Humidity-induced Electronic Conductivity of POM-based Porous Ionic Crystals

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Porous materials, due to their large surface area, are highly valuable for gas/vapor adsorption and separation. In particular, porous materials with electronic conductivity have attracted significant attention because they can modulate their electronic conductivity in response to guest sorption, such as water vapor, offering promise for sensor applications.[1] Among porous materials, porous ionic crystals (PICs) are crystalline porous composites formed by Coulomb interactions between anionic polyoxometalates (POMs) and macrocations such as oxo-centered trinuclear metal carboxylates.[2] The manipulation of the composition and structure of PICs enables the sorption of molecules/ions, proton conduction, and catalysis. However, the electron conduction of PICs remains relatively unexplored, although modulation of electronic conductivity through guest sorption in PICs is expected, as observed in other electroconductive porous materials.

In this study, Cr-complex cation, $[Cr_3O(OOCH)_6(4\text{-methylpyridine})_3]^+$, was assembled with two different POMs, $[H_3V_{10}O_{28}]^{3-}$ (**V_{10}**) and $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ (**SiW_{12}**) to construct two PICs, namely **PIC-V_{10}** and **PIC-SiW_{12}**. Single crystal XRD of each PIC revealed different arrangements of the Cr-complex (**Fig. 1**): **PIC-V_{10}** formed a hexagonal lattice, whereas **PIC-SiW_{12}** formed a rectangular lattice. The electronic conductivity of the PICs, measured by chronoamperometry (CA), was low under dry conditions but their conductivity increased with increasing humidity levels. Their trend and the value of electronic conductivity differed, suggesting a variation in conductivity with crystal structure. The relationship between the crystal structures and electronic conductivity, as well as the potential mechanism behind humidity-induced electronic conductivity, will be discussed.

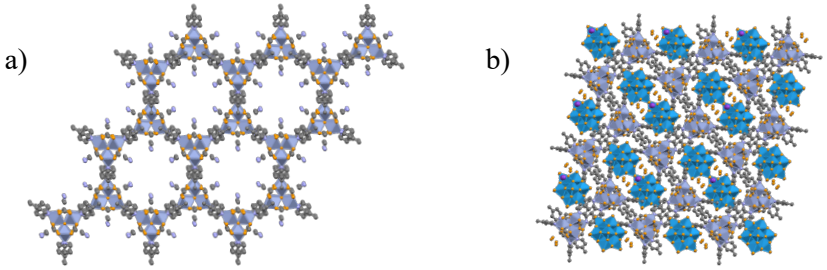

Fig 1. Crystal structure of a) **PIC-V_{10}** (**V_{10}** was disordered and could not be assigned by single crystal XRD) and b) **PIC-SiW_{12}**. Purple and blue polyhedra show the $[CrO_5N]$ unit of Cr-complex cation and the $[WO_6]$ unit of **SiW_{12}**, respectively.

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