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High Proton Conductivity of One-Dimensional Ferrous Oxalate Dihydrate

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Coordination polymers (CPs) have attracted much interest in the past two decades[1] because of their fascinating characteristics such as gas absorption,[2] electronic conduction,[3] or catalytic[4] properties. CPs have advantages of a highly ordered structure and a wide design latitude of frameworks by choosing various metal ions and bridging ligands. In addition, the hydrophilicity or acidity of the frameworks can be controlled by the design of the frameworks. Recently, a few works on the proton conductivity of CPs have been reported.[5] CPs also have several advantages for the construction of proton conductors. It is possible to make use of internal degrees of freedom of space (so-called coordination space[1]) in addition to the lattice (framework). Therefore, we can control the condensed state of the water cluster existing in a pore as a conducting media with changing hydrophilicity of the framework. By using both freedoms, we can also design hydrogen-bond networks as a conducting pathway and built-in acidic groups as a proton source and even tune pK_a of coordination space.

Ferrous oxalate dihydrate, so-called Humboldtine in the field of mineralogy, is one of the simplest CPs and was found in brown coal about a century ago and is able to found in soil. It has a one-dimensional (1D) chain composed of ferrous ions and oxalate, as shown in Figure 1, and a magnetic property as well as thermal stability had been reported.[6] Two water molecules coordinate axially to a ferrous ion and form a 1D ordered array of water molecules described in Figure 1. Lewis acidic ferrous ions have the potential to promote elimination of a proton from the coordination water. Therefore, the ordered array of water molecules coordinating to Lewis acidic ferrous ions is expected to make a pathway for proton transportation along with this array. Here, we report a highly proton-conductive property of ferrous oxalate dihydrate having a 1D chain of coordination water molecules.

Ferrous oxalate dihydrate (**1**) was synthesized by a simple mixing of ferrous sulfate and oxalic acid in water, according to the literature.[6] It was characterized by X-ray diffraction, infrared spectroscopy, and elemental analysis. For an electrical conductivity study, the powdered sample was compressed to ~0.5 mm in thickness and 2.5 mm in diameter. Both sides of the pellet were attached to gold wires with gold paste. The conductivity measurement was carried out using a Solartron 1260 impedance/gain-phase analyzer by a quasi-four-probe method at the frequency range 10 MHz to 1 Hz. A Debye semicircle was observed in the temperature range 5 to 45 °C. The proton conductivity was calculated from a diameter of the semicircle. Samples were placed in a temperature–humidity controlled chamber (SH221, ESPEC Corp.) during the measurement.

Figure 2 shows the Nyquist plot of **1** under ambient temperature and humidified conditions. A Debye relaxation process was observed at ~5 MHz. As shown in Figure 2, ferrous oxalate dihydrate showed a high proton conductivity of 1.3 mS cm^{-1} at 25 °C and RH 98%. The electric field dependence of proton conductivity was also measured, and **1** showed ohmic conductivity in the measured voltage range. The direct current electrical conductivity of **1** was also measured and found to be very low ($<10^{-10}$ S cm^{-1}), showing poor electronic conductivity, as reported previously.[6]

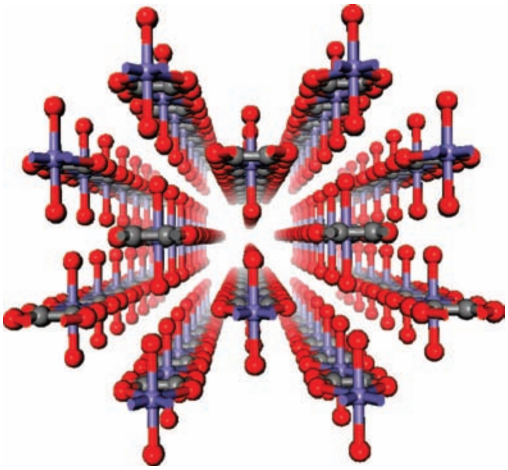

Figure 1. Crystal structure of Humboldtine.

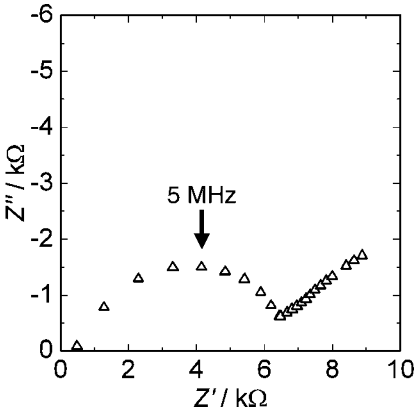

Figure 2. Nyquist plot of **1** at 25 °C and relative humidity 98%.

The proton conductivity of organic polymers with sulfonic acid, like Nafion, is reported to be $10^{-1}-10^{-5}$ S cm^{-1}.[7] Proton conductivities with other acidic functional groups have also been reported: $10^{-1}-10^{-4}$ for phosphate, $10^{-5}-10^{-6}$ for carboxylic acid, and $10^{-6}-10^{-8}$ S cm^{-1} for imidazole.[8] The proton conductivity of pure water is 5.5×10^{-8} S cm^{-1}. The proton conductivity of **1** is extremely high at ambient temperature without any strong acidic group and is comparable to Nafion.[8] In **1**, oxalic acid is totally coordinated to ferrous ion and there is no proton as a possible carrier at the bridging oxalate ligand. Thus a proton carrier is thought to originate from coordination water molecules.

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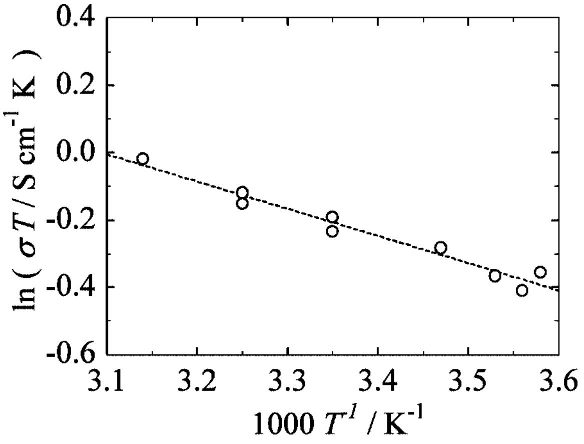

Figure 3. Arrhenius-type plot of **1** at various temperatures.

The ionic conductivity of a nanoscaled conduction pathway has been reported this decade, and a number of reports showed that the ionic conductivity of nanospace is more improved than that of bulk ion conduction compounds.[9,10] Maier and his co-worker reported the promotion of ionic conduction in a nanoscale interlayer of the ionic conductor.[10] The reason of the conductivity improvement was still under discussion, but ionic conductivity has a tendency to be enhanced when a thickness space−charge layers are comparable to the Debye length. CPs are featured as highly ordered nanoscale interfaces, and an interaction between framework and guest molecule becomes important. **1** contains a 1D nanoarray of coordination waters which form hydrogen bonds to oxygen atoms of the ferrous oxalate framework (2.71 Å[6]). Proton conduction is, therefore, considered to be much improved by this confined water nanoarray column.

Figure 3 shows the temperature dependence of the proton conductivity of **1** at 98% RH. The proton conductivity was increased with temperature. The activation energy (E_a) and pre-exponential factor (σ_0) were estimated to be 0.37 eV and $10^{5.75}$ S cm^{-1} K from the equation below.

$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \tag{1}$$

where σ is the ionic conductivity, σ_0 is the preexponential factor, k_B is the Boltzmann constant, and T is the temperature.

Colomban et al. described a superionic conductor (or fast ionic conductor) as a compound which has a conductivity above 0.1 mS cm^{-1} and an activation energy below 0.4 eV.[11] **1** shows a significantly high conductivity and relatively low activation energy, whose values are comparable with those of Nafion having a fluid water tube in the polymer.

In summary, a familiar 1D coordination polymer, ferrous oxalate dihydrate, exhibits a high proton conductivity of 1.3 mS cm^{-1} at ambient temperature. In general, ambient proton conductors possess strong acidic functional groups. In the present coordination polymer, a water molecule coordinating to ferrous ion is considered to be a proton source and proton conduction is extremely enhanced by the well-ordered 1D water nanoarray. This result provides us with a rational design of coordination polymers which are useful for solid electrolyte.

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Supporting Information Available: Synthetic procedure, PXRD patterns, water uptake measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

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