Anion Solvation in Carbonate-Based Electrolytes

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Supporting Information

ABSTRACT: With the correlation between Li^+ solvation and interphasial chemistry on anodes firmly established in Li-ion batteries, the effect of cation–solvent interaction has gone beyond bulk thermodynamic and transport properties and become an essential element that determines the reversibility of electrochemistry and kinetics of Li-ion intercalation chemistries. As of now, most studies are dedicated to the solvation of Li^+ , and the solvation of anions in carbonate-based electrolytes and its possible effect on the electrochemical stability of such electrolytes remains little understood. As a mirror effort to prior Li^+ solvation studies, this work focuses on the interactions between carbonate-based solvents and two anions (hexafluorophosphate, PF_6^- , and tetrafluoroborate, BF_4^-) that are most frequently used in Li-ion batteries. The possible correlation between such interaction and the interphasial chemistry on cathode surface is also explored.

INTRODUCTION

Li-ion intercalation chemistries are supported by the *ad hoc* formation of interphases on electrode surfaces.¹ Such interphases are solid electrolytes in nature, i.e., electronically insulating to prevent sustained electrolyte decomposition but ionically conductive to allow Li^+ -migration required by cell reactions. The existence of such interphases has been proven beyond doubt on graphitic anodes that operate at potentials far below the thermodynamic stability limit of any nonaqueous electrolyte components (0.2 V vs Li/Li^+ or -3.0 V vs standard hydrogen electrode, or SHE). On cathode surfaces, the existence of an interphase still incurs occasional controversy and seems to be highly dependent on the operating potentials and surface state of the cathode itself. For example, an interphase may never form on a LiFePO_4 -based cathode (3.5 V vs Li/Li^+ or 0.5 V vs SHE), but there is no doubt that electrolytes become unstable on either $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ or LiCoPO_4 (>4.5 V vs Li/Li^+ or >1.5 V vs SHE), resulting in surface deposits that could function as SEI.²

Given its importance, the interphase on graphitic anodes has been thoroughly investigated in the past two decades, from its key ingredients identification³ and formation mechanism⁴ to the more recent revelation on how the Li^+ -solvation sheath relates to the interphasial chemistry during the prerelation stage of cointercalation⁵ and the transport process through it thereafter.^{6,7} On the other hand, because of its conditional existence, little attention has been paid to cathode interphase

until rather recently, when high-voltage cathodes of >4.5 V came into consideration. Initial studies indicated a preference for EC vs DMC and enrichment of anion at the cathode surface.⁸ Thus, anions could play an active role in solvent oxidation⁹ or prevention of Al corrosion. A logical question thus extended is whether solvation of anions by electrolyte solvent affects passivation processes on the cathode surface. To seek an answer, the present work investigates how anion and solvent molecules interact in typical carbonate-based electrolytes. Attempts are also made to reveal the existence or absence of preferential solvation and whether a correlation that mirrors Li^+ solvation and anode interphasial chemistry exists for cathode interphases. Such fundamental understanding would be crucial to the efforts in designing electrolyte components and interphases that support high-voltage chemistries in Li-ion batteries.

EXPERIMENTAL SECTION

Lithium hexafluorophosphate (LiPF_6) and lithium tetrafluoroborate (LiBF_4) were purchased from Morita Chemical Industries and Ferro, respectively. They were stored in an argon-filled glovebox (Vacuum Atmospheres Nexus One, <1 ppm of O_2 , <1 ppm of H_2O) and used as received. Ethylene

carbonate (EC), ethylmethyl carbonate (EMC), and dimethyl carbonate (DMC) were purchased from BASF and dried over 3 Å molecular sieves that have been preactivated at 400 °C, followed by storage in the argon glovebox until needed. Anion receptor tris(pentafluorophenyl)borane (TPFPB) was synthesized at Brookhaven National Lab and purified by sublimation in the dryroom at the Army Research Lab before use. All electrolytes were prepared in the glovebox to minimize moisture inclusion.

Electrospray ionization mass spectrometry (ESI-MS) data were collected by a JEOL AccuTOF mass spectrometer operating in negative mode for anionic cluster detection. The sample injection chamber was filled with dry nitrogen and heated to 250 °C, with a needle-plate potential of 1000 V. Data were analyzed using JEOL mass spectrometry software, with peak height data culled from mass spectrometry spectrum intensity at expected anion–solvent m/z ranges. Nuclear magnetic resonance (NMR) experiments were performed with a 400 SB Bruker Avance III spectrometer (9.4 T). To avoid any interaction between the electrolyte and the NMR tube (borosilicate glass), the samples were placed in a 4 mm Teflon tube and inserted in a 5 mm NMR tube containing a chemical shift reference of deuterated solvent (setup depicted in the [Supporting Information](#)). This setup allowed both optimal chemical shift referencing and optimal adjustment of magnetic field homogeneity (i.e., shimming) using ^2H lock signal for each sample. CFCl_3 in CDCl_3 and boric acid in D_2O were used as external reference solutions (set to 0 ppm) for ^{19}F and ^{11}B experiments, respectively. Self-diffusion coefficients for ^1H , ^{19}F , and ^7Li nuclei were measured at 25 °C using a double stimulated echo pulse sequence to suppress convection effects.¹⁰ Gradient strength was arrayed (32 values, linear increase, $g = 0\text{--}45\text{ G/cm}$) for each experiment. Gradient pulse duration was $\delta = 1.5\text{--}4\text{ ms}$, and diffusion delay was $\Delta = 150\text{--}400\text{ ms}$.

Molecular dynamics (MD) simulations were performed on the $\text{LiPF}_6/\text{EC}/\text{DMC}$ (1:1 mol %) and $\text{LiBF}_4/\text{EC}:\text{DMC}$ (1:1 mol %) electrolytes in order to examine anion–solvent interactions. A modified APPLE&P many-body polarizable force field for EC/Li^+ and DMC/Li^+ was used in conjunction with the previously reported LiPF_6 and LiBF_4 force fields.¹¹ The functional form of APPLE&P force field is described elsewhere.¹² Briefly, it utilizes atomic charges centered on atoms and off-atom positions in conjunction with the atom-centered isotropic dipole polarizability to represent Coulomb and polarization interactions. The induced dipoles are smeared with the Thole screening parameter ($a_{\text{T}} = 0.4$) in order to prevent the so-called “polarization catastrophe” from occurring. The repulsion–dispersion interactions were described using a Buckingham (also called exp-6) potential. The interaction between an induced dipole and a partial charge was excluded for all atoms in EC, DMC, PF_6^- , and BF_4^- with the exception of interaction between $-\text{CH}_3$ groups in DMC. The 1–2 and 1–3 force centers were excluded from the charge–charge and repulsion–dispersion interactions. Partial charges for EC and DMC were refitted to reproduce the electrostatic potential from quantum chemistry calculations at the Møller–Plesset perturbation theory (MP2/aug-cc-pvTz) in the slab around the solvents, following a previously described methodology.¹² The solvent/ Li^+ repulsion parameters were fitted to describe the EC/Li^+ and DMC/Li^+ binding energy for 562 and 550 positions of Li^+ around EC and DMC, respectively. The

binding energy was calculated using M06-L functional and 6-31+G(d,p) basis set.

A modified MD simulation package WMI-MD was used that includes many-body polarization. Each simulation cell contained 320 EC, 320 DMC molecules, and 64 LiPF_6 for $\text{EC}:\text{DMC}$ (1:1 mol %)/ LiPF_6 and 480 EC, 352 DMC, and 64 LiBF_4 for $\text{EC}:\text{DMC}$ (1:1 vol %) doped with 1 M LiBF_4 . Electrolytes were equilibrated at 393 K for 4 ns, followed by NPT equilibration runs at 333 K for 2–9 ns. The $\text{EC}:\text{DMC}/\text{LiBF}_4$ was further equilibrated for 20 ns at room temperature in NPT ensemble followed by 25 ns production run in NVT ensemble. The Ewald summation method was used for the electrostatic interactions between permanent charges with induced dipole moments with $k = 6^3$ vectors. Multiple time step integration was employed with an inner time step of 0.5 fs (bonded interactions), a central time step of 1.5 fs for all nonbonded interactions within a truncation distance of 7.0–8.0 Å, and an outer time step of 3.0 fs for all nonbonded interactions between 7.0 Å and the nonbonded truncation distance of 14 Å. The reciprocal part of Ewald was updated only at the largest of the multiple time steps. A Nosé–Hoover thermostat and a barostat were used to control the temperature and pressure with the associated frequencies of 10^{-2} and 0.1×10^{-4} fs.

RESULTS AND DISCUSSION

Since Li-ion battery chemistry is driven by the insertion and removal of Li^+ in electrode lattice structures, the movement and solvation of Li^+ have been naturally considered key properties. The counterions, however, were often treated as invisible other than offering global electroneutrality. Their interaction with solvent and possible participation in interphasial chemistry often went unnoticed, until unexpected chemistries caused by anion reactions became impossible to ignore. Examples include superconcentrated electrolytes, in which the scarcity of solvent molecules at high concentrations of Li salts forced anions to appear more frequently in the Li^+ -solvation sheath and led to interphasial chemistries that are otherwise improbable in relatively dilute ($\sim 1.0\text{ M}$) electrolyte solutions.^{13–16} In fact, even in these conventional electrolytes for Li-ion batteries, an anion, though not directly participating intercalation reactions, must satisfy a series of requirements to support the cell reactions. Such requirements include low nucleophilicity or weak association with the cation (so that decent solubility and dissociation degree can be achieved in nonaqueous solvents), sufficient chemical and electrochemical inertness against electrodes, current collectors, and other cell components and, on occasion, being able to form a protective interphase on all of them.¹⁷ The short list of anions simultaneously meeting the above rigorous standards include hexafluorophosphate (PF_6^-), hexafluoroarsenate (AsF_6^-), tetrafluoroborate (BF_4^-), and perhaps perchlorate (ClO_4^-). Among these, PF_6^- became the current industry standard that can be found in almost all commercial Li-ion batteries because its lithium salt meets all these requirements in the most balanced manner,^{18,19} with LiBF_4 used only for niche applications. Other exotic anions, such as imides (as represented by bis(trifluoromethanesulfonyl)imide, TFSI $^-$) or bis(oxalato)borate (BOB^-), though providing certain unique advantages over PF_6^- , failed to balance these requirements and hence were confined to laboratory research applications. In this work we selected both PF_6^- and BF_4^- as candidates to investigate. Despite their extensive

Figure 1. Typical mass spectra via electrospray ionization for (a) 1.0 M LiPF₆ in EC/EMC (50:50) and (b) 1.0 M LiBF₄ in EC/EMC (30:70).

applications, little is known about their interactions with solvents with the exception of a few recent publications.^{20,21}

Electrospray-ionization Mass Spectra. In previous work, electrospray-ionization mass spectrometry (ESI-MS) was innovatively used in conjunction with ¹⁷O NMR and molecular dynamics as a powerful tool to map the Li⁺-solvation sheath structure both qualitatively and quantitatively. The combination of these techniques unambiguously revealed preferential solvation of Li⁺ and identified the solvent molecules most tightly coordinated.^{5b,19,22} When the negative mode of this technique was applied to electrolytes based on PF₆⁻ and BF₄⁻ anions in the full range of EC/EMC ratios, a striking difference was immediately noticed as compared to positive mode (Li⁺-solvent) spectra: the anion–solvent species detected were only present at low percentages (<1%) of the overall signal abundances. Figures 1a and 1b show the typical spectra collected from EC/EMC 50:50 and 30:70 solutions with 1 M LiPF₆ and 1 M LiBF₄, respectively. Spectra of all other solutions are shown in Figures S1 and S2.

This scarce presence of anion–solvent species agrees, in principle, with the knowledge that association of anion to solvent molecules is much weaker as compared with that between Li⁺ and solvent,^{21,23} as evidenced by the often higher transference number of anion than cation despite the smaller ionic radii of the cation.¹⁸ Of particular interest is the spectrum of LiPF₆ solution, where the most conspicuous species is the free anion itself (PF₆⁻) as given by *m/z* 144.9 in Figure 1a. Considering that naked cation was never detected in any ESI-MS spectra,^{5b,24} the presence of a free PF₆⁻ alludes to an extremely weak anion–solvent interaction. Meanwhile, the minor presence of cation–anion species, as represented by [Li(PF₆)₂]⁻ at *m/z* 297.01, indicates how well LiPF₆ is dissociated in the carbonate mixture at the concentrations investigated (~1.0 M). The weak association properties of PF₆⁻ result from the combined effects of highly electronegative fluorine attached to a polarizable phosphorus center, which consequently makes HPF₆ a superacid and hence confers on any salt based on such anions a low dissociation energy barrier. The peak at *m/z* 238.95 (with the second highest abundance in Figure 1a) seems to represent a decomposed species consisting of LiPF₆ adduct with a [EC-H]⁻ anion. This peak appears with varying abundances in all LiPF₆-based electrolytes with the exception in neat EMC solution and does not seem to depend on EC/EMC ratio. Its formation might undergo a transition state or intermediate involving the complexation between PF₆⁻

and EC, followed by the defluorination of PF₆⁻ and deprotonation of EC by the strong Lewis acid PF₆⁻. A possible mechanism is proposed in Scheme 1. The starting species can

Scheme 1. Proposed EC–PF₆ Complex Leading to Deprotonation of EC That Could Account for the ESI-MS Peak at *m/z* 238.95 Corresponding to the Complex LiPF₆·[EC-H]⁻

be viewed as a supermolecular complex formed among Li⁺, PF₆⁻, and an EC molecule, in which the interaction between Li⁺ and EC activates the H atoms on EC to form a hydrogen bond with F.

Interestingly, neither [LiPF₆·DMC-H]⁻ nor [LiPF₆·EMC-H]⁻ was found. Their absence might be related to the preference of EC by PF₆⁻ over acyclic carbonate molecules such as DMC and EMC, which is in accord with the higher binding energy of 18.4 kcal/mol for EC/PF₆⁻ compared to binding energy of 7.0 kcal/mol for DMC(cis-cis)/PF₆⁻ obtained from LC- ω PBE/6-31+G(d) DFT calculations with Grimme empirical dispersion included. More recently, using Raman, fluorescence, and NMR, Schroder et al. also concluded that H-bonding exists between PF₆⁻ and hydrogen in carbonate molecules, which is structurally similar to the starting intermediate species in the proposed mechanism.²⁵ In this sense, the intermediate in Scheme 1 not only constitutes the precursor for such deprotonation/defluorination reactions but also, more importantly, represents how anion and solvent species might exist with each other in the bulk electrolyte solution. Very likely, only under electrospraying conditions will such an intermediate become unstable and consequently break down, which might be catalyzed by the high temperature during injection (250 °C).

A quite different story resulted from ESI-MS of LiBF₄-based solutions. Although there is similarly little presence of anion–solvent interaction as indicated by the low abundance of [BF₄EC]⁻ at *m/z* 174.87 and [BF₄EMC]⁻ at *m/z* 190.91, the naked

BF_4^- (m/z 87) never appeared (Figure 1b and Figure S1). Instead, varying $\text{Li}^+(\text{BF}_4)_y$ aggregates dominate the spectra, as indicated by $[\text{Li}(\text{BF}_4)_3]^{2-}$ at m/z 133.00, $[\text{Li}(\text{BF}_4)_2]^-$ at m/z 181.01, and $[\text{Li}_3(\text{BF}_4)_5]^{2-}$ at m/z 227.03. This is consistent with the established knowledge that LiBF_4 dissociates to a lesser degree than does LiPF_6 ^{11b,26} as HBF_4 is a much weaker superacid than HPF_6 .^{18,27} Upon closer examination, m/z 181.01 could arise from two isobaric species, $[\text{Li}(\text{BF}_4)_2]^-$ and $[\text{LiBF}_4(\text{EC-H})]^-$, the latter of which could be produced in a mechanism similar to Scheme 1. This coincidence, caused by the almost identical molecular weights of BF_4^- and $(\text{EC-H})^-$, makes it difficult to quantitatively deconvolute the relative distributions of EC and EMC in close proximity to BF_4^- .

A quantitative analysis was conducted on ESI-MS spectra for both solutions in an attempt to identify whether preferential solvation exists for anions as it does for Li^+ . As pointed out in our previous Li^+ -solvation work, this information is critically important to commercial Li-ion batteries, where the electrolytes are almost always based on mixtures of solvents instead of single solvents, and any preferential solvation might lead to drastically different interphasial chemical compositions as well as electrochemical behavior. The population of EC molecules as found in the anion-solvent species is thus plotted against the electrolyte bulk composition for electrolytes containing both PF_6^- and BF_4^- anions (Figure 2). For PF_6^- solutions we

Figure 2. Comparison of EC populations as found in coordination complexes with PF_6^- and BF_4^- .

considered the population of decomposed species $[\text{LiPF}_6(\text{EC-H})]^-$ as a reflection of the population of $[\text{PF}_6\text{EC}]^-$ aggregates, based on the Raman interpretation by Schroder et al.,²⁵ for BF_4^- solutions, however, since it is impossible to distinguish the abundance of $[\text{BF}_4\text{EC}]^-$ aggregates at m/z 181.01, we simply excluded it from the calculation. It should be kept in mind that the contribution of EC population could be significantly underestimated in such analysis. In all electrolytes investigated here EC is found to be preferentially bonded with both anions, although the bias is not as significant when compared with the preferential solvation of Li^+ . We attribute this difference to the much weaker anion-solvent interactions. It has been hypothesized that the anions PF_6^- and BF_4^- would also exhibit preferential solvation in mixed cyclic/linear carbonate electrolytes as Li^+ does. For example, Ong et al. proposed that anions should prefer cyclic over linear carbonates through computa-

tion because the molecular configuration of the former is more polar due to the ring constraint.²⁸ The efforts to detect such a tendency accurately and quantitatively using ESI-MS, however, is challenged by the weak association between anion and solvent and the transient disintegration of such clusters during the flight stage of the electrospraying process.

NMR Characterization. Nuclear magnetic resonance (NMR) was also applied to the electrolytes containing both anions. Considering that these anions are highly fluorinated, ^{19}F NMR spectra were collected for these electrolytes at varying ratios of EC/DMC. Here DMC replaces EMC in all NMR experiments, and the difference incurred by this replacement is expected to be negligible in both bulk and interphasial properties^{1b,18} due to the structural similarity of the two acyclic carbonates. Figure 3 summarizes the change in ^{19}F chemical

Figure 3. Normalized ^{19}F chemical shifts of solutions of LiPF_6 and LiBF_4 referenced to the shift value at EC/DMC 80:20 for both salts.

shift ($\Delta\delta$) as the ratio of binary electrolytes varies, where $\Delta\delta$ was normalized as against the ^{19}F signals at DMC mole fraction of 0.2. The ^{19}F chemical shift of both anions exhibit an upfield shift as the solution dielectric constant decreases (i.e., with increasing DMC content), leading to a progressive shielding effect of ^{19}F nuclei. The upfield shift of ^{19}F of LiBF_4 with increasing of DMC content is a solvent effect similar to that observed by the work of Plakhotnyk et al.,²⁹ which confirmed that the ^{19}F chemical shift of BF_4^- in various solvents moves upfield as the solution dielectric constant decreases. The PF_6^- anion was expected to follow the same trend of this upfield shift, as observed in this work. The LiPF_6 salt in a spread of EC/DMC electrolytes showed a very small ^{19}F chemical shift range of less than 0.3 ppm over all tested electrolytes. A lack of ^{19}F chemical shift variation implies the composition of the solvents does not significantly change the surrounding environment of PF_6^- anions and in particular that the anion remains well separated from the Li^+ despite the decreasing permittivity of the solution. However, LiBF_4 displayed a significantly larger chemical shift range of about 0.9 ppm with the various amounts of DMC. This difference is attributed to the greater tendency of LiBF_4 to form ion pairs or higher aggregates, which is exacerbated by decreasing solvent polarity. The diffusion behavior of all species, either ions or solvent molecules, is largely dominated by the solution viscosity, which in turn is mostly determined by EC/DMC ratio. In order to eliminate the effect of viscosity as a variable, PF_6^- , BF_4^- , and Li^+ mobilities are expressed as the ratio between their respective diffusion coefficients and that of DMC. The ratios are presented in Figure 4. Li^+ shows a rather constant ratio around 0.4 in LiPF_6 systems, which is lower than that of the

Figure 4. Relative mobilities of Li and F in (a) 1 M LiPF₆ and (b) 1 M LiBF₄ solutions.

Scheme 2. (a) Anion Receptor Tris(pentafluorophenyl)borane (TPFPB) and (b) Interaction of Anions PF₆⁻ and BF₄⁻ with TPFPB Resulting in Fluorination of TPFPB and Creation of Neutral Species PF₅ and BF₃, Respectively

Figure 5. Effect of anion receptor TPFPB on the anion–solvent interaction: (a) LiPF₆ and (b) LiBF₄ in EC/DMC (50:50).

anion. This is due to the solvation sheath of Li⁺ being saturated by solvent molecules, EC in particular. In both LiPF₆ and LiBF₄, the relative mobility of fluorine is higher for low DMC content (i.e., high polarity), and it progressively converges toward the Li⁺ ratio as the polarity of the system decreases. This feature indicates that the decrease in solvent polarity favors association of cation and anion, as the less polar solvent molecules are much less effective in neutralizing the electric field exerted by ionic species (mainly Li⁺) on its surroundings. This weaker presence of anion–solvent interaction predicts that solvent molecules in such low-polarity media will be less likely to be found in the vicinity of both cation and anion. It is

noteworthy that the difference between the mobility of Li⁺ and BF₄⁻ is much smaller than in the LiPF₆ system, and BF₄⁻ has almost identical mobility as Li⁺ in EC/DMC 20/80 solution or higher DMC contents. This phenomenon again arises from the stronger ion association tendency of LiBF₄ compared to LiPF₆. Because of the interference from cation–anion interaction, at this time it is difficult to ascertain the specific preference of anion solvation via NMR methods.

Anion-Receptor Effect. So far we have been avoiding the term “anion-solvation sheath”, mainly because the weak interaction between the two leads to doubt whether a stable sheath structure could actually exist long enough. As pointed

Figure 6. Optimized geometries of TFPFB complexes with (a) BF_4^- and (b) PF_6^- anions from LC- ω PBE-GD3/6-31+G(d) DFT calculations.

Figure 7. Molecular dynamics simulation of the radial distribution function of LiPF_6 in EC and EC:DMC. (a) Li^+ and PF_6^-/F^- to solvent H and carbonyl oxygen (O_c), including F-H of EC and EC:EMC, Li- O_c in EC:EMC, and F- O_c in EC. Compared to the structured, close binding of Li^+ to carbonyl oxygens, the distribution of anion F to solvent H (F-H) peaks after 2 Å indicates much less structuring of anions. Comparing the F-H (solid line) distributions in Figure 6b predicts greater PF_6^- interaction with EC compared to DMC.

out by Chaban et al., with such loose attraction between anion and solvent, even the primary solvation sheath of anions would be difficult to define.²¹ The origin for the diffused structure of anion solvation can be attributed to the fact that the majority of polar aprotic solvents are nucleophilic in nature, and the dissolution of solutes relies mostly on the coordination of electropositive substructure in the solute by these nucleophiles. Thus, in Li-ion battery electrolytes, the point-charge Li^+ forms strong bonds with the lone-pair electrons in carbonyl moieties on carbonate, as revealed by both ESI-MS and ^{17}O NMR, while the absence of a strong electrophilic substructure in carbonate or ether solvents leads to insignificant solvation of anions.

In order to achieve the ideal situation of an unambiguous anion-solvent association, we introduced an anion receptor into the electrolytes, so that the intrinsic absence of anion-binding sites in the latter could be overcome. The structure of tris(pentafluorophenyl)borane (TFPFB, Scheme 2a) was designed to provide an electron-deficient boron center, and previous investigations have confirmed its efficiency in solvating various anions, including the anion for one of the least soluble lithium salts, LiF .³⁰

Upon addition of only 0.1 mol % TFPFB, dramatic changes occurred in the ESI-MS for both LiPF_6 and LiBF_4 -based electrolytes, resulting in much cleaner spectra (Figure 5) and distinct new species. However, in neither case was the expected simple adduct between TFPFB and anion detected, as indicated by the absence of species at m/z 654 [$\text{TFPFB} + \text{PF}_6^-$] and 596 [$\text{TFPFB} + \text{BF}_4^-$], respectively. Instead, the overwhelmingly abundant species found in both electrolytes is [$\text{TFPFB} + \text{F}^-$] (m/z 530.88), arising from the defluorination of these two anions by the anion receptor (Scheme 2b). The lability of P-

F/B-F bonds together with the strong affinity of TFPFB toward F^- makes such a defluorination process possible. DFT calculations performed using LC- ω PBE functional with GD3 empirical dispersion correction and 6-31+G(d) basis set indicated that the BF_4^- and PF_6^- interaction with TFPFB resulted in the spontaneous defluorination of anions with reaction free energies of -24.4 and -12.7 kcal/mol for $\text{TFPFB} + \text{BF}_4^-$ and $\text{TFPFB} + \text{PF}_6^-$ complex formation, respectively. As a result of anion complexation by TFPFB, the B-F bond in BF_4^- extends but less than the P-F bond in PF_6^- . In other words, fluorine is shared between BF_4^- and TFPFB, while it is largely transferred to the anion receptor in the $\text{TFPFB}-\text{PF}_6^-$ complex as shown in Figure 6. As fluorine is shared between TFPFB and BF_4^- in the complex, it could form either F-TFPFB complex or BF_4^- in ESI-MS experiments as shown in Figure 5. The free energy for PF_5 and BF_3 dissociation from the $\text{FPB} + \text{PF}_6^-$ and $\text{FPB} + \text{BF}_4^-$ complexes was 0.2 and 2.0 kcal/mol, respectively, indicating that both BF_3 and especially PF_5 could easily detach. Since both species are neutral in charge, ESI-MS is blind to them.

Suspicion has been raised previously regarding the stability of LiPF_6 or LiBF_4 against strong anion receptors like TFPFB;^{31,32} observations made in Figure 5 confirmed experimentally for the first time that a strong anion receptor does have the tendency of breaking down these highly fluorinated inorganic anions. The removal of fluorine incurs the question whether anion receptors are unsuitable for the electrolytes containing these anions because the strong Lewis acids generated from the process (PF_5 and BF_3) will very likely trigger a series of electrophilic reactions with the organic carbonate molecules,

leading to extensive electrolyte degradation.³³ A conclusive answer to this question requires further studies.

The most interesting, but somewhat unexpected, effect of the anion receptor is that naked BF_4^- anion could be detected now as an abundant species (Figure 5b), which was never observed in the ESI-MS of the electrolytes without TPFPB (Figure 1b) because of poorly dissociated LiBF_4 . Thus, it is reasonable to assume that in the bulk electrolytes the dissociation of LiBF_4 was indeed promoted by the anion receptor. We postulate that the adduct $[\text{TPFPB} + \text{BF}_4^-]$ formed in the electrolyte very likely experienced fragmentation during the electrospraying stage, losing the neutral TPFPB and leading to naked BF_4^- . We can even further infer that both $[\text{TPFPB} + \text{PF}_6^-]$ and $[\text{TPFPB} + \text{BF}_4^-]$ were formed in the electrolytes and served as precursor of fragmentation to produce the abundant species $[\text{TPFPB} + \text{F}^-]$ in both cases. The more labile P–F bond drives the fragmentation process to generate overwhelmingly $[\text{TPFPB} + \text{F}^-]$, while the more stable B–F bond manages to maintain an equilibrium between the two different fragmentation routes, producing both $[\text{TPFPB} + \text{F}^-]$ and $[\text{BF}_4^-]$, consistent with computational analysis.

Molecular Dynamic Simulations. To aid understanding of anion–solvent interaction, we employed computational simulations so that a mechanism at the atomic level could be derived. MD simulations were performed on EC:DMC (1:1 vol %) doped 1 M LiBF_4 (solvent:Li = 13) and EC:DMC(1:1 mol %) doped LiPF_6 (at solvent:Li = 10), with the purpose of examining how anion binds to either EC or DMC. Figure 7 compares radial distribution functions (RDFs) for both Li^+ with carbonyl oxygen ($\text{Li}-\text{O}_\text{C}$) and F with hydrogen ($\text{F}-\text{H}$). They serve as indicators for the solvent structuring around cation and anion. Consistent with previous studies, a highly structured solvation environment exists for Li^+ as evidenced by the high amplitude of the sharp first peak of $\text{Li}-\text{O}_\text{C}$ RDF. A similar strong peak was observed for F in PF_6^- and carbonyl oxygen O_C . However, the almost featureless RDFs for F in PF_6^- and H suggest much less structuring of solvent molecules around anions. A more detailed comparison of anion coordination in the single and mixed solvents is made in Figure 7b, where the $\text{F}-\text{H}$ RDFs indicate a much stronger association between H from EC with PF_6^- than H from DMC with PF_6^- , hinting at preferential interaction of anion with EC rather than DMC. This preference is in agreement with the slightly lower binding energy between EC and PF_6^- than DMC and PF_6^- (Table 1).

Table 1. G4MP2 Calculation of Anion–Solvent Binding and Free Energy

	binding energy (kcal/mol)	free energy (kcal/mol)
PF_6^- –EC	−16.7	−7.5
PF_6^- –DMC	−7.1	1.4
BF_4^- –EC	−18.0	−8.9
BF_4^- –DMC	−7.1	1.2

Interestingly, almost identical RDFs were obtained for the $\text{F}-\text{C}_\text{C}$ (carbonyl carbon) for both EC and DMC. As C_C is near the location of the solvent center of mass, it might indicate that from the point of view of the solvent center of mass both solvents have similar structuring with anions.

In a more visual representation, the distributions of F from PF_6^- in the vicinity of both EC and DMC molecules are calculated and shown in Figure 8. It shows two isosurfaces corresponding to $\rho/\rho_\text{bulk} = 5$ (in red) and $\rho/\rho_\text{bulk} = 3$ (in blue)

for EC–anion and $\rho/\rho_\text{bulk} = 3$ (in red) and $\rho/\rho_\text{bulk} = 2.3$ (in blue) for DMC–anion, where ρ is the local density of atom and ρ_bulk is the average density of atom in the whole simulation box. The red isosurface indicates the most probable position of F of anion, while the blue isosurface indicates a slightly less probably positions but still preferred compared to average number density. For DMC with its weaker dipole (Figure 8a), PF_6^- is most probable near its methyl group as well as its carbonyl carbon. In comparison, EC presents a much cleaner picture of PF_6^- location probability near the positive end of the EC dipole, which is the methylene end (Figure 8b). As shown by Schroder et al., F in anions prefers to coordinate with olefin Hs in EC and DMC and likely form hydrogen bond, and we believe that the supermolecular structure as shown in Figure 8b probably mediates the subsequent dehydrogenation of EC by PF_6^- , leading to the species $[\text{LiPF}_6^-(\text{EC}-\text{H})]$ at m/z 238.95 (Figure 1a).

The distribution of anions and Li^+ around solvent molecules in the EC:DMC/ LiBF_4 electrolyte is shown in Figure 9. It shows two isosurfaces: one corresponding to high probability of finding fluorine of BF_4^- $\rho/\rho_\text{bulk} = 4$ (in red in Figures 9a,c) and Li^+ $\rho/\rho_\text{bulk} = 33$ (in blue). The other two (Figures 9b,d) show the intermediate probability of finding fluorine of BF_4^- $\rho/\rho_\text{bulk} = 2$ (in red) and Li^+ $\rho/\rho_\text{bulk} = 33$ (in blue). While there are substantial similarities between the locations of PF_6^- (see Figure 8b) and BF_4^- (Figure 9a) near the ethylene part of EC, there are also noticeable differences. Specifically, some BF_4^- anions are located near carbonyl oxygens due to their coordination to the Li^+ cations and higher LiBF_4 salt aggregation compared to LiPF_6 . In contrast to the EC– BF_4^- most probable coordination via EC ethylene group, the most probable position of the BF_4^- anions is near the DMC carbonyl carbons, indicating that the DMC/ BF_4^- interactions are largely modulated by the DMC/ Li^+ and Li^+ / BF_4^- interactions. Interestingly, there is a substantial similarity between the solvent–lithium–anion packing found in our simulations in liquid electrolytes and the solvate structures obtained from crystal structures.³⁴ Higher probability of the direct $\text{H}\cdots\text{F}$ interaction in EC/ PF_6^- compared to solvent/ BF_4^- would indicate that at high potentials (>6 V vs Li/Li^+) kinetics of EC/DMC/ LiPF_6 oxidation might be higher than kinetics of EC/DMC/ LiBF_4 oxidation due to H-abstraction by anion during oxidation that requires formation of the $\text{H}\cdots\text{F}$ contracts.⁹

Implication to Electrochemistry. Considering the weak association, it will be safe to speculate that the solvation of anions imposes little influence on the overall anodic stability of the electrolytes, regardless if they exhibit preferential solvation or not. Note that this is not to state that anion has no effect on anodic stability; instead, what dictates the anodic stability limit should be the chemical and electrochemical stability of the anions and the solvent molecules altogether. To confirm this experimentally, EC/DMC-based electrolytes with both lithium salts are exposed to a LiFePO_4 cathodes surface that is progressively delithiated, where LiFePO_4 serves as a working electrode with redox peaks (~ 3.5 V vs Li) far below the decomposition region (>4.0 V) of electrolyte components. Using such composite working electrode, instead of more commonly used nonporous electrodes such as glassy carbon or platinum,³⁵ ensures more accurate evaluation of the decomposition onset potentials for electrolytes on active electrode surfaces that they will be exposed to in real-life Li-ion devices.³⁶ It is generally accepted that the anodic stability of the PF_6^- and its passivation of current collector (aluminum foil) outperform

Figure 8. 3D isosurface rendering of F in PF_6^- around (a) DMC and (b) EC, with most probable locations marked in red and less probable locations in blue.

Figure 9. 3D isosurface rendering for high (a, c) and intermediate (b, d) probability of fluorine of BF_4^- around EC (a, c) and DMC (c, d) (shown as red isosurfaces) in EC:DMC(1:1 vol %)/LiBF₄. Blue isosurfaces show high probability of Li⁺.

those of the BF_4^- , and Figure 10 confirms this difference; on the other hand, the variation in solvent ratio of electrolytes

Figure 10. Anodic stability of PF_6^- -based (solid lines) and BF_4^- -based (dotted lines) electrolyte as determined by linear sweep technique on a LiFePO_4 working electrode. The scan rate for all tested electrolytes was 0.05 mV/s.

exhibits little, if any, impact on the potential of electrolyte decomposition. The onset of significant current flow in Figure 10 occurs at about 4.5 V for both anions, but this is caused by anion intercalation into cathode graphite additive. Staging of BF_4^- is seen at 4.8 V, while staging of PF_6^- is seen at 4.6 and 5.1 V.³⁷ Coincidentally, the onset of oxidation for a similar electrolyte EC/DMC(1:1)/LiPF₆ was reported to occur around 4.6 V on glassy carbon,³⁸ indicating that the onset of staging and oxidation happens at a similar potential resulting in a lower Coulombic efficiency for anion intercalation for this electrolyte. The anodic peaks at 5.4 and 5.9 V are attributed to the solvent- BF_4^- and solvent- PF_6^- oxidation and were largely independent of electrolyte composition. Previous DFT calculations³⁹ predicted oxidation of the EC/ PF_6^- and DMC/ PF_6^- complexes to happen about 0.3 V higher than oxidation of the EC/ BF_4^- and DMC/ BF_4^- complexes, respectively, in good agreement with the difference between the experimentally measured peak positions. The anodic current at the peak was also higher for the LiPF₆-doped electrolyte than for the LiBF₄-doped one. It is possible that the PF_6^- peak has a higher current than BF_4^- is caused in part by faster oxidation kinetics as suggested by the higher probability of $\text{H}\cdots\text{F}$ interactions in PF_6^- compared to BF_4^- .

Ultimately, the near absence of solvent effect on anodic decomposition process, whether it is formation of interphase on cathode surface or passivation of current collector, apparently arises from the weak association between anions and their solvating molecules, which minimizes the effect of the solvent species on the electrochemical behaviors of electrolytes on cathode surfaces. The slight preferential solvation of anions by EC observed in this work is not strong enough to exert pronounced electrochemical significance analogous to the preferential solvation of Li⁺.

CONCLUSIONS

Using electrospray-ionization mass spectrometry (ESI-MS), nuclear magnetic resonance (NMR), and computational simulation, we investigated how anions of lithium salts (PF_6^- and BF_4^-) interact with carbonate molecules in typical electrolytes. Spectra indicate that these highly fluorinated anions exist relatively free with little solvation. For the small population of anions that are solvated, slight preferential solvation is found for both anions, with cyclic and more polar solvent EC favored over acyclic and less polar linear carbonates.

While ESI-MS revealed a few possible ways these anion react with either solvent molecule or added anion receptors, NMR indicates that F in these anions are the species that intensely interact with the weakly electropositive regions in solvent molecules. The weak anion–solvent interaction seems to at least minimize the solvent effect on the electrochemical behavior of electrolytes on cathode surfaces compared to the pronounced effect of the competitive solvation of EC and DMC to Li⁺ on the SEI formation on anode.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b08895.

Section 1: a more detailed description of the NMR procedures used to collect data presented in the [Results and Discussion](#) section; Figure S1: the NMR tube with Teflon sample insert for clarity in understanding the NMR experimental setup; Section 2: a presentation of all electrospray ionization mass spectrographs used to develop the solvation population information in [Figure 2](#) and composed of Figure S2a–j displaying LiPF₆ ESI-MS data and Figures S3a–j displaying LiBF₄ ESI-MS data; Section 3: composed of Figures S4–S7, providing additional isosurface views of both Li⁺ and F[−] from from the BF₄[−] anion around both EC and DMC; Figure S8: a closer view of the radial distribution function presented in [Figure 10](#) to more clearly show the magnitude of the F–H distribution values compared to the much larger Li–O distribution values ([PDF](#))

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Notes

The authors declare no competing financial interest.

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