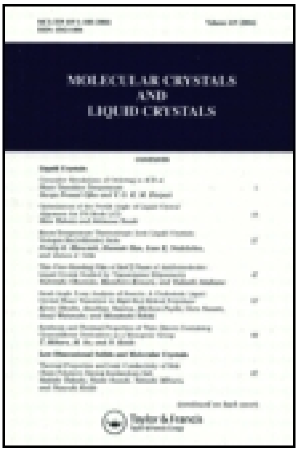

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Complex-Plane Impedance Study on a Hydrogen-Doped Copper Coordination Polymer: N,N′-bis-(2-hydroxyethyl)dithiooxamidato-copper(II)

Yuki Nagao [a], Ryuichi Ikeda [a], Seiichi Kanda [b], Yoshihiro Kubozono [c] & Hiroshi Kitagawa [a d e]

[a] Department of Chemistry, University of Tsukuba, Ibaraki, 305-8571, Japan

[b] Department of Chemistry, The University of Tokushima, Tokushima, 770-8506, Japan

[c] Institute for Molecular Science, Okazaki, 444-8585, Japan

[d] School of Materials Science, Japan Advanced Institute of Science and Technology, Ishikawa, 923-1292, Japan

[e] PRESTO, JST, Saitama, 332-0012, Japan

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Complex-Plane Impedance Study on a Hydrogen-Doped Copper Coordination Polymer: *N,N′*-bis-(2-hydroxyethyl)dithiooxamidato-copper(II)

YUKI NAGAO[a], RYUICHI IKEDA[a], SEIICHI KANDA[b],
YOSHIHIRO KUBOZONO[c] and HIROSHI KITAGAWA[a,d,e]

[a]*Department of Chemistry, University of Tsukuba, Ibaraki 305-8571, Japan,*
[b]*Department of Chemistry, The University of Tokushima,*
Tokushima 770-8506, Japan,
[c]*Institute for Molecular Science, Okazaki 444-8585, Japan,*
[d]*School of Materials Science, Japan Advanced Institute of Science*
and Technology, Ishikawa 923-1292, Japan and
[e]*PRESTO, JST, Saitama 332-0012, Japan*

AC conductivity measurements with an impedance analyzer were carried out for a hydrogen-doped coordination polymer, *N,N*'-bis-(2-hydroxyethyl)dithiooxamidatocopper(II), in order to estimate the protonic conductivity (σ_p). The log σ_p was linearly increased from 2.6×10^{-9} to 2.2×10^{-6} S cm^{-1} with relative humidity (RH) from 45 to 100 % at 300 K. A slight hysteresis of protonic conductivity was observed upon increasing and decreasing RH, which implies that H_3O^+ is generated by a reaction between water molecule and acid-base polymer near RH ~ 100 %.

Keywords: protonic conduction; coordination polymer; AC conductivity measurement; hydrogen doping; electronic conduction; inorganic-organic hybrids

INTRODUCTION

Inorganic-organic hybrids are one of the most promising materials because they possess a wide variety of inorganic and organic functionalities[1]. Protonic conduction is one of the unexplored and most attractive functionalities in inorganic-organic hybrids.

N,*N'*-bis-(2-hydroxyethyl)dithiooxamidatocopper(II), $(HOC_2H_4)_2$-*dtoa*Cu, is a two-dimensional coordination polymer (Figure 1)[2,3]. In the previous work, this polymer was revealed to be a protonic conductor[4]. The electronic conductivity of $(HOC_2H_4)_2$*dtoa*Cu is increased by about nine orders of magnitude as the hydrogen doping proceeds[5]. The hydrogen is doped to $(HOC_2H_4)_2$*dtoa*Cu according to the proton-coupled redox property, as shown in Figure 2. The hydrogen doped to the coordination polymer reduces Cu(II) to Cu(I), and bonds the nitrogen sites of the ligands as a proton. The protonic conductivity of hydrogen-doped $(HOC_2H_4)_2$*dtoa*Cu is expected to be higher than that of the non-doped one. In this paper, we report on proton transport properties of the hydrogen-doped polymer by AC conductivity measurements.

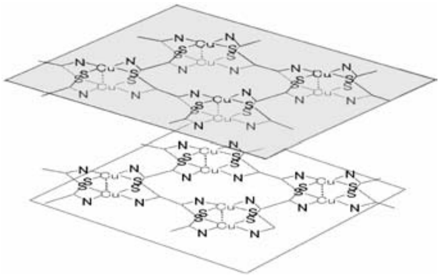

FIGURE 1 Proposed structure of $(HOC_2H_4)_2$*dtoa*Cu[2,3].

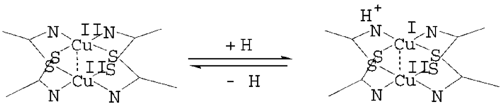

FIGURE 2 Proton-coupled redox property of $(HOC_2H_4)_2$*dtoa*Cu.

EXPERIMENTAL

The title coordination polymer was prepared by a simple stoichiometric mixing of 5 % C_2H_5OH*aq* solution of $(HOC_2H_4)_2$*dtoa* and $CuSO_4$*aq*. Hydrogen doping was electrochemically performed by generated hydrogen gas on the cathode's surface with a KCl solution of 0.1 mol/l under vigorous stirring for 3 hours. The qualities of samples were checked by powder X-ray diffraction measurements. The X-ray diffraction patterns were measured with synchrotron radiation at the BL-1B in the Photon Factory of High Energy Accelerator Research Organization (KEK-PF). The X-ray wavelength λ used was 0.8500(4) Å.

For AC conductivity measurements, the powdered sample was processed into pellets of 0.57 mm thickness and 2.5 mm ϕ under pressure (~ 1 GPa) and vacuous condition. The impedance measurements were carried out by a conventional quasi-four-probe method using gold paste and gold wires (25 μm ϕ) with an Agilent Technologies 4294A impedance analyzer in the frequency range of 40 Hz – 4 MHz at 300 K. Relative humidity (RH) was changed in the range of 45 – 100 % by using water and saturated solution of salts, generating an atmosphere of a defined RH[6]. The measurements were carried out with decreasing RH from 100 to 45 % (the first series), and then with increasing it from 45 to 100 % (the second series).

RESULTS AND DISCUSSION

Figure 3 shows the X-ray diffraction patterns of hydrogen-doped $(HOC_2H_4)_2$*dtoa*Cu and non-doped one. The two-dimensional framework of the coordination polymer is maintained during hydrogen doping because main intense peaks are unchanged. The lattice of non-doped $(HOC_2H_4)_2$*dtoa*Cu is tetragonal with constants of a = 8.54 and c = 9.85 Å.

The protonic conductivity was obtained by the complex-plane impedance plots. Figure 4 shows the real (Z') versus imaginary (Z") parts of the complex-impedance data for the hydrogen-doped $(HOC_2H_4)_2$*dtoa*Cu under RH of 100 % in the first series. The plots consist of a depressed semicircular arc followed by a low frequency tail. The bulk resistance of this polymer is directly given by the intersection of depressed semicircle with the real axis. The conductivity estimated in this manner is 2.2 × 10^{-6} S cm^{-1}, which is in principle the sum of the protonic (σ_p) and electronic (σ_e) contributions. The σ_e is 2.0 × 10^{-10} S cm^{-1} measured by DC electrical conductivity, which is negligible compared to the σ_p. So the protonic conductivity is determined to be 2.2 × 10^{-6} S cm^{-1}.

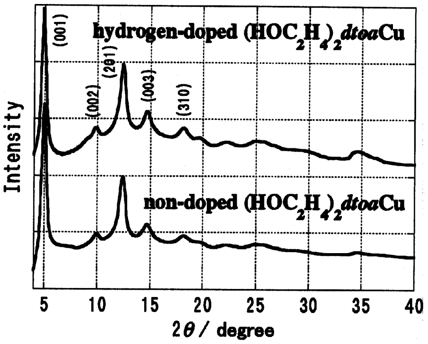

FIGURE 3 X-ray diffraction patterns of the hydrogen-doped and non-doped $(HOC_2H_4)_2$*dtoa*Cu.

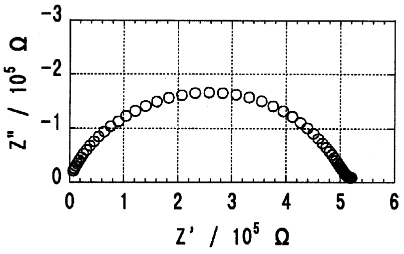

FIGURE 4 Complex-plane impedance plots of hydrogen-doped $(HOC_2H_4)_2$*dtoa*Cu under RH of 100 % and 300 K.

Figure 5 shows the RH dependence of protonic conductivity for the hydrogen-doped $(HOC_2H_4)_2$*dtoa*Cu. The log σ_p are linearly decreased from 2.2×10^{-6} to 2.6×10^{-9} S cm^{-1} with decreasing RH from 100 to 45 % (the first series). The conductivities in the second series are a little lower although the conductivity is almost equal to that in the first one under RH of 100 %. This implies that H_3O^+ is generated near RH ~ 100 % by a reaction between water molecule and the hydrogen at NH bonds of the acid-base polymer. The protonic conductivity of hydrogen-doped $(HOC_2H_4)_2$*dtoa*Cu is lower by about two orders of magnitude than that of non-doped one under RH of 83 %[4], which is due to the larger pK_a of hydrogen-doped $(HOC_2H_4)_2$*dtoa*Cu than non-doped one.

The concentration of water molecules included in the non-doped $(HOC_2H_4)_2$*dtoa*Cu was also found to increase with RH[4]. This fact implies that the protonic conductivity depends on the quantity of water molecules containing in the polymer. The lattice constant c of $(HOC_2H_4)_2$*dtoa*Cu was found by the X-ray diffraction measurements to become slightly longer with RH[7]. It is reported that the proton conductor "Nafion®", which is used as solid electrolyte in the fuel cell, also contains much water clusters and these make pathway of the protonic conduction[8,9]. This coordination polymer is supposed to have the same mechanism. Detailed investigation on the mechanism of the protonic conduction of this polymer is in progress.

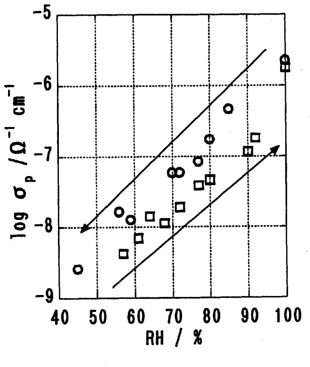

FIGURE 5 Log (protonic conductivity) vs. RH plots of hydrogen-doped $(HOC_2H_4)_2$*dtoa*Cu at 300 K. ○: the first series; □: the second series (See EXPERIMENTAL).

CONCLUSION

In this work, AC conductivity measurements were carried out for the hydrogen-doped coordination polymer, *N,N'*-bis-(2-hydroxyethyl)-dithiooxamidatocopper(II). The protonic conductivity was found to increase from 2.6×10^{-9} to 2.2×10^{-6} S cm^{-1} with RH (45 - 100 %). A slight hysteresis was observed, which implies that H_3O^+ is generated by the reaction between water molecule and acid-base polymer near RH ~ 100 %.

Acknowledgments

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