Composition-Dependent Solvation Structure and Ion Dynamics in $Pyr_{14}FSI$ and $Pyr_{12O1}FSI$ Ionic Liquid Electrolytes for High-Voltage Lithium Metal Batteries

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Ionic liquid electrolytes (ILEs) are promising candidates for high-voltage lithium metal batteries (LMB) due to their wide electrochemical stability windows (ESW), high thermal stability, and non-flammability. However, ILEs often suffer from high viscosity and strong ion pairing, which can hinder the lithium-ion mobility and thus limit the ionic conductivity. The incorporation of a co-solvent has emerged as an effective strategy to mitigate these issues by weakening ion pairing interactions and reducing viscosity, thus enhancing Li^+ transport and interfacial performance [1-2]. Nevertheless, the influence of lithium salt concentration and co-solvent ratio on Li^+ solvation structures and their subsequent impact on ion transport properties in ILEs remains insufficiently understood. Clarifying these mechanisms is crucial for the rational design and optimization of ionic liquid electrolytes system for next-generation high-voltage batteries. In this study, experimental investigations and molecular dynamics (MD) simulations were conducted to investigate the effects of lithium bis(fluorosulfonyl)imid (LiFSI) salt concentration and bis(2,2,2-trifluoroethyl) ether (BTFE) co-solvent ratio on the Li^+ solvation sheath and self-diffusion properties in pyrrolidimium-based $[Pyr_{14}][FSI]$ and $[Pyr_{12O1}][FSI]$ ILEs. The coordination environment of Li^+ was analyzed to evaluate how increasing lithium salt concentration and BTFE ratio affect solvation structure and ion dynamics. The simulation results validated against the experimental results and confirmed the predicted Li^+ solvation behaviors. Subsequently, micelle-like solvation structure ionic liquids were successfully used in LNMO high-voltage lithium metal battery to achieve 150 stable cycling [3].

The results revealed that the lithium salt concentration and co-solvent addition distinctly influences the Li^+ solvation sheath structures, significantly dependent on the ionic liquid cation chemistry. Increasing lithium salt concentration weakens the Li^+–FSI^- coordination interactions in both $[Pyr_{14}][FSI]$- and $[Pyr_{12O1}][FSI]$-based ionic liquid electrolytes, whereas the addition of the co-solvent BTFE strengthened these interactions in both systems. Moreover, in the ether-functionalized $[Pyr_{12O1}][FSI]$-based electrolyte, the polar oxygen atom of the Pyr_{12O1}^+ cation actively participated in forming the Li^+ peripheral solvation sheath, further enhancing the Li^+ coordination. Notably, BTFE did not directly coordinate with Li^+ in the primary solvation sheath but indirectly modified the overall solvation environment by altering the electrolyte structure.

In addition, self-diffusion analysis revealed that the lithium salt concentration and co-solvent addition signifycantly impacted the Li^+ transport dynamics, with distinct behavior observed in $[Pyr_{14}][FSI]$- and $[Pyr_{12O1}][FSI]$-based ILEs. Increasing the lithium salt concentration generally reduces the Li^+ mobility due to enhanced ion interactions in both electrolyte systems. However, introducing BTFE notably enhances the mobility of all electrolyte components. In the $[Pyr_{12O1}][FSI]$-based ILEs system, the Li^+ diffusion is continuously improved with increasing BTFE ratio, reflecting the pronounced enhancement at high BTFE content. In contrast, $[Pyr_{14}][FSI]$- based electrolytes exhibited an optimal Li^+ mobility enhancement at moderate BTFE ratios, beyond that further improvements became limited. These observations highlight the critical role of electrolyte composition and cation structure in controlling ion transport dynamics, providing valuable insights for optimizing ionic liquid electrolyte formulations for advanced battery technologies.

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