10th Congress on Ionic Liquids (COIL-10)
17th – 21st November 2025 • Perth • Australia

Polymer-assisted Deep Supercooling of Li Salt: Effects of Polymer Additives on Suppression of Crystallization

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Lithium secondary batteries capable of fast charging require electrolytes with both high ionic conductivity and high Li^+ transference number.[1] Inorganic solid-state electrolytes used in all-solid-statebatteries meet both of these requirements, but achieving intimate electrolyte-electrode interfacial contact still remains a challenge.[2] In contrast, in liquid electrolytes, the interface chemistry can be well controlled, but the lithium transference number (t_{Li}) is usually low. The presence of solvent that can diffuse freely causes a concentration gradient of Li salt under anion blocking conditions. Recent studies suggested lithium molten salts as a potential solution to achieve $t_{Li} \sim 1$ in a battery cell.[3, 4] However, the high melting point and crystallinity make most of these salts unsuitable for battery applications at room temperature. Stabilizing the supercooled liquid state is an effective way to extend the liquid temperature range of lithium molten salts. In pharmaceutical fields, polymeric additives have been utilized to inhibit unfavorable crystalliztion and stabilize amorphous formulations of drugs. Inspired by this technology, we developed a novel approach to extend the liquidus temperature of Li salt by adding a small amount of polymer.The addition of 10 mol% of poly(methyl methacrylate) (PMMA) by repeating unit to lithium (fluorosulfonyl)(trifluoromethanesulfonyl)amide (Li[FTA]) resulted in the successful preparation of a viscous liquid at room temperature. In the resulting 90 mol% Li[FTA]/PMMA, differential scanning calorimetry does not show the melting peak characteristic for Li[FTA], and it remains a supercooled liquid for several months at ambient temperature (deep supercooling). This mixture, deeply supercooled Li salt (Li-DSS), is composed almost entirely of Li salt and liquified by deep supercooling effect. We measured the Li^+ transference number of DSS under anion blocking conditions to apply for single Li ion conducting liquid electrolyte. Our result showed $t_{Li} \sim 1$ in liquid electrolytes at lower temperature. In the presentation, the suppression of crystallization of Li-DSS will be discussed with particular attention to the effects of polymer additives on structure and dynamics obtained by using both experimental and computational methods.

References

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Taku Sudoh is a Ph.D. candidate at Yokohama National University in the Department of Chemistry and life Science. He is currently supported by a JSPS Research Fellowship for Young Scientists (DC1), working on material science of liquid electrolytes for Li secondary batteries. His research interests include transport properties and dynamics of ions.