

Effects of polymer structure on supercooling behavior and ion transport of deeply supercooled Li salts containing polymer additives

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To realize the rapid charge-discharge performance of Li secondary batteries, it is essential to enhance the Li⁺ transference number (t_{Li}) of electrolytes as well as improve ionic conductivity (σ_{ion})¹. Recently, all-solid-batteries with inorganic solid-state electrolytes, which achieve high σ_{ion} and $t_{\text{Li}} \sim 1$, are considered as a promising next-generation rechargeable battery, even though the designing of the electrolyte-electrode interface remains a challenge². Molten Li salts enable $t_{\text{Li}} \sim 1$ as liquid electrolytes³ because they do not contain solvents and cannot generate a concentration gradient of Li salts in a battery during operation. However, their high melting point ($T_{\text{m}} > 100$ °C) and crystallinity typically impede their efficacy as electrolytes near ambient temperature. It has been recently found that the addition of small amounts of polymers with coordination properties to Li salts, lithium (fluorosulfonyl)(trifluoromethanesulfonyl)amide (LiFTA) or binary mixture of LiFTA and lithium bis(fluorosulfonyl)amide (LiFSA), can yield deeply supercooled Li salt (Li-DSS). These electrolytes remain a stable supercooled liquid at an ambient temperature, with a low glass transition temperature (T_{g}) and significantly suppressed crystallization. Li-DSS demonstrated comparable t_{Li} values to those observed in the pure molten Li salts, while facing a challenge related to ionic conductivity. This study investigated how the chemical structure of the polymer additive and the ratio of the binary LiFTA/LiFSA mixture affect the transport properties and supercooling behavior. Li-DSS containing an anionic polymer additive exhibited a longer duration of supercooled liquid state in comparison to Li-DSS containing non-ionic poly(methyl methacrylate) additive. Additionally, the anionic polymer-based Li-DSS showed higher ionic conductivity at a higher LiFSA content in the LiFTA/LiFSA binary mixtures. Based on the above results of the systematic study, we discuss the key factors for improving the ionic conductivity and the stability of the metastable Li-DSS.

References

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