

## PLASTIC CRYSTALS FOR FUTURE BATTERIES

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Electrochemical systems, especially lithium based battery technologies, are promising devices for providing clean and sustainable energy for next generation automobiles. To make safe and effective energy storage devices, our group has been working on developing and understanding novel ionic conductive materials, among which Organic Ionic Plastic Crystals (OIPCs) are increasingly drawing attention as a new type of solid-state electrolyte. OIPCs have definitive 3D crystalline lattices but with short-ranged rotational or orientational motion of the ions. When used as the solid electrolyte in lithium batteries, OIPCs can act as hosts allowing the added lithium ions to shuffle between the positive and negative terminals. As OIPCs are solid at ambient temperature, with high thermal and electrochemical stability, negligible vapor pressure and low flammability, they can provide a solution to the challenging safety concerns of the present commercial lithium batteries and pave the way towards more robust energy sources for electric vehicles.

**Aims**

In the present work, we selected a particularly low melting OIPC named diethyl(methyl)(isobutyl)phosphonium bis(fluorosulfonyl)imide ([P1,2,2,4][FSI], 1) to understand the ionic conduction mechanisms in systems with various amounts of added LiFSI salt and 2) to develop prototype ambient temperature lithium metal cells using this electrolyte material.

**Methods/Techniques**

For Aim 1: we used Differential Scanning Calorimetry (DSC) and Impedance Spectroscopy (EIS) to measure the temperature dependent conductivity of the material. Moreover, we used Solid-state Nuclear Magnetic Resonance (NMR) and synchrotron X-Ray powder Diffraction (XRD) to reveal the structure and dynamics of various phases, which is believed strongly correlated to the conduction mechanisms.

For Aim 2: we had charging/discharging cycling tests of the prototypical coin cells at room temperature.

**Results and Discussion**

Thermal analysis (DSC) showed that the pure OIPC has two solid-solid phase transitions (at 10°C and 25°C, respectively) before melting (37°C). These transitions are corresponding to subtle crystal structure change indicated by the XRD analysis and interestingly, both transitions accompanied by sudden increases of the bulk ions' mobility as indicated by solid-state NMR. However, the conductivity of the pure material is more likely governed by those energetic ions in the vicinity of lattice defects like vacancies, dislocations or grain boundaries. By adding only 4mol% Li salt, the room temperature conductivity increased to  $> 10^{-4} \text{ Scm}^{-1}$ , which is the threshold for a device application. This high conductivity is largely attributed to translational motion of the  $\text{Li}^+$  ions, as shown by 7Li static NMR measurements. It is worth noting that by introducing the Li salt, we may create eutectic and even amorphous phases apart from the original OIPC phases. At 22°C, the charging/discharging cycling of a prototypical cell had been carried out up to 50 cycles with excellent capacity retention and efficiency. Importantly, the cell also worked well under considerable current density.

**Conclusions**

This work represents important progress towards the development of safer and long-lasting lithium batteries: For the first time, at ambient temperature we have realized a prototypical lithium metal cell using an advantageous OIPC electrolyte to achieve excellent cell performance. We have carried out a series of in-depth characterizations to understand the ionic conduction mechanism of the Li salt doped OIPC. We found that the dramatic increase of ionic conductivity achieved by adding the Li salt may due to the creation of highly  $\text{Li}^+$  conductive eutectic and amorphous phases.