

# pH-dependent electrocatalysis for proton reduction by bis(2,2':6',2''-terpyridine) cobalt(II) complex embedded in Nafion<sup>®</sup> membrane

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## Abstract

Electrocatalysis for H<sup>+</sup> reduction by a bis(2,2':6',2''-terpyridine) cobalt(II) complex ([Co(terpy)<sub>2</sub><sup>2+</sup>]) dispersed in a Nafion<sup>®</sup> membrane coated on a basal-plane pyrolytic graphite (BPG) electrode was studied. It was found that the electrocatalysis for H<sup>+</sup> reduction varies with the pH conditions employed. Under acidic pH conditions (pH ≲ 4), the electrocatalytic H<sup>+</sup> reduction was induced by [Co(terpy)<sub>2</sub><sup>+</sup>] (Co(I)), while under weakly acidic–neutral pH conditions (pH ≳ 4), H<sup>+</sup> reduction took place after forming [Co(terpy)<sub>2</sub><sup>+•</sup>] Co(0)). The pH-dependent electrocatalysis was attributable to weak basicity of the electrogenerated Co(I): under low pH conditions (pH ≲ 4) Co(I) can coordinate H<sup>+</sup> resulting in an intermediate (Co(I)–H). However, since the reduction potential of Co(II) is pH-independent above pH ∼ 4, the H<sup>+</sup> reduction took place by Co(0) via Co(0)–H. The electron transfer to generate catalytically active species at the polymer-coated electrode was also studied by potential-step chronoamperometry. Similar to the concentration dependence of the turnover number of the catalyst, the apparent diffusion coefficient (*D*<sub>app</sub>) of the electrons decreased with increasing the complex concentration. It is most probable that the overall kinetics in the electrocatalytic H<sup>+</sup> reduction is dominated by the reduction of the complex. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Electrocatalysis; Proton reduction; Terpyridyl cobalt complex; Polymer-coated electrode; Electron transfer

## 1. Introduction

Water photolysis to produce H<sub>2</sub> and O<sub>2</sub> is a promising model for an artificial photosynthetic system [1–3], but real example of such an artificial photosynthetic system has not been reported. Both O<sub>2</sub> and H<sub>2</sub> formations by water photolysis must take place via a multi-electron transfer, so that, toward this goal, it is important that highly active catalysts are developed to form O<sub>2</sub> and H<sub>2</sub> at the oxidation/reduction sites

[4]. Although there have been no highly active oxidation/reduction catalysts capable of efficient O<sub>2</sub> and H<sub>2</sub> formation, we have been developing efficient catalyst systems using molecular aggregates composed of a metal complex and a polymer membrane [5–11]. Molecular aggregates can often show unique and active catalysis that cannot be observed in a homogeneous solution [12], mostly due to the arrangement of the reaction components within a matrix as seen in nature. Therefore, developing an efficient catalyst site by molecular aggregates may also be expected to open a breakthrough in constructing a molecule-based photosynthetic model.

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$H^+$  reduction is a fundamental chemical reaction and has been attracting attention a great deal in both basic science and technology. One of the important subjects in the related research is to develop much more active catalyst than a conventional Pt one. Although colloidal Pt has been known as the most active catalyst in reducing  $H^+$  [13–17], a few examples of highly active molecular catalyses for  $H^+$  reduction have been found recently by the present authors: Prussian White [8] as well as metallo-porphines incorporated in a polymer film [9,10] can function as molecule-based  $H^+$  reduction catalysts with much higher activity than a conventional Pt catalyst. It is important to investigate and accumulate fundamental knowledge on molecular catalyst for designing much more active catalyst system. Polypyridyl metal complexes may also be one of the promising candidates for constructing a catalyst site because of their stability during the redox process [1].

In the present work, electrocatalysis and its mechanism for  $H^+$  reduction by a bis(2,2':6',2''-terpyridine) cobalt(II) complex embedded in a Nafion<sup>®</sup> membrane coated on a basal-plane pyrolytic graphite (BPG) electrode (denoted as BPG/Nf[Co(terpy)<sub>2</sub><sup>2+</sup>]) were studied by voltammetry as well as potential-step chronoamperometry. If  $H^+$  reduction takes place by a molecular catalyst, the molecule itself needs to coordinate  $H^+$  prior to its catalytic reduction, so that the relationship between electrocatalysis by Nf[Co(terpy)<sub>2</sub><sup>2+</sup>] and pH was firstly investigated. Furthermore, the electrocatalysis should follow electron transfer to the catalyst molecule through the matrix. The electron transfer to generate electrocatalytically active species is a key process affecting the overall kinetics, so that it must be essential to understand the electron transfer process. The electrocatalysis will be discussed in combination with the electron transfer of Nf[Co(terpy)<sub>2</sub><sup>2+</sup>].

## 2. Experimental

A 5 wt.% Nafion<sup>®</sup> (Nf) alcoholic solution and a basal-plane pyrolytic graphite (BPG) plate were purchased from Aldrich Chemical Co., Ltd., and Union Carbide Co., Ltd., respectively. Co(terpy)<sub>2</sub>I<sub>2</sub> ([Co(terpy)<sub>2</sub><sup>2+</sup>]) was synthesized according to a pre-

vious procedure [18]. The purest grade reagents were used without further purification.

Electrode modification was carried out as follows. A methanol solution containing 2.5 wt.% Nf was at first prepared. A 6  $\mu$ l of this solution was cast onto a BPG electrode (effective area, 0.21 cm<sup>2</sup>), followed by solvent evaporation under air. The Nf-coated BPG was dipped into pure water for 30 min to improve its cation exchange ability. The introduction of the [Co(terpy)<sub>2</sub><sup>2+</sup>] was carried out by a cation exchange method by dipping the Nf-coated BPG into an aqueous solution containing a known concentration of [Co(terpy)<sub>2</sub><sup>2+</sup>], and the amount of the adsorbed [Co(terpy)<sub>2</sub><sup>2+</sup>] was estimated by the visible absorption spectral change of the solution before and after the adsorption. The membrane thickness of Nf was ca. 3  $\mu$ m by considering the density of the Nf membrane (2 g cm<sup>-3</sup>) [19].

An electrochemical cell was equipped with the BPG/Nf[Co(terpy)<sub>2</sub><sup>2+</sup>] working, a spiral Pt counter electrode and a silver/silver chloride (Ag/AgCl, in saturated KCl electrolyte) reference electrode in a phosphate buffer solution. Electrochemical study was carried out using a potentiostat (HOKUTO DENKO, HA-301) equipped with a function generator (HOKUTO DENKO, HB-104), a coulometer (HOKUTO DENKO, HF-201) and a recorder (YOKOGAWA, 3025). Typical potentiostatic electrolyses at the polymer-coated BPG electrode were run for 1 h.

Electrochemistry was also studied in a [Co(terpy)<sub>2</sub><sup>2+</sup>]/dimethylacetamide (DMA) or [Co(terpy)<sub>2</sub><sup>2+</sup>]/(DMA + H<sub>2</sub>O) (DMA:H<sub>2</sub>O = 4:1) solution containing electrolyte (NaClO<sub>4</sub>) with a BPG working, a Ag/AgCl reference and a Pt wire counter electrode.

The H<sub>2</sub> produced in the electrolysis was analyzed by a gas chromatograph (Shimadzu, GC-8A) with a molecular sieve 5 Å-column and Ar carrier gas. Faradaic efficiency (%) for the H<sub>2</sub> formation in the electrolysis always exceeded 80%.

## 3. Results and discussion

### 3.1. Electrochemistry of [Co(terpy)<sub>2</sub><sup>2+</sup>] solution

Fig. 1(a) shows a typical cyclic voltammogram (CV) of a homogeneous 1 mM Co(terpy)<sub>2</sub><sup>2+</sup>/DMA solution (aprotic solvent) containing 0.1 M NaClO<sub>4</sub>.

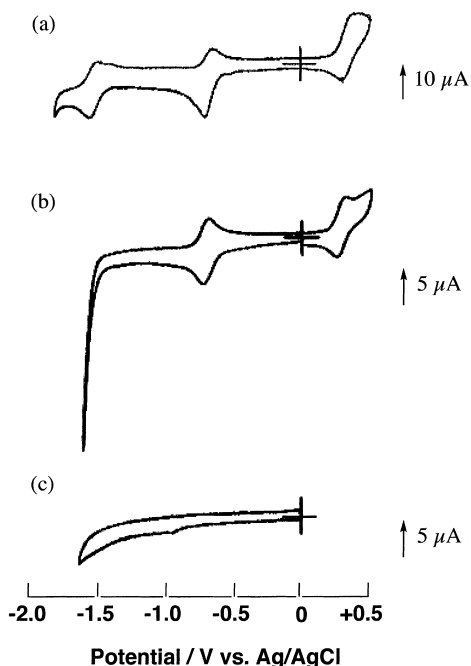


Fig. 1. CVs of  $[\text{Co}(\text{terpy})_2]^{2+}$  in DMA (a) and DMA +  $\text{H}_2\text{O}$  (DMA: $\text{H}_2\text{O}$ , (v/v = 4:1)) (b), and in the absence of the complex (c).  $[\text{Co}(\text{terpy})_2]^{2+}$  concentration, 1 mM;  $\text{NaClO}_4$ , 0.1 M; scan rate,  $5 \text{ mV s}^{-1}$ .

Three redox couples were observed at  $+0.36 \text{ V}$  (Co(III)/Co(II)),  $-0.67 \text{ V}$  (Co(II)/Co(I)) and  $-1.51 \text{ V}$  (Co(I)/Co(0)), where the third reduction takes place on the ligand, and the formed  $\text{Co}(\text{terpy})_2^{+\bullet}$  is denoted as Co(0). The assignment of the redox couples is the same as the previous report [20]. A similar CV measurement was carried out in a  $\text{Co}(\text{terpy})_2^{2+}/\text{DMA}$  solution containing 20% water, and the CV is shown in Fig. 1(b). Different from Fig. 1(a), the redox couple of Co(I)/Co(0) disappeared due to  $\text{H}^+$  reduction, where a growth of cathodic currents started to occur below  $-1.5 \text{ V}$ . Almost no increase of cathodic currents can be observed in the absence of the complex (see Fig. 1(c)), supporting that the electrocatalytic  $\text{H}^+$  reduction takes place after forming Co(0) species. In a separate experiment, it was confirmed that the electrocatalytic  $\text{H}_2$  formation in a  $\text{Co}(\text{terpy})_2^{2+}/(\text{DMA} + \text{water})$  system occurs (the amount of  $\text{H}_2$  produced was ca. 1.5 ml at  $-1.70 \text{ V}$  for 0.5 h, and turnover number of the complex was estimated as  $2.5 \times 10^2 \text{ h}^{-1}$ ). The appearance of reversible redox peaks of Co(II)/Co(I)

shows that Co(0) species is responsible for the  $\text{H}_2$  formation. Therefore, in the present case Co(0) must work as an one-electron reductant for the  $\text{H}_2$  formation which is a two-electron reduction process. Such a bimolecular electrocatalysis would be difficult to take place by a homogeneous Co(0) in a solution. The electroreduction of Co(I) into Co(0) is most probably followed by coordination of  $\text{H}^+$  resulting in an intermediate formation (Co(0)–H) attributable to high basicity of Co(0). In addition, with increasing the reduction state of the complex, the catalyst molecule itself would become insoluble in an aqueous solution due to the reduced charge. Therefore, it is most probable that adsorption of the intermediate complex (Co(0)–H) onto the electrode surface occurs due to hydrophobic interaction, leading to the bimolecular catalysis.

### 3.2. Electrocatalysis for $\text{H}^+$ reduction by $[\text{Co}(\text{terpy})_2]^{2+}$ embedded in a Nafion membrane

Fig. 2 shows CVs at a BPG electrode coated with a Nafion membrane incorporating  $[\text{Co}(\text{terpy})_2]^{2+}$  (denoted as BPG/Nf $[\text{Co}(\text{terpy})_2]^{2+}$ ). When the CV was measured in a pH 6.6 electrolyte solution (Fig. 2(a)), two redox couples of both Co(III)/Co(II) and Co(II)/Co(I) were observed at  $+0.08$  and  $-0.93 \text{ V}$ , and moreover, on a more reductive scan, remarkable growth of the currents was observed below  $-1.3 \text{ V}$ . The electrocatalytic  $\text{H}_2$  formation was confirmed below  $-1.3 \text{ V}$  as mentioned later. Similar to a homogeneous  $[\text{Co}(\text{terpy})_2]^{2+}/(\text{DMA} + \text{H}_2\text{O})$  solution, the electrocatalytic  $\text{H}^+$  reduction at BPG/Nf $[\text{Co}(\text{terpy})_2]^{2+}$  (pH 6.6) started to take place after forming Co(0) below  $-1.3 \text{ V}$ . Under acidic pH conditions (see Fig. 2(b) and (c)), the CVs are entirely different compared with the pH 6.6 system. Different from Fig. 2(a), only a cathodic peak was observed for the redox process of Co(II)/Co(I), and the electrocatalytic currents due to  $\text{H}^+$  reduction began to increase below approx.  $-1.1 \text{ V}$ . The reoxidation peak of the Co(I) was absent, indicating that under acidic pH conditions, Co(I) induces the catalytic  $\text{H}^+$  reduction. It should be noted here that the electrocatalysis for the  $\text{H}^+$  reduction by Nf $[\text{Co}(\text{terpy})_2]^{2+}$  varies with the pH conditions employed. Comparing the CV in Fig. 2(b) and (c) (pH 2–3) with that in Fig. 2(a) (pH 6.6), the reduction peak shifts to positive potentials on

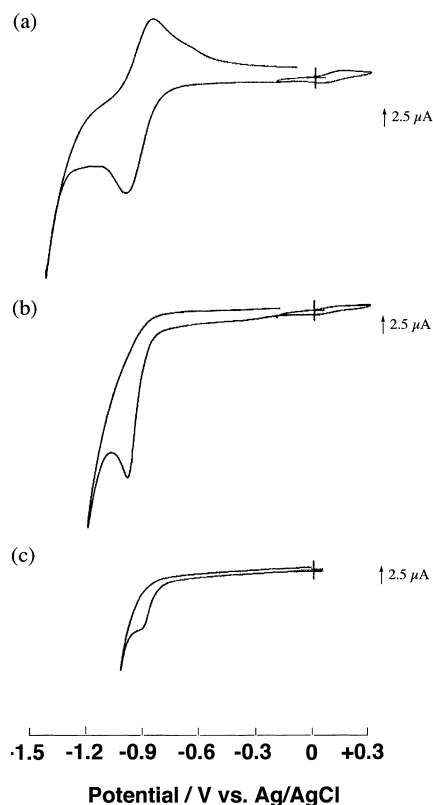
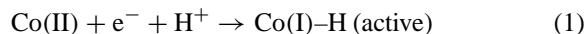


Fig. 2. CVs at BPG/Nf[Co(terpy)<sub>2</sub><sup>2+</sup>] in an aqueous electrolyte solution. [Co(terpy)<sub>2</sub><sup>2+</sup>] concentration in membrane: (a) 0.83 M; (b) 0.69 M; and (c) 0.52 M. pH: (a) 6.6; (b) 3.0; (c) 2.1. Scan rate, 5 mV s<sup>-1</sup>.

lowering pH. The detailed electrocatalysis mechanism will be discussed later.

The reduction potential of Co(II) was investigated over the pH range from 1 to 7, and the result is shown in Fig. 3. The reduction potential of the Co(II) to Co(I) showed a pH dependence of approx. -59 mV per pH when the pH was below 3.8, and then it became almost pH-independent and reached a constant value. This result reveals that the Co(I) is weakly basic. From Fig. 3, the following relations can be introduced:

At pH < 3.8,



and at pH > 3.8,

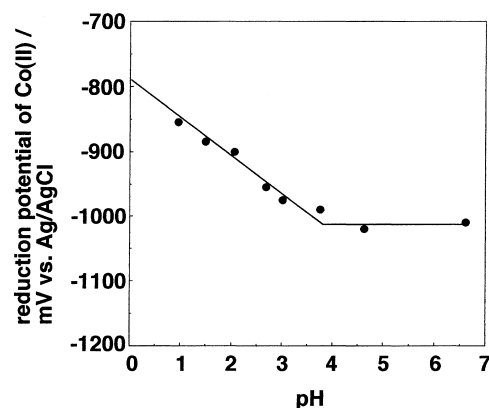
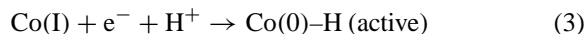
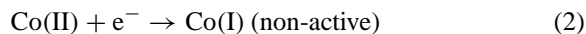


Fig. 3. The pH dependence of the reduction potential of Co(II). The reduction potential of [Co(terpy)<sub>2</sub><sup>2+</sup>] was obtained by measuring the CV at 5 mV s<sup>-1</sup>.

Eq. (1) shows that one-electron reduction of Co(II) into Co(I) is accompanied by one-proton coordination to compensate the charge, resulting in an intermediate formation of Co(I)-H. While, under weakly acidic-neutral pH conditions, Co(I) is present stably without H<sup>+</sup> coordination (Eq. (2)). Therefore, under weakly acidic-neutral pH conditions, further electroreduction of the Co(I) must take place to reduce H<sup>+</sup> (Eq. (3)). Nf has a highly acidic property due to the sulfonic acid groups on the side chain, which is called a super-strong acid [21,22]. However, it is likely that the reduction process of the complex in this acidic matrix is affected by bulk pH conditions, showing that the charge compensation needs to be achieved by H<sup>+</sup> migration from the bulk electrolyte solution to the redox site in the matrix.

Typical electrolysis data at both pH 2.9 and pH 6.6 are summarized in Table 1. Their electrolyses were carried out under similar conditions of the complex concentration. At pH 2.9 the potential at which the Co(I) is present (-1.00 V) was applied during the electrolysis. While, at pH 6.6 H<sub>2</sub> formation is expected to take place by Co(0), so that potential of -1.45 V was applied. The electrolysis data exhibited clearly that the electrocatalytic H<sup>+</sup> reduction is induced by the Co-complex dispersed in the Nafion membrane. The net H<sub>2</sub> amount at BPG/Nf[Co(terpy)<sub>2</sub><sup>2+</sup>] was calculated by subtracting the amount of H<sub>2</sub> produced at a blank Nf-coated BPG (BPG/Nf), and then the intrinsic turnover number (TN) of a complex for H<sub>2</sub> formation was estimated.

Table 1  
The amount of H<sub>2</sub> produced at BPG/Nf[Co(terpy)<sub>2</sub><sup>2+</sup>]

pH	Applied potential (V) vs. Ag/AgCl	Active species	H <sub>2</sub> produced (μlh <sup>-1</sup> )	TN (h <sup>-1</sup> ) <sup>a</sup>
pH 2.9 <sup>b</sup>	-1.00	Co(I)	7.4	13.9
pH 7.0 <sup>c</sup>	-1.45	Co(0)	20.3	20.7

<sup>a</sup> TN was estimated by subtracting the amount of H<sub>2</sub> at Nf-coated BPG (BPG/Nf).

<sup>b</sup> Complex concentration in the membrane, 0.19 M ( $1.2 \times 10^{-8}$  mol); applied potential, -1.10 V (vs. Ag/AgCl).

<sup>c</sup> Complex concentration in the membrane, 0.23 M ( $1.4 \times 10^{-8}$  mol); applied potential, -1.45 V (vs. Ag/AgCl).

### 3.3. Electron transfer of [Co(terpy)<sub>2</sub><sup>2+</sup>] embedded in a Nafion membrane

A heterogeneous electrocatalysis by a functional molecule at a polymer-coated electrode should be discussed in combination with its electron transfer process to generate electrocatalytically active species, since the overall kinetics are affected by the electron transfer. Therefore, the information obtained by the electron transfer analysis is of importance in considering the catalysis mechanism. In the present work, potential-step chronoamperometry was carried out to analyze the electron transfer process at BPG/Nf[Co(terpy)<sub>2</sub><sup>2+</sup>] according to Cottrell's equation (Eq. (4)) [23,24] based on a semi-infinite diffusion process:

$$i = \frac{nFc(D_{\text{app}})^{1/2}}{(\pi t)^{1/2}} \quad (4)$$

where  $D_{\text{app}}$  (cm<sup>2</sup> s<sup>-1</sup>) is the apparent diffusion coefficient,  $i$  (A cm<sup>-2</sup>) the current density,  $n$  the number of electrons (in the present case it is 1) and  $F$  is the Faraday's constant ( $9.65 \times 10^4$  C mol<sup>-1</sup>). The electron transfer process of Co(II) into Co(I) in a pH 6.6 electrolyte solution was studied by a potential step from -0.3 to -1.1 V. The relationship between  $i$  and  $t^{-1/2}$  was linear, showing that the electroreduction of Co(II) into Co(I) fits the Cottrell's equation. From the slope,  $D_{\text{app}}$  was estimated as a function of the complex concentration in the film, as shown in Fig. 4. The  $D_{\text{app}}$  values decreased remarkably with the increasing complex concentration. Electron transfer in a heterogeneous system takes place either by a physical diffusion of the redox molecule or by an electron self-exchange. The  $D_{\text{app}}$  value is represented by the sum of an intrinsic diffusion coefficient ( $D_p$ ) in the absence of any electron self-exchange reaction

and a contribution of electron self-exchange ( $D_{\text{et}}$ ; this includes a term of concentration as a function) [25–27]. The  $D_{\text{app}}$  value increases with the concentration if the electron self-exchange rate is dominated, but this is not the case in the present system. The inverse concentration dependence in Fig. 4 shows that electron self-exchange is negligible compared with physical diffusion. Moreover, the decrease of  $D_{\text{app}}$  with concentration shows that diffusion of the redox molecules is strongly prohibited by increasing its concentration. Similar concentration dependencies of  $D_{\text{app}}$  have been observed for a film in which the redox molecule is embedded [28–30]: for example, Watanabe et al. have exhibited that Li-TCNQ (TCNQ, 7,7,8,8-tetracyanoquinodimethane) dissolved in a poly(ethylene oxide) film is the case in the reduction of TCNQ<sup>-</sup> into TCNQ<sup>-2</sup>. The present authors have

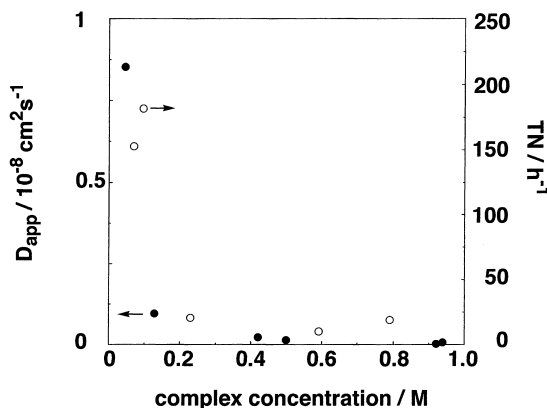


Fig. 4. Concentration dependence of  $D_{\text{app}}$  and TN in a pH 6.6 electrolyte solution. The chronoamperometry to obtain the  $i-t^{-1/2}$  plot was carried out by stepping the potential from -0.3 to -1.1 V. The potentiostatic electrolysis was carried out at -1.45 V, and turnover number (TN) of [Co(terpy)<sub>2</sub><sup>2+</sup>] for the electrocatalytic H<sub>2</sub> formation was calculated by subtracting the amount of H<sub>2</sub> produced at a blank Nf-coated BPG (BPG/Nf).

also reported that, in electroreduction of  $\text{Co}^{\text{II}}\text{TPP}$  dispersed in Nf matrix, the electroactive ratio of the complex ( $R_{\text{et}}$ ), which is a parameter reflecting the electron transfer process, decreases with increasing the concentration. As for such the concentration dependencies of  $D_{\text{app}}$ , further explanations should be given for the present case. The  $[\text{Co}(\text{terpy})_2^{2+}]$  molecule itself is hydrophobic, so that the property of the polymer matrix would become more hydrophobic with the increasing complex concentration. The hydrophobicity would further increase by reducing the complex. As has been known, the Nf film involves both hydrophilic columns composed of the sulfonic acid groups on the side chain and hydrophobic columns composed of the polymer backbone [21,22]. It seems that the increase of the hydrophobicity prohibits the charge transfer of ion or complex, as has also been indicated in the literature [31].

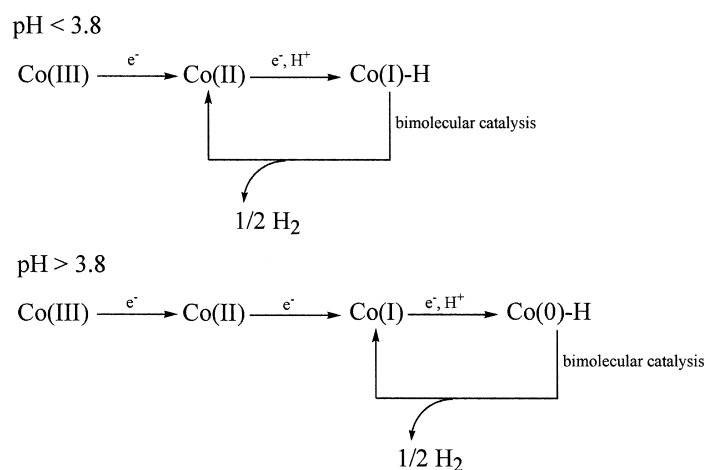
In Fig. 4, the TN for the electrocatalytic  $\text{H}_2$  formation based on the electrolysis data (pH 6.62) at BPG/Nf $[\text{Co}(\text{terpy})_2^{2+}]$  is also plotted against the complex concentration. The concentration dependencies of both  $D_{\text{app}}$  and TN are almost the same, supporting that the overall kinetics in the Nf $[\text{Co}(\text{terpy})_2^{2+}]$  system is controlled by the electron transfer process.

The electron transfer process of Co(I) into Co(0) in a pH 6.6 electrolyte solution cannot be studied because the electrocatalytic  $\text{H}^+$  reduction takes place on forming Co(0). It has recently been found by our group that the charge transfer mechanism in a polymer ma-

trix can be associated with the charge transfer product [28,32–36]: when the interaction of the charge transport product with the matrix is strong, charge transport takes place by a hopping (electron self-exchange) mechanism, but when it is weak, charge transport occurs by a physical diffusion mechanism. In the present case, it can be predicted that the interaction of the charge transport product with the matrix is weak for Co(0), which supports a diffusion mechanism for the electron transport.

### 3.4. Electrocatalysis mechanism of $[\text{Co}(\text{terpy})_2^{2+}]$ embedded in a Nafion membrane

The electrocatalysis mechanism by Nf $[\text{Co}(\text{terpy})_2^{2+}]$  is summarized as shown in Scheme 1. The different catalytically active species with the pH conditions employed should be noticed. Under higher pH conditions (pH  $\gtrsim$  4), the electrocatalytic  $\text{H}^+$  reduction occurs after forming Co(0). This is explained by the pH independence of the reduction potential of Co(II) showing no formation of Co(I)–H in these pH regions. When electrocatalysis by the Co(0) takes place to reduce  $\text{H}^+$ , the electroreduction process of Co(I) into Co(0) should be accompanied by  $\text{H}^+$  coordination. A reference study in Fig. 1(b) exhibited that electrocatalytic  $\text{H}^+$  reduction by Co(0) occurs even in a non-acidic (DMA +  $\text{H}_2\text{O}$ ) solution, indicating that the  $\text{p}K_{\text{a}}$  value of Co(0)–H is much higher than that of Co(I)–H ( $\text{p}K_{\text{a}} \sim 3.8$  obtained from Fig. 3).



Scheme 1. Electrocatalysis Mechanism for  $\text{H}^+$  reduction by  $[\text{Co}(\text{terpy})_2]$  embedded in a Nafion membrane.

Therefore, it is reasonable that the electrocatalysis is caused by Co(0) above pH 3.8. Considering the concentration dependencies of both the  $D_{app}$  and TN (see Fig. 4), the rate-determining step could be the electroreduction process of the complex. The  $D_{app}$  value essentially reflects not only the electron transfer but also the  $H^+$  or counter ion migration from the bulk solution to the redox site in the matrix. The hydrophobicity of the catalyst would increase with the reduction of the complex, so that the  $D_{app}$  value for the reduction of Co(I) to form Co(0)–H would be smaller than that for the Co(II)/Co(I) process because of the higher hydrophobic interaction of the Co(0) with matrix. In addition to no formation of Co(I)–H at pH > 3.8, the appearance of the reversible peak for Co(II)/Co(I) couple (see Fig. 2(a)) supports that Co(I) is not responsible for the electrocatalysis to reduce  $H^+$ , so that the electrocatalysis occurs by Co(0).

Under acidic pH conditions below 3.8, the electroreduction of Co(II) is conjugated with  $H^+$  migration (from the bulk electrolyte solution) to compensate the charge resulting in the Co(I)–H formation as an intermediate for the  $H^+$  reduction. It can be confirmed that the potential at which only the Co(I) is present (pH 2.9,  $-1.00$  V versus Ag/AgCl) induces the electrocatalytic  $H_2$  formation. Formal potential of  $H^+/H_2$  (pH  $\sim$  3) is  $-0.37$  V (versus Ag/AgCl), so that Co(I) works as a reductant to form  $H_2$ . In the CV at the lower pH (Fig. 2(c)), a shoulder peak for the Co(II) reduction appeared, showing that the electrocatalysis takes place on forming Co(I)–H. The reoxidation peak of Co(I) was absent supporting that the electrocatalysis by Co(I) could occur quickly.

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