

Investigation of the key role of DMF solvent in PVDF-based electrolytes

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The development of high-performance Lithium-ion batteries has long been at the forefront of energy technologies, given the urgent need for large-scale deployment of renewable energy sources, together with the electrification of transportation.

The electrolyte, which is a fundamental component of such electrochemical systems, is often the limiting factor directly affecting the performance and safety of the battery [1,2]. In this context, Poly(vinylidene difluoride)-based electrolytes have attracted huge attention due to their interesting ionic conductive properties and capability to overcome safety issues by replacing flammable organic liquid electrolytes [3]. Despite the interest in these polymer electrolytes, the mechanism of Li-ion diffusion in PVDF-based electrolyte is not well understood. Recent experimental studies [4] have argued that residual DMF solvent, which is used during the electrolytes preparation to dissolve the polymer-salt system, solvates Li⁺ and contributes to the ionic diffusion.

Here we have used Density Functional Theory (DFT) to elucidate the role of DMF in the solvation and diffusion of Li⁺. The interaction of Li⁺ with DMF molecules and PVDF chains has been computed by constructing Li⁺(DMF)_n(PVDF)_m complexes. In addition, molecular dynamics simulation has been performed in order to obtain additional insights on the diffusion of Li⁺(DMF)_n(PVDF)_m complex.

The atomic structures and formation energies of Li⁺(DMF)_n(PVDF)_m complexes, shown in Figure 1, demonstrate that Li⁺ tends to coordinate up to three DMF molecules rather than directly binding PVDF, indicating that the interaction Li⁺-DMF is stronger than the interaction of Li⁺ with PVDF. Increasing the number of ligands, *e.g.* n+m > 4, Li⁺(DMF)_n complex interacts with PVDF as the second solvation shell.

Moreover, our molecular dynamics simulations confirm that the amount of DMF molecules coordinating Li⁺ affects the mobility of Li⁺ through PVDF chains. Our results represent a step forwarding in understanding the diffusion mechanism of Li-ion in PVDF-based electrolytes and can be used for the rational design of novel electrolytes with improved performances.

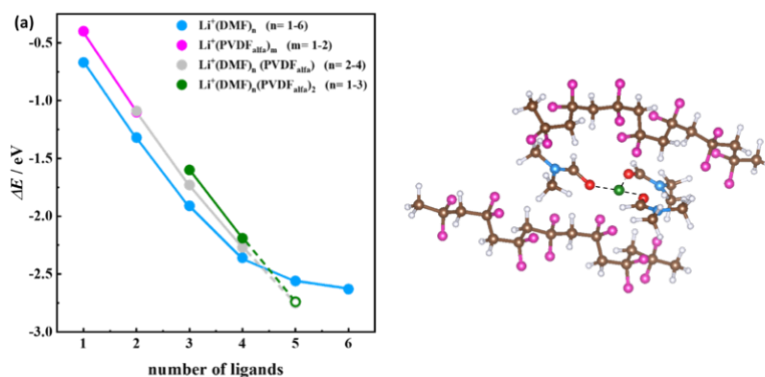


Figure 1. Formation Energy (ΔE) and a representative structure of Li⁺(DMF)_n(PVDF)_m complexes.

References

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