

Electrocatalytic proton reduction by phthalocyanine cobalt derivatives incorporated in poly(4-vinylpyridine-co-styrene) film

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Received 10 August 1998; accepted 15 December 1998

Abstract

The electrocatalytic proton reduction by phthalocyanine cobalt derivatives such as non-substituted phthalocyanine cobalt(II) (CoPc), octacyanophthalocyanine cobalt(II) (CoPc(CN)₈), and tetrasulfonatophthalocyanine cobalt(II) (CoPc(SO₃H)₄) incorporated in a poly(4-vinylpyridine-co-styrene) (P(VP-St)) film coated on a graphite electrode has been studied. Under the applied potential of -0.90 V (Ag/AgCl), the turnover number of the catalyst for hydrogen production reached 2×10^5 h⁻¹ for the P(VP-St)[CoPc] system. The catalytic efficiency of the three complexes is in the order, CoPc > CoPc(CN)₈ > CoPc(SO₃H)₄. The electron propagation through the polymer matrix has been studied by the potential-step chronoamperometry (PSCAS). The result demonstrated that the electron transfer occurs through a physical diffusion mechanism. The apparent diffusion coefficient decreased in the order of CoPc > CoPc(CN)₈ > CoPc(SO₃H)₄ which is in accordance with that of the catalytic efficiency. The catalytic proton reduction was strongly suggested to be dominated by the electron transfer within the matrix. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Electrocatalytic proton reduction; Phthalocyanine cobalt derivatives; Poly(4-vinylpyridin-co-styrene) (P(VP-St)); Turnover number (TN); Electron transfer

1. Introduction

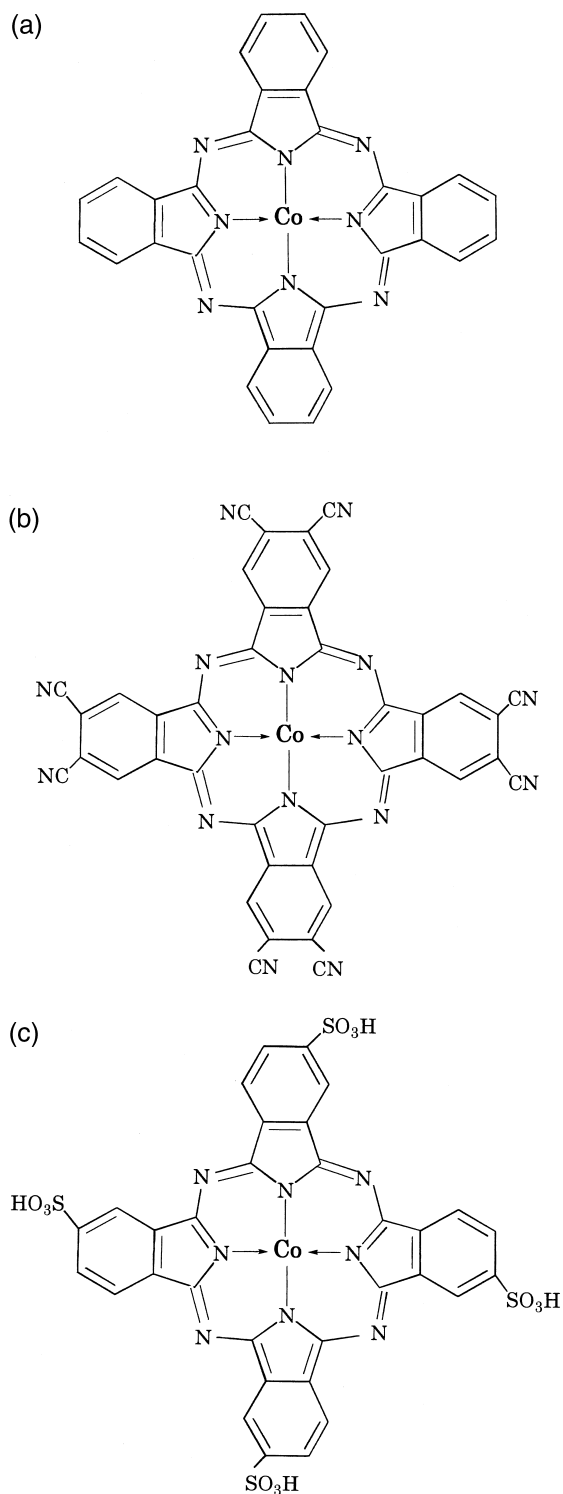
In the natural photosynthetic system, the photosensitizer, chlorophyll molecule, absorbs sunlight to oxidize water to oxygen and synthesizes carbohydrates from carbon dioxide [1–5]. The water oxidation works as an electron donating

step and carbon dioxide as an electron acceptor. To solve the energy crisis, it is of importance to mimic the natural photosynthesis to produce fuels from sunlight and water [6–16]. Water photolysis brings about simultaneous evolution of hydrogen and oxygen. This reaction is regarded as one of the most promising ways for solar energy conversion because hydrogen is a clean fuel as well as a basic chemical compound. To realize an artificial water photolysis, highly efficient catalyst is needed [16–20].

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Porphyrin and phthalocyanine derivatives have been widely studied as potential candidates for solar energy conversion devices because they absorb visible light efficiently and then electron transfer within them occurs with a high efficiency [21–26]. It has been reported that these complexes can catalyze proton reduction to generate hydrogen in sacrificial donor systems [26,27]. Our recent research revealed that tetraphenylporphyrin cobalt(II) (CoTPP) when incorporated into a Nafion film exhibited highly electrocatalytic effect for proton reduction [28–30]. In the present work, phthalocyanine cobalt(II) (CoPc) derivatives were employed to study the electrocatalysis in proton reduction. These complexes were incorporated into a polycation, poly(4-vinylpyridine-co-styrene) (P(VP-St)). Besides the non-substituted CoPc, octacyanophthalocyanine cobalt(II) (CoPc(CN)₈) and tetrasulfonatophthalocyanine cobalt(II) (CoPc(SO₃H)₄) were also used to investigate the catalysis of the phthalocyanine cobalt derivatives as well as the effect of the substituted groups on the Pc ring and their interaction with the matrix (Scheme 1).

Because the complexes are incorporated in a polymer film, electron propagation in the matrix is an important factor to influence the proton reduction. Such electron transfer is generally considered to occur via a physical diffusion or/and electron hopping mechanism [31–50]. If the complexes are attached to macromolecular structure either by chemical bonding or by strong physical interaction, the physical diffusion becomes so weak that it can be neglected in comparison with the electron hopping. In this case, the electron transfer occurs through an electron hopping mechanism. Otherwise, physical diffusion takes place. Because of the poor solubility of the CoPc and CoPc(CN)₈ in organic solvents, CoPc(SO₃H)₄ was employed as the redox probe to study the electron propagation through the matrix by a potential-step chronoamperometry (PSCAS) measurement [46–49].



Scheme 1. Structure of the CoPc derivatives. (a) CoPc. (b) CoPc(CN)₈. (c) CoPc(SO₃H)₄.

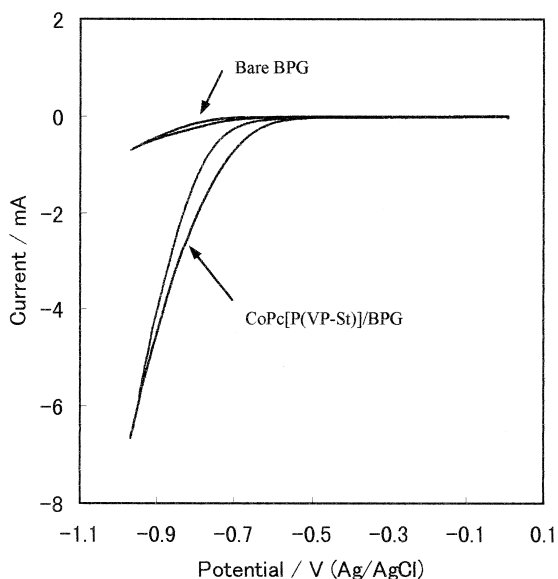


Fig. 1. Cyclic voltammogram of the P(VP-St)[CoPc] coated on BPG electrode dipped in a 0.1 M buffer $\text{NaH}_2\text{PO}_4/\text{H}_3\text{PO}_4$ aqueous electrolyte solution (pH 1.0) at scan rate 20 mV s^{-1} .

2. Experimental

Poly(4-vinylpyridine-co-styrene) (P(VP-St), a random copolymer with a molar ratio 9:1 of 4-vinylpyridine:styrene, and CoPc were purchased from Aldrich. $\text{CoPc}(\text{CN})_8$ and $\text{CoPc}(\text{SO}_3\text{H})_4$ were synthesized and purified.

The non-substituted CoPc-containing P(VP-St) (abbreviated as P(VP-St)[CoPc]) and Co(II)- $\text{Pc}(\text{CN})_8$ -containing P(VP-St) (abbreviated as P(VP-St)[Co(II) $\text{Pc}(\text{CN})_8$]) films were prepared by a mixture casting method [50]. P(VP-St) was dissolved in *N,N*-dimethylacetamide (DMAc) to prepare a 0.5 wt.% solution (density 0.8 g cm^{-3}). Non-substituted CoPc or $\text{CoPc}(\text{Pc})_8$ was dissolved in the P(VP-St)/DMAc solution. A $5 \mu\text{l}$ of such solution was cast on a basal-plane pyrolytic graphite (BPG) electrode (effective area 0.2 cm^2). After drying at room temperature

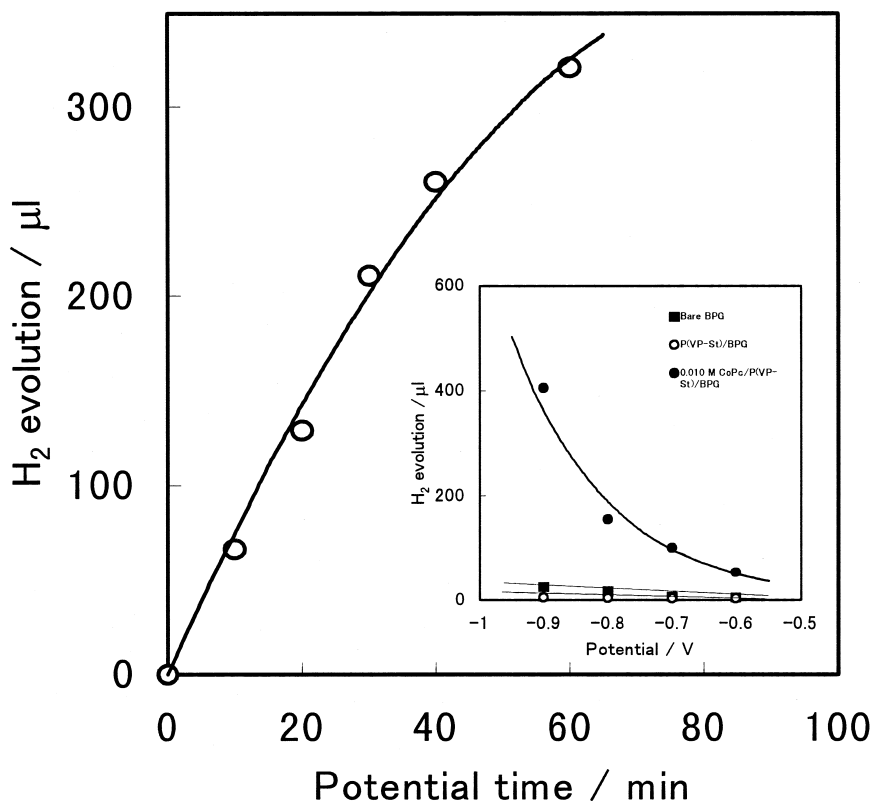


Fig. 2. Correlation between the hydrogen evolution and the time in a potentiostatic electrolysis at -0.90 V (Ag/AgCl) for the P(VP-St)[CoPc]. The inset represents the dependence of the hydrogen evolution on the applied potentials for the P(VP-St)[CoPc] in 1 h.

under vacuum, the thickness of the dry film was about 1 μm (density 1.0/g cm^{-3}). The complex concentration in the P(VP-St) film was estimated from the complex amount and the film volume.

The P(VP-St)[CoPc(SO₃H)₄] system was prepared by an adsorption method [50]. A 5 μl of a 0.5 wt.% P(VP-St)/DMAc solution was cast on a BPG electrode. A 1 μm film was formed by drying under vacuum. By dipping the polymer-coated BPG electrode in a CoPc(SO₃H)₄ aqueous solution at pH 1.0, CoPc(SO₃H)₄ could be adsorbed from the solution into the polycation matrix by anion exchange. The complex concentration in the matrix became saturated after 1 h. The amount of

CoPc(SO₃H)₄ in the P(VP-St) was determined by the absorbance change in the solution before and after the absorption. A transparent indium tin oxide (ITO) electrode (effective area 1.0 cm^2) coated with a 1 μm P(VP-St) film containing CoPc(SO₃H)₄ complex was prepared by the similar method.

The electrochemical measurement was carried out by using a potentiostat (Hokuto Denko, HA-301) with a function generator (Hokuto Denko, HB-104), a coulomb meter (Hokuto Denko, HF-201), and a recorder (Shimadzu, XY-50). A single-compartment electrochemical cell was equipped with a modified BPG electrode, an Ag/AgCl reference, and a spiral platinum wire counter electrode. A 0.1 M

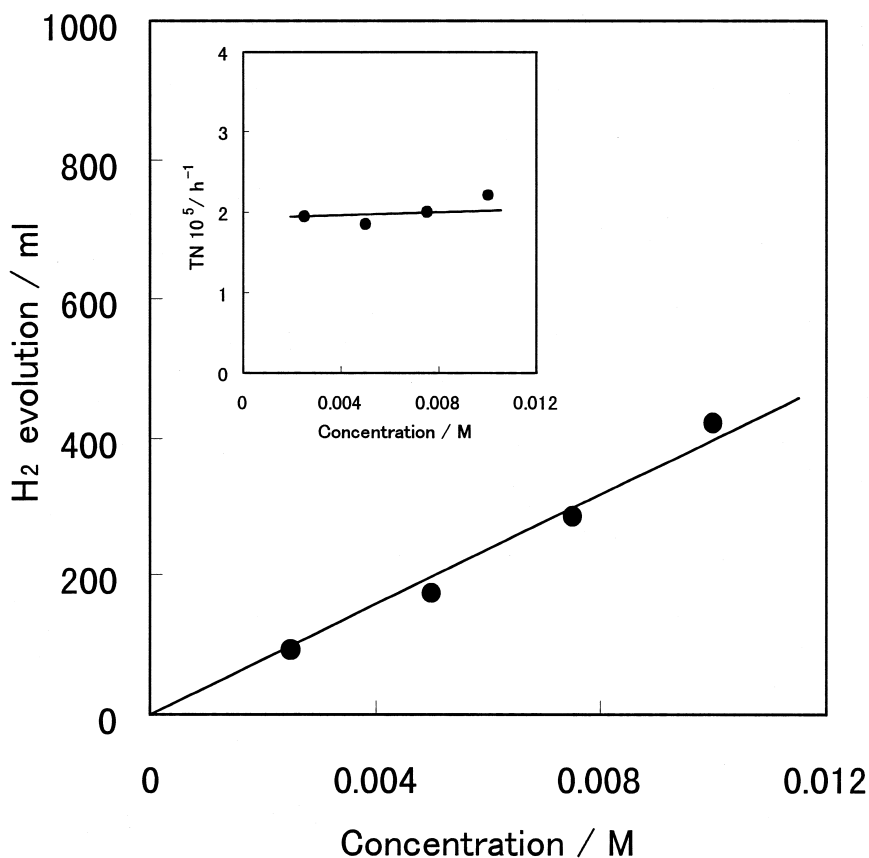


Fig. 3. Dependence of the hydrogen evolution on the complex concentration for the P(VP-St)[CoPc] in a potentiostatic electrolysis at -0.90 V (Ag/AgCl) in 1 h. The inset represents the relation between the turnover number and the complex concentration for the P(VP-St)[CoPc].

$\text{NaH}_2\text{PO}_4/\text{H}_3\text{PO}_4$ (pH 1.0) aqueous buffer solution was used. The amount of hydrogen evolution was measured by a gas chromatography (Shimadzu, GC-4CPT) with a molecular sieve 5 Å column and argon carrier gas. The PSCAS was carried out by combining a multichannel photodiode array spectrophotometer (Otsuka Electronic, IMUC-7000) with the voltammetric apparatus. A conventional single-compartment quartz cell was equipped with a modified ITO electrode, an Ag/AgCl reference, and a spiral platinum wire counter electrode. A 0.1 M NaClO_4 aqueous solution at pH 1.2 was used.

All the reaction systems were deaerated by bubbling argon gas for 30 min before measurement. Ion-exchange water was used in all the experiments.

3. Results and discussion

The concentrations of the CoPc and $\text{CoPc}(\text{CN})_8$ in the P(VP-St) were 2.5–10 mM, and that of the $\text{CoPc}(\text{SO}_3\text{H})_4$ 0.04–0.28 M. Different from the CoPc and $\text{CoPc}(\text{CN})_8$, $\text{CoPc}(\text{SO}_3\text{H})_4$ was incorporated into the P(VP-St) matrix by an electrostatic interaction. Therefore, the concentration of $\text{CoPc}(\text{SO}_3\text{H})_4$ in the matrix can reach a higher value than that of the CoPc and $\text{CoPc}(\text{CN})_8$.

Cyclic voltammogram (CV) of the P(VP-St)[CoPc] on a BPG electrode is shown in Fig. 1. When the applied potential is lower than -0.60 V (Ag/AgCl), the CoPc exhibited high cathodic currents due to the proton reduction in comparison with the bare BPG electrode indicating that the complex works as a catalyst for

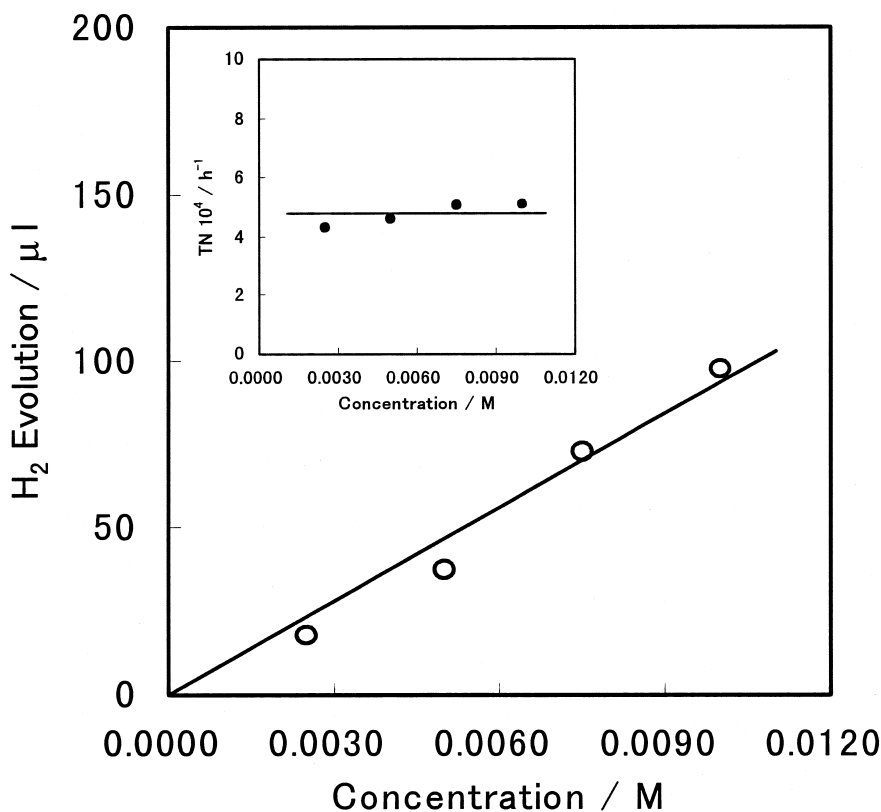


Fig. 4. Dependence of the hydrogen evolution on the complex concentration for the P(VP-St)[CoPc(CN)₈] in a potentiostatic electrolysis at -0.90 V (Ag/AgCl) in 1 h. The inset represents the relation between the turnover number and the complex concentration for the P(VP-St)[CoPc(CN)₈].

proton reduction. When the potentiostatic electrolysis was applied at -0.90 V (at $\text{pH} = 1.0$), the evolved amount of hydrogen increased with time (Fig. 2), showing that the complex is electrochemically stable as a catalyst in the proton reduction. The amount of hydrogen increased with decreasing the applied potentials as shown in the inset of Fig. 2. Overpotential was necessary for the electrocatalysis. The hydrogen evolved at -0.90 V in 1 h was plotted against the CoPc concentration in the matrix as shown in Fig. 3. The linear relation demonstrates that the hydrogen evolved is of first order with respect to the complex concentration. Since all the complexes were electroactive in the matrix as will be shown later, the turnover number (TN) of the catalyst was estimated from the hydrogen evolution; it was almost independent of the complex concentration (inset of Fig. 3).

Instead of the CoPc, the $\text{CoPc}(\text{CN})_8$ and $\text{CoPc}(\text{SO}_3\text{H})_4$ were also used as the catalyst to study the proton reduction by potentiostatic electrolysis. The evolved hydrogen was plotted against the complex concentration in the matrix as shown in Figs. 4 and 5. The TN was plotted against the complex concentration in the insets of Figs. 4 and 5. Similar to the CoPc, the $\text{CoPc}(\text{CN})_8$ expresses a first order function for the hydrogen evolution with respect to the complex concentration. The TN values were almost independent of the concentration of the complex. Similar results were obtained for the $\text{CoPc}(\text{SO}_3\text{H})_4$, except that the TN number showed a small downward deviation against the complex concentration.

The redox reaction of these CoPc derivatives should be a crucial factor for their electrocatalytic activities of proton reduction [51,52]. The

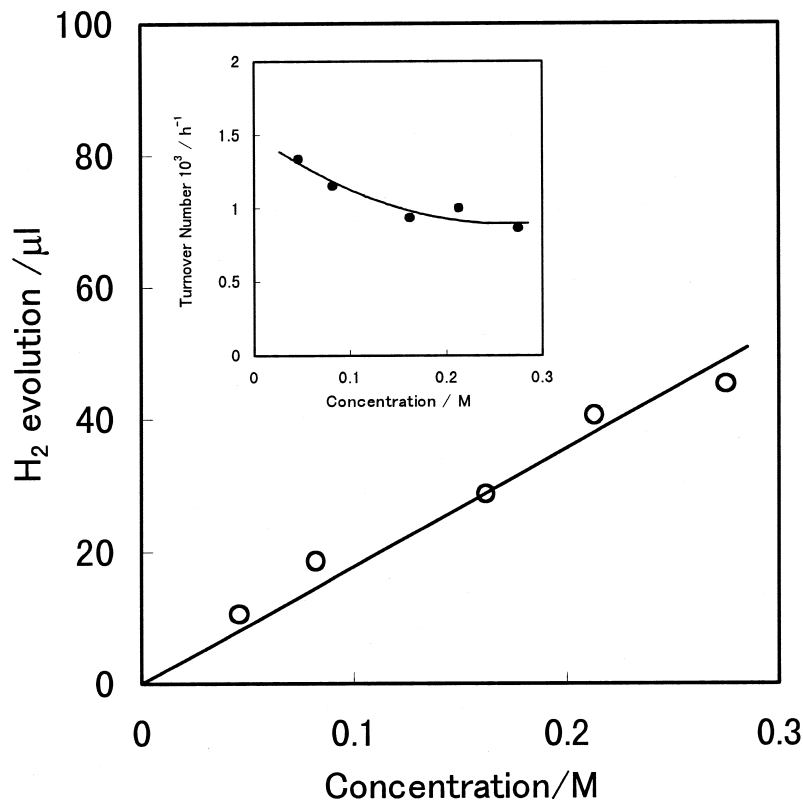


Fig. 5. Dependence of the hydrogen evolution on the complex concentration for the $\text{P}(\text{VP-St})[\text{CoPc}(\text{SO}_3\text{H})_4]$ in a potentiostatic electrolysis at -0.90 V (Ag/AgCl) in 1 h. The inset represents the relation between the turnover number and the complex concentration for the $\text{P}(\text{VP-St})[\text{CoPc}(\text{SO}_3\text{H})_4]$.

CVs of the CoPc, CoPc(CN)₈, and CoPc(SO₃H)₄ in the P(VP-St) coated on a BPG electrode are shown in Fig. 6a–c, respectively. For the P(VP-St)[CoPc] (Fig. 6a), the first redox couple corresponding to Co(II)Pc(–2)/[Co(I)Pc(–2)][–] is at –0.25 V (Ag/AgCl), and then proton reduction seems to take place after the second reduction of the complex at –0.5 V. For the P(VP-St)[CoPc(CN)₈], the first reduction is at –0.2 V and the second one at –0.45 V (Fig. 6b). Proton reduction seems to take place after the third reduction at –0.55 V. Although the first redox couple of Co(II)Pc(–2)(CN)₈/[Co(I)Pc(–2)(CN)₈][–] is not very clear in the present voltammogram, this redox reaction has been demonstrated unambiguously by a visible absorption spectral change [53,54]. The P(VP-St)[CoPc(SO₃H)₄] exhibits the first reduction around –0.5 V, and the proton reduction would take place after the second reduction at –0.65 V (Fig. 6c), but the reoxidation peaks for the first and second reduction are absent. For the CoPc derivatives, the first reduction is generally considered to occur on the cobalt centers, while the second and third on the macrocyclic ring [51,52].

Redox potentials of CoPc derivatives are dependent on the characteristics of the substituted groups on their macrocyclic Pc ring. Compared with the CoPc, the redox potential of CoPc(CN)₈ is positively shifted due to the eight electron-withdrawing substituents. On the contrary, the redox potential of CoPc(SO₃H)₄ is negatively shifted due to the four electron-donating substituents. An important factor of the catalytic proton reduction is to decide which redox state of the complex catalyzes the proton reduction. According to the CVs, it is most probable that the second reduced complexes are effective for the CoPc and CoPc(SO₃H)₈ and that the third reduced complex for the CoPc(CN)₈.

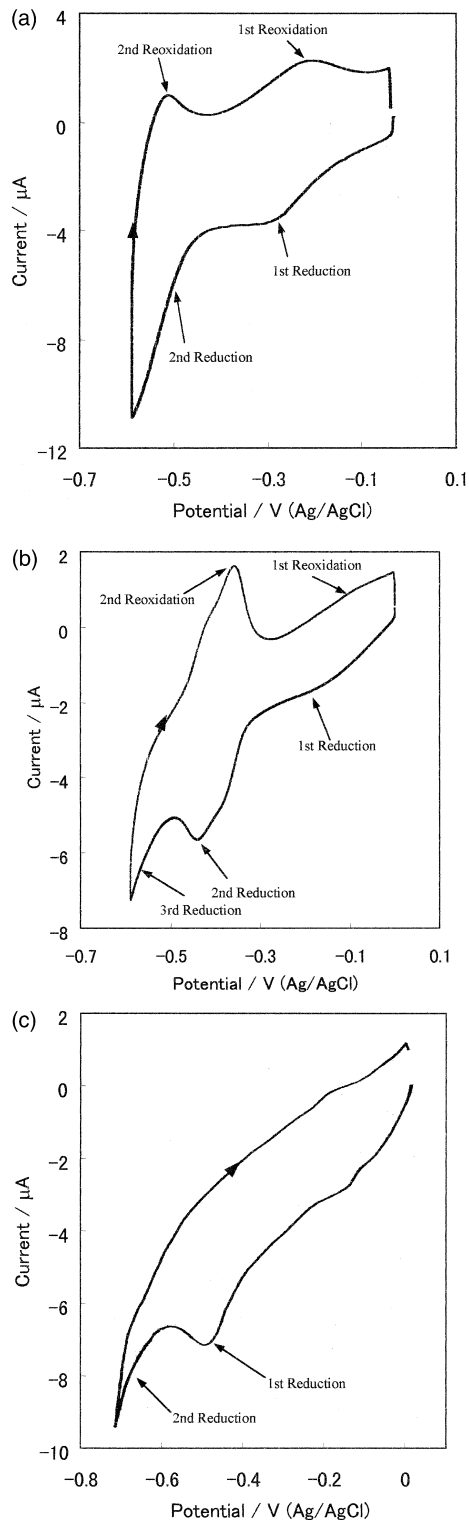
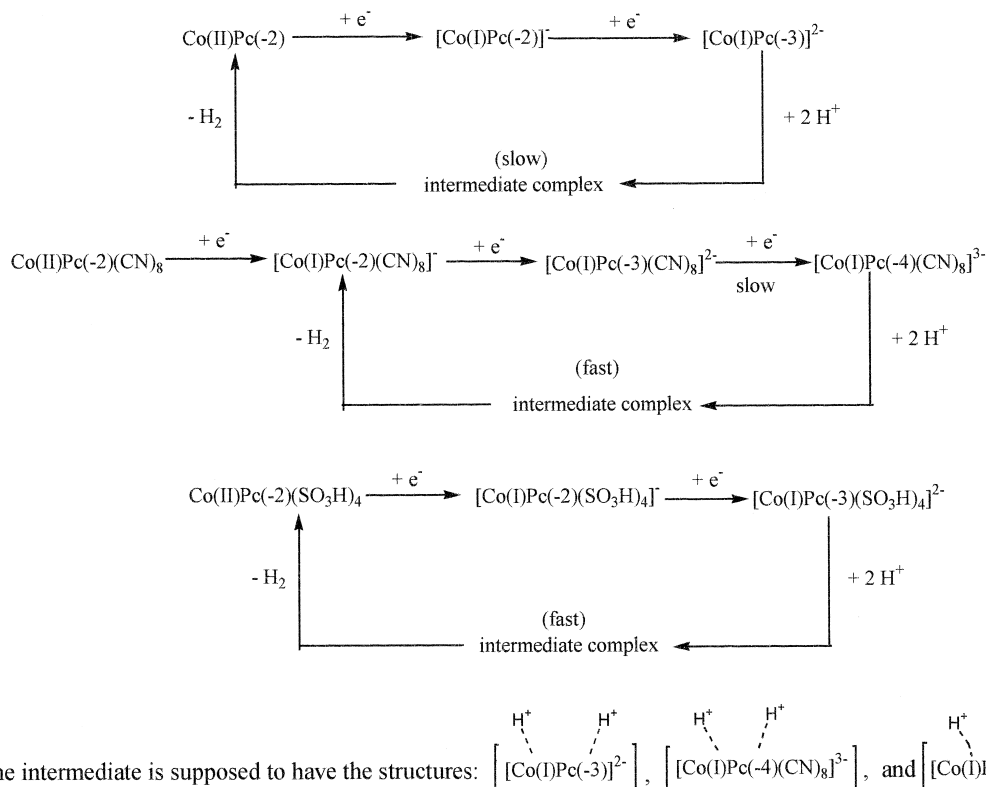


Fig. 6. CVs of the P(VP-St)[CoPc derivatives] coated on the BPG electrode at scan rate 20 mV s⁻¹. (a) P(VP-St)[CoPc]. (b) P(VP-St)[CoPc(CN)₈]. (c) P(VP-St)[CoPc(SO₃H)₄].

There exist at least two steps for hydrogen evolution; one step is reduction of the complex including electron propagation through the polymer matrix, and the second one is the proton reduction by the reduced complex. The appearance of the reoxidation peak for the second reduction of CoPc (Fig. 6a) shows that the rate-determining step is the catalytic proton reduction by the reduced complex. No reoxidation peak for the third reduction of the $\text{CoPc}(\text{CN})_8$, the clear reoxidation waves for the 2nd and 1st reductions indicate that the third reduction is rate-determining. For the $\text{CoPc}(\text{SO}_3\text{H})_8$, both the first and the second reoxidation peaks are absent demonstrating that proton reduction proceeds rapidly. These results are summarized as Scheme 2. As for the monomolecular or bimolecular mechanism for the proton reduction, discussion will be given later.

When adopting the TN value for evaluating the catalytic efficiency, the following order is obtained: $\text{CoPc} > \text{CoPc}(\text{CN})_8 > \text{CoPc}(\text{SO}_3\text{H})_4$. The catalytic efficiency of CoPc is the highest with the TN value of $2 \times 10^5 \text{ h}^{-1}$. From the above discussion, it is concluded that the electron transfer in the matrix can influence the electrocatalytic efficiency for the proton reduction by the complex. The electron transfer is dependent on the interaction of the redox complex with the polymer framework. Our recent research reveals that when the interaction is relatively weak such as $[\text{Co}(\text{III})(-2)]^+ / \text{Co}(\text{II})$ TPP(-2) in the P(VP-St) and Nafion [47] or the methylviologen $\text{MV}^{2+} / \text{MV}^{\cdot+}$ in the Nafion [49], the electron transfer takes place by a diffusion mechanism. While, if the interaction is relatively strong such as $\text{Ru}(\text{bpy})_3^{3+} / \text{Ru}(\text{bpy})_3^{2+}$ in the Nafion, the charge transfer occurs by a



Scheme 2. Electrocatalytic mechanism of proton reduction by the CoPc derivatives incorporated in the P(VP-St) matrix. (a) P(VP-St)[CoPc]. (b) P(VP-St)[CoPc(CN)₈]. (c) P(VP-St)[CoPc(SO₃H)₄].

hopping mechanism [46]. The charge transfer rate by the diffusion mechanism is generally faster than that by the hopping mechanism. Even though the charge propagates through the matrix by the same mechanism, the charge transfer rate is also affected obviously by the interaction of the redox molecule with the polymer framework [49]. Proton reduction was catalyzed by the 2nd reduced CoPc, while catalyzed by the 3rd reduced CoPc(CN)₈. As a more negatively charged center, the electrostatic interaction of the 3rd reduced CoPc(CN)₈ with the cationic P(VP-St) should be stronger than that of the 2nd reduced CoPc. Therefore, the electron transfer rate by reduction of CoPc(CN)₈ is relatively lower, rationalizing that the rate-determining step in the P(VP-St)[CoPc(CN)₈] is third reduction. After ionization, the CoPc(SO₃H)₄ has four negative charges so that the electrostatic interaction with the cationic matrix is the strongest in these three complexes. The migration of the complex through the matrix would be the slowest, so that the reduction would be the rate-determining step.

Electron transfer mechanism by redox molecules in a matrix can be studied by a real concentration change from the visible absorption spectrum under the potential-step. Because of the high solubility in the P(VP-St), CoPc(SO₃H)₄ was chosen as the redox probe for the PSCAS measurement. The P(VP-St)[CoPc] and the P(VP-St)[CoPc(CN)₈] systems were measured by the PSCAS. [Co(II)Pc(-2)(SO₃H)₄] in the P(VP-St) film displayed a maximum absorbance at 630 nm (molar absorption coefficient is $5.0 \times 10^3 \text{ mol}^{-1} \text{ m}^2$) as shown in Fig. 7. The potential step was applied from 0 to -0.50 V (Ag/AgCl) to study its first reduction. The band at 630 nm decreased with the simultaneous increase of the band at 440 nm under the potential step until the band at 440 nm saturates and that at 630 nm disappears completely after 5 min (Fig. 7). Such spectral change is similar to that of the first reduction by the CoPc or CoPc(CN)₈ as studied in the previous reports [54–56].

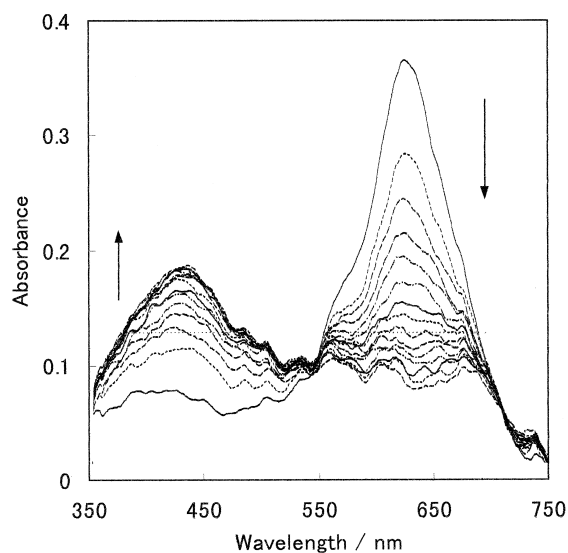


Fig. 7. Absorption spectral change of the 0.07 M P(VP-St)[CoPc(SO₃H)₄] coated on ITO electrode with the time after the potential step from 0 to -0.50 V (Ag/AgCl).

The initial formation rate of [Co(I)Pc(-2)(SO₃H)₄]⁻ (v_{CT}) estimated from the absorbance decrease at 630 nm was of first order with respect to the complex concentration in P(VP-St) matrix as shown in the inset of Fig. 8. The electron transfer for the first reduction of [Co(II)Pc(-2)(SO₃H)₄] is concluded to take place through a diffusion mechanism. A similar phenomenon has been observed for the first reduction of methylviologen (MV²⁺) and CoTPP in the Nafion in which the electron transfer occurs through a diffusion mechanism [47,49]. Since CoPc and CoPc(CN)₈ are incorporated in the polymer matrix mainly by hydrophobic interaction, which is much weaker than the electrostatic interaction of the CoPc(SO₃H)₄ with protonated pyridine groups, the electron transfer of CoPc and CoPc(CN)₈ systems would most probably take place also by a diffusion mechanism.

The fraction of the electroactive complex R_{ct} can be obtained by the absorbance change at 630 nm under the applied potential by Eq. (1) [46–50]

$$R_{\text{ct}} = (A_0 - A_t) / (\epsilon_{\text{II}} - \epsilon_{\text{I}}) cl \quad (1)$$

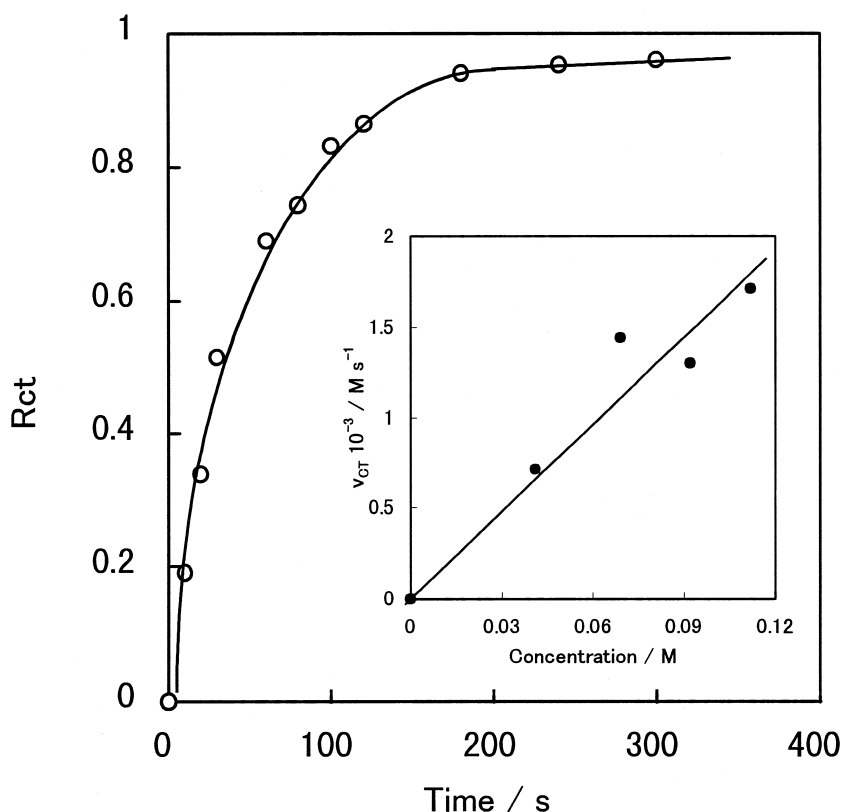


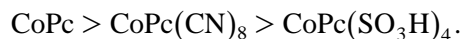
Fig. 8. Correlation between the R_{ct} and the time after the potential step from 0 to -0.50 V (Ag/AgCl) for the electrode with 0.07 M $\text{CoPc}(\text{SO}_3\text{H})_4$ in the P(VP-St). The inset represents plot of the initial formation rate for the first reduction of $\text{Co}(\text{II})\text{Pc}(-2)(\text{SO}_3\text{H})_4$ against the complex concentration.

where A_0 and A_t are the absorbances at 630 nm at the start and after t seconds, ε_{II} and ε_{I} are the molar absorption coefficient at 630 nm of $\text{Co}(\text{II})$ and $\text{Co}(\text{I})$ complex, c is the complex concentration in the matrix, and l is the thickness of the film. The calculated R_{ct} value of the $\text{CoPc}(\text{SO}_3\text{H})_4$ increased with reaction time and approached one after 180 s (Fig. 8), indicating that almost all the complexes are electroactive in the matrix.

Generally, the charge propagation rate through the polymer matrix can be represented by the apparent diffusion coefficient (D_{app}) [39,40]. This data is estimated by the Cottrell's equation, Eq. (2), by the chronoamperometry based on a semi-infinite diffusion process

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

where i is the current density, n is the number of electron involved in the reaction which in this case is 1, F is the Faraday's constant. In the presents systems, the linear relation between i and $t^{-1/2}$ indicates that the charge propagation in the matrix fits the Cottrell's equation. From the slope, D_{app} values were estimated and listed in Table 1. It should be noticed that the D_{app} values are almost independent of the complex concentration in the matrix for the CoPc and $\text{CoPc}(\text{CN})_8$, while they decreased slightly with increasing the complex concentration for the $\text{CoPc}(\text{SO}_3\text{H})_4$. D_{app} of the three complexes decreases in the following order:



This order is in accordance with that of the catalytic efficiency shown by TN values. D_{app}

Table 1

The apparent diffusion coefficient (D_{app}) of the P(VP-St)[CoPc], P(VP-St)[CoPc(CN)₈] and P(VP-St)[CoPc(SO₃H)₄] in a 0.1 M NaH₂PO₄/H₃PO₄ buffer aqueous solution at pH 1.0

	Concentration (mM)	$D_{\text{app}} \times 10^9$ (cm ² s ⁻¹)
CoPc ^a	2.5	23
	5.0	17
	7.5	20
	10	24
CoPc(CN) ₈ ^b	2.5	7.2
	5.0	6.3
	7.5	6.8
	10	6.0
CoPc(SO ₃ H) ₄ ^c	40	0.48
	70	0.43
	90	0.36
	110	0.22

^a Potential step from 0 to -0.4 V (vs. Ag/AgCl).

^b Potential step from 0 to -0.5 V (vs. Ag/AgCl).

^c Potential step from 0 to -0.55 V (vs. Ag/AgCl).

of the CoPc(SO₃H)₄ is one hundred times less than that of the CoPc. This fact demonstrates that the electrocatalytic proton reduction is dominated by the electron transfer of the redox complex within the matrix.

The catalytic proton reduction to hydrogen molecule by the CoPc derivatives can take place either through a monomolecular or a bimolecular mechanism. It should be noted that the turnover numbers (TN) are almost independent of the complex concentration in the matrix (Figs. 3–5) showing that the rate-determining step is a monomolecular process. There are two possible explanations: One possibility is that the rate-determining step of the reaction is the electron transfer through the matrix by a diffusion mechanism. In this case, the proton reduction may be catalyzed by either a monomolecular or a bimolecular mechanism. The other possibility is that the rate-determining step is the catalytic proton reduction which takes place by a monomolecular mechanism. Because the electron transfer has been regarded to be the rate-determining step for the P(VP-St)[CoPc(CN)₈] and P(VP-St)[CoPc(SO₃H)₄] systems as discussed above, it is difficult to decide whether the catalytic proton reduction take place by a

monomolecular or a bimolecular mechanism. The results of CVs demonstrates that the effective catalyst species for proton reduction are the second reduced complexes of the CoPc and the CoPc(SO₃H)₄, and the third reduced complex of CoPc(CN)₈. Therefore, the monomolecular mechanism seems to be more reasonable. Model catalytic schemes for proton reduction by the monomolecular mechanism are shown in Scheme 2. An intermediate consisting of one reduced complex and two protons is suggested to exist. A hydrogen molecule is evolved when the intermediate decomposes and leaves a neutral molecule CoPc and CoPc(SO₃H)₄ or a first reduced molecule [Co(I)Pc(-2)(CN)₈]⁻.

Acknowledgements

The authors acknowledge the Grant-in-Aid for the Scientific Research Priority Area of 'New Polymers and Their Nano-Organized System' (No. 277/10126207) from Ministry of Education, Science, Sports and Culture.

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