学位論文の要約

題目　Study on Novel Proton Conducting Behavior in Free-Standing Coordination Polymer Membranes

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序論

It is known that the introduction of flexibility, namely, excellent mechanical stability against external force such as compressive, tensile, and flexural forces into the CPs not only increases the feasibility of the foregoing applications but also expands the range of their practical use. However, the framework structure formed by directional covalent or coordination bonds is fraught with drawbacks of the difficulty in the introduction of mechanical flexibility. To overcome the drawback, researchers have utilized low-dimensional CPs with open-framework structure, in which each chain or sheet unit is connected by weak van der Waals interactions. Whereas the flexural properties of needle-shaped crystalline CPs with one-dimensional (1D) coordination structure have been extensively investigated, mechanically flexible crystalline CPs with two-dimensional (2D) coordination structure have been almost unexplored despite their high surface-to-volume ratio is potentially beneficial for various applications mentioned above. Although there are several flexible polymer composites embedded with CPs, it is known that the chemical/physical properties of the composites depend largely on the kinds of the polymer and the loading amount of CPs. Therefore, the realization of a flexible membrane composed solely of CPs is in high demand for not only the rational design of mechanically flexible proton-conducting CPs but also their future protonic applications. We note that a key issue to push forward the applications is to maintain the structural and proton-conducting properties during the repetitive sequences between flat and bending states; however, there is no report on how the application of the external force affects the proton conductivity of the 2D CPs. This thesis aims to fabricate flexible CP membranes composed of 2D nanosheet, and investigate specific proton conducting behavior in it.

１． High-Performance All-Solid-State Proton Rectifier Using a Heterogeneous Membrane Composed of Coordination Polymer and Layered Double Hydroxide

This part is focused on the fabrication of all-solid-state proton rectifier. by the facile mechanical lamination of two free-standing membranes; namely, a proton-conducting PCP, Cu_2(CuTCPP), and hydroxide ion-conducting LDH, Mg-Al-LDH(NO_3). The *I–V* characteristics provide a rectification ratio as high as > 200 at 25 °C under 90% RH, which is the highest recorded value. These results will open the way for the exploration of new and more advanced all-solid-state proton rectifiers through rational design.

２． Robust Proton Conduction against Mechanical Stress in Flexible Free-Standing Membrane Composed of Two-Dimensional Coordination Polymer

We fabricated highly flexible free-standing membranes composed of 2D CP, Cu_2(NiTCPP). The membrane is highly oriented and excellent mechanical properties by virtue of weak interlayer interactions of van der Waals type. The proton conductivity of the membrane remains almost unchanged even by applying bending stress. The proton-conducting properties, as well as the structural features, in different bending states strongly indicate that proton-conducting pathway through the hydrogen bonding network is kept intact during the bending operation. This is the first study to demonstrate the robust proton conduction of 2D CP against the applied bending stress.

３． Proton Conducting Behavior in Flexible Coordination Polymer Free-Standing Membranes

We fabricated highly flexible free-standing membranes composed of 2D CPs, Cu_2(NiTCPP), Cu_2(CuTCPP) and Cu_2(ZnTCPP). The membrane was highly oriented and had excellent mechanical properties owing to the weak interlayer interactions of van der Waals type. The σ value of the membrane reached 4.53×10^{-5}, 2.00×10^{-5} and 4.73×10^{-5} S cm^{-1} at 45 °C and 98% RH condition. This is the first study to fabricate a series of flexible CP free-standing membranes. The prominent advantage of the present membrane for future flexible protonic devices is that it can be fabricated free from any substrate and shows excellent bending stability even without blending with the polymer matrix.