

# 学位論文の要約

## 題目

### Studies on Highly Ion-conductive Metal–Organic Frameworks by Postsynthetic Modification Methods

(合成後修飾法を用いた高イオン伝導性金属–有機構造体の開発に関する研究)

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## 序論

Metal–Organic Frameworks (MOFs), also known as porous coordination polymers (PCPs) are a subclass of coordination polymer (CPs) composed of metal clusters and organic ligands, forming self-assembled 2D or 3D structures containing potential voids. Due to their inherent regular structure and high designability, MOFs have been widely studied for a variety of applications such as gas storage, catalysis, and in particular, ionic conductivity. In general, studies for high proton conductivity, a special case of ionic conductivity, in MOFs have been focused on the increase in charge carrier concentration and mobility. Therefore, some MOFs exhibit a high proton conductivity ( $\sigma > 10^{-2} \text{ S cm}^{-1}$ ) with strong acidic species (e.g., HCl, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub>) as part of the framework, guest molecules, or both. However, most approaches to proton conductive MOFs are detrimental to the stability of the framework. Therefore, the purpose of this thesis is to provide new approaches for ionic conductivity in MOFs and to study the ion conduction mechanism.

### **Superprotonic Conductivity in Metal–Organic Framework via Solvent-Free Coordinative Urea Insertion**

We report superprotonic conductivity ( $\sigma > \sim 10^{-2} \text{ S cm}^{-1}$  at 298 K and 95% RH) achieved through the post synthetic modification of the MOF-74 [M<sub>2</sub>(dobdc), M = Ni<sup>2+</sup> and Mg<sup>2+</sup>, dobdc = 2,5-dioxido-1,4-benzenedicarboxylate] with the non-acidic molecule urea, four samples were prepared: MOF-74II(Ni)–H<sub>2</sub>O, MOF-74II(Ni)–H<sub>2</sub>O–Urea, MOF-74II(Ni)–Urea and MOF-74II(Mg)–Urea. The MOFs structure was studied using IR, XPS, TGA, EA, and PXRD. The N<sub>2</sub> gas and water vapor sorption indicated the dramatic decreased in porosity and a twostep water

adsorption profile for the MOF-74–Urea. The proton conductivity and its activation energy were studied using AC impedance spectroscopy. It was found that MOF-74(Ni)–Urea proton conductivity improves dramatically at 70% relative humidity with a change in proton conduction mechanism. Furthermore, the Solid-state  $^2\text{H}$  NMR confirmed that the hydrogen bonding in the interface between the polarized urea and the confined water is a key factor in the change in conduction mechanism. In summary, Urea assisted proton diffusion by stabilizing and strengthening the hydrogen bonding between guest water molecules which is reflected in the Grotthuss mechanism under the high humidity condition.

## **2. Void Space vs. Surface Functionalization for Proton Conduction in Metal–Organic Frameworks**

The effect of void space and pore surface modification on proton conduction in MOFs were studied. The solvent-free coordinative insertion of urea was applied to the isorecticular MOF-74II(Ni) [ $\text{Ni}_2(\text{dobpdc})$ ,  $\text{dobpdc} = 4,4'$ -dihydroxy-(1,1'-biphenyl)-3,3'-dicarboxylate], three samples were prepared: MOF-74II(Ni)– $\text{H}_2\text{O}$ , MOF-74II(Ni)– $\text{H}_2\text{O}$ -Urea and MOF-74II(Ni)–Urea. The IR, XPS, TGA, EA, and PXRD confirmed the successful insertion of urea. Subsequently, the water vapor sorption and  $\text{N}_2$  gas sorption were measured. All MOF-74II samples showed high porosity and similar vapor sorption profiles in stark difference with the MOF-74 samples. The MOF-74II samples showed lower proton conductivity than the MOF-74 samples, indicating that large porosity reduces the effectiveness of urea as an assistant for proton conductivity. Furthermore, the density functional theory calculations suggest that strong hydrogen bonding between conducting media under high porosity is inefficient for realizing high proton conductivity, and indeed, in large pore the guest water approaches the bulk water behavior. Thus, we demonstrated that a strong Hydrogen bond network supported by confinement of the proton carrier molecules is a priority factor in proton conduction.

## **3. Li salts assisted ionic conductivity in 2D-layered Ti MOF**

We studied the ionic conductivity in the 2-D layered Ti-dobdc framework by the intercalation of LiX salts (X = Cl, Br, I). We incorporated LiX into the Ti-dobdc [ $\text{Ti}_2(\text{C}_8\text{O}_6\text{H}_3)_3(\text{CH}_3\text{CN})_{1.15}(\text{C}_4\text{H}_{10}\text{O})_{0.3}(\text{H}_2\text{O})_{2.5}$ ] framework by mechanical mixing at different MOF:LiX molar ratios (1:1, 1:3, 1:5). The PXRD patterns showed that the optimal molar ratio is 1:1. The water vapor sorption of all samples was measured. It was observed that the incorporation of LiX increases the water sorption property dramatically due to the

deliquescence of the LiX. Subsequently, the ionic conductivity was explored by AC impedance spectroscopy of pelletized samples. In the AC impedance measurements, the Ti-dobdc-LiX samples showed a trend of ionic conductivity similar to the profile observed in water vapor sorption measurements, indicating that proton may be the major charge carrier in the Ti-dobdc-LiX. Furthermore, AC impedance measurements at temperatures higher than the boiling point of water show a drop in ionic conductivity for all samples indicating that proton may be the charge carrier. In conclusion, we have achieved superionic conductivity by intercalating hydrated LiX salts in the 2-D Ti-dobdc framework. However, further studies on the charge carrier identity are required. It was found that the high covalent character of Li-I is beneficial for high ionic conductivity at low humidity and mild temperature condition. However, the weaker Li-I bond strength has a negative impact on the stability of the conductivity at high temperatures. As a result, Ti-dobdc-LiBr, which has a moderate covalent/ ionic character, can be the best ionic conductor. This study will provide a strategy for the design of electrolytes in an aqueous battery system.