Transparent Coordination Polymer Monolith for Intermediate Temperature Proton Conductivity

([1]*Graduate School of Engineering, Kyoto University,* [2]*Institute for Advanced Study, Kyoto University*) ○Ellan Berdichevsky,[1] Nattapol Ma,[1] Satoshi Horike,[1,2]

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Solid-state proton conductors are important materials for next generation electrolyte materials in battery, fuel cell, and electrochemical sensor technologies.[1] Conventional sulfonated fluoropolymers such as Nafion® achieve remarkable conductivities, however they require high humidity conditions to maintain effectiveness.[2] Higher operating temperatures would improve process thermodynamics at the cost of lower relative humidity. Thus, new materials that can reach high proton conductivities at intermediate (>120°C) temperatures and relatively low humidity are needed. Metal-organic frameworks and coordination polymers are attractive candidates, with their tailorable structures and functionalities.[3] Nonetheless, a key challenge in using CP/MOFs lies with their high crystallinity leading to grain boundaries, which inevitably result in disjointed conduction pathways and lower bulk conductivity. With this in mind, we examined CP/MOFs with good thermal/water stabilities and intrinsic proton carriers as suitable candidates, while also investigating material processability.

We examined $[(CH_3NH_2)_3SO_4]_2[Zn_2(C_2O_4)_3]$ (**DMAS-Znox**), previously shown to exhibit high proton conductivity at elevated temperatures under anhydrous conditions.[4] A facile and rapid synthesis by use of microwave irradiation was developed. The obtained highly crystalline product gave lower than expected proton conductivity as measured by impedance spectroscopy, a result of the numerous grain boundaries in the pressed compact. To improve bulk homogeneity, mild mechanical grinding of **DMAS-Znox** prior to pellet formation was performed. Grinding, followed by uniaxial pressing resulted in highly homogenous, transparent monoliths that retain crystallinity, as observed by SEM and PXRD. The reduction of grain boundaries in the bulk led to a significant increase in proton conductivity (10^{-7} to 10^{-5} $S\cdot cm^{-1}$ at 120°C). Humidity was also found to play an important role at elevated temperatures; exposure of the material to as little as 5% relative humidity at 150°C was enough to increase conductivity by a few orders of magnitude over anhydrous conditions. Finally, to take advantage of the transparency, **DMAS-Znox** could be doped with photo-acid molecules, such as pyranine, to further control proton conduction.

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