

Li Ion Solvation Study Using DFT

The performance of a Li ion battery varies with the electrolytes employed which is determined by Li⁺-solvent interactions. Understanding how solvent molecular structure affects coordination strength provides insight into electrolyte design for improved ion mobility and stability. In this project, I have used basic computational tools and DFT to analyse some of these interactions to systematically understand how binding of the Li⁺ ions differ with different carbonate based electrolytes, extending the study to analyse incremental solvation by analysing small Li⁺ clusters. I carried out vibrational frequency calculations to confirm the stability of the optimised structures, and confirmed the robustness of the methodology by recalculating binding energies using a different set of exchange-correlation (XC) functionals. Ethylene carbonate (EC) and dimethyl carbonate (DMC) are the electrolytes used.

Binding Energy Analysis

1. Li⁺-EC system

After constructing Li⁺ and EC on Avogadro, and optimising their structures on ORCA, I calculated their single point energies using DFT with a B3LYP functional and def2 TZVP, def2 SVP basis sets respectively in a consistent gas phase. I constructed an Li⁺-EC cluster system and repeated the same.

Single Point Energies:

$$E[\text{Li}^+] = -7.278559087059 \text{ Eh}$$

$$E[\text{EC}] = -341.985564495677 \text{ Eh}$$

$$E[\text{Li}^+-\text{EC}] = -349.354884632141 \text{ Eh}$$

Using their individual single point energies, the binding energy was calculated using the given formula

$$E_{\text{bind}} = E[\text{Li}^+-\text{EC}] - (E[\text{Li}^+] + E[\text{EC}])$$

$$\begin{aligned} E_{\text{bind}} &= -349.354884632141 - (-7.278559087059 + -341.985564495677) \\ &= -0.090761049405 \text{ Eh} = \mathbf{-56.9 \text{ kcal/mol}} \end{aligned}$$

Gas-phase DFT calculations show that Li⁺ binds strongly to ethylene carbonate, with a computed binding energy of -56.9 kcal/mol , indicating significant electrostatic stabilization through coordination to the carbonyl oxygen.

2. Li⁺-DMC system

Repeating the same process with DMC as solvent, binding energy was calculated.

Single Point Energies:

$$E[\text{Li}^+] = -7.278559087059 \text{ Eh}$$

$$E[\text{DMC}] = -343.188477609013 \text{ Eh}$$

$$E[\text{Li}^+-\text{DMC}] = -350.549440942088 \text{ Eh}$$

To find binding energy

$$E_{\text{bind}} = E[\text{Li}^+\text{-DMC}] - (E[\text{Li}^+] + E[\text{DMC}])$$

$$E_{\text{bind}} = -350.549440942088 - (-7.278559087059 + -343.188477609013)$$

$$E_{\text{bind}} = -0.082404246016 \text{ Eh} = \mathbf{-51.7 \text{ kcal/mol}}$$

DFT calculations reveal Li binds strongly to dimethyl carbonate as well with a binding energy of -51.7 kcal/mol. This value is however less than that of the Li⁺-EC system.

$$E_{\text{bind}}[\text{Li}^+\text{-EC}] > E_{\text{bind}}[\text{Li}^+\text{-DMC}]$$

This difference can be attributed to the rigid cyclic structure of EC, which facilitates more effective electrostatic stabilization of Li⁺ compared to the flexible linear DMC molecule. These results highlight how solvent molecular structure influences lithium-ion coordination strength and transport properties in carbonate-based electrolytes.

Li-O Bond Length

Comparing the Li-O bond length of the two systems,

$$\text{Li-O(EC)} = 1.827 \text{ \AA}$$

$$\text{Li-O(DMC)} = 1.856 \text{ \AA}$$

$$d\text{Li-O(EC)} < d\text{Li-O(DMC)}$$

Geometric analysis of the optimized Li⁺-solvent complexes reveals a shorter Li-O coordination distance for ethylene carbonate (1.827 Å) compared to dimethyl carbonate (1.856 Å). This structural difference correlates directly with the stronger binding energy calculated for Li⁺-EC (-56.9 kcal/mol) compared to Li⁺-DMC (-51.7 kcal/mol), implying how solvent molecular rigidity and dipole alignment influence lithium-ion coordination strength in carbonate-based electrolytes.

Incremental Solvation Analysis

With insight into the varying effect of different solvents, I redid the calculations by constructing a system Li(EC)₂ to analyse the effect of Li⁺ binding energy with addition of a solvent molecule into its coordination shell.

$$E[\text{Li(EC)}_2] = -691.404808210147$$

$$\Delta E = E[\text{Li(EC)}_2] - (E[\text{Li(EC)}] + E[\text{EC}])$$

$$\Delta E = -691.404808210147 - (-691.340449127818) = -0.064359082329 \text{ Eh} = \mathbf{-40.4 \text{ kcal/mol}}$$

Incremental solvation analysis further reveals non-additive stabilization in the first solvation shell of Li⁺. While the first ethylene carbonate molecule binds strongly (-56.9 kcal/mol), coordination of the second EC molecule causes reduced stabilization (-40.4 kcal/mol). This could be a result arising from electrostatic hindrance and solvent-solvent competition.

Li Transport Descriptor

With data on the repercussions of strong Li^+ -solvent coordination, it is clear that stronger binding leads to stiffer Li-O interactions which hinder ion mobility. I looked into this through stretching frequency values.

Stretching Frequencies:

$$\nu_{\text{Li-O(EC)}} = 237\text{cm}^{-1}$$

$$\nu_{\text{Li-O(DMC)}} = 198.97\text{cm}^{-1}$$

Vibrational frequency analysis reveals a clear difference in Li^+ coordination stiffness between carbonate solvents. The Li-O stretching mode appears at a higher frequency in ethylene carbonate ($\sim 237\text{ cm}^{-1}$) compared to dimethyl carbonate ($\sim 199\text{ cm}^{-1}$), indicating a stiffer coordination environment in EC. This supports the conclusion that stronger Li^+ solvation in EC may impede lithium-ion mobility relative to DMC, demonstrating how solvent molecular structure influences transport-related properties.

Robustness of Methodology

To reconfirm the robustness of the functionals used, I redid the calculations using PBE correlation exchange functionals to check the magnitude of difference in values.

$$\text{Li}^+ = -7.256652951183\text{ Eh}$$

$$\text{EC} = -341.781287836788\text{ Eh}$$

$$E[\text{Li}^+-\text{EC}] = -349.125021898754\text{ Eh}$$

$$E_{\text{bind}} = -0.087081110783\text{ Eh} = \mathbf{-54.6\text{ kcal/mol}}$$

$$\Delta E = -54.6 - (-56.9) = \sim 2.3\text{ kcal/mol}$$

Methodological robustness was assessed for the strongest coordinating system (Li^+-EC). Due to the very small energy difference, it is confirmed that qualitative binding trends are preserved across XC functionals.

Conclusion

The project gives quantitative insight about the Li-solvent interactions that govern its efficiency as an ion-electrolyte system using quantum computational softwares. Binding energy analysis reveals ethylene carbonate's greater affinity to Li^+ than with dimethyl carbonate, which is further evidenced by comparing the Li-O bond lengths and stretching frequencies. Incremental solvation effects of the $\text{Li}(\text{EC})_2$ cluster gave a lower binding energy as compared to Li^+-EC , implying non additive stabilisation in the first solvation shell. To confirm qualitative trends are consistent with different XC functionals used during DFT calculations, recalculation of the binding energy of the strongest coordinating system Li^+-EC confirmed the obtained results.