

Conduction of Li^+ cations in ethylene carbonate (EC) and propylene carbonate (PC): comparative studies using density functional theory

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Abstract Density functional theory is used to study the interaction of Li^+ cation with ethylene carbonate (EC) and propylene carbonate (PC) comparatively, which are the most popular solvents used in lithium-ion battery composite. In our theoretical calculations, we use DFT hybrid parameter B3LYP5 with a basis set 6–31G** by means of PCGAMESS/Firefly software package. We analyze the optimized structures of EC, PC, and their clusters including lithium-ion. We then calculate solvation energy, desolvation energy, electron affinity, Gibbs free energy, heats of formation of Li^+ solvated by EC and PC, and the charge on Li^+ . From the above analysis, we observe EC as a better solvent than PC in applications of lithium-ion batteries.

Keywords Propylene carbonate · Density functional theory · Lithium-ion battery · Solvation energy · Electron affinity

Introduction

Lithium-ion rechargeable batteries are widely used in electronic devices, tools, and vehicles as compared to the conventional batteries [1–6]. However, there are many challenges remain still regarding the safety requirements.

One of the key points regarding the safety concern is the use of organic solvents in lithium-ion batteries. The major solvents used for electrolytes are ethylene carbonate (EC), propylene carbonate (PC), and other linear carbonates such as diethyl carbonate. Experimental works report that EC could not cointercalate Li ion into graphite anode due to its high melting point (37 °C) [7], but enhances the intercalation of Li ion into the anode by forming a solid electrolyte interphase (SEI) film [8] of thickness 30–50 nm near the graphite anode, which is formed due to an interaction of electrolyte with solid anode metal. However, in case of PC, lithium-ion can cointercalate into the anode [9, 10], resulting in the exfoliation of the graphite accompanied by the formation of propene and hydrogen [10–14]. The reason is its high permittivity, which provides the electrolytes with high ionic conductivity and its low melting point (–49 °C), which provides a battery with better performance under low temperature [7, 15, 16]. At the same time, the reduction of PC on graphite anode has been well understood in applications of lithium-ion batteries [6, 7, 17, 18]. Due to different properties of EC and PC, EC-based solvent mixtures containing a large amount of linear carbonates such as dimethyl carbonate are widely used in lithium-ion batteries [8, 19]. The reductive decomposition of the solvent on graphite anode may also be enhanced by using SEI forming additives such as vinylene carbonate [20, 21]. The chemical stability of organic solvents directly affects the capacity, the cyclic stability, and the safety issues.

It is considered that Li^+ cation in the electrolyte solution consisting of organic solvent and supporting electrolyte is surrounded with a certain number of solvent molecules, known as solvation. Previous researches have reported the solvation number for Li^+ -organic solvent complexes by Raman intensity study [22, 23]. The solvation numbers for Li^+ has also theoretically been examined for EC and methyl

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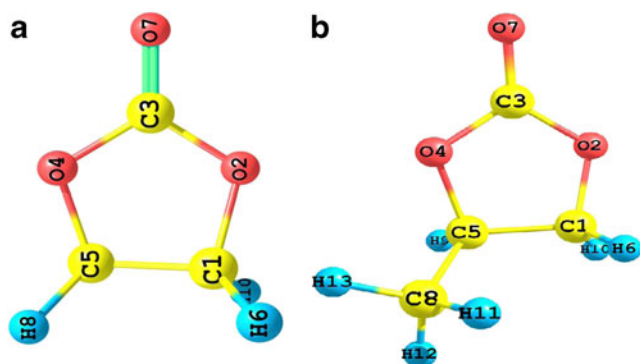
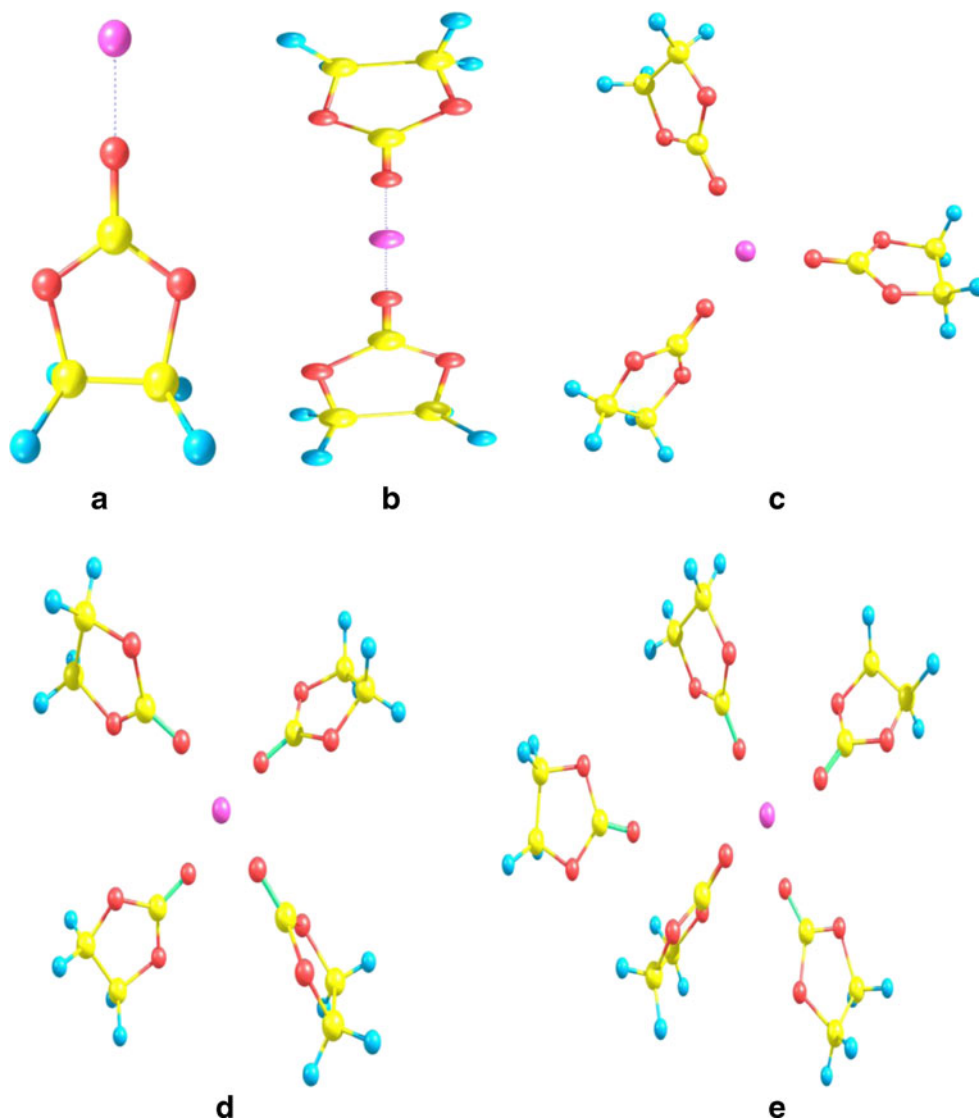


Fig. 1 Optimized structure of **a** EC molecule, **b** PC molecule

ethyl carbonate molecules using Hartree–Fock method [24]. From these experimental and theoretical investigations, the solvation number of Li^+ -EC complex has been estimated to be four [22, 24]. Solvation of Li^+ with PC molecules has not been investigated by sufficient researchers. Hence, in

Fig. 2 Optimized structure of **a** $[\text{Li}^+(\text{EC})_1]$ complex, **b** $[\text{Li}^+(\text{EC})_2]$ complex, **c** $[\text{Li}^+(\text{EC})_3]$ complex, **d** $[\text{Li}^+(\text{EC})_4]$ complex, and **e** $[\text{Li}^+(\text{EC})_5]$ complex

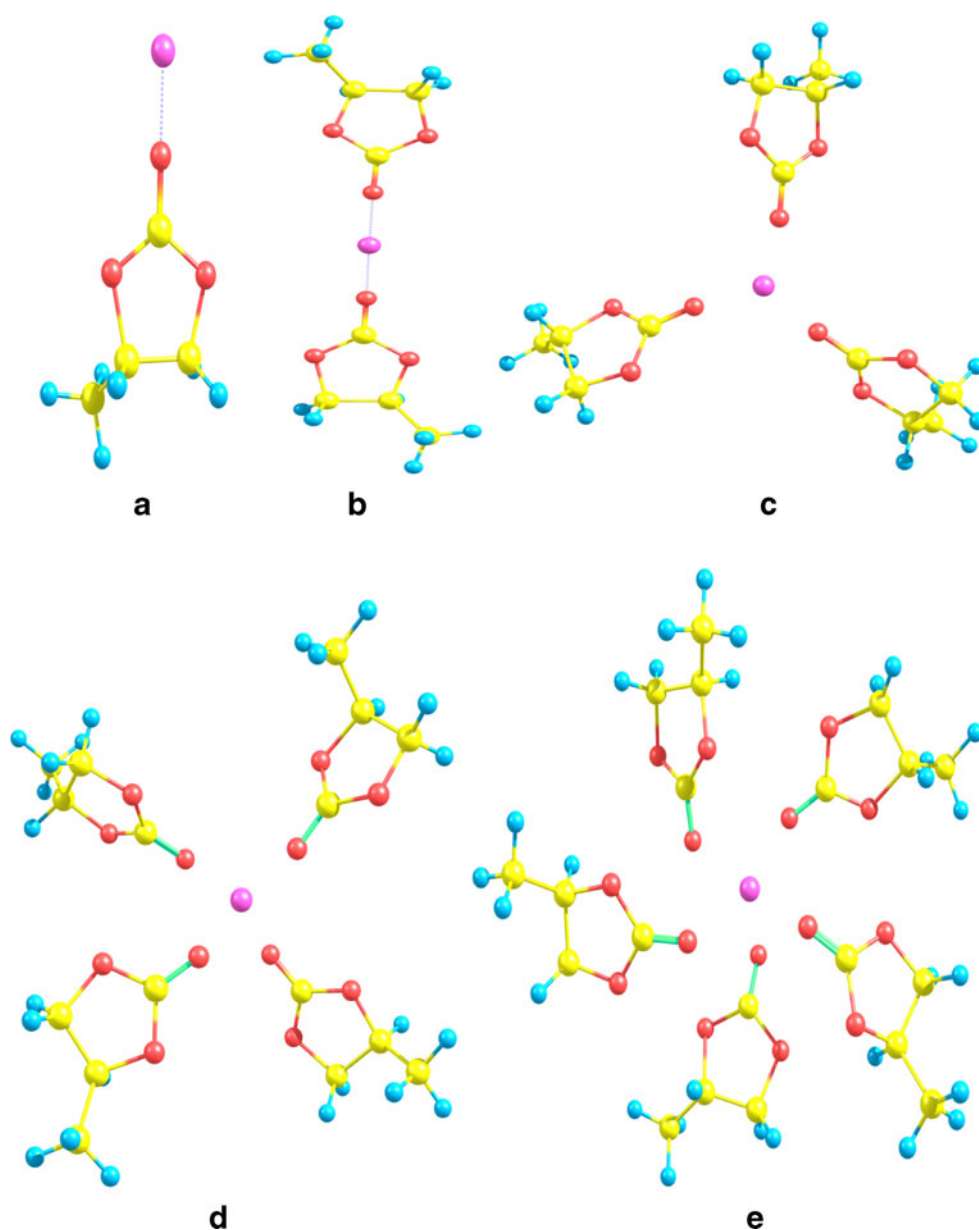


this research work, we perform density functional theory (DFT) calculations to clarify the electronic structures of the solvated Li^+ when PC is used as the solvent and also clarify the most appropriate number of PC molecules solvated to Li^+ . Besides these electronic structures, we calculate the comparative analysis of both EC and PC solvated to Li^+ regarding the solvation energy, desolvation energy, electron affinity, Gibbs free energy, heats of formation, and charge on Li^+ . The optimized structure of EC and PC with numerical labeling of atoms is shown in Fig. 1.

Computational details

The DFT calculations are performed with hybrid parameter B3LYP5 as implemented in PCGAMESS/Firefly software package [25]. The hybrid parameter B3LYP5 consists of exchange correlation function generalized gradient approxi-

Fig. 3 Optimized structure of **a** $[\text{Li}^+(\text{PC})_1]$ complex, **b** $[\text{Li}^+(\text{PC})_2]$ complex, **c** $[\text{Li}^+(\text{PC})_3]$ complex, **d** $[\text{Li}^+(\text{PC})_4]$ complex, and **e** $[\text{Li}^+(\text{PC})_5]$ complex



mation in the Becke [26], Lee-Yang-Parr [27], and VWN formula 5 [28]. The basis set is chosen as 6–31G** in our calculations. The approximate basis set superposition error [29] for all $[\text{Li}^+(\text{EC})_n]$ and $[\text{Li}^+(\text{PC})_n]$ complexes is calculated at the B3LYP5/6–31G** level using counterpoise method and is observed to be negligibly small.

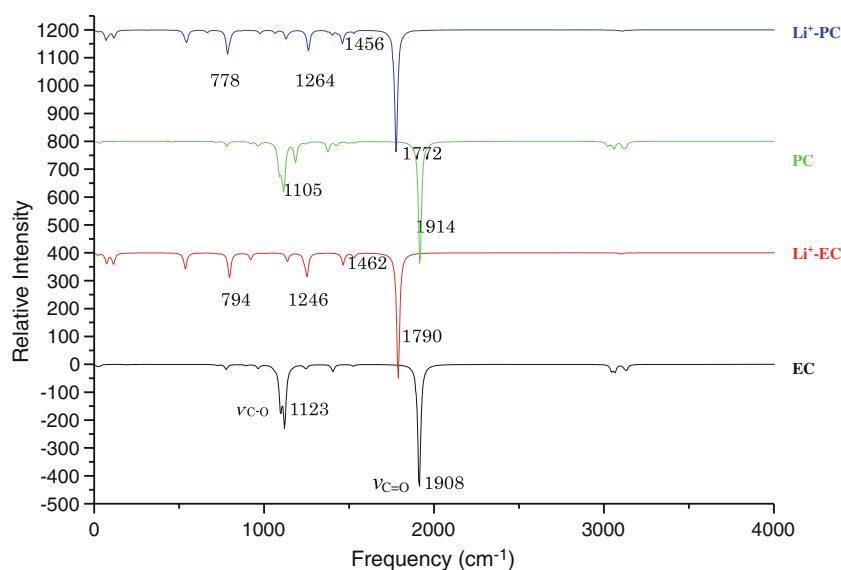
An isolated EC and PC molecule and their clusters including Li^+ are optimized at the B3LYP5/6–31G** level. The optimized structures of all clusters of EC and PC including lithium-ion are shown in Figs. 2 and 3, respectively. Once the optimized geometry is obtained, we analyze the optimized parameters in the first step. To confirm each optimized and stationary points and make zero-point energy corrections, frequency analyses are done with the same basis set. Enthalpy and Gibbs free energy are

obtained at 298.15 K. The charge distribution is analyzed by Mulliken population analysis. We calculate the solvation energy, desolvation energy, electron affinity of Li^+ solvated by EC and PC, and charge on Li^+ in the second step.

Results and discussion

The equilibrium geometry of an isolated solvent molecule, for example, EC is a topic that has received a considerable attention over experimental and theoretical research for a long time. To our knowledge, Angell [30] reported a planar structure of EC by observing the disappearance of some spectral lines in passing from solid to liquid and gas phases and attributed this to the enhanced symmetry when EC

Fig. 4 Simulated IR spectra of EC, Li⁺-EC, PC, and Li⁺-PC systems on the basis of B3LYP5/6–31 G (d, p) calculations



molecule passes from C₂ to C_{2v}. In contradiction, Alonso et al. [31, 32] and Matias et al. [33] reported a nonplanar structure of EC with microwave spectroscopy and neutron diffraction study. From the geometry optimization of EC, we have also found that the ring shows a nonplanar structure with C₂ symmetry. In organic electrolytes of lithium-ion batteries, carbonate molecules solvate Li⁺ ions and such solvation not only considerably affects salt dissociation, but also the solvent reduction potentials and their subsequent decompositions. For example, the solvent molecules coordinated to lithium-ions react more actively with the electrode [34]. Hence, due to its complexity, the solvation of lithium-ions in electrolyte solutions of lithium-ion batteries has been an interesting and still controversial topic [35, 36]. Only one type of Li⁺ coordination has been found with EC, through Li⁺-O. The interaction between Li⁺ and a solvent molecule can also be analyzed by the IR spectra, as illustrated in Fig. 4 for the Li⁺-EC and Li⁺-PC systems. In both cases, the asymmetric stretching frequency of C=O ($\nu_{C=O}$) is significantly decreased (1,908 vs. 1,790 cm⁻¹ for EC; 1,914 vs. 1,772 cm⁻¹ for PC), indicating that C=O is weakened by the interaction of Li⁺-O=C, whereas that of O-C (ν_{C-O} , O, linked with CH₂; C, carbonyl group) is increased (1,123 vs. 1,246 cm⁻¹ for EC; 1,105 vs. 1,264 cm⁻¹ for PC). Such variations are in line with the corresponding bond changes, i.e., C=O is

stretched (1.24 vs. 1.21 Å for EC; 1.25 vs. 1.21 Å for PC), and O-C (1.34 vs. 1.39 Å for EC; 1.34 vs. 1.40 Å for PC) is contracted. Table 1 lists the bond lengths R_1 and R_2 (in Å), and vibrational frequencies ν_1 and ν_2 (in cm⁻¹) of C=O before and after interaction with Li⁺ calculated at the B3LYP5/6–31G** level. It is also interesting to note that the coordination with Li⁺ changes the conformation of EC molecule slightly towards a more planar geometry. However, C1–C5 bond length does not seem to undergo any significant change as easily explainable by the proximity of Li⁺ to the carbonyl oxygen and its neighboring atoms. This is also true in case of PC molecule.

Because all complexes are found to be highly symmetrical, equilibrium values of internal coordinates are equal for all coordinating EC molecule in each cluster as reported in Table 2. The most dramatic effect of coordination appears in Li⁺(EC)₁ complex, where the O7–C3 bond is maximally stretched. With increasing number of EC molecules, Li⁺-O distance increases and its geometry approaches the value of isolated molecule. This is also true for Li⁺-PC complexes as shown in Table 3. It can be seen from Tables 2 to 3 that there is a good agreement between theory and experiment for optimized parameters of an isolated EC molecule [37]. For Li⁺(EC)₂, the EC ligands were positioned 180° from each other. For Li⁺(EC)₃, the EC molecules are trigonal planar, tetrahedral for Li⁺(EC)₄, and trigonal bipyramidal for Li⁺(EC)₅. The orientation of the molecules in each of the coordinated systems is selected to give the highest symmetry. This is also true for Li⁺(PC)_{2–5} complexes.

The structure of [Li⁺(S)_n] complexes is obtained by evaluating the solvation energy (ΔE_{solv}) of Li⁺ solvated by solvent S (EC and PC) using the equation:

$$\Delta E_{\text{solv}} = E_{\text{total}}[\text{Li}^+(\text{S})_n] - E_{\text{total}}[\text{Li}^+] - n \times E_{\text{total}}[\text{S}]$$

Table 1 Bond lengths R_1 and R_2 (in Å), and vibrational frequencies ν_1 and ν_2 (in cm⁻¹) of C=O before and after interaction with Li⁺ calculated at the B3LYP5/6–31G** level

Solvent	R_1	R_2	ΔR	ν_1	ν_2	$\Delta\nu$
EC	1.21	1.24	0.03	1,908	1,790	-118
PC	1.21	1.25	0.04	1,914	1,772	-142

Table 2 Results of the geometry optimization (bond lengths in ångstrom, and bond angles in degree) for the structure of EC (theory and experiment) and Li⁺(EC)_{1–5} complexes

Geometries	EC		Li ⁺ (EC) ₁	Li ⁺ (EC) ₂	Li ⁺ (EC) ₃	Li ⁺ (EC) ₄	Li ⁺ (EC) ₅
	Cal	Expt[37]					
Bond length in angstrom							
Li ⁺ -O	–	–	1.73	1.78	1.84	1.92	1.98
C3-O7	1.21	1.20	1.24	1.24	1.23	1.22	1.23
C3-O4	1.39	1.36	1.34	1.36	1.37	1.37	1.37
O4-C5	1.47	1.46	1.50	1.50	1.49	1.49	1.48
C1-C5	1.54	1.52	1.54	1.55	1.55	1.55	1.54
Bond angle in degree							
Li ⁺ O7-C3	–	–	179.9	179.1	178.5	152.5	148.6
O2-C3-O7	125.2	124.2	123.4	123.7	124.1	124.6	124.5
O4-C3-O2	109.5	111.7	113.2	112.5	111.8	111.4	111.5

where, $E_{total} [Li^+(S)_n]$, $E_{total} [Li^+]$, and $E_{total} [S]$ are total energy of Li⁺-S cluster, Li⁺, and solvent (EC and PC) molecule respectively. The value of n ranges 1–5. The variation of solvation energy of Li⁺ solvated by EC and PC is shown in Fig. 5. It is evident from Fig. 5 that EC has higher solvation energy (–53.48 kcal/mol) for its complex with Li⁺ than PC (–51.78 kcal/mol). Therefore, we conclude that Li⁺-EC complexes are more stable than Li⁺-PC complexes, which is caused due to the strong binding of Li atom with EC molecules as compared to PC molecules.

Moreover, the desolvation energy (ΔE_{desolv}) of Li solvated by solvent S (EC and PC) using the equation:

$$\Delta E_{desolv} = E_{total} [Li(S)_n] + E_{total} [S] - E_{total} [Li(S)_{n+1}]$$

where, $E_{total} [Li(S)_n]$, $E_{total} [S]$ and $E_{total} [Li(S)_{n+1}]$ are total energy of Li(S)_n cluster, solvent (S) molecule, and Li(S)_{n+1} cluster, respectively. The variation of desolvation energy of Li solvated by EC and PC is shown in Fig. 6. It is evident from Fig. 6 that PC gives rise to a higher desolvation energy than EC, which suggests that the Li⁺ may have more difficulty in inserting into the anode in PC than in EC. We know that the ability of one molecule to lose an electron depends on the energy of the highest occupied molecular

orbital (HOMO). The HOMO energy of EC and PC is –8.15 and –8.07 eV, respectively, indicating that the oxidative decomposition activity is in the order PC>EC. On the basis of this, EC is more stable against the oxidation than PC. However, due to the higher dielectric constant of EC, Li⁺ coordinates more easily with EC than with PC. The positive charge on lithium tends to transfer to the anode when the battery is charged.

In addition, the electron affinity of Li⁺ solvated by EC and PC is calculated using the equation:

$$EA = E_{total} [N+1] - E_{total} [N]$$

where, $E_{total} [M]$ and $E_{total} [N+1]$ represent the total energy of Li⁺-EC complexes with N and $(N+1)$ electrons, respectively. The variation of electron affinity of Li⁺ solvated by EC and PC as a function of solvation number is shown in Fig. 7. We observed, from Fig. 7, that Li⁺-EC complexes are more reducible than Li⁺-PC complexes. We know that the ability of one molecule to gain an electron depends on the energy level of the lowest unoccupied molecular orbital (LUMO). The LUMO energy of EC and PC is –0.31 and –0.33 eV, respectively, indicating the reductive decomposition activity is in the order EC>PC. On the basis of this, it seems that EC is more stable against

Table 3 Results of the geometry optimization (bond lengths in angstrom, and bond angles in degree) for the structure of PC and Li⁺(PC)_{1–5} complexes

Geometries	PC	Li ⁺ (PC) ₁	Li ⁺ (PC) ₂	Li ⁺ (PC) ₃	Li ⁺ (PC) ₄	Li ⁺ (PC) ₅
Bond length in angstrom						
Li ⁺ -O	–	1.73	1.77	1.84	1.93	2.02
C3-O7	1.21	1.25	1.24	1.23	1.23	1.23
C3-O4	1.40	1.34	1.36	1.36	1.37	1.38
O4-C5	1.48	1.53	1.52	1.51	1.51	1.50
C1-C5	1.54	1.55	1.55	1.55	1.55	1.54
Bond angle in degree						
Li ⁺ -O7-C3	–	179.2	179.2	172.2	141.5	125.9
O7-C3-O2	125.3	122.9	123.3	123.9	124.0	125.8
O2-C3-O4	109.5	113.3	112.6	111.8	111.3	110.8

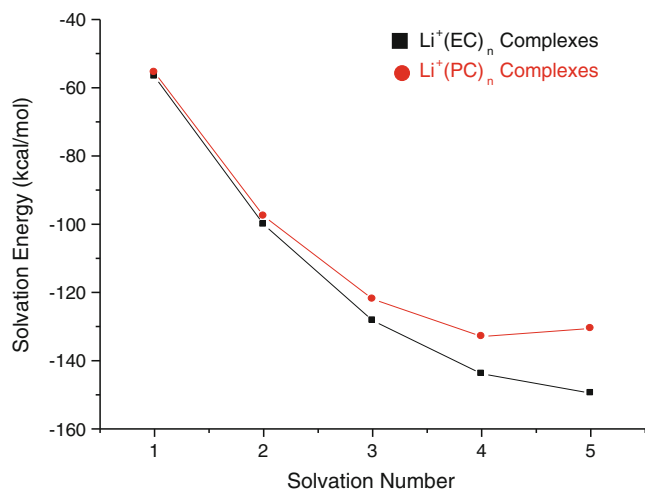


Fig. 5 Plot of solvation energy of Li⁺ solvated by EC and PC as a function of solvation number

reduction than PC molecules. The positive charge on lithium tends to transfer to the cathode when the battery is discharged. This calculated solvation energy, desolvation energy, and electron affinity of Li⁺ for EC and PC is in agreement with reference results [33].

Regarding the electrical analysis, we calculate the charge on Li⁺ for all complexes using Mulliken charge analysis. The plot of charge on Li⁺ as a function of solvation number is shown in Fig. 8. As in Fig. 8, it is clear that the charge on Li⁺ decreases significantly as the coordination increases. However, for coordination 4–5, there is no further decrease in charge of Li⁺. Finally, the question of the number of solvent (EC and PC) molecules in the primary solvation shell of the cation is outstanding. The number of solvent

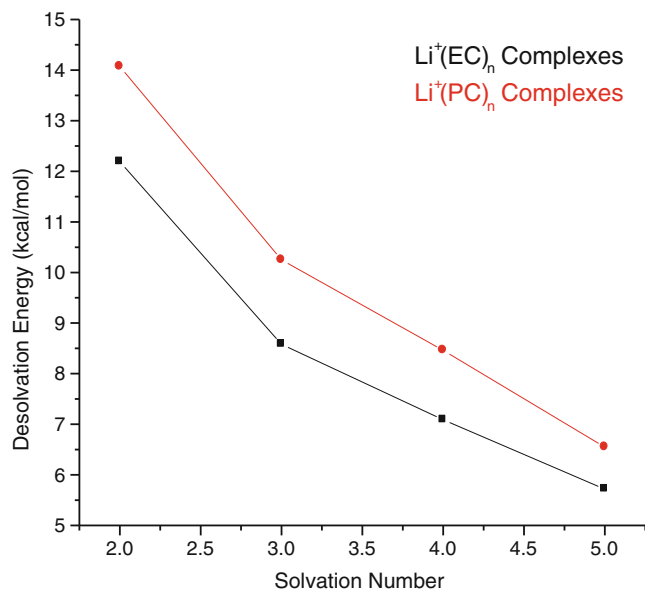


Fig. 6 Plot of desolvation energy of Li⁺ solvated by EC and PC as a function of solvation number

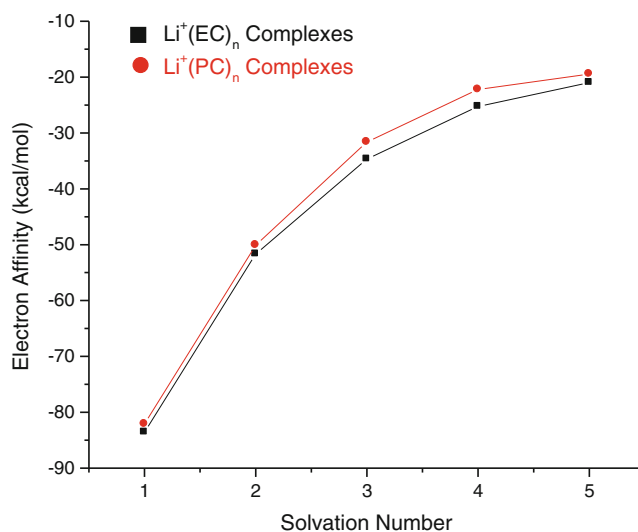


Fig. 7 Plot of electron affinity of Li⁺ solvated by EC and PC as a function of solvation number

molecules that can coordinate the lithium cation may be determined using an approximate enthalpy of reaction for coordination:

$$\Delta H = E[\text{Li}^+(\text{S})_n] - E[\text{Li}^+(\text{S})_{n-1}] - E(\text{S})$$

where E represents the ground-state calculated energies, n is the number of solvent molecules, ΔH is the enthalpy of the coordination reaction. The coordination reaction that corresponds to the enthalpy of reaction can be written as $\text{Li}^+(\text{S})_{n-1} + \text{S} = \text{Li}^+(\text{S})_n$

Results for the calculated Gibbs free energies of reaction and heats of formation for complexes of solvents with Li⁺ are presented in Table 4. Although the heats of formation reaction for Li⁺(EC)₅ is also exothermic, instead of

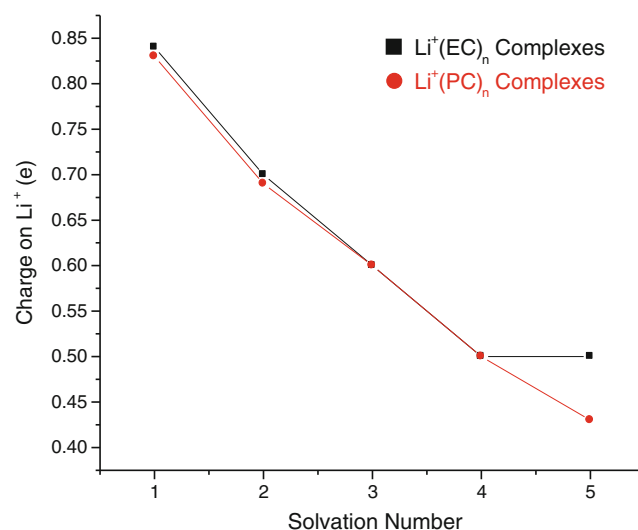


Fig. 8 Plot of charge on Li⁺ solvated by EC and PC as a function of solvation number

Table 4 Gibbs free energies and heats of formation for the coordination of EC and PC to Li⁺ calculated at the B3LYP5/6–31G** level

Reaction	ΔG (kcal/mol)	ΔH (kcal/mol)
Li ⁺ +EC=Li ⁺ (EC) ₁	–43.5	–49.7
Li ⁺ (EC) ₁ +EC=Li ⁺ (EC) ₂	–30.6	–39.3
Li ⁺ (EC) ₂ +EC=Li ⁺ (EC) ₃	–12.9	–23.8
Li ⁺ (EC) ₃ +EC=Li ⁺ (EC) ₄	–5.4	–13.3
Li ⁺ (EC) ₄ +EC=Li ⁺ (EC) ₅	9.6	–5.4
Li ⁺ +PC=Li ⁺ (PC) ₁	–43.2	–49.5
Li ⁺ (PC) ₁ +PC=Li ⁺ (PC) ₂	–28.4	–36.7
Li ⁺ (PC) ₂ +PC=Li ⁺ (PC) ₃	–11.6	–19.8
Li ⁺ (PC) ₃ +PC=Li ⁺ (PC) ₄	2.2	–11.2
Li ⁺ (PC) ₄ +PC=Li ⁺ (PC) ₅	7.8	–4.6

endothermic as predicted by with HF/6–31G* [35], its Gibbs free energy of formation (ΔG) is positive. Thereby, we conclude that the leading component is the four-coordinated complex, Li⁺(EC)₄. This result agrees with the conclusion from Raman intensity data [35] and classical molecular dynamics simulations [38]. The similar result is also obtained for Li⁺-PC complexes. It is evident from Table 4 that the Gibbs free energy of formation and heats of formation for Li⁺-EC complexes are larger than those for Li⁺-PC complexes, indicating EC as a better electrolyte than PC in applications of lithium-ion batteries.

Conclusions

Electronic structures of Li⁺-EC and Li⁺-PC complexes are studied by DFT. The structural and electrical properties of Li⁺-EC and Li⁺-PC complexes are studied comparatively. We analyze the optimized structures of EC, PC, and their clusters including one lithium-ion. We then calculate solvation energy, desolvation energy, electron affinity, Gibbs free energy, and heats of formation of Li⁺ solvated by EC and PC; and the charge on Li⁺. Our analysis shows EC as a more stable electrolyte than PC in applications of lithium-ion batteries.

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