

Deciphering the Ethylene Carbonate–Propylene Carbonate Mystery in Li-Ion Batteries

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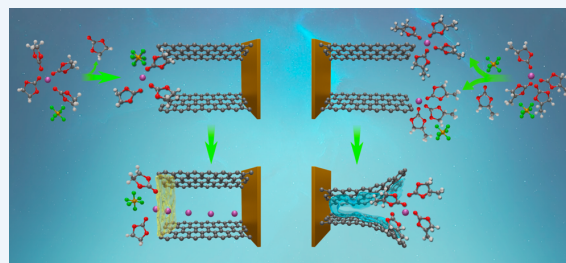
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Supporting Information

CONSPECTUS: As one of the landmark technologies, Li-ion batteries (LIBs) have reshaped our life in the 21st century, but molecular-level understanding about the mechanism underneath this young chemistry is still insufficient. Despite their deceptively simple appearances with just three active components (cathode and anode separated by electrolyte), the actual processes in LIBs involve complexities at all length-scales, from Li^+ migration within electrode lattices or across crystalline boundaries and interfaces to the Li^+ accommodation and dislocation at potentials far away from the thermodynamic equilibria of electrolytes. Among all, the interphases situated between electrodes and electrolytes remain the most elusive component in LIBs.

Interphases form because no electrolyte component (salt anion, solvent molecules) could remain thermodynamically stable at the extreme potentials where electrodes in modern LIBs operate, and their chemical ingredients come from the sacrificial decompositions of electrolyte components. The presence of an interphase on electrodes ensures reversibility of Li^+ intercalation chemistry in anode and cathode at extreme potentials and defines the cycle life, power and energy densities, and even safety of the eventual LIBs device. Despite such importance and numerous investigations dedicated in the past two decades, we still cannot explain why, nor predict whether, certain electrolyte solvents can form a protective interphase to support the reversible Li^+ intercalation chemistries while others destroy the electrode structure. The most representative example is the long-standing “EC–PC Disparity” and the two interphasial extremities induced therefrom: differing by only one methyl substituent, ethylene carbonate (EC) forms almost ideal interphases on the graphitic anode, thus becoming the indispensable solvent in all LIBs manufactured today, while propylene carbonate (PC) does not form any protective interphase, leading to catastrophic exfoliation of the graphitic structure. With one after another hypotheses proposed but none satisfactorily rationalizing this disparity on the molecular level, this mystery has been puzzling the battery and electrochemistry community for decades.

In this Account, we attempted to decipher this mystery by reviewing the key factors that govern the interaction between the graphitic structure and the solvated Li^+ right before interphase formation. Combining DFT calculation and experiments, we identified the partial desolvation of the solvated Li^+ at graphite edge sites as a critical step, in which the competitive solvation of Li^+ by anion and solvent molecules dictates whether an electrolyte is destined to form a protective interphase. Applying this model to the knowledge of relative Li^+ solvation energy and frontier molecular orbital energy gap, it becomes theoretically possible now to predict whether a new solvent or anion would form a complex with Li^+ leading to desirable interphases. Such molecular-level understanding of interphasial processes provides guiding principles to the effort of tailor-designing new electrolyte systems for more aggressive battery chemistries beyond Li-ion.



Formed during the initial charging cycles of Li-ion batteries (LIBs) and situated between the graphitic anode and the electrolytes, the solid–electrolyte interphase (SEI) in LIBs is the key component that enables the reversible Li^+ intercalation chemistry at a potential (~ 0.20 V vs Li) far beyond the

reduction limit of the electrolyte components (solvents, anions).^{1–3} Twenty-five years after the birth of LIBs chemistry,

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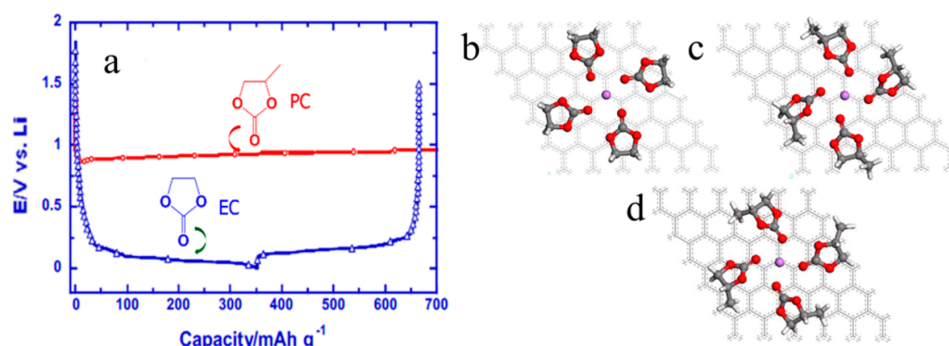


Figure 1. (a) “EC–PC Disparity” represents two extremes of interphasial chemistry on graphitic anodes, which are induced by the minuscule structural difference between the two carbonate molecules. Reproduced with permission from ref 8. Copyright 2009 Electrochemical Society. Optimized conformational structures (top views) of (b) $\text{Li}^+(\text{EC})_4\text{C}_{72}$, (c) *trans*- $\text{Li}^+(\text{PC})_4\text{C}_{72}$, and (d) *cis*- $\text{Li}^+(\text{PC})_4\text{C}_{72}$. Reproduced with permission from ref 18. Copyright 2011 Elsevier.

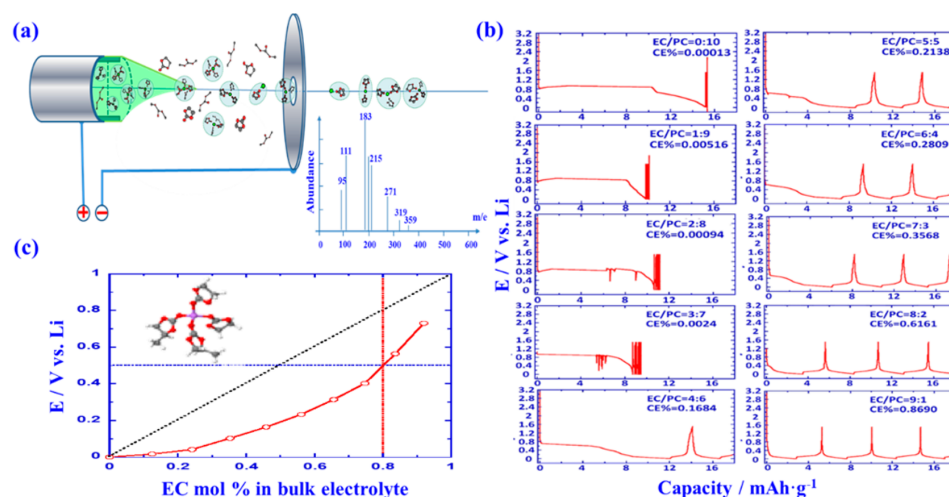


Figure 2. (a) Schematic illustration of quantitative measurement of Li^+ solvation sheath structure using electrospray ionization mass spectra. (b) Effect of successive replacement of PC with EC on interphase effectiveness, where EC/PC molar ratios and Coulombic efficiency (CE%) were labeled in individual graphs. Note that a sudden change in CE% occurs at bulk composition of EC/PC = 80:20. Reproduced with permission from ref 16. Copyright 2012 American Chemical Society; (c) The statistical correlation between the EC% in Li^+ solvation sheath as identified by ESI-MS and the EC/PC molar ratio in bulk electrolyte. Note that at the bulk composition of EC/PC = 80:20, there is exactly 50% EC in the Li^+ solvation sheath, which constitutes the threshold of forming a protective SEI. Reproduced with permission from ref 16. Copyright 2012 American Chemical Society.

despite its omnipresence in our life, researchers still struggle to understand most of the processes happening around this interphase, as well as the mechanisms and chemistry governing its formation.^{4,5} Quoting Winter, the SEI remains “the most important but least understood” component in LIBs.⁶ We do not fully understand how Li^+ migrates through the interphase, and we cannot explain why, let alone predict whether, certain electrolyte compositions can eventually form a protective SEI or instead lead to sustained irreversible reactions that destroy the fragile graphitic structure. The most classical example is perhaps the “EC–PC Disparity”, where the minuscule structural difference caused by a single methyl group between ethylene carbonate (EC) and propylene carbonate (PC) results in two extremities of interphasial behavior:^{7,8} the incessantly irreversible reduction of PC-based electrolyte at ~0.7 V and the consequent “exfoliation” of the graphite structure, in sharp

contrast to the reversible Li^+ interaction/deintercalation enabled by EC-based electrolyte at ~0.1 V (Figure 1a). Given the size of methyl (~0.2 nm), one could intuitively infer that the above selectivity must be related to the graphitic structure, whose 0.33 nm edge-site most likely serves as a sensitive sub-nanometer probe to the structural difference between EC and PC.

Most of the investigated aprotic solvents demonstrate similar electrochemical behaviors as PC, that is, endless decomposition followed by graphite exfoliation. This limitation reluctantly makes EC the indispensable electrolyte solvent in all LIBs manufactured today, despite its many intrinsic disadvantages, such as high melting point, high viscosity, narrow liquid range, and low anodic stability. In the absence of molecular-level understanding about interphasial chemistry, the efforts of

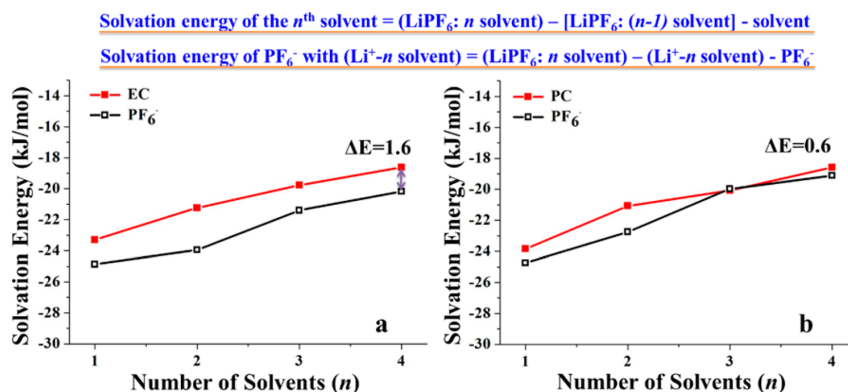


Figure 3. Solvation energy of solvent molecules and PF_6^- with Li^+ in (a) EC- and (b) PC-based electrolytes.

developing new electrolytes have not been a rigorous science but semiempirical trial-and-error.

Chemically speaking, the SEI has been known to consist of salt-like products from the sacrificial decomposition of electrolyte components, the most dominant of which are lithium alkylcarbonates originating from the single-electron reduction of carbonate molecules. This solvent-originated SEI is often decorated with sporadic inorganic species such as LiPO_xF_y and LiF , apparently originating from the lithium salt anion PF_6^- . The role of these inorganic species in SEI was never clear and has been controversial.^{2,3,9} More uncertain is the formation mechanism. Besenhard and Winter et al. were the first to realize the critical role of electrode surface structure in directing the arrangement of ions and solvent molecules before the interphase formation. They suggested that the solvated Li^+ co-intercalates into the edge-sites of graphite,¹⁰ forming a transient “ternary graphite intercalation compound (GIC)” with expanded interlayer distance, whose eventual decomposition leads to the formation of a 3D-interphase with slight penetration into the graphitic structure. Inspired by Besenhard and Winter, Xu et al. further inferred that the primary solvation sheath of Li^+ must constitute the chemical precursor for the interphase formed thereafter.^{11,12} This “solvation–co-intercalation–decomposition” model successfully explains the correlations existing among electrolyte bulk composition, Li^+ solvation sheath structure, and the eventual interphase chemistry, as supported later on by diverse experiments.^{13–16} Some of the work even achieved quantitative rationale for the correlation between Li^+ solvation sheath structure as measured by EC % found within the solvation sheath and interphase effectiveness as quantified by the Coulombic efficiencies, as exemplified by the electrolytes based on EC–PC mixtures (Figure 2).

However, this elegant model still stops short of either rationalizing the difference between EC and PC in interphasial chemistry or predicting what solvent structure can eventually lead to a protective interphase. During the past two decades there have been very rare efforts that directly address the EC–PC disparity. Zhuang et al. once argued that the reductions of PC and EC might follow different electrochemical pathways, with PC favoring a two-electron reduction process that directly produces Li_2CO_3 and propylene, which destroys the graphitic structure.¹⁷ However, this hypothesis contradicts the spectral studies by Xu et al, who showed that single-electron pathway was actually followed by both EC and PC, as evidenced by the alkylcarbonates generated.¹² Tasaki et al. approached this

interphasial mystery from the ternary GICs as proposed by Besenhard and Winter and held the bulkier geometry of $[\text{Li}(\text{PC})_n]^+$ responsible for the graphite exfoliation (Figure 1b,c,d),¹⁸ because the presence of the methyl group would force the graphite interlayer distance in the ternary GIC to increase from 0.69 to 0.85 nm if PC replaces EC in the solvation complex $\text{Li}^+(\text{solv})_4$. This additional strain is sufficient to exfoliate the graphene layers from each other. However, EC-like behavior has been observed with molecules bulkier than PC, which apparently rules out the pure geometric consideration as a convincing rationale.¹⁹ Interestingly, although Tasaki’s calculation already considers the existence of PF_6^- in the graphitic interlayer, its role in reduction was completely ignored, which counters the fact that the reduction products of PF_6^- often abound in the inner layer of the SEI.

We believe that, while the solvation–co-intercalation–decomposition model and its variations correctly described how a 3D-SEI is formed at graphite edge sites facing the electrolyte, its imperfection arises from its oversimplification when visualizing how a solvated Li^+ approaches the graphitic structure and interacts with it thereafter. First, its co-intercalation has been treated as if the whole primary solvation sheath would remain intact, while partial desolvation very likely occurs before solvated Li^+ enters the interlayer of the graphitic structure. Second, the anion presence has been almost completely neglected in the previous models proposed by Xu^{11,12} or Tasaki,¹⁸ while global electroneutrality requires that anion is within a certain distance from the Li^+ primary solvation sheath, although such anion presence could be simultaneously “transient” and “partial”, due to the solvation of Li^+ by the polarizable lone-pairs sitting on solvent molecules. Hence, when a solvated Li^+ approaches the graphitic edge sites, the competition between solvent molecule and anion might decide what species remain with the solvated Li^+ and become the subsequent SEI precursors.

To investigate such interplay, we conducted a thought experiment similar to that of the Born–Haber cycle, that is, simulating the dissolution process of LiPF_6 by adding the investigated solvent molecules one by one until its complete ionization. During the process, various possible solvation structures are considered, with only the most stable optimized structures presented in Figure S1. Clearly, for both solvents a “contact ion pair solvation structure” prevails whenever the solvent number is less than 4. Only when the solvent number increases to 4 does the solvent– Li^+ interaction become strong

enough to segregate Li^+ from PF_6^- , generating a “solvent-separated ion structure”. Further increasing the solvent number to 5 drives the solvation energy into the positive realm, which is energetically unfavorable. Hence, the maximal number of solvent molecules should be considered 4. Such a “solvent-separated ion structure” consists of a Li^+ tetrahedrally solvated by 4 solvent molecules forming a primary solvation shell, with an anion in the vicinity but outside of the primary sheath. The complex species, although remaining globally electroneutral, should be the prevailing entity transporting in the electrolyte bulk, because the anion actually does not belong to a discrete solvation sheath and instead should be shared by multiple solvated Li^+ ; therefore its contribution to each solvation sheath accounts only for a fraction of its formal charge. Upon application of an electric field, instantaneous polarization of the solvent-separated Li^+ –anion complex would induce its migration.

During the very first lithiation process, the decreasing potential of graphite anode generates such an electric field, attracting the solvated Li^+ to the edge sites of graphite.²⁰ Since the interlayer distance of pristine graphite (0.33 nm) cannot directly accommodate a solvated Li^+ complex (>1.0 nm), the graphitic structure would expand under the strain, as observed by Besenhard and Winter et al. with both dilatometry and in situ XRD.^{10,15} Meanwhile, the solvated Li^+ faces the stripping force from the narrow interlayer pathway and is forced to lose a member of the solvent-separated Li^+ –anion complex so that the energy barrier of co-intercalation could be minimized. How this partial desolvation proceeds significantly depends on the competitive interaction of solvents and anion with Li^+ , as quantified by the solvation energy shown in Figure 3 a,b.

For EC, in the entire solvation number range 1 through 4, its solvation energy is always smaller (weaker) than PF_6^- (Figure 3a), indicating that during this partial desolvation process, EC solvent will statistically lose to PF_6^- in its attempt to remain in the primary Li^+ solvation sheath. Such a partially desolvated Li^+ containing PF_6^- would then co-intercalate into the graphitic structure and form a ternary GIC, whose fate is to become the chemical precursors to the final SEI via reductive decomposition. Needless to say, such an SEI would bear the chemical signature of both solvent origin (lithium ethylene dicarbonate, LEDC) and anion origin (LiF), with substantial presence of the latter.

In stark contrast, the solvation energy of the fourth PC is only 0.6 kJ/mol smaller than PF_6^- (Figure 3b), suggesting that during the partial desolvation, the probability of the Li^+ solvation sheath losing PF_6^- is slightly lower than that of PC. Hence, comparing with that of EC, the anion-free solvation structure of $\text{Li}^+(\text{PC})_4$ has higher chance to occur during the co-intercalation from PC based electrolyte. Naturally, such co-intercalation would predominantly lead to ingredients from the solvent reductive decomposition, or lithium propylene dicarbonate (LPDC), with LiF being a relative minority. In other words, the key difference between the EC- and PC-based Li^+ solvation sheath is how they generate the precursor to co-intercalation at graphite: the former apparently tends to form a GIC with higher anion population than the latter. These different GIC intermediates naturally lead to different surface products, and what differentiates the two extremes of interphasial chemistries as shown in Figure 1a is the LiF-content in each case.

To experimentally confirm the above prediction made by DFT calculation, graphitic anodes were electrochemically

cycled in various electrolytes based on neat EC, neat PC, or a mixture of EC and ethylmethyl carbonate (EMC), the latter being a typical representative of the electrolytes used in commercial LIBs. The lithium salts selected are lithium hexafluorophosphate (LiPF_6 , the industry standard) and lithium bis(fluorosulfonyl) imide (LiFSI), which is a new favorite for beyond-Li-ion battery chemistries. These graphite anodes were recovered for chemical analysis using X-ray photoelectron spectra (XPS). The voltage-profiles of the electrochemical cycling and XPS are shown in Figures S2 and S3, while Table 1

Table 1. LiF Content as Found on the Surface of Cycled Graphite Anode

sample	pristine graphite	1.0 M LiPF_6 EC	1.2 M LiPF_6 EC/ EMC	1.0 M LiPF_6 PC	3.5 M LiPF_6 PC	3.5 M LiFSI PC
LiF % ^a	0	67.11	65.47	54.53	68.94	70.14
PVDF %	100	32.89	34.53	45.47	31.06	29.86

^aRelative content vs poly(vinylidene fluoride) (PVDF), which is used as binder in the graphite anode and serves as reference for LiF content estimation.

quantitatively summarizes the relative content of LiF found on surfaces of graphite as identified by F 1s at ~687 eV. The SEI formed in electrolytes based on both neat EC and EC/EMC (3:7) are apparently richer in LiF than that formed in neat PC at similar salt concentration.

The above scenario could be reversed when there is an unusually high anion population in the electrolyte to compete with PC, such as the so-called “super-concentrated electrolyte”. Experiment found that when LiPF_6 or LiFSI were used at >3 M, the graphite electrode can be reversibly cycled in neat PC electrolytes with almost ideal Li^+ intercalation behavior (Figure S2), an indication that protective SEI has been formed. XPS confirmed the accompanied higher LiF content in the resultant SEI (Figure S3, Table 1). In this sense, the reported “abnormal interphasial behavior” observed at ultrahigh salt concentrations was rooted in the changed Li^+ solvation structure.^{9,21–24}

Thus, we conclude that LiF content in the SEI, as result of the competitive solvation toward Li^+ between solvent and anion, constitutes the key factor responsible for the “EC–PC Disparity”. While the rationale behind how LEDC, LPDC, and LiF work on a molecular level in the interphase will be discussed later, the reason causing the difference in initial desolvation processes of EC and PC is the atomic charge density of =O and alkyl groups in these solvents, as shown in Figure S4. Hence, a methyl group of sub-nanosize induces a “mighty” difference in solvating power of these two solvent molecules, resulting in a drastic change in their macroscopic electrochemical behaviors.

It should be emphasized that the above model is specific to the typical LIBs electrolytes that are based on LiPF_6 dissolved in carbonate solvents. When the model is applied to a broader context, this model actually hints at the balanced contribution between solvent molecules and anion. For example, when the salt anion does not contain fluorine, whether PC-based electrolytes exfoliate graphite depends on several factors, such as the reduction potential of the anion carbonate solvent and especially whether the reduction product can stabilize graphitic structure. A typical example is lithium bis(oxaloborate) (LiBOB), whose high reduction potential at 1.7 V vs Li and the subsequent oxalate products enable PC electrolytes to support the lithiation chemistry of graphitic anode with

electrochemical behaviors (voltage profile, Coulombic efficiency) similar to EC, even when LiBOB concentration is <1.0 M.²⁵

In our previous works, we have demonstrated how PF_6^- significantly reduces the oxidative stability of electrolyte.^{26,27} In this work, how PF_6^- participates the reductive decomposition of Li^+ solvation sheath and how it affects the reductive activity of carbonate molecules become the topic of interest. Single-electron reduction of isolated solvent or anion was calculated and shown in Figure S5. The decomposition of PF_6^- directly generates PF_5 and F^- , which would form LiF with Li^+ . Interestingly, the reductive activity of PF_6^- is found to be lower than both EC and PC; hence it is thermodynamically improbable for an isolated PF_6^- to gain an electron (be reduced, expressing as +e in this work). The only possibility for PF_6^- to gain an electron is to present in a complex with Li^+ . The optimized structure of Li^+ solvation sheath without PF_6^- before and after one electron reduction is presented in Figure S6 and Figure S7, respectively, while the calculated electron affinity energy is given in Figure S8. In comparison with Figure S5 and Figure S8, it becomes clear that the existence of Li^+ significantly increases the reductive activity of solvents, although it does not change their reaction activity order. This obtained order is in excellent agreement with that reported using B3LYP/6-311+G(2d,p) and GGA-PBE/TNP methods.¹⁸ The effect of Li^+ on the reductive activity of both solvent and anion suggests that in electrolyte the electrochemical reactions of isolated solvent or ion is unlikely; instead, coordination or interaction with Li^+ provides an ideal reactant complex that could accept electron via the most probable pathway.

Figure 4 presents the optimized structure of PF_6^- -containing Li^+ solvation complex after single-electron reduction. For the

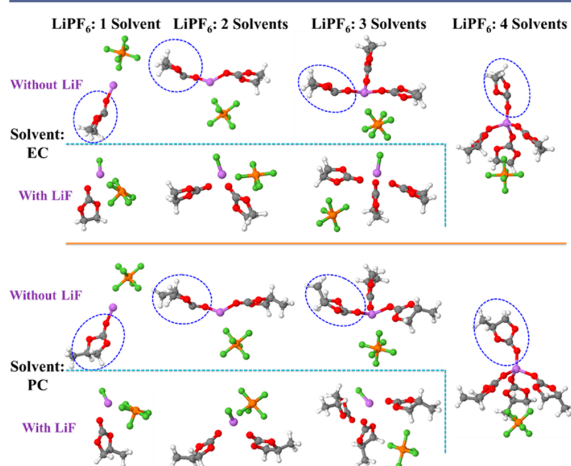


Figure 4. Optimized structures of $(\text{LiPF}_6/n \text{ solvent})$ ($n = 1-4$) solvation complexes after single-electron reduction. The reduced solvent is highlighted with dotted circle.

contact ion pair solvation structure ($n \leq 3$), the reductive reaction is more complicated, because the electron can either distribute on one solvent or PF_6^- ; while for the solvent-separated ion structure, the electron can only distribute on one solvent. Electron distribution on PF_6^- directly leads to the breakage of P–F bond, and most importantly, generates LiF. Figure 5a shows the calculated electron affinity energy of the corresponding solvation complexes. Surprisingly, although the

reductive activity of the isolated PF_6^- is lower than individual solvents, the gained electron prefers to reside on PF_6^- instead of solvent molecule ($n \leq 3$), leading to dramatically higher electron affinity energy of the former than the latter. This suggests that increasing the salt concentration of PC-based electrolyte would increase the reductive activity of electrolyte, which is exactly what is observed in experiments as reported by Nie et al.⁹ and Suo et al.²² as well as this work (Figure S2). The higher LiF-content generated at higher LiPF_6 concentration in PC (Table 1) directly supports the correlation between a LiF-rich SEI and a well-protected graphite anode.

It is important to point out that a solvation sheath of lower reductive activity would result in more serious solvent co-insertion. An extreme example is the solvation sheaths consisting of ether solvents such as dimethoxyethane (DME), whose unique cathodic stability allows almost reversible intercalation/deintercalation of $\text{Li}^+(\text{DME})_4$ or $\text{Na}^+(\text{DME})_4$ in the graphitic anode.²⁸ For practical battery considerations, a more protective SEI requires less cathodic stability, and hence approaches of increasing the reactivity of the Li^+ solvation sheath were often adopted in development of new electrolyte formulations, including using electrolyte components of lower LUMO (lowest unoccupied molecular orbital) energy level or lithium salts at concentrations higher than what ion conductivity considerations would require.

After decomposition happens to the co-intercalated Li^+ solvation complex, is there difference between the reduction products from EC and PC?

It has been well-known that the single-electron reduction of solvents would lead to LEDC (from EC), LPDC (from PC), or other alkylcarbonate salts generated from linear carbonate molecules, while F-containing anion generates LiF and other inorganic species. A composite SEI formed during the initial cycles of LIBs would be highly heterogeneous consisting of all these products. The structure–property relationship among these SEI components has been comprehensively reviewed by Qi et al.²⁹ Nevertheless, how these species arrange themselves in the SEI and how Li^+ transports through them remain to be understood. While the above analysis identifies LiF as a key-factor in determining whether a protective interphase forms at the graphite/electrolyte junctions, other salts with carbonate origin should not be neglected, simply because an SEI consisting of LiF alone would certainly fail, given that LiF is an insulator not only to electron but also to ion conduction.

In order to constitute a compact, insoluble, and protective interphase, ideal SEI components should have flat configuration, low solubility in electrolytes, high ion conduction, and high electronic insulation. Earlier reports have described that LPDC inclines to remain as monomer,³⁰ which shows weaker intermolecular cohesion and results in higher solubility in electrolyte than that of LEDC,⁸ while LEDC has a strong tendency to form dimer and is significantly less soluble. On the other hand, to the best of our knowledge, there has been no serious discussion over the electronic insulation capability of these interphasial components to date. The optimized structure and frontier molecular orbital energy of the above products is hence calculated (Figure 5b). As comparison we also calculated Li_2CO_3 , which is also often found in SEI either as chemical or electrochemical decomposition products of alkylcarbonates but was never considered as an effective SEI component, despite its similar solubility and compact configuration to LEDC.

As shown in Figure 5b, the curving chain structure of LPDC tends to build loose deposit products, leading to poor cohesion

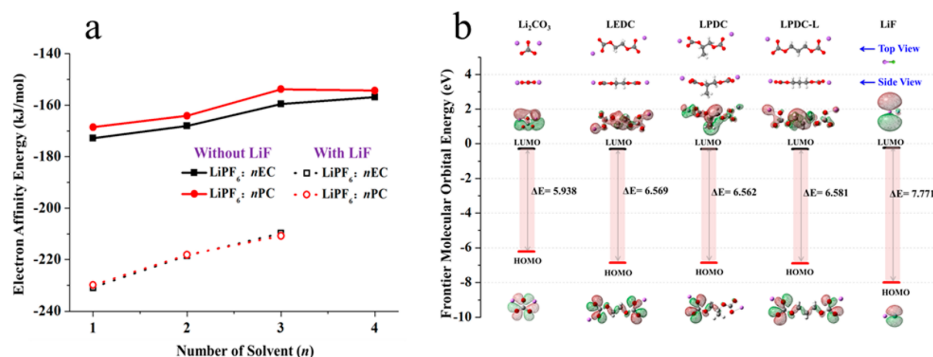


Figure 5. (a) Calculated electron affinity energy of (LiPF₆/n solvent) ($n = 1-4$) solvation sheaths and (b) frontier molecular orbital energy and the LUMO–HOMO energy gap of Li₂CO₃, LEDC, LPDC, LPDC-L and LiF, together with their corresponding optimized structure and molecular orbital diagrams.

and poor resistance against dissolution. However, the structures of Li₂CO₃, LEDC, and LiF all enable sufficiently flat configurations that lead to compact insoluble products. A question is thus raised regarding why Li₂CO₃ does not effectively serve as SEI component to protect graphitic anode even though it should generate a compact film. We found that the answer may lie in the electronic insulation capability, which can be quantified by the energy gap between the LUMO and HOMO (highest occupied molecular orbital). Figure 5b clearly shows that such gap for the investigated components decreases in the order of LiF > LPDC ≈ LEDC > Li₂CO₃. Obviously, Li₂CO₃ cannot effectively insulate the electron tunneling from the highly negatively charged electrode to the electrolyte components, resulting in sustained decomposition of electrolyte at low electrode potential. Among those, LiF shows the best electrical insulation. The LUMO–HOMO energy gap of LPDC is comparable to that of LEDC, indicating similar electron insulating capability for the two. Therefore, the main reason that LPDC fails to passivate the electrode surface is ascribed to its bent structure. Any external factors that help LPDC to pack densely would increase the passivation capability of LPDC. On the other hand, LPDC may reform its configuration via a radical transfer to generate an isomeric LPDC-L with a flat structure (Figure S9 and 10). In this case, LPDC-L could passivate the electrode surface as reported recently.³¹ However, the energy barrier for such radical transfer reaction is rather high (181.7 kJ/mol), which makes the majority of the decomposition products from PC to be LPDC rather than LPDC-L.

In conclusion, combining DFT calculation with electrochemical and spectral experiments, we vigorously examined the process of a solvated Li⁺ interacting with graphitic structure and successfully explained on the molecular level the origin of the so-called “EC–PC disparity”, which is actually created by the difference in EC and PC’s relative competitiveness to solvate Li⁺ against F-containing anion. It is revealed that the partial desolvation behavior of Li⁺ solvation complex during its initial co-intercalation into graphite structure predetermines which solvent is destined to form a protective SEI. High salt concentrations could reverse the above disparity, as relative competitiveness could be altered due to increase in anion population or F-donation capability. In a broader sense, the Li⁺ solvation complex serves as a precursor for electrode surface reductions, which provides a variety of reaction pathways with different energy barriers, and EC–PC disparity just reflects the

options of the lowest energy barriers in each case. By comparing frontier molecular orbital energy, we also found the correlation between the HOMO–LUMO gap and the effectiveness of various solvent/anion decomposition products in protecting the graphitic anode. Such understanding not only modifies the established laws regarding interphase formation. As a very insightful tool to predict whether a new electrolyte component, no matter whether solvent or anion, could lead to a desirable interphasial chemistry, it also provides guiding principles to custom-design an ideal electrolyte system and interphases for new battery chemistries beyond Li-ion.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.accounts.7b00474.

Computational details, definition of various energies, optimized structures of (LiPF₆/n solvent) ($n = 1-5$) solvation shells, first discharge/charge curves of the investigated electrolytes, high resolution F 1s XPS spectra of graphite electrodes after sixth discharge, NBO atomic charge distribution of the investigated ions and solvents and solvation energy of solvent with Li⁺ and with PF₆[−], optimized structures and calculated electron affinity energies of Li⁺, PF₆[−], EC, and PC before and after reduction, optimized structures of (Li⁺/n solvent) ($n = 1-4$) solvation shells before and after one electron reduction reaction, calculated electron affinity energy of (Li⁺/n solvent) ($n = 1-4$) solvation shells, possible decomposition paths of EC–Li⁺ + e and PC–Li⁺ + e, and possible termination reactions of the main decomposition products of EC–Li⁺ + e and PC–Li⁺ + e. (PDF)

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