



Cation–Solvent, Cation–Anion, and Solvent–Solvent Interactions with Electrolyte Solvation in Lithium Batteries

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Electrolyte solvation is a fundamental issue that regulates the lithium (Li) ion solvation sheath structure, the formation of cathode/anode–electrolyte interphase, and the plating/stripping behavior of Li ions in working Li batteries. Herein, we probe the cation-solvent, cation-anion, and solvent-solvent interactions under both vacuum and electrolyte conditions through density functional theory calculations. The solvation effects can significantly weaken the aforementioned interactions in electrolytes as well as increase the Li–O/F distances in Li⁺-containing complexes. The dissolution behaviour of Li salts in electrolytes was further explored and experimentally validated by dissolving lithium nitrate in different solvents. This work affords a mechanistic understanding of electrolyte microstructure and highlights the significant role of electrolyte solvation in regulating battery performance, affording fruitful insights into emerging electrolyte design for high-performance batteries.

Solvation exists widely and renders very different and significant phenomena in vast chemical and material systems.^[1] The current chemistry is also originated from our growing knowledge of solutions to some degree.^[2] The electrolyte solvation and its effects on battery performance have been always one key fundamental and essential issue in working lithium (Li) batteries, which attracts increasing attention recently.^[3]

The solvation structure of Li ions in electrolyte directly determines the formation of solid electrolyte interphase (SEI) on anode as well as cathode–electrolyte interphase (CEI). This can render significant impacts on anode and cathode performance, respectively.^[4] The different voltage–capacity curves corresponding to varied charge–discharge mechanisms. For instance, the electrochemical pathways of lithium–sulfur batteries with ester or ether electrolytes are largely depended on the dissolution behaviors of polysulfides.^[5] The dissolution behavior of solute is largely dependent on solvation effects. Besides, the stripping and plating behaviors of Li metal anode are accompanied with the solvation and desolvation processes of Li ions.^[4b,6]

There have been a lot of pioneering works in lithium batteries to probe the electrolyte solvation structure and understand its effects on battery performance.^[7] For example, Xu, Borodin, and co-workers investigated the solvation structure of Li ions through both theoretical simulations and experimental nuclear magnetic resonance tests, confirming the preferential solvents inside solvation sheath as well as the transport behavior of Li ions.^[7a,b,8] We proposed the concept of ion-solvent complex and explored the origin of the reduced reductive stability of the complex comparing with pure solvent.^[7g,9] Fluoroethylene carbonate (FEC) was thus introduced into Li ion solvation sheath and a LiF-rich and stable SEI was formed, rendering the long cycling performance of Li metal anodes.^[10] Zhang and co-workers comprehensively studied high-concentration electrolytes, in which the electrolyte solvation is very different from routine electrolytes, and correlated the solvation effects with electrochemical performance of lithium batteries.^[6b,11]

There are great achievements in understanding electrolyte solvation structure and promoting battery performance.^[12] If the solvation effect on fundamental interactions in electrolytes, such as the cation-solvent, cation-anion, and solvent-solvent interactions, can be built, a deep understanding of electrolyte solvation at the atomic level can be achieved. This is of great importance for further electrolyte exploration and interfacial regulation of working rechargeable batteries.

In this contribution, the interactions of cation-solvent, cation-anion, and solvent-solvent in both vacuum and solution conditions were systematically investigated through density functional theory (DFT) calculations. Typical ester (ethylene carbonate [EC], diethyl carbonate [DEC]), and ether (1,3-dioxolane [DOL] and 1,2-dimethoxyethane [DME]) solvents, and widely used Li salts (lithium hexafluorophosphate [LiPF₆], lithium bis(fluorosulfonyl)imide [LiFSI], lithium bis(trifluoromethanesulfonyl)imide [LiTFSI], and lithium nitrate [LiNO₃]) were considered in the current modeling contribution. All cation-solvent, cation-anion, and solvent-solvent complexes exhibit a much-reduced binding energy in solutions comparing with vacuum condition. Besides, the reduced level of binding energy is directly related with the dielectric constant of solvents, determined by the nature of electrostatic interactions. Based on these results, a deep understanding of Li salt dissolution behavior in different electrolytes was explored.

Electrolytes are typically composed by Li ions, anions from Li salts, and solvents. Li ions in electrolytes are commonly solvated with solvents and anions. The solvation structure is determined by the Li⁺-solvent and Li⁺-anion interactions (Figure 1). Besides, there is solvent-solvent interaction in most

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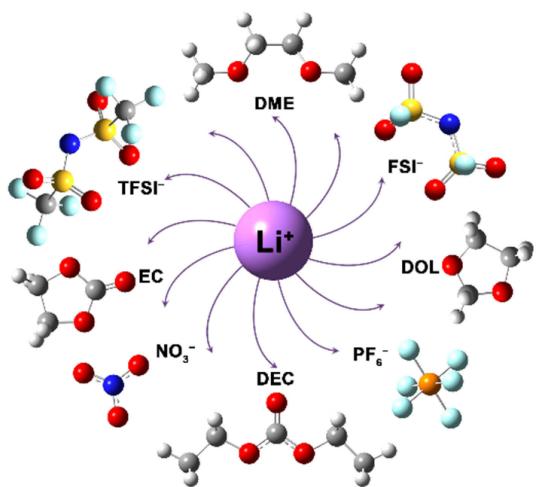


Figure 1. Schematic representation of electrolyte solvation. The interaction between Li^+ and anion or solvent species is shown. The hydrogen, lithium, carbon, nitrogen, oxygen, fluorine, phosphorus, and sulfur atoms are represented by white, purple, grey, blue, red, green, orange, and yellow, respectively.

dilute electrolyte, while the solvent-solvent interaction will be disappeared in very high-concentration electrolytes due to the loss of free solvent.^[13] These three interactions can be attributed to electrostatic interactions, including ion–ion interaction, ion–dipole interaction, and dipole–dipole interaction. Therefore, the dielectric constant of solvent has a very significant impact on the binding energy of these interactions according to classical physical laws (Formula 1–3).^[2]

$$U_{\text{ion-ion}} = -\frac{1}{4\pi\epsilon} \times \frac{z_1 z_2 e^2}{r} \quad (1)$$

$$U_{\text{ion-dipole}} = -\frac{1}{4\pi\epsilon} \times \frac{ze\mu\cos\theta}{r^2} \quad (2)$$

$$U_{\text{dipole-dipole}} = -\frac{1}{(4\pi\epsilon)^2} \times \frac{2\mu_1^2 \mu_2^2}{3k_B T r^6} \quad (3)$$

where ϵ is the dielectric constant, $z\cdot e$ the charge on ion, μ the dipole moment of dipole, r the distance between ion and ion/ion and the center of dipole/the center of dipole and the center of dipole, θ the dipole angle relative to the line r joining the ion and the center of the dipole, k_B the Boltzmann constant, and T the temperature.

The optimized geometrical structures of cation-solvent, cation-anion, and solvent-solvent complexes are presented in Figure 2. Li ions prefer to interact with the carbonyl oxygen of EC/DEC solvent and ether oxygen of DOL/DME solvent (Figure 2a–d) in both vacuum and solution conditions. While the Li–O bond length is enlarged by the solvation effects (Figure S1). Consequently, the binding energy of Li^+ -solvent complexes is reduced in solutions comparing with that in vacuum (Figure 3a). Specifically, the binding energies of Li^+ -DOL, Li^+ -DEC, Li^+ -EC, and Li^+ -DME in vacuum are -1.71 , -2.09 , -2.24 , and -2.84 eV, respectively. While in solutions, the binding energies of Li^+ -DOL, Li^+ -DEC, Li^+ -EC, and Li^+ -DME are reduced to -0.81 , -1.15 ,

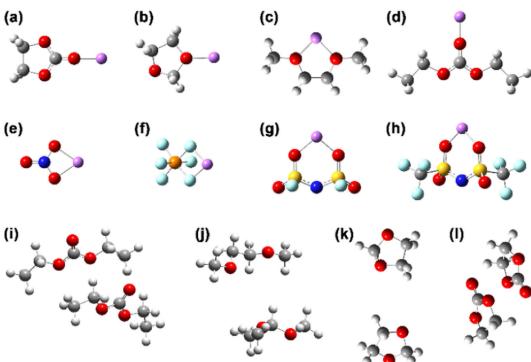


Figure 2. Optimized geometrical structures of the: a) Li^+ -EC, b) Li^+ -DOL, c) Li^+ -DME, d) Li^+ -DEC, e) Li^+ -NO₃, f) Li^+ -PF₆⁻, g) Li^+ -FSI⁻, h) Li^+ -TFSI⁻, i) DEC-DEC, j) DME-DME, k) DOL-DOL, and l) EC-EC complexes. The hydrogen, lithium, carbon, nitrogen, oxygen, fluorine, phosphorus, and sulfur atoms are represented by white, purple, grey, blue, red, green, orange, and yellow, respectively.

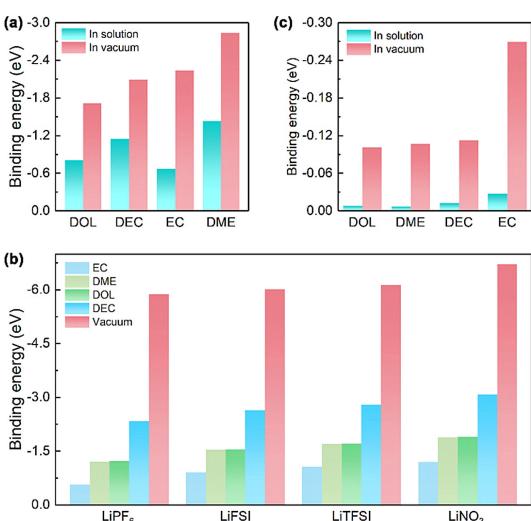


Figure 3. Comparison of binding energies in vacuum and solution: a) Li^+ -DOL/DEC/EC/DME, b) Li^+ -PF₆⁻/FSI⁻/TFSI⁻/NO₃, and c) DOL-DOL/DME-DME/DEC-DEC/EC-EC.

–0.67, and –1.43 eV, respectively. As the dielectric constant of EC is largest, the solvation effect of EC on binding energy is the most significant among these four solvents. Similarly, the solvation effect of DEC is the slightest.

The situations of Li^+ -anion complexes (Figure 2e–h) are analogous to that in Li^+ -solvent complexes. The solvation can also significantly increase the Li–O/F bond length (Figure S2) and simultaneously reduce the binding energy of Li^+ -anion (Figure 3b). Besides, the trend of binding energy of a specific Li^+ -anion is agreed with the dielectric constant trend of solvents. The larger dielectric constant of solvent, the smaller binding energy of the Li^+ -anion complex. For instance, the binding energies of Li^+ -PF₆⁻ complex in EC, DME, DOL, DEC, and vacuum are –0.56, –1.21, –1.22, –2.34, and –5.88 eV, respectively. Simultaneously, the dielectric constants of EC, DME, DOL, and DEC are 89.8, 7.2, 7.1, and 2.8, respectively (Table S1). However, the electrolyte solvation can change the

geometrical structure of Li^+ -anion complexes. Specifically, Li ion prefers to simultaneously interact with three F atoms of PF_6^- (similar to hollow site) in vacuum but two F atoms of PF_6^- (similar to bridge site) in all solutions.

The interaction between electrolyte solvents was also further considered (Figure 2i–l) although their interactions are much weaker than that of the other two complexes. The interactions between electro-positive hydrogen and electro-negative oxygen play the major role in solvent-solvent complexes. This is much more complicated than that of Li^+ -anion/solvent complexes. As expected, the solvation effect can also largely reduce the binding energy of solvent-solvent complexes in solutions comparing with that in vacuum (Figure 3c). Specifically, the binding energies of DOL-DOL, DME-DME, and DEC-DEC can be reduced from around -0.10 eV to around -0.01 eV when introducing the solvation effect into simulations. While the binding energy of EC-EC changes from -0.270 to -0.028 eV. The appropriate large binding energy of EC-EC can explain its solid state at room temperature (T_r) as the $k_B T_r$ is around 0.026 eV.

The solvation can obviously reduce interaction strength among electrolyte components, including the Li^+ -solvent, Li^+ -anion, and solvent-solvent interactions. Simultaneously, the solvation can also increase the $\text{Li}-\text{O}/\text{F}$ bond length in Li^+ -solvent and Li^+ -anion complexes and even change the interaction forms (*i.e.* $\text{Li}^+-\text{PF}_6^-$ complex). Consequently, the existence form of Li^+ in electrolyte can be largely regulated by electrolyte solvation, which can directly control the dissolution behavior of Li salts in different electrolytes.

Although both salt and solvation play an important role in determining the Li^+ -anion interaction, the binding energies between Li^+ and salt anions keep the same trend in all solvents: $\text{Li}^+-\text{NO}_3^- > \text{Li}^+-\text{FSI}^- > \text{Li}^+-\text{TFSI}^- > \text{Li}^+-\text{PF}_6^-$ (Figure 4a). A large

Li^+ -anion binding energy indicates a worse dissolution of the salt to some degree. This is consistent with experimental cognitions that LiPF_6 can be much easier dissolved in most solvents than LiNO_3 . Basically, the dissolution behavior of Li salt is regulated by the Li^+ -solvent and Li^+ -anion interactions, which compete with each in electrolytes. On one hand, solvents with a large dielectric constant significantly can weaken the Li^+ -anion interaction, favoring the dissolving of Li salt. This is one of the reasons why EC based electrolytes are widely used. On the other hand, solvents with a large Li^+ -solvent can strongly compete with anion to coordinate with Li ions. Therefore, DME is expected to be a good solvent in this respect.

More importantly, the dissolution behavior of LiNO_3 in different solvents has been strongly considered recently.^[14] The binding energy of $\text{Li}^+-\text{NO}_3^-$ in DEC and DOL solvent is -3.09 and -1.89 eV respectively. This is much larger than that of Li^+-DEC (-1.15 eV) and Li^+-DOL complexes (-0.81 eV). The huge binding energy differences indicate LiNO_3 can hardly be dissolved in DEC and DOL solvents as Li ions prefer to interact with NO_3^- rather than DEC or DOL molecule. Although the binding energy differences in EC and DME electrolytes are 0.52 and 0.47 eV, respectively, a small amount of LiNO_3 can be expected to be dissolved.

Solvent takes a major part in electrolytes and can compete with salt anions due to the quantity advantages if the binding energy difference is small enough. Besides, the small binding energy differences in EC and DME electrolytes are induced by the large dielectric constant of EC and the large binding energy of Li^+-DME , respectively.

In order to validate the theoretical inference, 20 mg LiNO_3 was added into 1.0 mL EC, DEC, DOL, and DME solvents. As EC is solid at room temperature, EC solvent was heated to 40°C and the other solvents are kept at room temperature. As expected, the LiNO_3 can be only dissolved in EC and DME solvents (Figure 4b). Besides, a mixture of EC and DEC (EC/DEC solvent, $v:v=1:1$) was also considered for its wide applications in conventional lithium ion batteries. As results, LiNO_3 can hardly be dissolved, agreeing with previous experimental reports.^[14]

In conclusion, the solvation effects on fundamental interactions in electrolytes were probed through DFT calculations as well as experimental verifications. The binding energy of Li^+ -solvents, Li^+ -anions, and solvent-solvent can be significantly reduced by solvation effects, in which the dielectric constant of solvents plays an important role. The electrolyte solvation can also enlarge the $\text{Li}-\text{O}/\text{F}$ bond length in Li^+ -solvent/anion complexes. The dissolution behaviour of Li salts in different electrolytes can also be regulated by solvation effects. Specially, the dissolution behaviour of LiNO_3 was predicted and also verified by experiment results herein. This work uncovers the important role of solvation effect in regulating electrolyte structures and dissolution behaviour of Li salts at the atomic level, affording fruitful insights into new electrolyte design as well as understanding its roles in battery performance.

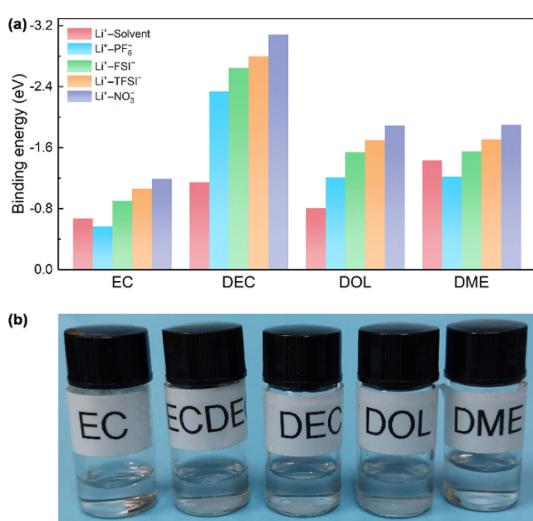


Figure 4. a) Comparison of $\text{Li}^+-\text{PF}_6^-/\text{FSI}^-/\text{TFSI}^-/\text{NO}_3^-$ and Li^+ -solvent binding energies in EC/DEC/DOL/DME electrolytes. b) The experimentally observed dissolution behaviour of LiNO_3 in EC, EC/DEC, DEC, DOL, and DME solvents. The EC solvents were melted at 40°C while the other solvents were maintained at room temperature.

Experimental Section

DFT Calculation Details

The cluster-based DFT calculations were performed in Gaussian (G09)^[15] suite of program with Becke's three-parameter hybrid method using the Lee–Yang–Parr correlation functional (B3LYP).^[16] The geometrical structures and the vibrational modes were calculated at 6-311+G(d, p) level. Simultaneously, the solvation effect was considered with integral equation formalism variant of the Polarizable Continuum (IEPCM) model.^[17] The used parameters for IEPCM models are listed in Table S1. The binding energy (E_b) between two components was defined as following: $E_b = E_{\text{total}} - E_A - E_B$, where E_{total} , E_A , and E_B are the total energy of the A–B complexes, A component, and B component, respectively. A and B can be Li ion, salt anion, and solvents.

Experimental Details

The EC and DEC solvents were purchased from Sigma-Aldrich Co., LTD. The DOL and DME solvents were purchased from Alfa Aesar Chemical Co., Ltd. LiNO₃ (99.99% metals basis) was purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. 20 mg LiNO₃ was added into 1.0 mL solvents when observing the dissolution behaviour of LiNO₃. The preparation of electrolytes was performed at room temperature in an Argon-filled glovebox (Mikrouna) with water and oxygen content less than 0.1 ppm.

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Conflict of Interest

The authors declare no conflict of interest.

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