

Thermal and Electrochemical Properties of Ionic Clathrate Hydrates

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The ionic clathrate hydrates are known to create numerous clathrate structures by hydrophobic inclusion of cations into confined cage space and hydrophilic incorporation of relatively small monatomic anions with hydrogen-bonded water framework, or both hydrophilic and hydrophobic incorporations of polyatomic anion with hydrophilic and hydrophobic components. In particular, tetramethylammonium hydroxide (Me_4NOH) clathrate hydrates have been confirmed to possess peculiar crystalline structures, largely depending on hydration number as well as temperature. Recently, we observed that the water content in the double ($\text{CH}_4 + \text{Me}_4\text{NOH}$) clathrate hydrate plays a significant role in inducing structure transformation and thus affecting its phase behavior. An additional observation is that the co-inclusion of secondary host species in Me_4NOH clathrate hydrate matrix makes the host-water lattice reorganized and reconstructed, creating the fresh cage dimension. Due to their ionic characteristics, the Me_4NOH clathrate hydrates have been particularly explored as a potential solid ionic conductor, which exhibit relative high ionic conductivities even low temperature. However, its low melting temperature hinders practical application to solid ionic conductor. In this work, we present the melting point increase of Me_4NOH clathrate hydrate by simply adding secondary molecules. More importantly, we observed that the co-inclusion of secondary guest in Me_4NOH clathrate hydrate tends to induce a drastic increase of melting temperature from $-26.5\text{ }^\circ\text{C}$ to $+31.0\text{ }^\circ\text{C}$ via structural distortion. In addition, we found that the ionic conductivity is greatly enhanced when the co-guest THF is included in terapropylammonium hydroxide ($(n\text{-Pr})_4\text{NOH}$) hydrate, forming structure-II (sII) clathrate hydrate.