Polyiodides in Room-Temperature Ionic Liquid

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Non-stoichiometric [C₃mim][I₃.66] demonstrated an entirely different phase behavior at LT. In the cooling process, the crystallization of [C₃mim][I₃.66] was not observed. While, upon heating, metastable frozen [C₃mim][I₃.66] exhibited cold crystallization. In order to interpret the complicated behaviors, we introduce the following assumption. Since [C₃mim][I₃] crystallized simply, [C₃mim][I₃] is defined newly to be pure RTIL system considering I₃⁻ anion as a crystal forming factor. Then, [C₃mim][I₃.66] is rewritten by [C₃mim][I₃] – 7.1 mol% I₂. Thus, 7.1 mol% I₂ is regarded as an additive to new defined pure system of [C₃mim][I₃]. In some binary system, 7 mol% additive changes the phase behaviors drastically. It is pointed out that fluctuations of excess iodine occurs between C₃mim⁺ and I₃⁻. Thus, we deduce that complicated phase behaviors of non-stoichiometric [C₃mim][I₃] – 7.1 mol% I₂ are originated from the dynamic fluctuations of excess iodide/iodine.

Excess iodide/iodine of non-stoichiometric [C₃mim][I₃.66] (or [C₃mim][I₃] – 7.1 mol% I₂) caused complicated behavior in the HP phases; (i) HP crystal polymorph, (ii) spatial heterogeneous solid phases (edge or central parts), and (iii) decompression crystallization.[4]

In the liquid state, the excess iodide/iodine destabilizes by propagating between cation and anion. The unbalanced fluctuation contributes to the non-stoichiometric anomalies at LT and HP. A significant finding of effect of the non-stoichiometric anomalies provides a new insight to polyiodide migration inside RTILs assembled in the DSSCs devices.

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References

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Fig. 1: Phase behaviors of [C₃mim][I₆] at LT and HP.