Published in final edited form as:

Phys Chem Chem Phys. 2017 March 01; 19(9): 6861–6870. doi:10.1039/c6cp07646g.

New Insights into the Electroreduction of Ethylene Sulfite as Electrolyte Additive for Facilitating Solid Electrolyte Interphase of Lithium Ion Battery

Yumin Sun^{a,b} and Yixuan Wang^{b,*}

^aSchool of Environmental Engineering, Shandong Jianzhu University, Jinan 250101, P. R. China

^bComputational Chemistry Laboratory, Department of Chemistry and Forensic Sciences, Albany State University, Albany, GA31705, US

Abstract

To help understand the solid electrolyte interphase (SEI) formation facilitated by electrolyte additives of lithium-ion batteries (LIB) the supermolecular clusters $[(ES)Li^+(PC)_m](PC)_n$ ($m=1-2$; $n=0, 6$, and 9) were used to investigate the electroreductive decompositions of the electrolyte additive, ethylene sulfite (ES), as well as the solvent, propylene carbonate (PC) with density functional theory. The results show that ES can be reduced prior to PC, resulting in a reduction precursor that will then undergo a ring opening decomposition to yield a radical anion. A new concerted pathway (path B) was located for the ring opening of the reduced ES, which has much lower energy barrier than the previously reported stepwise pathway (path A). The transition state for the ring opening of PC induced by the reduced ES (path C, indirect path) is closer to that of path A than path B in energy. The direct ring opening of the reduced PC (path D) has lower energy barrier than those of paths A, B and C, yet it is less favorable than the latter paths in terms of thermodynamics (vertical electron affinity or the reduction potential dissociation energy). The overall rate constant including the initial reduction and the subsequent ring opening for path B is the largest among the four paths, followed by paths $A > C > D$, which further signifies the importance of the concerted new path in facilitating the SEI. The hybrid models, the supermolecular cluster augmented by polarized continuum model, $PCM-[(ES)Li^+(PC)_2](PC)_n$ ($n=0, 6$, and 9), were used to further estimate the reduction potential by taking into account both explicit and implicit solvent effects. The second solvation shell of Li^+ in $[(ES)Li^+(PC)_2](PC)_n$ ($n=6$, and 9) partially compensates the overestimation of solvent effects arising from the PCM model for the naked $(ES)Li^+(PC)_2$, and the theoretical reduction potential with $PCM-[(ES)Li^+(PC)_2](PC)_6$ (1.90–1.93V) agrees very well with the experimental one (1.8–2.0V).

Keywords

Li ion battery; electrolyte additive; solid electrolyte interphase; electroreduction mechanism

* yixuan.wang@asurams or yixuanwang64@gmail.com.

1. Introduction

Lithium ion batteries (LIBs) have been popular power resources in the recent two decades as a result of their excellent performance in terms of cycle life, energy density, power capability and charge rate.^{1–5} The stability, safety, and durability of the LIBs significantly depends on the quality of the solid electrolyte interphase (SEI) between the graphite anode surface and the electrolyte.^{3, 6–8} The SEI layer was believed to be resulted from the reduction of the electrolyte during the first few cycles.³ Thus, many studies on its formation, composition, and morphology have been conducted by both experiments and theories in the past decades.^{4, 9–12}

Propylene carbonate (PC) is an attractive solvent for the LIBs because of its liquid state at room temperature and relatively high polarity. However, PC alone as a solvent can easily exfoliate the graphite anode and reduce its reversible capacity.^{13, 14} An efficient way to solve the problem is to add an additive to PC-based electrolyte, which can significantly facilitate the formation of the SEI layer. The explored additives including 3-propane sultone (PS), vinylene carbonate (VC), vinyl ethylene carbonate (VEC), 1,3-propane sultone (PS), and ethyl vinyl sulfone (EVS) can effectively generate SEI layer in the presence of small amount (e.g., 5% weight) together with PC, ethylene carbonate (EC) or a mixture of the cyclic and acyclic carbonates.^{15–18} To explain the various experimentally observed SEI compositions, the reductive decompositions of the additives for PC(EC)-based electrolytes were extensively investigated with *ab initio* molecular dynamics and traditional quantum mechanics methods.^{19–22} The electro-reduction of the additives is generally initiated by accepting an electron from the electrode to form a decomposition precursor (initiation step,

E -the energy of the precursor relative to the neutral additive), and the homolytic ring opening reaction will then occur on the precursor through a transition state with an energy barrier of E_a (ring opening step). In general, $-E$ (i.e., vertical electron affinity, EA) of the additives is generally higher than those of the solvents, suggesting that the additives are thermodynamically favorable to be reduced prior to PC. However, on the other hand, the higher energy barrier E_a for the ring opening of the additive, like VC being almost twice higher than those of PC and EC, indicates that the ring opening step of the additive is kinetically unfavorable.¹⁹ Thermodynamics and kinetics of the two steps for the additives and solvents of the electrolyte for LIB are opposite. *Thus, the open questions are 1) the initial reduction or the consequent ring opening, which step plays more important role in the first electron decomposition path, and 2) the additive or solvent, which one has larger overall reaction rate for the generation of the ring opening radical?*

Since ethylene sulfite (ES) was introduced as an additive for the PC-based electrolyte,²³ sulfite additives for the LIB have been attracting much attention.^{18, 21, 24} To explain the mechanism by which ES can promote the formation of a stable SEI layer on the anode, using density functional theory Li et al investigated the reduction mechanism of ES only in the gas phase.²⁵ Jiang used the cluster models $(ES)Li^+(PC)_n$ ($n=0-2$) to further theoretically explore the electroreduction of ES in vacuum as well as in solvent that was described with an implicit model (PCM).²⁶ Similar to other additives, it was revealed that ES has higher electron affinity or reduction potential than PC (-79.5^{26} vs -44.9 kcal/mol¹⁹); however, the energy barrier of the reductive decomposition of ES in $ES-Li^+-PC$ is much higher than those

of PC and even VC (36.6^{26} vs 10.9 and 19.1 kcal/mol¹⁹). Experiments also detected some new surface species that may be attributed to the reduction of PC.^{3, 6} In the present investigation, density functional theory (DFT) calculations were extensively carried out on the supermolecular clusters $[(ES)Li^+(PC)_m](PC)_n$ ($m=1-2$; $n=0, 6$, and 9) clusters. Our objectives are (1) to determine the most favorable paths of the ES reductive decomposition; (2) to calculate the overall reaction rate for the generation of ring opening radical; (3) to discuss explicit solvent effects on the thermodynamics and kinetics. On the basis of these results, the above mentioned questions can be well addressed.

2. Computational details

To realistically model a small amount of ES in PC-based electrolyte solutions, the Gibbs free energy change for the clusters of $(ES)Li^+(PC)_n$ ($n=0-3$) shows that $(ES)Li^+(PC)$ and $(ES)Li^+(PC)_2$ are the most probable solvated lithium ion species.^{26, 27} To explore the effect of anode interface on the cluster, the adsorptions of $Li^+(ES)(PC)_{1-2}$ on graphite, modeled by $C_{150}H_{30}$, were also investigated with B3PW91/6-31G* in the present work. $Li^+(ES)(PC)$ can be well adsorbed by the interface (Li^+ -graphite = 2.48 Å), while due to the coordination competition of Li^+ with PC and interface with $Li^+(ES)(PC)_2$ is rather separated from the interface (Li^+ -graphite = 5.12 Å). Therefore, the following investigation will focus on the clusters $(ES)Li^+(PC)$ and $(ES)Li^+(PC)_2$ for the reductive decomposition mechanism. All the calculations were performed using the Gaussian09 package.²⁸ The stationary points for the clusters were fully optimized with density functional theory B3PW91 method with the 6-311++G(d,p) basis set. In order to confirm the transition states and make zero-point energy (ZPE) corrections, frequency analyses were carried out at the same level. IRC was also done to confirm a few key transition states. Charges were predicted by fitting the molecular electrostatic potential (CHELPG method).²⁹ The implicit solvent effect was accounted for by using the polarized continuum model (PCM)³⁰ as implemented in Gaussian09 in which a conventional set of Pauling radii was used for all calculations. We adopted the dielectric constant of PC (64.9) in relation to the conditions implemented in experiments for the PCM. In 1M electrolyte solution of $LiPF_6$ and the mixture of EC/PC widely used in experiments, the ratio of solvent molecules to Li^+ is approximately 11 to 1. DFT (B3PW91/6-31G*) investigation shows that the transition from the closely contact ion-pair ($Li^+-PF_6^-$) to solvent shared ion-pair $Li^+ \cdots (PC)_4 \cdots (PF_6^-)$ occurs upon 4 PC molecules, and the shortest distance from Li^+ to PF_6^- is 4.3 Å as increase PC molecules to six, i.e., resulting in the solvent separated ion pair $(PC)_4 \cdots Li^+ \cdots (PC)_2 \cdots (PF_6^-)$. At 1M electrolyte solution solvated Li^+ and anion is rather separated. Thus, the role of the counter ion in the relevant calculation may be less important.

To gain more insights into the solvent effects, 6 and 9 PC solvent molecules were also explicitly added to cluster $(ES)Li^+(PC)_2$, forming the supermolecules $[(ES)Li^+(PC)_2](PC)_n$ ($n=6$ and 9). Through the supermolecules, each solvent molecule in the first solvation shell of Li^+ interacts with 2 or 3 PC molecules through 2 or 3 weak hydrogen bonds (C-H $\cdots$ O). The full geometry optimization for the supermolecules was done with the B3PW91/6-31G(d,p) method in a vacuum. Then, the single-point energies were obtained at the B3PW91/6-311++G(d,p)//B3PW91/6-31G(d,p) level. A hybrid solvent model including implicit solvent PCM and the superclusters consisting of the explicit solvent molecules

$[(\text{ES})\text{Li}^+(\text{PC})_2](\text{PC})_n$ ($n=0, 6$ and 9), was finally applied to evaluate the role of PCM as well as the explicit solvent molecules in the solvent effects.

3. Results and Discussion

3.1 The electroreductive decomposition of ES and PC in cluster $(\text{ES})\text{Li}^+(\text{PC})$

The potential energy profile for the two-electron reduction pathways of cluster $(\text{ES})\text{Li}^+(\text{PC})$ **1** was shown in Figure 1, and the relative energetic data were summarized in Table 1 together with major characteristics. Accepting an electron, **1** is firstly reduced to a radical precursor, $(\text{ES})\text{Li}^+(\text{PC})^-$ **2** or $(\text{ES})^-\text{Li}^+(\text{PC})$ **3**, which corresponds to the reduction of PC and ES, respectively. A charge population analysis shows that the spin density is mainly located at the carbonyl carbon (C9) in PC moiety of **2**, and the sulfur (S2) atom in ES moiety of **3** with a coefficient of 0.77 and 0.67, respectively. The distributions of spin density confirm that PC is reduced in **2**, while the excess electron goes to ES in **3**. Upon accepting an electron, one of C-O bonds in **2** is slightly prolonged by $\sim 0.2\text{\AA}$ (1.528 vs $1.320\text{\AA}$ in **1**), while one S-O bond is significantly stretched to $2.702\text{\AA}$ in **3** ($1.635\text{\AA}$ in **1**). According to Figure 1, **3** is more stable than **2** by approximately 45.7 kcal/mol in vacuum (down to 40.1 kcal/mol in solution with PCM model). Similar to other additives such as VC, the result implies that the ES has a superior electron-accepting ability to PC. This observation agrees very well with a recent study by Jiang et al. that the reduction potential or vertical electron affinity (EA_V) of ES is larger than PC (2.99 vs 0.92 eV in solution, the difference close to 47.0 kcal/mol).²¹ The Fermi level for LiC6 has been reported to be -2.80 eV versus vacuum, respectively. The predicted LUMO of ethylene sulfite (ES), -4.50 eV in the presence of Li^+ ions (ESLi^+PC), is more negative than the Fermi level of the graphite electrode and, consequently, ES will be reduced assuming that electrons can cross the energy barrier for electron tunneling.

Starting from **3**, the ring opening of ES^- in $(\text{ES})^-\text{Li}^+(\text{PC})$ in vacuum (through the cleavage of C4–O3 that is rather separated from S by $2.702\text{\AA}$) was reported by Xing et al, which is a stepwise path and has two transition states (TS) and one intermediate.²⁵ The stepwise path was also confirmed in the present study, Path A as shown in Figure 1. **3** initially converts into an intermediate **4** that has higher energy than **3** by 13.5 kcal/mol. The transition state connecting **3** and **4** is rather similar to intermediate **4** (the unique imaginary frequency $\sim 202\text{cm}^{-1}$), and its energy ($E+\text{ZPE}$) is only 0.1 kcal/mol higher than that of the intermediate **4**, which is consistent with Xing et al's result.²⁵ **4** proceeds to a ring opening radical **6a** through a transition state **5** (**TS5**) with an energy barrier of 26.3 kcal/mol, similar to that obtained by Xing et al (28.0 kcal/mol). **TS5** was also located by Jiang et al in both vacuum and solution (PCM model),²¹ but the path connecting the reduced precursor of ES and the ring opening radical was described as an elementary step because of the unique transition state. The predicted energy barrier by Jiang et al was consequently high relative to the reduction precursor **3** ($(\text{ES})^-\text{Li}^+(\text{PC})$), 41.5 kcal/mol with B3LYP/6–311++G(d,p), and 36.6 kcal/mol with PCM-B3LYP/6–311++G(d,p). The present energy barrier from **3** to **6** via **TS5** is 40.9 and 28.6 kcal/mol respectively in vacuum and solution.

The most interesting is that a new path (path **B**) is located via the cleavage of C5–O6, along which transition state **7** (**TS7**) connects **3** and **6b** with a low energy barrier of only 25.1 kcal/mol (20.4 in solution), much lower than that of path A (40.9 kcal/mol in vacuum, and 28.6 in solution) as compared with the reduction precursor of ES, **3**. As shown in Figure 1, **TS7** has lower energy than **TS5** by 14.7kcal/mol in vacuum, and 8.2kcal/mol in solution. Another difference from path A is that this process is indeed a concerted pathway, and the unique imaginary frequency shows that the displacement vector predominantly correlates with the stretch of the C5–O6 bond of ES with a weak stretch of S2–O3. The other bonds of ES in **7** have a little change, although the S2–O3 distance is relatively shorter than that in **3** (2.230 vs 2.702 Å). The spin density of **TS7** mainly locates on S2 and the leaving C (C5) with respective coefficient of 0.31 and 0.69e. Although the ultimate ring opening anion radical (**6b**) from path B has only 1.4kcal/mol lower in energy than that from path A, i.e., similar dissociation energy (energy of ring opening radical **6** relative to the precursor **3**), in terms of the kinetics (energy barrier, and the ring opening rate that will be shown below) of the ring opening reaction of (ES) $\cdot$ Li $^{+}$ (PC), path B (the concerted pathway) is more favorable than the step-wise pathway (path A).

Figure 2 further illustrates the energy and geometry differences along with spin density for paths A and B. Although C4–O3 and C5–O6 bonds are the same, and that is also true for the two S–O bonds (S2–O3, S2–O6) at **1**, after ES is reduced to yield the reduction precursor (**3** in Figure 1) the excess electron considerably alters the symmetry of **1**. The significantly stretched S2–O3 (2.702Å) is accompanied by a variation of C4–O3 (1.370 Å) and C5–O6 (1.446 Å). In addition, the Li $^{+}$ coordinates with O3 and O1, yet far from O6. Transition states **5** and **7** correspond to the cleavage of C4–O3 and C5–O6, respectively. In terms of the geometry, relative to the precursor (**3**) primary changes of transition state **7** are the concerted stretching of C5–O6 and S2–O3, whereas much more variations occur on transition state **5**, significant contraction of S2–O3, extension of S2–O6 and extension of C4–O3. Thus, for the reorganization of three bonds between transition state **5** and precursor **3** there is another transition state. The distance between O and leaving C in **TS7** is longer than that in **TS5** (2.072 vs 1.865Å), i.e., the transition state for the concerted path B is later than that for the stepwise path A. The close inspection indicates that the spin density distribution of **TS7** is more similar to that of **6** than **TS5**. These factors may be responsible to the lower energy in **TS7** than **TS5**. The transition states **5** and **7** were confirmed by the IRC calculations, which are shown in Figures S1.

The ring opening product (radical anion, **6a** or **6b**) is indeed the same as or similar to the previously reported one. The SEI components mainly arise from the termination reactions of the radical anion **6** via the second electron process, the self-association, or the reactions with the reactant and other intermediates. Thus, the mechanism for the formation of the radical anion is very crucial for the growth of the SEI film. The present investigation locates a new pathway for the generation of the radical anion, the precursor of the SEI, and provides new insights to understand the SEI facilitated by the additive.

Our previous study on cluster (VC)Li $^{+}$ (PC) showed that the reduced additive VC can induce the ring opening of PC through an electron transfer, and the process even has a lower energy barrier than that of the reduced VC.¹⁹ For cluster (ES)Li $^{+}$ (PC), can the reduced ES also

induce a homolytic ring opening of PC to avoid a high-energy barrier path? To answer this question, path C is located as shown in Figure 1, in which an electron transfer induces a homolytic ring opening of PC ring instead of the ES ring. According to the natural orbital analysis, the spin density of the transition state (TS8) is located at the carbonyl carbon of PC with a coefficient of 0.51, and at the sulfur atom of ES with 0.36. The distance of C12 and O13 on TS8 is stretched to 2.069 Å. The characteristics of **8** as a transition state connecting **3** and the ring open radical **9** can be further confirmed by the vibrational mode of its unique imaginary frequency. Although TS8 has lower energy than TS5 by 5.1 kcal/mol in vacuum, it is less stable than TS7 by 9.6 kcal/mol in vacuum (10.8 kcal/mol in solution). This trend is quite different from that in the case of (VC)Li⁺(PC).¹⁹ For the electroreductive decomposition process (path C), ES is not consumed; it just catalyzes the homolytic ring opening of PC via an electron transfer. Bulk solvent effects on the reduction potential of (ES)Li⁺(PC) and ring-opening energy barriers of the reduction precursor (ES)⁻Li⁺(PC) have also been estimated by the PCM model (dielectric constant, 63.9). The cluster-PCM predicted ring opening barriers for TS5, **7**, and **8** are decreased differently by 11.2, 4.7 and 4.1 kcal/mol, respectively (Table 1).

It was reported that the reductive decomposition of PC has a lower energy barrier than the additive VC has.¹⁹ To directly and consistently compare with ES, the reduction path of PC was also investigated for cluster (ES)Li⁺(PC) in the present study (path D in Figure 1). PC is reduced to (ES)Li⁺(PC)⁻ (**2**) with a vertical electron affinity of 71.7 kcal/mol in vacuum (38.7 kcal/mol in solution) that is much smaller than that of ES to (ES)⁻Li⁺(PC) (**3**) (117.4 and 78.8 kcal/mol for ES respectively in vacuum and in solution). The decomposition path of (ES)Li⁺(PC)⁻ proceeds through transition state TS10 to generate a secondary radical **9**. The energy barrier of C12–O13 cleavage in TS10 is relatively low (12.0 and 11.2 kcal/mol in respective vacuum and solution.), which is close to that of PC-reduction process in the cluster (VC)Li⁺(PC) (11.5 kcal/mol).¹⁹ The formation of **9** is less exothermic than **6** (–106.2 vs –108.8 kcal/mol in vacuum, and –67.9 vs –76.7 kcal/mol in solution), indicating that the generation of the ring opening radical is thermodynamically more favorable from the reduced ES than the reduced PC. Similar to the comparison between VC and PC, the reductive decomposition of PC is also more favorable than additive ES in terms of kinetics (energy barrier), yet less favorable in the aspects of thermodynamics (vertical electron affinity, dissociation energy).

The termination reactions of the one-electron reduction product, anion radical **6b** were also investigated, including the second CO bond cleavage to result in ethylene and the second electron reduction. The CO bond cleavage undergoes via a transition state **11** (TS11) to bring about **12**, which is a weak complex of the ethylene gas and ROSO₂Li. It is also possible for **6** to further accept the second electron from the polarized electrode. As shown in Figure 1, further reduction of **6** with adding another Li⁺ generates an intermediate **13**. The decomposition of **13** produces an inorganic product RSO₃Li₂ and ethylene gas (**15**) through a transition state **14** with a relative small energy barrier. The energy barrier for the formation of **15** is much lower than that for the formation of **12** (1.4 vs 13.7 kcal/mol in vacuum), suggesting that the termination of radical anion **6b** prefers the two-electron reduction process via transition state **14** to the direct dissociation of the one-electron process via TS11.

The termination reactions can also take place either with other intermediates or self-dimerization, bringing about lithium carbides species to participate in the formation of SEI film.^{8, 12, 19}

3.2 The electroreductive decompositions of ES and PC in cluster (ES)Li⁺(PC)₂

With an extra PC molecule, the reductive decomposition paths of cluster (ES)Li⁺(PC)₂ (**16**) in Figure 3 are very similar to those of **1**. However, because of further solvation of Li⁺ the initial reduction potentials (vertical electron affinity) are further decreased by approximately 10 kcal/mol, -103.5 and -61.6 kcal/mol in vacuum (-74.7 and -37.3 kcal/mol in solution) for the respective reduction of ES and PC in **16**, bringing about the radical anions (ES)^{•-}Li⁺(PC)₂ (**18**) and (ES)Li⁺(PC)^{•-} (**17**). The formation energies of the ring opening radical anions are also decreased (-89.1 vs -106.2 kcal/mol for PC ring opening (**24**), -98.3 vs -108.8 kcal/mol for ES ring opening (**21**)). The most important is that for the decomposition of ES^{•-} in (ES)^{•-}Li⁺(PC)₂ a transition state TS22 for the concerted pathway (**B**) still has lower energy than TS20 for the stepwise pathway (**A**) by 12.5 and 7.3 kcal/mol in vacuum and in the solution, respectively. The direct reductive decomposition pathway of PC (**D**) is still favorable with respect to kinetics, lower barrier (12.4 and 9.6 kcal/mol in respective vacuum and solution) than paths A and B, yet again its thermodynamic aspects are unfavorable (lower electron affinity and dissociation energy). The ring opening radical intermediate **21b** can still undergo a homolytic CO cleavage via a transition state **26** to give a weak complex of the ethylene gas and ROSO₂Li. However, the barrier **21b**→TS26→**27** is considerably higher than that of **6**→TS11→**12** (29.2 vs 13.7 kcal/mol). The radical anion **21b** has very strong tendency to accept an electron and Li⁺, generating a complex **28**. The homolytic CO cleavage of **28** undergoes through a transition state **29** with a minor energy barrier of 1.5 kcal/mol, rather similar to that of **8** via **9** (1.4 kcal/mol) and much smaller than the path (**21b**→TS26→**27**), suggesting the two electron reduction is kinetically more favorable than the one electron reduction path, bringing about an inorganic product RSO₃Li₂ **30**, an efficient component for the formation of SEI.^{31, 32}

3.3 The rate constant of electroreductive decomposition pathways

According to the above analysis, similar to another additive VC the reductive decomposition of ES is thermodynamically favorable, while that of PC is kinetically controlled. It is interesting therefore to deal with the rate constant for the entire one-electron reduction decomposition consisting of the electrochemistry equilibrium and kinetic aspects,³³ which can be shown as follows.

According to the steady-state approximation, the overall rate constant k is

$$k = K \cdot k' \quad (3)$$

K is the equilibrium constant for the formation of reduction precursors $[(ES)Li^+(PC)_n]^-$ (Eq. 1) and k' the rate constant for the ring opening reaction (Eq. 2). The equilibrium constant K for the first step reaction of accepting an electron can be written as

$$K = \exp \frac{-\Delta G}{RT} \quad (4)$$

G is the Gibbs free energy change for Eq. (1). According to the classical transition state theory, the kinetic rate constant k' at a certain temperature can be calculated with the following equation:

$$k' = \frac{ek_B T}{h} \cdot e^{\frac{-E_a}{RT}} \cdot e^{\frac{\Delta S^\ddagger}{R}} \quad (5)$$

where k_B is the Boltzmann constant, h the Planck constant, E_a and $\Delta S^\ddagger$ the energy barrier and activation entropy for the ring opening reaction, respectively. The overall rate constants for the electroreduction decomposition process of the clusters $(ES)Li^+(PC)$ and $(ES)Li^+(PC)_2$ in solvent for the four pathways are listed in Table 3. The equilibrium constants K for the formations of PC- and ES-reduction precursors of cluster $(ES)Li^+(PC)$ are very different, 3.04×10^{57} vs 9.48×10^{27} . Although the ring opening rate constant k' for path D is the highest among the four loaded paths, due to the rather small K for the initial reduction of PC in $(ES)Li^+(PC)$ the overall rate constant k of the path D is the smallest ($4.44 \times 10^{32} s^{-1}$). Regarding the three paths from the ES-reduction precursor, path A has much lower ring opening rate constant k' than path D (10^{-10} vs $10^4 s^{-1}$), however, the high equilibrium constant K for the formation ES-reduction precursor compensates the low rate constant to bring about a relatively high overall rate constant ($3.27 \times 10^{48} s^{-1}$) for path A. Moreover, another path (path C) from the ES-reduction precursor yet inducing PC ring opening has similar overall rate constant k to that of the path A, suggesting that the ring opening taking place on the unreduced PC molecule is an alternative pathway. It is the most interesting that high equilibrium constants K and mild the ring opening rate constant k' (between those of paths D and A) result in the highest overall rate constant for path B. The rate constants for interfacial electron transfer from highly ordered pyrolytic graphite (HOPG), to redox couples in solution range from 10 to 10^{-9} cm/s, but most of them are approximately 10^{-2} cm/s.³⁵ The ring opening rate for path B (10^{-1}) lies within this range, and the ring-opening may be faster than or comparable with the electron transfer.

As discussed above the inclusion of PC in cluster $(ES)Li^+(PC)_2$ decreases the vertical electron affinities of ES and PC (less negative for G_{sol}) as compared with $(ES)Li^+(PC)_2$, the equilibrium constants K for the formation of reduction precursors $(ES)^-Li^+(PC)_2]^-$ are therefore smaller. The rate constants k' of the ring opening reactions also become smaller for paths A, B and C, while it becomes bigger for path D. The overall rate constants k for all of

four paths are much smaller than those of (ES)Li⁺(PC). In line with cluster (ES)Li⁺(PC), the overall rate constant for path B is still the highest, followed by paths A, C, and D. The result indicates that path B located in the present investigation is the most probable reductive decomposition pathway of ES in PC-based electrolyte of the LIB.

For the first-order reduction reactions, the remaining reactants can be estimated by the following equation,

$$\frac{[A]_0 - x}{[A]_0 - y} = e^{(k_2 - k_1)t} \quad (6)$$

$$y = [A]_0 - \frac{[A]_0 - x}{e^{(k_2 - k_1)t}} \quad (7)$$

Where [A]₀ is the initial concentration of the solvent, x and y are the concentrations for the ring opening anion for the path with the rate constant *k*₁ and *k*₂, respectively. The rate constant difference for path B (*k*₂=10⁴⁶) and path D (*k*₁=10³⁰) is so big that the reduction product of PC can be omitted, implying that the reduction of PC can be significantly suppressed by the additive.

3.4 Explicit solvent effects on reduction pathways- A hybrid solvent model

As a result of the inclusion of one solvent molecule in Li⁺ solvation shell or implicitly accounting for solvent with PCM model, the vertical electron affinities of **ES** and **PC** are significantly decreased as shown above. 6 PC and 9 PC molecules were therefore respectively added to the cluster (ES)Li⁺(PC)₂ to explicitly describe the solvent effect on the most favorable path of the ES reductive decomposition (path B). The potential energy profile for the reductive decomposition of the supermolecules was shown in Figure 4. The energetic and geometry data were listed in Table 4. Comparing (ES)Li⁺(PC)₂ with [(ES)Li⁺(PC)₂](PC)_n (n=6 and 9), the average distances of Li⁺-O in the clusters slightly change, induced by the weak hydrogen bond (C-H...O) between the extra PC and the first Li solvation shell.³⁴ The C₅-O₆ distance in the transition state doesn't change much with more PC. In line with the trend that the inclusion of the implicit solvent model (PCM) decreases the vertical electron affinity of ES and PC of [(ES)Li⁺(PC)₂], the ability to accept an electron of ES is downtrend as more PC molecules are added to [(ES)Li⁺(PC)₂] (94.1 and 97.6 kcal/mol for [(ES)Li⁺(PC)₂](PC)_n (n=6 and 9) vs 101.9 kcal/mol for [(ES)Li⁺(PC)₂]). The energy barrier of the ring opening of the ES-reduction precursor is also slightly decreased as compared with that of the naked cluster (ES)Li⁺(PC)₂ (23.0 and 25.4 vs 25.9 kcal/mol). The effect of explicit solvent molecules on the reduction of PC (path D) was also shown Figure 4. The energetic shifts are similar to those of path B. For example, the reduction potentials decrease by 2–7 kcal/mol as 6 and 9 PC molecules are included, and the dissociation energy for the formation of radical anion also decrease by 2–5 kcal/mol.

The PCM model was also added to the supermolecules $[(ES)Li^+(PC)_2](PC)_n$ ($n=0,6$ and 9), i.e., using hybrid model to deal with solvent effect by jointly applying explicit solvent molecules and implicit polarized continuum model. The electron affinities of ES of the supermolecules are further decreased by approximately 20kcal/mol, yielding 75.0 and 77.5 kca/mol, which are also higher by 5–8 kcal/mol than that predicted by PCM for the naked $[(ES)Li^+(PC)_2]$ (~ 70.4 kcal/mol that is ~ 30 kcal/mol lower than in vacuum.). The solvent effects arising from PCM for the supermolecules $[(ES)Li^+(PC)_2](PC)_n$ ($n=6$ and 9) are partially (~ 10 kcal/mol) screened by the second solvation shell of Li^+ . PCM has similar relative performance on the transition states and the ring opening radicals for $[(ES)Li^+(PC)_2](PC)_n$ ($n=0,6$ and 9), i.e., higher solvent effect by ~ 10 kcal/mol for the naked $[(ES)Li^+(PC)_2]$. The reduction potentials for the reduction of ES were estimated with a thermodynamic cycle for PCM- $[(ES)Li^+(PC)_2](PC)_n$ (the standard reduction potential φ^0 , relative to Li^+/Li 1.39V²²). The reduction potentials (1.90–1.93V) of ES for PCM- $[(ES)Li^+(PC)_2](PC)_n$ are in much better agreement with experimental one (1.8–2.0V²³) than those from the PCM- $[(ES)Li^+(PC)_2]$ (1.42–1.58V). We suggest that the inclusion of the second solvation shell of Li^+ via the supermolecules $[(ES)Li^+(PC)_2](PC)_n$ (6 and 9) can compensate the overestimation of the solvent effects arising from the PCM model.

The thermodynamic cycle was used for the calculation of reduction potentials (φ^0/V), S and S_{stand} for $[(ES)Li^+(PC)_2](PC)_n$ and $[(ES)^-Li^+(PC)_2](PC)_n$, respectively.

$$\Delta G_{sol} = \Delta G_{gas} + \Delta G_{sol}(S^-) - \Delta G_{sol}(S) \quad (8)$$

$$\varphi^0 = -\Delta G_{sol}/F - 1.39 \quad (9)$$

4. Conclusion

Density functional theory (B3PW91) has been applied to the supermolecular clusters $[(ES)Li^+(PC)_m](PC)_n$ ($m=1,2$; $n=0, 6$ and 9) to get new insights into the electroreductive decompositions of the electrolyte additive (ES) and solvent (PC). It is confirmed that the additive ES has higher vertical electron affinity than solvent PC, i.e., high reduction potential, signifying that ES can be reduced prior to PC to bring about a reduction precursor that then undergoes a ring opening decomposition to yield a radical anion. A new concerted pathway (path B) was located for ES electroreductive decomposition that has much lower energy barrier than the previously reported stepwise pathway (path A). The transition state for the decomposition of PC induced by the reduced ES (path C, indirect path) is closer to that of path A than path B in energy. The direct electroreductive decomposition of PC (path

D) has lower energy barrier than those of paths A, B and C, yet it is less favorable than the latter paths in the aspect of vertical electron affinity (reduction potential). To comprehensively assess the reaction paths the overall reaction rates were calculated including the initial reduction and the subsequent ring opening. The path B has the largest overall rate constant followed by the paths A>C>D, which further signifies the importance of the concerted path. The second solvation shell of Li⁺ in [(ES)Li⁺(PC)₂](PC)_n (n=6, and 9) partially compensates the overestimation of solvent effects arising from PCM model, and the theoretical reduction potential (1.90–1.93V) for the additive ES from the hybrid solvent model PCM-[(ES)Li⁺(PC)₂](PC)₆ agrees well with the experimental one (1.8–2.0V).

Acknowledgments

The project described here was supported by the National Institute of General Medical of the National Institute of Health (GM105576) for development objective.

References

1. Armstrong AR, Bruce PG. *Nature*. 1996; 381:499–500.
2. Dominey, LA. *Lithium Batteries. New Materials, Developments and Perspectives*. Elsevier; 1994.
3. Aurbach DJ. *J. Power Sources*. 2000; 89:206–218.
4. Xu K. *Chem. Rev*. 2014; 114:11503–11618. [PubMed: 25351820]
5. Busche MR, Drossel T, Leichtweiss T, Weber DA, Falk M, Schneider M, Reich M-L, Sommer H, Adelhelm P, Janek J. *Nature Chem*. 2016; 8:426. [PubMed: 27102676]
6. Bar-Tow D, Peled E, Burstein L. *J. Electrochem. Soc*. 1999; 146:824–832.
7. Trarascon J-M, Armand M. *Nature*. 2001; 414:359–367. [PubMed: 11713543]
8. An SJ, Li J, Daniel C, Mohanty D, Nagpure S, Wood DL III. *Carbon*. 2016; 105:52–76.
9. Schroder K, Alvarado J, Yersak TA, Li J, Dudney N, Webb LJ, Meng YS, Stevenson KJ. *Chem. Mater*. 2015; 27:5531.
10. Bhatt MD, O'Dwyer C. *Phys. Chem. Chem. Phys*. 2015; 17:4799–4844. [PubMed: 25613366]
11. Hoz, JMMdl, Balbuena, PB. *Phys. Chem. Chem. Phys*. 2014; 16:17019–17098.
12. Haregewoin AM, Wotango AS, Hwang B-J. *Energy Environ. Sci*. 2016; 9:1955–1988.
13. Zheng HH, Liu G, Battaglia V. *J. Phys. Chem. C*. 2010; 114:6182–6189.
14. Märkle W, Colin JF, Goers D, Spahr ME, Novák P. *Electrochimica Acta*. 2010; 55:4964–4969.
15. Wang Y, Nakamura S, Ue M, Balbuena PB. *J. Amer. Chem. Soc*. 2001; 123:11708–11718. [PubMed: 11716728]
16. Ein-Eli Y, Thomas SR, Koch VR. *J. Electrochem. Soc*. 1997; 144:1159–1165.
17. Jung HM, Park S-H, Jeon J, Choi Y, Yoon S, Cho J-J, Oh S, Kang S, Han Y-K, Lee H. *J. Mater. Chem. A*. 2013; 1:11975–11981.
18. Wagner R, Brox S, Kasnatscheew J, Gallus DR. *Electrochem. Commun*. 2014; 40:80–83.
19. Wang YX, Balbuena P. *J. Phys. Chem. B*. 2002; 106:4486–4495.
20. Keisuke U, Keitaro S, Yukihiro O, Yoshitaka T. *J. Amer. Chem. Soc*. 2013; 135:11967–11974. [PubMed: 23901789]
21. Leggesse EG, Jiang J-C. *RSC Advances*. 2012; 2:5439–5446.
22. Purushotham U, Takenaka N, Nagaoka M. *RSC Advances*. 2016; 6:65232.
23. Wrodnigg GH, Besenhard JO, Winter M. *J. Electrochem. Soc*. 1999; 146:470–472.
24. Yao W, Zhang Z, Jun G, Li J, Xu J, Wang Z, Yang Y. *Energy Environmental Sci*. 2009; 2:1102–1108.
25. Xing L, Li W, Xua M, Li T, Zhou L. *J. Power Sources*. 2011; 196:7044–7047.
26. Leggesse EG, Jiang J-C. *J. Phys. Chem. A*. 2012; 116:11025–11033. [PubMed: 23078373]
27. Bhatt MD, O'Dwyer C. *J. Electrochem. Soc*. 2014; 161:A14115–A14121.

28. Frisch, MJ., Trucks, GW., Schlegel, HB., Scuseria, GE., Robb, MA., Cheeseman, JR., Zakrzewski, VG., Montgomery, JAJ., Stratmann, RE., Burant, JC., Dapprich, S., Millam, JM., Daniels, AD., Kudin, KN., Strain, OFMC., Tomasi, J., Barone, B., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, GA., Ayala, PY., Cui, Q., Morokuma, K., Malick, DK., Rabuck, AD., Raghavachari, K., Foresman, JB., Ciolovski, J., Ortiz, JV., Stefanov, VV., Liu, G., Liashenko, A., Piskorz, P., Komaroni, I., Gomperts, R., Martin, RL., Fox, DJ., Keith, T., Al-Laham, MA., Peng, CY., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, PMW., Johnson, B., Chen, W., Wong, MW., Andres, JL., Head-Gordon, M., Replogle, ES., Pople, JA. Gaussian09 D01 edn. Pittsburgh, PA: Gaussian Inc.; 2009.
29. Breneman CM, Wiberg KB. J. Comput. Chem. 1990; 11:361.
30. Barone V, Cossi M. J. Phys. Chem. A. 1998; 102:1995–2001.
31. Ota H, Sato T, Suzuki H, Usami T. J. Power Sources. 2001; 97–98:107–113.
32. Ota H, Akai T, Namita H, Yamaguchi S, Nomura M. J. Power Sources. 2003; 119–121:567–571.
33. McQuarrie, DA., Simon, JD. Physical Chemistry: A Molecular Approach. Sausalito, CA: 1997.
34. Wang YX, Balbuena PP. J. Phys. Chem. A. 2001; 105:9972–9982.
35. Royea WJ, Hamann TW, Brunschwig BS, Lewis NS. J. Phys. Chem. B. 2006; 110:19433–19422. [PubMed: 17004802]

Figure 1.

The potential energy ($E + ZPE$ in vacuum) profile for the electroreductive decomposition of $(PC)Li^+(ES)$ with B3PW91/6–311++G(d,p).

Figure 2.

The potential energy profile with spin density (isovalue=0.005) for paths A and B. The data refer to G in solution with PCM-B3PW91/6-311++G**.

Figure 3.

The potential energy profile for the two-electro reductive decomposition paths of $(\text{PC})_2\text{Li}^+(\text{ES})$ with B3PW91/6-311++G(d,p)

Figure 4.
The potential energy profile for paths B and D of the superclusters $[(ES)Li^+(PC)_2](PC)_n$ ($n=0, 6$ and 9) with B3PW91/6-311++G(d,p)//B3PW91/6-31G(d,p)

Relative energies (E , kcal/mol) and Gibbs free energies (G , kcal/mol), charge (q /e), main coefficients of spin densities (sd/e) for stationary points, and imaginary frequency (ω /cm⁻¹) of transition states for the reductive decomposition of (PC)Li⁺(ES) with B3PW91/6-311++G(d,p) method

Table 1

Structures	sd ^c											
	E + ZPE ^a		G _{vac}	G _{sol} ^b	q		S2 (C9)	C12	C5	ω	E ^d	E+ ZPE ^e
1	0		0	0	+0.81							0
2	-71.7 (-38.7)		-71.6	-38.4	+0.81	(0.77)						
3	-117.4 (-78.8)		-118.1	-78.9	+0.81	0.67					0	-121.5 (-79.5)
4	-103.9 (-69.2)		-104.5	-69.7	+0.70	0.60					15.6	
5(TS,4↔6)	-77.6 (-50.2)		-76.5	-49.5	+0.79	0.42			0.59	908i	43.0	-80.2 (-42.9)
6a	-107.4 (-76.5)		-109.7	-78.8	+0.78				1.10 ^f		12.6	-110.4 (-70.0)
6b	-108.8 (-76.7)		-112.0	-80.0	+0.78				1.10			
7(TS,3↔6)	-92.3 (-58.4)		-94.5	-60.0	+0.81	0.31			0.69	577i		
8(TS,3↔9)	-82.7 (-47.6)		-83.8	-48.5	+0.70	0.36		0.51		485i		
9	-106.2 (-67.9)		-107.2	-68.3	+0.76			1.1				
10 (TS,2↔9)	-59.7 (-27.6)		-59.2	-26.8	+0.79	(0.48)		0.44		922i		
11(TS,6↔12)	-95.1 (-66.5)		-90.6	-69.6	+0.78	0.13			0.61	537i	22.8	-110.3 (-60.2)
12	-112.2 (-77.1)		-116.9	-81.8	+0.70	0.60					6.2	-116.7 (-76.4)
13	-305.9 (-169.1)		-299.4	-271.1								
14(TS,13↔15)	-304.4 (-168.9)		-297.2	-270.2							386i	
15	-339.5 (-204.9)		-334.5	-308.3								

^aThe data in the parentheses are from PCM-B3PW91/6-311++G(d,p);

^b $G_{sol} = G_{vac} + \text{relative solvation free energies}$;

^cSee the atom label in Figure 1 and the data in parentheses refer to the corresponding atom of PC moiety;

^dData in vacuum are from ref.²⁵ with B3LYP/6-311++G(d,p);

^eData are from ref.²¹ and data in the parentheses were calculated with PCM-B3LYP/6-311++G(d,p) method.

^fC4

Table 2

Relative energies and Gibbs free energies (kcal/mol), charge (q/e), main coefficients of spin densities (sd/e) for stationary points and imaginary frequency (ω/cm^{-1}) of transition states for the reductive decomposition of (ES)Li⁺(PC)₂ calculated with B3PW91/6-311++G(d,p) method

Structures	E + ZPE ^a	G _{vac}	G _{sol} ^b	Charge		sd ^c				
				Li	S2 (C9)	C12	C5	C5	C5	ω
16	0	0	0	+0.78						
17	-61.6 (-37.3)	-57.1	-32.7	+0.73	(0.79)					
18	-103.5 (-74.7)	-99.2	-70.7	+0.78	0.67					
19	-92.8 (-66.8)	-87.8	-61.6	+0.76	0.62					
20(TS,19 $\leftrightarrow$ 21)	-67.2 (-43.1)	-61.3	-37.2	+0.79	0.40			0.57	817i	
21a	-96.1(-67.9)	-92.7	-64.5	+0.71				1.00		
21b	-98.7 (-73.0)	-96.6	-71.0	+0.71				1.00		
22(TS,18 $\leftrightarrow$ 21)	-79.7 (-50.4)	-74.8	-45.5	+0.72	0.31			0.68	621i	
23(TS,18 $\leftrightarrow$ 24)	-68.2 (-39.3)	-63.0	-4.7	+0.78	0.38	0.56			472i	
24	-89.1 (-67.6)	-87.6	-66.1	+0.73		1.00				
25(TS,17 $\leftrightarrow$ 24)	-49.2 (-27.7)	-45.2	-23.7	+0.74	(0.46)	0.41			917i	
26 (TS,21 $\leftrightarrow$ 27)	-69.1 (-41.9)	-80.8	-53.6	+0.68	0.14		0.63		507i	
27	-102.4 (-74.1)	-103.1	-74.8	+0.79	0.63					
28	-293.4 (-163.5)	-280.3	-258.9							
29(TS,28 $\leftrightarrow$ 30)	-291.5 (-160.9)	-278.0	-255.9							372i
30	-326.5 (-203.0)	-316.8	-302.7							

^aThe data in the parentheses are from PCM-B3PW91/6-311++G(d,p)

^b $G_{\text{sol}} = G_{\text{vac}} + \text{relative solvation free energies.}$

^cSee the atom label in Figure 1 and the data in parentheses refer to the corresponding atom of the PC moiety.

Table 3

Equilibrium constant K for the reduction, kinetic rate constant k' for the ring opening and the entire rate constant k for four paths of clusters $(\text{ES})\text{Li}^+(\text{PC})$ and $(\text{ES})\text{Li}^+(\text{PC})_2$ in solution.

	K	k' (s^{-1})	k (s^{-1})
$(\text{ES})\text{Li}^+(\text{PC})$			
path A	3.04×10^{57}	6.15×10^{-10}	3.27×10^{48}
path B	3.04×10^{57}	2.29×10^{-1}	6.95×10^{56}
path C	3.04×10^{57}	9.42×10^{-10}	2.86×10^{48}
path D	9.48×10^{27}	4.61×10^4	4.44×10^{32}
$(\text{ES})\text{Li}^+(\text{PC})_2$			
path A	3.23×10^{51}	1.33×10^{-12}	4.31×10^{39}
path B	3.23×10^{51}	5.69×10^{-6}	1.84×10^{46}
Path C	3.23×10^{51}	6.29×10^{-14}	2.03×10^{38}
path D	7.25×10^{23}	5.69×10^6	4.12×10^{30}

Table 4

Relative energies (E , kcal/mol), Gibbs free energies (G), reduction potentials (ϕ/V), and the characteristics of the cluster (ES)Li⁺(PC)₂(PC)_n (n=0,6, and 9) at B3PW91/6-311++G(d,p)/B3PW91/6-31G(d,p)

compound	E ^a	G _{sol} ^b	φ ⁰	Bond distance				ν/cm ⁻¹
				Li ⁺ -O ₁	Li ⁺ -O ₈	Li ⁺ -O ^c	C ₅ -O ₆	
(ES)Li ⁺ (PC) ₂								
16	0	0		1.912	1.883	1.890	1.447	
18	-101.9 (-70.4)	-68.5	1.58	1.898/2.032	2.002	2.031	1.440	
22(TS,18↔21)	-76.0 (-43.7)	-43.8		1.934/2.009	1.997	2.007	2.038	623i
21	-95.7 (-64.2)	-64.9	1.42	1.996/2.010	1.971	1.985		
[(ES)Li ⁺ (PC) ₂](PC) ₆								
31	0	0		1.885	1.864	1.864	1.445	
32	-94.1 (-75.0)	-75.8	1.90	1.880/2.003	1.997	2.020	1.443	
33(TS,32↔34)	-71.1 (-47.8)	-52.9		1.931/1.985	1.941	2.050	2.034	643i
34	-86.4 (-67.8)	-76.5	1.93	1.972/1.990	1.978	1.941		
1.80-2.0 ²³								
[(ES)Li ⁺ (PC) ₂](PC) ₉								
35	0	0		1.914	1.890	1.896	1.452	
36	-97.6 (-77.5)	-80.6	2.10	1.872/2.023	1.990	2.000	1.444	
37(TS,36↔38)	-72.2 (-50.8)	-51.4		1.929/1.990	1.978	2.001	2.024	657i
38	-89.5 (-69.3)	-72.6	1.76	1.951	1.939	1.981		

^aThe data in the parentheses are calculated at the PCM-B3PW91/6-311++G(d,p)/B3PW91/6-31G(d,p) level;

^b G_{sol} =E(PCM-B3PW91/6-311++G(d,p))+ thermal correction to Gibbs free energy at B3PW91/6-31G(d,p);

^cthe average distance from Li⁺ to oxygen of PC.