

Polyiodides in Room-Temperature Ionic Liquid

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1 Introduction

Polyiodides (I_m^-) have been studied in various scientific fields since a long time.[1] Dye-sensitized solar cells (DSSCs) have been examined for high conversion efficiency. Recently, room-temperature ionic liquids (RTILs) were assembled into DSSCs on the basis of their electrochemical stability.[2] In redox couples, polyiodides combined with the RTILs were fabricated in the DSSCs. Very recently, ^{127}I -NMR experiments in the $[\text{C}_n\text{mim}][\text{I}_m]$ system have supported the Grotthuss exchange mechanism by the doublet and triplet peak splitting at a relatively large m . [3] Here, the C_nmim^+ cations were 1-alkyl-3-methylimidazolium, and n denoted the alkyl-side chain length of C_nmim^+ .

2 Experiment

High pressure (HP) behavior of transparent pure $[\text{C}_3\text{mim}][\text{I}]$ was examined using diamond anvil cell (DAC) in BL-18C. In the mixed system, we performed HP experiments in NE5C with a multi-anvil assembly (MAX80), since ruby inside the DAC is useless as a pressure marker in the dark colored $[\text{C}_n\text{mim}][\text{I}_m]$.

3 Results and Discussion

Low-temperature phase (LT) behaviors were investigated using simultaneous X-ray diffraction and differential scanning calorimetry.[4] Crystallization of pure $[\text{C}_3\text{mim}][\text{I}]$ was suppressed both at LT and HP (Fig. 1). In contrast, stoichiometric $[\text{C}_3\text{mim}][\text{I}_3]$ having polyiodide easily crystallized at LT and HP. Hence, I_3^- (one of polyiodides) is regarded as a crystal forming factor, although I^- contributes to glass forming. This is a significant finding of an essential property of polyiodides.

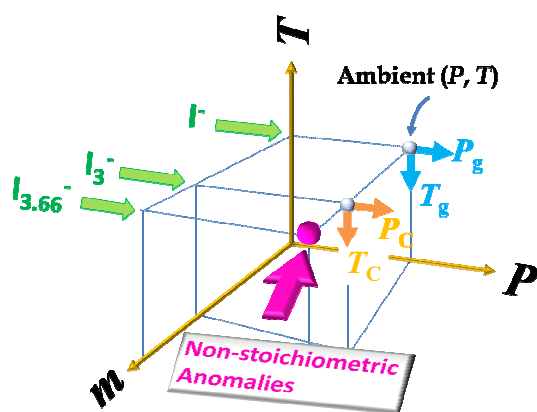


Fig. 1: Phase behaviors of $[\text{C}_3\text{mim}][\text{I}_m]$ at LT and HP.

Non-stoichiometric $[\text{C}_3\text{mim}][\text{I}_{3.66}]$ demonstrated an entirely different phase behavior at LT. In the cooling process, the crystallization of $[\text{C}_3\text{mim}][\text{I}_{3.66}]$ was not observed. While, upon heating, metastable frozen $[\text{C}_3\text{mim}][\text{I}_{3.66}]$ exhibited cold crystallization. In order to interpret the complicated behaviors, we introduce the following assumption. Since $[\text{C}_3\text{mim}][\text{I}_3]$ crystallized simply, $[\text{C}_3\text{mim}][\text{I}_3]$ is defined newly to be pure RTIL system considering I_3^- anion as a crystal forming factor. Then, $[\text{C}_3\text{mim}][\text{I}_{3.66}]$ is rewritten by $[\text{C}_3\text{mim}][\text{I}_3] - 7.1 \text{ mol\% } \text{I}_2$. Thus, 7.1 mol% I_2 is regarded as an additive to new defined pure system of $[\text{C}_3\text{mim}][\text{I}_3]$. In some binary system, 7 mol% additive changes the phase behaviors drastically. It is pointed out that fluctuations of excess iodine occurs between C_3mim^+ and I_3^- . Thus, we deduce that complicated phase behaviors of non-stoichiometric $[\text{C}_3\text{mim}][\text{I}_3] - 7.1 \text{ mol\% } \text{I}_2$ are originated from the dynamic fluctuations of excess iodide/iodine.

Excess iodide/iodine of non-stoichiometric $[\text{C}_3\text{mim}][\text{I}_{3.66}]$ (or $[\text{C}_3\text{mim}][\text{I}_3] - 7.1 \text{ mol\% } \text{I}_2$) 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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