Galvanostatic Transient Studies on Copper Coordination Polymer under Hydrogen Absorption

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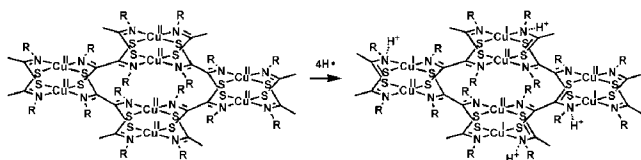[4]*National Institute for Materials Science, 3-13 Sakura, Tsukuba 300-0003*

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Hydrogen electrode reaction (HER) was investigated for a copper coordination polymer, catena-μ-N,N'-bis(hydroxyethyl)dithiooxamidatocopper(II) (CuCP) by galvanostatic transient measurements using a palladium cathode. Individual steps in the Volmer–Tafel reaction were successfully observed for the colloidal CuCP in alkaline solution under hydrogen absorption. The Volmer step was found to be promoted with CuCP and its hydrogen-absorbed polymer (CuCPH) from shorter decay times in transient curves and smaller overpotentials in Tafel plots. In contrast, the inhibition of the Tafel step was observed, which is due to the larger overpotentials. Difference in reducibility between the polymers and plausible reduction mechanisms is discussed.

Development of hydrogen-storage materials is one of the most important subjects in the field of hydrogen technology.[1–5] In previous studies, we reported hydrogen absorption property in a copper coordination polymer, catena-μ-N,N'-bis(hydroxyethyl)dithiooxamidatocopper(II) (CuCP).[6,7] The interesting feature was that CuCP absorbs hydrogen in a quite unique way based on proton-coupled redox property. This was confirmed by the fact that the valence state of copper(II) is reduced to the copper(I, II) mixed-valence state under hydrogen absorption, and N–H bonds are simultaneously formed at the ligand, as illustrated in Figure 1. The two-dimensional framework of CuCP was maintained under hydrogen absorption.[6] Moreover, outstanding changes in physical properties were induced with hydrogen absorption, i.e., an increase in electrical conductivity (up to $\sigma_e \approx 1 \times 10^0\,\mathrm{S\,cm^{-1}}$) derived from the mixed valency of Cu and Pauli paramagnetism from the metallic conduction. These hydrogen-induced properties have been firstly observed phenomena in coordination polymers.
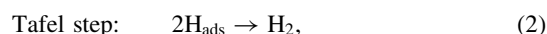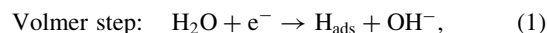
In our previous studies,[6,7] hydrogen absorption was carried out by using a hydrogen electrode reaction (HER) method on a platinum cathode in a process of water electrolysis. Hydrogen at its moment of birth on electrode is often called "nascent hydrogen,"[8] which is known to have much stronger reducing power than atmospheric hydrogen. Its reactivity can be controlled electrochemically.[9]

In alkaline solution, HER on the platinum cathode obeys the Volmer–Tafel reaction, which consists of two kinds of elementary steps as follows,

$$\text{Volmer step:} \quad H_2O + e^- \rightarrow H_{ads} + OH^-, \quad (1)$$

$$\text{Tafel step:} \quad 2H_{ads} \rightarrow H_2, \quad (2)$$

where H_{ads} indicates atomic hydrogen adsorbed on the cathode surface. The Volmer and the Tafel steps result from a discharge of the electric double layer and a recombination of atomic hydrogens on the cathode surface, respectively. Enyo has reported the electrochemical reduction mechanism for some organic substances by analyses of the Volmer–Tafel reaction with galvanostatic transient measurements.[9]

In this study, HER in colloidal CuCP solution was investigated in order to reveal the reduction mechanism. CuCP and its hydrogen-absorbed polymer (CuCPH) were prepared with $CuSO_4 \cdot 5H_2O$ (Nacalai Tesque, Inc.) and N,N'-bis(hydroxyethyl)dithiooxamide (Pfalz & Bauer, Inc.) by the method previously reported.[7] Colloidal solutions were obtained by dispersing the polymers ($2.0\,\mu$mol) into 0.1 M aqueous NaOH solutions (100 ml). Diameters of the colloids were smaller than $0.3\,\mu$m. Their stabilities were checked by FT-IR measurements. Galvanostatic transient measurements were carried out using three-electrode system controlled by a galvanostat (Hokuto Denko Co., Ltd. HA-301). Overpotential decay transients were produced by the interruption of cathodic currents with a single square pulse (pulse width was 100 ms). A thin palladium foil ($10\,\mathrm{mm} \times 2.5\,\mathrm{mm} \times 5.0\,\mu\mathrm{m}$ in thickness, The Nilaco Corp.) was employed as a working electrode because its hydrogen absorption property enables the Volmer and the Tafel steps to be observed separately.[10] Polymers are considered to influence overpotentials and decay times of the respective steps.

Figure 2 shows overpotential decay transient curves under 10 mA cathodic currents for colloidal dispersions of CuCP and CuCPH with 0.1 M aqueous NaOH solution. They consist of rapidly and slowly decaying components, which can be assigned to the Volmer and the Tafel steps, respectively. The decay time for the rapid component was estimated to be 1.4 ms for CuCP and 1.2 ms for CuCPH, which are about one tenth of the value (12 ms) observed for 0.1 M NaOH control solution. The observed shorter decay time can be considered to be attributed to the promotion of the Volmer step by the polymers. That is, the

Figure 1. Schematic representation of proton-coupled redox property in CuCP (R = C_2H_4OH).
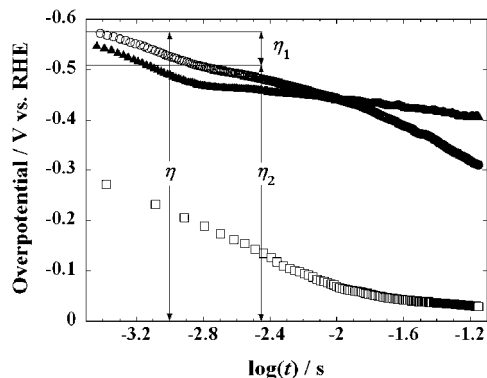
Figure 2. Overpotential decay transient curves under 10 mA cathodic current for colloidal CuCP (○) and CuCPH solutions (▲) and 0.1 M NaOH control solution (□). Total overpotential η, overpotential components of the Volmer and the Tafel steps, η_1 and η_2, are illustrated for the transient curve of CuCP.
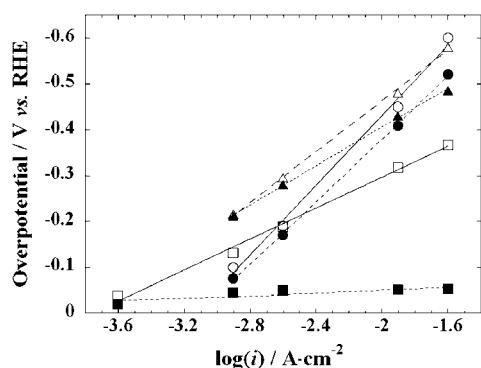

Figure 3. Tafel plots of total overpotentials η (opened symbol) and overpotential components η_2 (closed symbol) for colloidal CuCP (circle) and CuCPH (triangle) solutions and 0.1 M NaOH control solution (square).

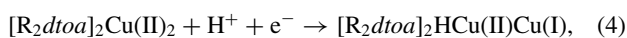discharge of the electric double layer is accelerated by the polymers.

Figure 3 gives Tafel plots for total overpotential η and overpotential component for the Tafel step η_2. Tafel plot for the control solution shows a typical behavior for the Volmer–Tafel reaction.[10] Tafel plots for the polymers, on the other hand, gave much greater values in η_2 than the value for the control solution. This implies the inhibition of the Tafel step by the polymers. The overpotential component for the Volmer step η_1 is defined as a difference between η and η_2. The smaller η_1 for the polymers would be derived from the promotion of the Volmer step. In addition, η of CuCPH is greater than that of CuCP in the $\log(i) < -1.7$ region. This can be explained by the fact that CuCPH is less reducible than CuCP because it is reduced form.

In the process of hydrogen doping into CuCP, following three kinds of reduction mechanisms can be proposed,
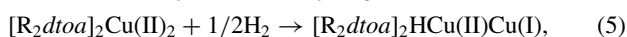
(i) Radical mechanism[11]

$$[R_2dtoa]_2Cu(II)_2 + H\bullet \rightarrow [R_2dtoa]_2HCu(II)Cu(I), \qquad (3)$$

(ii) Ionic mechanism[11]
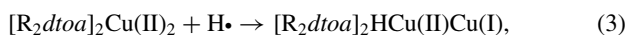
$$[R_2dtoa]_2Cu(II)_2 + H^+ + e^- \rightarrow [R_2dtoa]_2HCu(II)Cu(I), \quad (4)$$

(iii) Reduction by molecular hydrogen

$$[R_2dtoa]_2Cu(II)_2 + 1/2H_2 \rightarrow [R_2dtoa]_2HCu(II)Cu(I), \qquad (5)$$

where CuCP and CuCPH are expressed respectively as $[R_2dtoa]_2Cu(II)_2$ and $[R_2dtoa]_2HCu(II)Cu(I)$ ($R_2dtoa = N,N'$-

bis(hydroxyethyl)dithiooxamide anion).

The radical mechanism (i) proceeds on the cathode surface, on which CuCP is reduced by atomic hydrogen. The ionic mechanism (ii) also proceeds on the cathode in a manner that CuCP is reduced by an electron accompanied or preceded by the addition of a proton. In the mechanism (iii), CuCP is reduced by generated molecular hydrogen in the neighborhood or the offing of the cathode. Since the reducing power of molecular hydrogen is much weaker than that of atomic hydrogen or an electron,[9] the last mechanism is less possible.

From the experimental results mentioned above, hydrogen absorption is considered to occur under the radical mechanism rather than the ionic mechanism. In fact, the polymers were highly aggregated on the surface of the cathode in a process of water electrolysis. If such the polymers absorb atomic hydrogens, they should lower hydrogen concentration on the cathode surface and disturb the Tafel step. In order to keep the hydrogen concentration enough for the Tafel step, more negative potential is needed, resulting in increase of η_2. The polymers are also supposed to disturb the Tafel step by blocking the supply of atomic hydrogens from the inside of the electrode. The less negative potential and the shorter decay time for the Volmer step may be attributed to electronic and ionic conductions of the polymers.[12–16] They should make the Tafel step to be rate-determining, serving to prolong the lifetime of atomic hydrogens on the electrode.

In this study, the Volmer–Tafel reactions in colloidal CuCP and CuCPH solutions have been investigated by the overpotential decay transient curves. The shorter decay times and the smaller overpotentials for the Volmer step, and the larger overpotentials for the Tafel step were observed, indicating that the hydrogen absorption occurs under the radical mechanism. In the preceding studies,[9,10] discrimination between (i) and (ii) was carried out by analysis of the overpotentials, which is now in progress.

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