Solvating Power Series of Electrolyte Solvents for Lithium Batteries

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Complete List of Authors:	Su, Chi-Cheung; Argonne National Laboratory, He, Meinan; Argonne National Laboratory, Chemical Science & Engineering Amine, Rachid; University of Illinois at Chicago, Chemical Engineering; Argonne National Laboratory, Materials Science Division Rojas, Tomas; Argonne National Laboratory Cheng, Lei; Argonne National Laboratory Ngo, Anh; Argonne National Laboratory Amine, Khalil; Argonne National Laboratory,

Solvating Power Series of Electrolyte Solvents for Lithium Batteries

Chi-Cheung Su,[a†] Meinan He,[a†] Rachid Amine,[b] Tomas Rojas,[b,c] Lei Cheng,[b] Anh T. Ngo,[b] and Khalil Amine[a,d*]

[a] Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Avenue, Lemont, IL 60439, USA

[b] Materials Science Division, Argonne National Laboratory, 9700 S. Cass Avenue, Lemont, IL 60439, USA

[c] Department of Physics and Astronomy and Ohio Materials Institute, Ohio University, Athens, Ohio 45701-2979, USA

[d] Material Science and Engineering, Stanford University, Stanford, CA 94305, USA

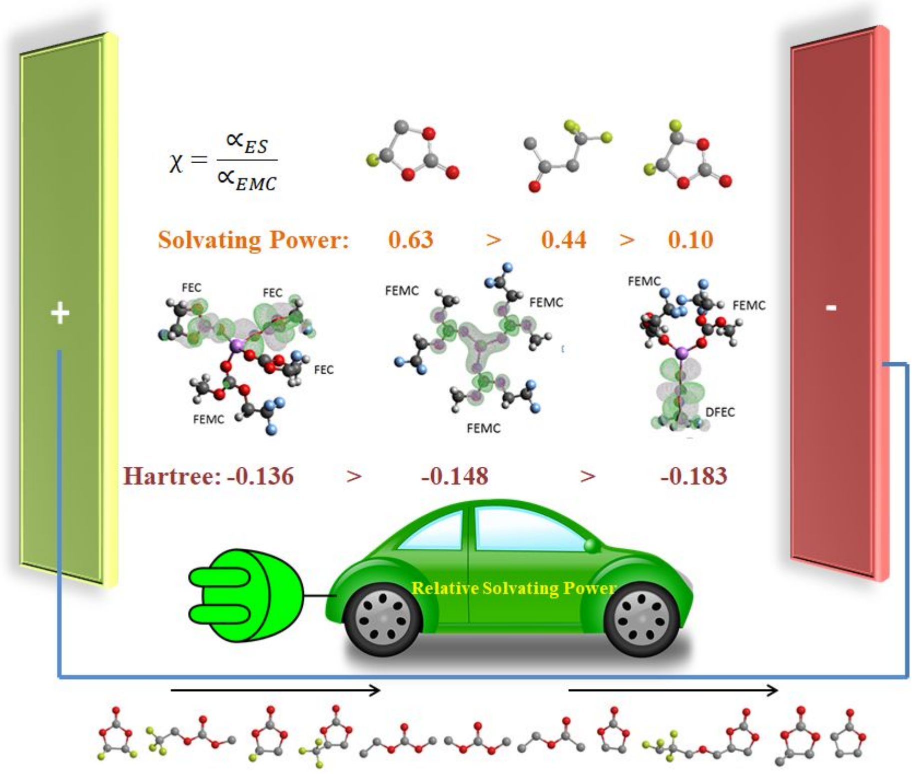
[†] *These authors contributed equally to this work.*

E-mail: amine@anl.gov

ABSTRACT

From dictating the redox potential of electrolyte solvents to shaping the stability of solid-electrolyte interfaces, solvation plays a critical role in the electrochemistry of electrolytes. To efficiently design functional electrolytes for lithium batteries, it is particularly important to understand the relative solvating ability of each individual organic solvent, because most of the electrolyte systems are comprised of two or more electrolyte solvents. Using a newly developed internally referenced diffusion-ordered spectroscopy technique and diffusion coefficient-coordination ratio (D-α) analysis, we successfully constructed a solvating power series for common electrolyte solvents. We demonstrated the usefulness of this solvating power series in designing more reliable electrolyte system by selecting an appropriate fluorinated electrolyte solvent for a high-voltage lithium metal battery (LMB) as an example. For a methyl (2,2,2-trifluoroethyl) carbonate-based electrolyte, we identified fluoroethylene carbonate as a more desirable cyclic carbonate co-solvent than difluoroethylene carbonate for LMB due to its significantly higher ability to solvate lithium ions.

TOC Graphic



Lithium-ion batteries (LIBs) are indispensable for modern consumer electronic devices due to their relatively high specific capacity and operating voltage. [1–3] To meet the demands of current electric vehicle applications, researchers worldwide are endeavoring to enhance the energy density of state-of-the-art lithium batteries. [4–6] Recently, high-voltage lithium metal batteries (LMBs) have received tremendous attention due to the low electrochemical potential and extremely high specific capacity of lithium metal anodes. [7–9] However, the massive commercialization of LMBs is still hindered by the interfacial instability between lithium and electrolyte, which creates severe safety problems. [7,10–11] A reliable electrolyte is crucial for the operation of any new battery system. [12–13] Several studies illustrate a strong correlation between physicochemical properties, such as the ability to form solid-electrolyte interphase (SEI) and an electrochemical window with the solution structure of the electrolyte. [14–20] In other words, the electrochemical performance of a lithium battery is profoundly affected by the solvation state of its electrolyte system. One example is a super-concentrated electrolyte, which has a salt concentration larger than 3.0 M and exhibits abnormal properties compared with its normal-concentration counterpart (1.0 M). [21–25] The solvation behavior of electrolyte solvents is also critical in controlling lithium polysulfide dissolution and the cell performance of lithium-sulfur batteries. [26-28] Therefore, understanding the basic solvation ability of various electrolyte solvents is the first step to developing a new functional electrolyte system.

In this study, we constructed a solvating power series consisting of different common electrolyte solvents for LIBS/LMBs according to the relative solvating power of each solvent. Similar to our previous report, [28] we define the relative solvating power (χ) of individual solvent as the ratio between the coordination percentage of a test solvent (α) and the coordination percentage of a reference solvent (α_0). We chose one of the most common electrolyte solvents for LIBs, ethyl methyl carbonate (EMC), as the reference solvent. Unlike the dielectric constant, which indicates the electronic polarizability of a solvent, the relative solvating power reveals the solvating ability of a solvent molecule to solvate lithium ions and is dictated by the organic structure of the solvent. The dielectric constant of a solvent does not necessarily correlate with its ability to solvate lithium ions, because the former is not heavily influenced by features of the solvent molecule such as denticity and steric hindrance, which can drastically alter the molecule's lithium solvating ability. [28] Although donor number is another commonly used parameter that reflects the Lewis basicity of a solvent, it is also not able to indicate the lithium solvating ability accurately. Donor number is actually measured by the negative enthalpy of the formation of 1:1 adduct of antimony pentachloride and the testing solvent. [29] Since antimony is significantly larger than lithium and antimony pentachloride only has one empty orbital for a pair of electrons, the measured donor number is not sensitive to steric hindrance and chelate effect of a solvent, which are important determining factors in lithium cations solvation. This can be corroborated by the fact that the donor number of (17.2) dimethyl carbonate (DMC) is even higher than that of (16.4) ethylene carbonate (EC), [29] although EC has higher solvating ability towards lithium than DMC. [14-15] It is clear that the steric bulkiness of a ligand in binding antimony is not as critical as in binding lithium. Experimental results showed that lactone and cyclic carbonate possess higher relative solvating power than linear carbonate and that they render a higher coordination ratio of cyclic carbonate in the conventional LIB electrolyte system. Moreover, fluorination causes a drastic decrease in a solvent's lithium solvating ability, which causes large decreases in the solvating ability of fluorinated carbonate solvents. The solvating power series serves as an important guideline for evaluating the solvation status of individual electrolyte solvents and the selection of appropriate co-solvents. The determination of a suitable cyclic carbonate co-solvent for a methyl (2,2,2-trifluoroethyl) carbonate (FEMC) based electrolyte served as a representative application of the series. For FEMC-based electrolyte system, we discovered that fluoroethylene carbonate (FEC) was a more desirable cyclic carbonate co-solvent for LMBs than difluoroethylene carbonate (DFEC). Because FEC displays a higher solvating power than FEMC, a large portion of lithium cations are solvated by FEC in the FEC-FEMC electrolyte, whereas the dominant solvent in the DFEC-FEMC electrolyte is FEMC. Therefore, FEMC is more prone to reduction in the DFEC-

FEMC system. Because the reduction products that FEMC generates are detrimental to the solid-electrolyte interphase (SEI) on the lithium metal anode, the DFEC-FEMC system displays inferior cycling performance compared to the FEC-FEMC electrolyte system.

Conventionally, vibrational spectroscopy such as Fourier-transform infrared (FTIR) or Raman spectroscopy is used to evaluate solvent solvation state. [30–33] However, the determination of solvation state using these conventional techniques involves either complicated deconvolution of overlapping peaks or is simply impossible for a binary electrolyte system, especially for electrolyte solvents sharing the same functional groups such as EC and EMC. [14,33-34] Therefore, in this study we employed the internally referenced diffusion-ordered spectroscopy (IR-DOSY) technique, which overcame the limitation of conventional vibrational spectroscopy, [28,34] to determine the solvation state of individual solvents in a binary electrolyte system. Detailed deduction of D-α analysis and the calculation of χ are presented in the supporting information (SI).

Figure S1 shows the Raman spectra of the C-O single bond absorption in FEC and EMC. It is obvious that Raman spectroscopy is not an effective way to investigate the solvation behavior of FEC and EMC, because both molecules contain four different C-O single bonds even if structural conformers are not taken into consideration. Although FEC only has one carbonyl group, the interpretation of its FTIR spectrum is seriously hindered by the existence of strong Fermi resonance for cyclic carbonate. [33–35] As shown in Figure S2, the carbonyl absorption for FEC is broad and splits into several peaks. Although the carbonyl absorption of FEC changed significantly after lithium hexafluorophosphate ($LiPF_6$) was added to FEC, it is impossible to perform any meaningful deconvolution to decipher the spectrum. In contrast, the

NMR proton signals of FEC, EMC, and toluene, which was added as the internal reference due to its unique non-coordinating property, [28,34] are clearly separated as shown in Figure S3. Due to the clear separation of distinctive proton resonance peaks, IR-DOSY provides an effective way to probe the solvation state of individual electrolyte solvent in all binary electrolyte systems. [34] We added toluene as an internal reference into the $LiPF_6$:FEC:EMC 1:4:4 (molar ratio) electrolyte system because of its non-coordinating property. [34] As illustrated in Figure 1a, EMC diffuses slightly faster than FEC before the addition of $LiPF_6$ salt. However, the diffusion coefficient of EMC decreases significantly after the addition of $LiPF_6$ and is smaller than that of FEC, as depicted in Figure 1b, indicating that EMC has a higher affinity toward lithium cations than FEC. Table S1 summarizes the diffusion coefficients and coordination ratios of FEC and EMC, as well as the coordination number of lithium in 1:4:4 $LiPF_6$:FEC:EMC electrolyte. Several studies show that regular cyclic carbonates such as EC or propylene carbonate (PC) have a higher tendency to solvate lithium cations than regular linear carbonates such as EMC. [14,16,17,34] However, the strong electron withdrawing effect of fluorine atoms on FEC largely reduces its affinity toward lithium ions. Therefore, FEC has a lower tendency to solvate EMC despite its cyclic carbonate nature.

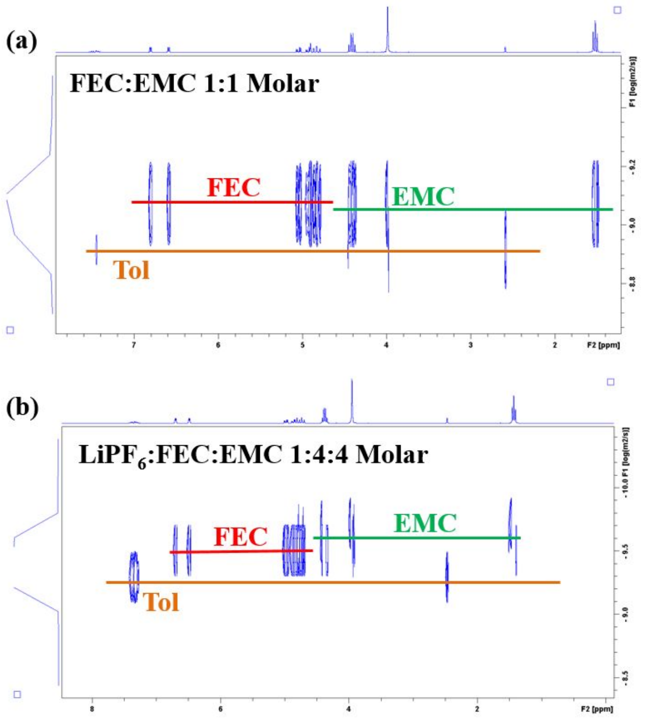


Figure 1. ^{1}H DOSY-NMR spectra of (a) 1:1 FEC:EMC and (b) 1:4:4 LiPF$_6$:FEC:EMC electrolyte with toluene added as an internal reference.

Tables S2 through S10 outline the coordination number of lithium and the coordination ratios of EMC and other common electrolyte solvents (ESs), including gamma-butyrolactone, 4-((2,2,3,3-tetrafluoropropoxy)methyl)-1,3-dioxolan-2-one (HFEEC), PC, EC, ethyl acetate (EA), DMC, 4-(trifluoromethyl)-1,3-dioxolan-2-one (TFPC), FEC, FEMC, and DFEC in a 1:4:4 (molar ratio) LiPF$_6$:ES:EMC solution. Figure S4 depicts the detailed chemical structures of all common electrolyte solvents. Figure 2 displays the solvating power series of these common electrolyte solvents according to their relative solvating power (χ), which is the ratio between the coordination percentage of individual electrolyte solvent and the coordination percentage of

EMC. As previously reported, relative solvating power presents a more accurate parameter of the ability of electrolyte solvent to solvate lithium ions than the commonly used dielectric constant, which only indicates the electronic polarizability of a solvent molecule. [28] Lactone and regular cyclic carbonate are unsurprisingly on the top of the solvating power series due to their high polarity. Note that HFEEC has a higher relative solvating power than both PC and EC, probably due to the bidentate coordination of its alkoxy group. The lithium solvating power of EMC is very similar to the solvating power of dimethyl carbonate but smaller than that of EA. Although cyclic carbonate usually has greater lithium solvating power than linear carbonate, the solvating power of TFPC and FEC is significantly lower than that of EMC due to the presence of a strong electron withdrawing group. For carbonate with the same strong electron withdrawing group, linear fluorinated carbonate FEMC exhibits lower lithium affinity than its cyclic counterpart TFPC. DFEC displays the lowest lithium solvating power in the list because it has two strong electron-withdrawing fluorine atoms.

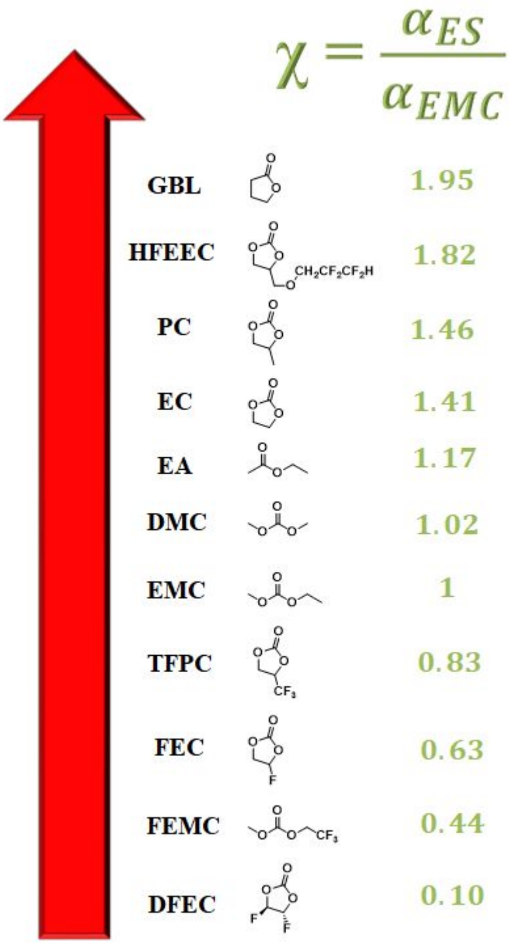


Figure 2. Solvating power series of common electrolyte solvents.

To demonstrate the usefulness of the established solvating power series, we assembled various lithium metal cells and subjected them to galvanostatic cycling tests. Figure 3a shows the specific discharge capacity of the $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622)/Li cells employing conventional electrolyte (1.2M $LiPF_6$ in EC:EMC 3:7) and two different fluorinated electrolytes (1.2M $LiPF_6$ in FEC:FEMC 3:7 v/v and 1.2M $LiPF_6$ in DFEC:FEMC 3:7 v/v). We conducted three formation cycles at C/10 rate before the higher current density C/3 rate cycling. Both DFEC- and FEC-based cells displayed enhanced stability toward the lithium metal anode compared to the cell employing a conventional EC-based electrolyte. Recently, various research groups have independently studied the beneficial effects of using FEC as an SEI enabler on lithium metal anodes. [36–39] Their results indicate that fluorine atoms attached to the EC backbone facilitate the formation of a compact lithium fluoride (LiF) rich SEI layer, which stabilizes the cycling of the lithium metal anode. DFEC was found to be an even better SEI enabler because it has two fluorine atoms and forms an even more compact SEI layer. [40] However, when fluorinated linear carbonate FEMC was used as a co-solvent instead of EMC, the capacity retention of the DFEC-based cell (43% after 400 cycles) was significantly lower than that of the FEC-based cell (73% after 400 cycles) as illustrated in Figure 3a. The average 100-cycle Coulombic efficiency (CE) of the NMC622/Li cell using a conventional electrolyte was 97.1%, as shown in Figure 3b. Although the average 400-cycle CE of the DFEC-based cell (99.7%) was significantly higher than the average CE of the conventional cell, it was smaller than the average 400-cycle CE of the FEC-based cell (99.9%). We speculate that the formation of detrimental components as a result of the gradual decomposition of FEMC in the DFEC/FEMC electrolyte may be the major reason for this unusual phenomenon. This proposed decay mechanism was supported not only by the results of the solvation study, but also by the Li/Li symmetric cell, Cu/Li cell, and density functional theory (DFT) calculations results.

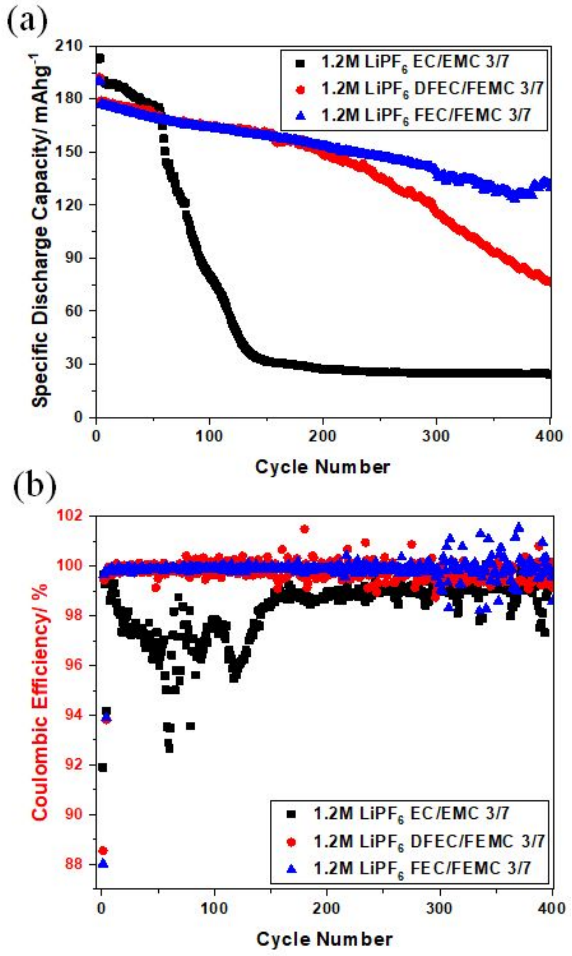


Figure 3. (a) Capacity retention and (b) CE of NMC622/Li cells using 1.2M LiPF$_6$ in EC:EMC 3:7, 1.2 M LiPF$_6$ in FEC:FEMC 3:7 and 1.2 M LiPF$_6$ in DFEC:FEMC 3:7 electrolytes.

To evaluate the plating/stripping stability of the Li metal electrode 1.2 M LiPF$_6$ in pure FEMC electrolyte, we conducted both a Li/Li symmetric cell test and a Cu/Li cell test. The results are depicted in Figures S5 and S6, respectively. Unlike the FEC- and DFEC-based electrolytes, which showed very stable cycling with low polarization, [40] the Li/Li symmetric cell using pure FEMC electrolyte exhibited very high voltage polarization (>5 V) after just two cycles. Moreover, the CE of the Cu/Li cell using pure FEMC electrolyte was less than 10%, while the CEs of cells using FEC- and DFE-based electrolytes are normally >90%. [40] These results unambiguously demonstrate the deleterious effect of FEMC decomposition on lithium metal anodes. The introduction of a trifluoromethyl group significantly enhanced the oxidation potential of FEMC compared to EMC at the expense of cathodic stability, rendering the FEMC molecule much more susceptible to reduction. [41] To better understand the reductive decomposition of FEC/FEMC and DFEC/FEMC electrolytes, the solvation status must be first resolved. According to the solvating power series, the lithium solvating ability of FEC (0.63) is significantly higher than that of FEMC (0.44), while the lithium affinity of FEMC is much greater than that of DFEC (0.10). Because the solvation number of lithium in an electrolyte at a normal concentration is usually around 2.5–4.5 and FEC is slightly more attracted to lithium ions, we predict that mixed aggregates solvated by both FEC and FEMC will be the major species in the FEC-based electrolyte. For the DFEC-based electrolyte, because FEMC possesses much higher lithium affinity than DFEC, mixed aggregates solvated by both DFEC and FEMC coexist with aggregates solvated only by FEMC. This prediction is supported by the results of IR-DOSY, which measured the actual solvation status of FEC/FEMC and DFEC/FEMC electrolytes, as illustrated in Tables S11 and S12. The coordination percentages of FEC and FEMC are 0.56 and 0.44, respectively, in 1:4:4 (molar ratio) $LiPF_6$:FEC:FEMC electrolyte. The coordination number of lithium is 3.99, which indicates that mixed aggregates solvated by four solvent molecules including two to three FEC molecules are major species. However, the coordination percentage of DFEC is only 0.13 in a 1:4:4 (molar ratio) $LiPF_6$:DFEC:FEMC electrolyte, whereas the coordination percentage of FEMC is 0.48 and the coordination number of lithium is 2.45. Because the ratio of coordination percentage of FEMC to DFEC

($\alpha_{FEMC}/\alpha_{DFEC}$) is 3.69, which is noticeably higher than the coordination number of lithium (2.45), the existence of a significant amount of aggregates solvated only by FEMC is inevitable. Note that the ratios of the measured coordination percentages of cyclic fluorinated carbonate (FC) and FEMC are similar to the ratios of their relative solvating power, as shown in Table 1. Thus, the solvating power series provide accurate estimates of the solvation behavior of individual solvent molecules.

Table 1. Coordination percentages and ratios of coordination percentages for 1:4:4 $LiPF_6$:FEC:FEMC and 1:4:4 $LiPF_6$:DFEC:FEMC electrolytes.

Solution	α_{FC}[a]	α_{FEMC}	$\alpha_{FC}/\alpha_{FEMC}$	χ_{FC}/χ_{FEMC}[b]
1:4:4 $LiPF_6$:FEC:FEMC	0.56	0.44	1.26	1.42
1:4:4 $LiPF_6$:DFEC:FEMC	0.13	0.48	0.28	0.23

[a] α_{FC} is the coordination percentage of fluorinated cyclic carbonate.
[b] χ_{FC} is the relative solvating power of fluorinated cyclic carbonate.

To further validate the proposed mechanism, we performed DFT calculations to determine the lowest unoccupied molecular orbital (LUMO) level of specific lithium solvating aggregates. Figure S7 displayed the Hartree LUMO of (a) $Li^+(FEC)_3(FEMC)$, (b) $Li^+(DFEC)(FEMC)_2$ and (c) $Li^+(FEMC)_3$. It is clear that inside the mixed aggregates solvated by both FEC and FEMC, the LUMO lies on FEC molecule while the LUMO can only lie on FEMC if the aggregates are solvated only by FEMC. We also conducted DFT calculations to unveil the LUMO level of an FEMC molecule in both electrolytes. Figure S8 and S9 display respectively the unit cell of both electrolytes and the projected density of states (PDOS) of optimized structures of FEMC in 1.2 M $LiPF_6$ FEC:FEMC 3:7 and 1.2 M $LiPF_6$ DFEC:FEMC 3:7 electrolytes. When the conduction band of FEMC that account for the reduction behavior is considered, the energy level of FEMC in the DFEC-based electrolyte is significantly lower than the energy level in the FEC-based electrolyte, which indicates that FEMC molecule is more prone to reduction in the DFEC-based electrolyte. Numerical integration of the PDOS up to 3 eV reveals that the unit cell of DFEC based electrolyte has about 0.5 more states than that of FEC based electrolyte. Thus, a larger number of FEMC molecules are reduced in the DFEC electrolyte in comparison to FEC electrolyte. Figure S10 shows the lowest energy configuration of FEMC adsorbed on a lithium surface. The calculation result indicates strong interaction exists between the carbonyl oxygen and the lithium surface. After the adsorption, transfer of electron from lithium to FEMC can easily occur, resulting in the formation of radical anion. By DFT calculation, this FEMC radical anion can further decompose to form methoxide or trifluoroethoxide and carbonates as illustrated in Figure S11. These decomposition pathways are similar to the pathways proposed by Seo *et. al*. [42] It is very common for the decomposition products such as methoxide and trifluoroethyl carbonate to further react with the electrolyte solvents, [43] forming significant amount of by-products that can impair the compact SEI formed by the reductive decomposition of DFEC. Detailed theoretical calculation about the decomposition of FEMC is presented in SI. All in all, the subsequent slow reduction of molecular FEMC in the DFEC-based electrolyte creates detrimental effects for the SEI on lithium metal surfaces, resulting in an inferior performance of the DFEC-based electrolyte compared to the performance of the FEC-based electrolyte due to the absence of aggregates solvated only by FEMC.

In conclusion, we constructed a solvating power series, which comprises all the common electrolyte solvents for LIBs, according to the lithium solvating affinity of the electrolyte solvents. Undoubtedly, the solvating power series established in this work provides important guidelines to help understand and evaluate the solvation behavior of solvent molecules in different electrolyte systems, as evidenced by its capability to reveal the solvation behavior of different fluorinated carbonate electrolyte systems, which heavily influences the electrochemical performance of lithium batteries.

ASSOCIATED CONTENT

Supporting Information

Experimental section, NMR data, FTIR data, Raman data, and DFT calculation. This material is available free of charge via the Internet.

AUTHOR INFORMATION

Corresponding Author

*Email: amine@anl.gov

Notes

The authors declare no competing financial interest.

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Broader context

In pursuit of high-energy lithium-based rechargeable batteries, many new electrode materials such as nickel-rich layered cathodes and silicon anodes have been developed. However, conventional electrolyte ($LiPF_6$ dissolved in EC and DMC/EMC/DEC) designed for the graphite/$LiCoO_2$ system is not able to maintain the stable cycling of these new high-energy systems. Thus, functional electrolytes have been actively pursued by researchers. Although it is well-known that the electrochemical property of an electrolyte is heavily influenced by its solvation state, insight into the lithium solvating ability of various electrolyte solvents is limited. In this report, we construct a solvating power series, which provides a reliable quantitative measure of the lithium solvating power of common electrolyte solvents. Using the as-established solvating power series, researchers can easily evaluate the solvation state of an individual solvent in a binary or ternary electrolyte system. A representative application of the series is illustrated by the determination of a suitable cyclic carbonate co-solvent for FEMC based electrolyte. This newly constructed solvating power series will provide insightful guidance for the future design of functional electrolyte system and will be especially instructive in the selection of suitable solvent/co-solvent for lithium batteries.