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A First-Principles Molecular Dynamics Study on Li+ Solvation Structures in THF/MTHF Containing Electrolytes for Lithium Metal Batteries.

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Abstract : In lithium-ion batteries (LIBs) the solid–electrolyte interphase (SEI) layer, which forms on the anode surface, plays a crucial role in stabilizing battery performance. Over the past two decades, efforts to enhance LIB electrolytes have primarily focused on refining the quality of SEI components. Despite these endeavors, several observed phenomena remain inadequately improved the SEI layer. Consequently, there has been a significant surge in research interest regarding the behavior of electrolyte solvation structures to elucidate improvements in battery performance. Thus, in this study, we aimed to explore the solvation structures of $LiPF_6$ in a mixture of organic solvents, tetrahydrofuran (THF) and 2-methyl-tetrahydrofuran (MTHF) using ab-initio molecular dynamics (AIMD) simulations. Our work investigated the solvation structure of electrolytes with different salt concentrations: low-concentration electrolyte (1.0M LiPF6 in 1:1v/v mixture of THF and MTHF), and high-concentration electrolyte (2.0M $LiPF_6$ in 1:1v/v mixture of THF and MTHF) and compared them with that of conventional electrolyte (1.0M $LiPF_6$ in 1:1v/v mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC)). Furthermore, the reduction stability of Li+ solvation structures in these electrolyte systems are investigated. It is found that the first solvation shell of Li+ primary consists of THF. We also analyzed the molecular orbital energy levels to understand the reducing stability of these solvents. Compared with the solvation sheath of commercial electrolyte, the THF/MTHF-containing electrolytes have a higher lowest unoccupied molecular orbital (LUMO) energy level, resulting in improved reduction and interface stability. It has been shown that Li-Al alloy can significantly improve cycle life and promote the formation of a dense SEI layer. Therefore, this study aims to construct the solvation structures obtained from calculations of the pure electrolyte system on the surface of Al-Li alloy. Additionally, AIMD simulations will be conducted to investigate chemical reactions at the interface. This investigation aims to elucidate the composition of the SEI layer formed. Furthermore, Bader charges are used to determine the origin and flow of electrons, thereby revealing the sequence of reduction reactions for generating SEI layers.

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