Density functional theory molecular dynamics simulation on the tetraglyme based electrolytes for lithium batteries

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New electrolytes with high stability and condcutivity are pivotal for developing the next-generation lithium-ion/metal batteries. Glyme based electrolytes are of interest due to the ionic-liquid-like behavior at a high concentration of lithium salt. The fundamental properties of glyme electrolytes, such as the solvation process and ionic diffusion kinetics, have not been adequately understood. Considering the experimental difficulties, first-principles simulations could be helpful to address these fundamental problems.

Herein we employ density functional theory (DFT) based molecular dynamics (MD) simulation of lithium bis(trifluoromethylsulfonyl)-amide (LiTFSA, Li salt) and tetraglyme (G4, solvent), to comparatively investigate the solvation structure of Li^+ ions at both low concentration (1mol/L) and high concentration (equimolar), as shown in the Figure below. For each Li-salt concentration, different initial models were constructed to show the dependence of simulation results on the conformation of G4 molecules. Our results show that the initial conformation of G4 molecules has no prominent influence on the electrolyte properties at a low concentration of Li salt. In the case of high concentration (equimolar), all G4 molecules prefer the crown-ether-like structure enclosing a Li^+ ion, and the one-to-one correspondence between Li^+ ions and G4 molecules is maintained during the entire DFT-MD simulation, suggesting an ionic-liquid-like nature that is consistent with experimental reports.[1]

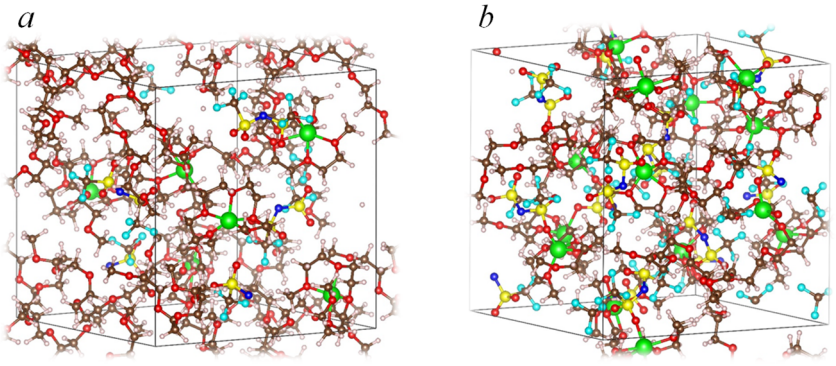

Figure. Snap shot of the low concentration (a) and high concentration (b) LiTFSA@G4 electrolyte during the DFT-MD simulation. Colour scheme: green-Li, red-O in G4, grey: C, blue: O in TFSA, light blue: F, yellow: S.

References:

[1] K. Yoshida, M. Nakamura, Y. Kazue, N. Tachikawa, S. Tsuzuki, S. Seki, K. Dokko, M. Watanabe, J. Am. Chem. Soc. 133 (2011) 13121–13129.