1,2,4-Triazolium perfluorobutanesulfonate as an archetypal pure protic organic ionic plastic crystal electrolyte for all-solid-state fuel cells

1,2,4-Triazolium perfluorobutanesulfonate (1), a novel, pure protic organic ionic plastic crystal (POIPC) with a wide plastic crystalline phase, has been explored as a proof-of-principle anhydrous proton conductor for all-solid-state high temperature hydrogen/air fuel cells. Its physicochemical properties, including thermal, mechanical, structural, morphological, crystallographic, spectral, and ion-conducting properties, as well as fuel cell performances, have been studied comprehensively in both fundamental and device-oriented aspects. With superior thermal stability, 1 exhibits crystal (phase III), plastic crystalline (phase II and I) and melt phases successively from 173 °C to 200 °C. Differential scanning calorimetry and temperature dependent powder X-ray diffraction (XRD) measurements together with polarized optical microscopy and thermomechanical analysis reveal the two solid–solid phase transitions of 1 at 76.8 °C and 87.2 °C prior to the melting transition at 180.9 °C, showing a wide plastic phase (87–181 °C). Scanning electron microscopy displays the morphology of different phases, indicating the plasticity in phase I. Single-crystal XRD studies reveal the molecular structure of 1 and its three-dimensional N–H/O hydrogen bonding network. The influence of the three-dimensional hydrogen bonding network on the physicochemical properties of 1 has been highlighted. The temperature dependence of hydrogen bonding is investigated by variable-temperature infrared spectroscopy. The sudden weakening of hydrogen bonds at 82 °C seems to be coupled with the onset of orientational or rotational disorder of the ions. The temperature dependence of ionic conductivity in the solid and molten states is measured via impedance spectroscopy and current interruption technique, respectively. The Arrhenius plot of the ionic conductivity assumes a lower plateau region (phase I, 100–155 °C) with a low activation energy of 36.7 kJ mol⁻¹ (i.e. 0.38 eV), suggesting likely a Grotthuss mechanism for the proton conduction. Variable-temperature infrared analysis, optical morphological observations, and powder XRD patterns further illustrate the structural changes. Electrochemical hydrogen pumping tests confirm the protonic nature of the ionic conduction observed in the lower plateau region. Finally, measurements of the open circuit voltages (OCVs) and the polarization curves of a dry hydrogen/air fuel cell prove the long-range proton conduction. At 150 °C, a high OCV of 1.05 V is achieved, approaching the theoretical maximum (1.11 V).

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