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Ionic conductivity on cyano-bridged bimetal assemblies

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Various interesting functionalities have been reported on Prussian blue analogues, such as humidity sensitive magnetism. Prussian blue analogues have two types of cubic crystal structures. One of them is $M_A^{II}[M_B^{III}(CN)_6]_{2/3}\bullet zH_2O$ type (M_A, M_B: transition metal ions). There are vacancies of $[M^B(CN)_6]$ in $M_A[M_B(CN)_6]_{2/3}\bullet zH_2O$, and water molecules are coordinated to M_A ions and/or exist in the vacancy sites. Herein we report high ionic conductivities (σ) of 1.2×10^{-3} S cm^{-1} for $Co[Cr(CN)_6]_{2/3}\bullet zH_2O$ (1) and 1.6×10^{-3} S cm^{-1} for $V[Cr(CN)_6]_{2/3}\bullet zH_2O$ (2) at 293 K, 100%RH, respectively. As the humidity decreased, σ of 1 drastically decreased to 3.2×10^{-8} S cm^{-1} at 8%RH. This result indicates that the origin of ionic conduction is explained by Grotthuss mechanism, i.e., proton transfer is mediated by hydrogen-bonding network of water molecules. σ at 100%RH of 1 and 2 increased as temperature was increased. The plot of $\ln(\sigma T)$ vs T^{-1} of 1 was linear and gave an activation energy (E_a) of 0.22 eV, whereas, the slope of the plot of 2 changed at an intermediate temperature. The E_a values in the high- and low-temperature regions were 0.10 and 0.19 eV, respectively. The folding point of 313 K corresponds to the magnetic transition temperature of 2, which indicates that an interference effect between magnetic ordering and proton conduction was observed.

Biography

K. Nakagawa has completed his PhD at the age of 27 years from The University of Tokyo. He studies as a postdoctoral researcher at The University of Tokyo, School of Science.

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