

Solvation: Why Lithium Trifluoromethanesulfonate in Common Battery Solvents Makes a Poor Electrolyte

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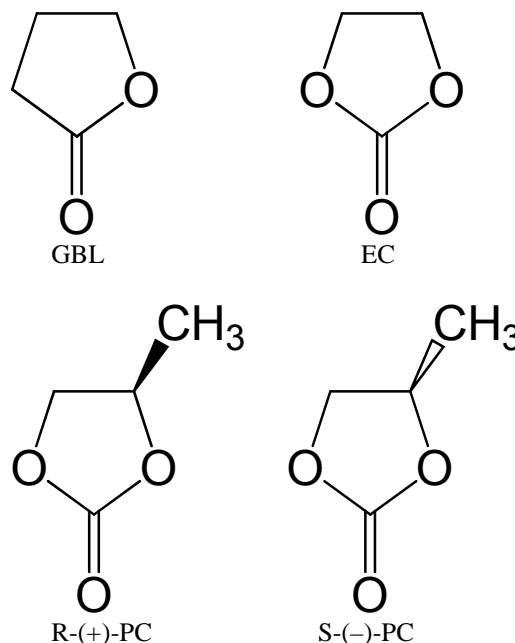
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Three figures of merit governing the selection of a Li-ion battery electrolyte are cost, reactivity, and charge transport. Ideally an electrolyte would be cheap, unreactive towards other battery components (electrode materials, membranes, solvent, etc.), and transport charge efficiently. Considering these categories, lithium bis(trifluoromethanesulphonyl)imide (Li-TFSI) has found success and application in an array of Li-ion batteries whereas lithium trifluoromethanesulfonate (LiTf) has not. Why? Both LiTf and Li-TFSI meet the first two criteria: inexpensive and inert to common battery materials. However, LiTf has failed when used as a salt in battery electrolytes due primarily to inadequate charge transport. The question is why does the lithium salt with the Tf⁻ anion exhibits poor transport behavior in common electrolyte solvents whereas the salt with the TFSI⁻ anion does not? The key to this puzzle lies in the solvation of the LiTf.

In this work we investigated the solvation of LiTf in several common electrolyte solvents to improve our understanding of the impact of the anion structure on solvation state. By employing differential scanning calorimetry (DSC), Raman spectroscopy, and X-ray crystallography we were able to monitor changes of solvation state(s) with respect to both temperature and concentration were. The phase behavior of mixtures of LiTF with common organic solvents found in battery electrolytes were interrogated with the aid of DSC, and the solvation environment of the salt in an organic solvent was elucidated through Raman spectral analysis. Finally, X-ray diffraction analysis of available crystallized solvates was obtained to provide supporting structural information to the DSC and Raman analyses. Correlating these three pieces of chemical information enables us to

shed some light as to the fundamental cause(s) of the poor electrolyte performance of LiTF in the organic solvents studied.

Our work has shown that the inadequate charge transport behavior of LiTF arises predominately from its highly associative nature. In ethylene carbonate (EC), γ -butyrolactone (GBL), R-(+)-propylene carbonate (R-(+)-PC) or S-(-)-propylene carbonate (S-(-)-PC) the LiTf exists predominately in either aggregated form or as contact ion pairs under all concentration and temperature conditions studied.¹⁻³ Only in the most dilute solutions did we find a significant presence of solvent-separated ion pairs.



References

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