

Role of Side Chains in Determining the Electrochemical Properties of Pyrrolidinium-based Electrolytes

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Current lithium-ion batteries typically use organic electrolytes that pose safety risks such as ignition and explosion. Alternative materials are needed to address these problems. Ionic liquids (ILs) and ionic plastic crystals (IPCs) have shown promising ionic conductivity while offering improved safety. In this study, lithium salts were incorporated into ILs and IPCs to improve their characteristics, and the properties of the composites were evaluated for comparison.

A quarternization reaction of *N*-ethylpyrrolidine and iodoethane was performed, followed by anion exchange using lithium bis(fluorosulfonyl)amide (LiFSA) to produce [C₂epyr][FSA] (Fig. 1). A similar reaction was done with *N*-methylpyrrolidine and iodopropane to produce [C₃mpyr][FSA] (Fig. 1). Pre-determined amounts of LiFSA were added to [C₂epyr][FSA] and [C₃mpyr][FSA], to produce [C₂epyr]*x* and [C₃mpyr]*x* (*x* represents mol% of LiFSA). Thermal properties were characterized using differential scanning calorimetry. Ionic conductivity was obtained through impedance spectroscopy, while DC polarization measurements were performed to obtain the lithium transference number (*t*_{Li+}).

[C₂epyr][FSA] showed a melting point (*T*_m) at 128 °C and a solid-solid transition (*T*_{s-s}) at -34 °C. For [C₃mpyr][FSA], *T*_m was observed at -11.8 °C while *T*_{s-s} was observed at -19.0 °C. The ionic conductivity of [C₂epyr][FSA] was magnitudes lower compared to [C₃mpyr][FSA] because of the difference in ionic mobility in solids and liquids. Upon the addition of LiFSA, the *T*_m lowered, and a phase change was observed. Their ionic conductivity also increased initially, and at very high LiFSA concentrations, the ionic conductivity values of the composites decreased. The *t*_{Li+} increased linearly vs. LiFSA concentration for both systems (Fig 2). High LiFSA concentrations gave high *t*_{Li+} but with a trade-off of low ionic conductivity.¹

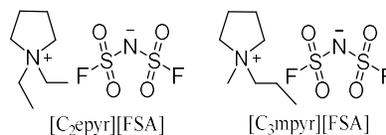


Fig 1. Structures of IPC and IL used in this study.

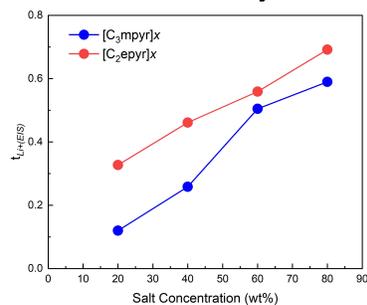


Fig 2. Relationship between *t*_{Li+} and LiFSA concentration for [C₂epyr]*x* and [C₃mpyr]*x*.

References

1. Al-Masri, D.; Yunis, R.; Zhu, H.; Jin, L.; Bruce, P.; Hollenkamp, A. F.; Pringle, J. M. *J. Mater. Chem. A* **2019**, *7* (44), 25389-25398.



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