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Protic Organic Ionic Plastic Crystals: Fast Solid-State Proton Conductors

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High temperature polymer electrolyte membrane fuel cells (PEMFCs) operating between 100 °C and 200 °C are desirable because they offer significant benefits, such as improved electrode kinetics, simpler water and heat management, and better tolerance to fuel impurities, leading to higher overall system efficiencies [1]. However, state-of-the-art high temperature PEMFCs suffer from leakage problems associated with liquid electrolytes, such as H_3PO_4 and protic ionic liquids.

Recently, organic ionic plastic crystals (OIPCs) [2–6], which are unique electrolyte materials due to their superior properties such as intrinsic ionic conductivity, non-flammability, negligible vapor pressure, plasticity (mechanical flexibility), high thermal stability, and wide electrochemical window, are promising ionic conductors for electrochemical devices. While the OIPCs used as electrolytes for PEMFCs should be proton-conducting, they are often doped plastic crystals, which employ acids, protic ionic liquids or bases as the dopants for doping the matrix of certain neat plastic crystals.

In order to obviate the use of dopants that may be incompatible with the host matrix of plastic crystals, we have developed some highly proton-conductive pure plastic crystals which are protic OIPCs (abbreviated as "**POIPCs**", Figure 1) [3–6] and in essence are solid protic organic salts formed by proton transfer from a Brønsted acid to a Brønsted base. In this talk, we will present our recent work on some pure POIPCs with wide plastic crystalline phases as novel, fast solid-state proton conductors for the realization of all-solid-state high temperature PEMFCs [3–6]. The physicochemical properties of POIPCs, including thermal, mechanical, structural, morphological, thermodynamic, crystallographical, spectral and ion-conducting properties, as well as proton conducting mechanisms, isotope effects and fuel cell performances, are studied comprehensively in both fundamental and device-oriented aspects.



Figure 1. Schematic of POIPC-based fuel cells.

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