Electrochemistry of Ruthenium Purple Confined in a Polymer Matrix: Voltammetry, Electrocatalysis for Hydrogen Evolution, and Electron-Transport Characteristics

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The synthesis of iron(III) ruthenocyanide (Ruthenium Purple, RP) in a Nafion (Nf) membrane was carried out. The visible-light absorption spectrum of the resulting RP exhibited an inter-valent charge-transfer band around 550–570 nm similar to that of neat RP, evidently showing that RP is formed in a polymer matrix. The voltammetric characteristics of the RP confined in the Nf matrix (Nf[RP]) were investigated compared with the neat RP. When Nf[RP] was used as an electrocatalyst to reduce H^+, efficient H_2 formation was found to originate from its molecular catalysis. In order to investigate the dominant factor that affects the overall kinetics in H^+ reduction catalysis, the dependencies of both the catalytic activity (represented by the turnover number (TN) of a RP unit) and the diffusion coefficient of electron (D_{app}) were studied as a function of the RP concentration in the matrix. The D_{app} value decreased with increasing the concentration. The dependence of TN on the concentration was similar to that of D_{app}, indicating that the overall kinetics is dominated by electron transport by RP.

Water photolysis, called artificial photosynthesis, has been attracting attention as one of the most promising candidates to create a renewable energy resource in the near future.[1–3] However, such an artificial photosynthetic system has not been achieved. Because water photolysis involves a series of redox reactions composed of a multi-electron transfer process of water, the development of active and efficient catalysts for forming H_2 and O_2 is one of the most important approaches towards this goal.[4,5] As for the reduction catalyst to form H_2, colloidal Pt has been recognized to be the most active catalyst.[6–10] However, the activity of a colloidal Pt catalyst often changes with the preparation methods because its activity strongly depends on the particle size and effective area. In order to stabilize and improve the catalytic activity, the preparation of Pt colloids protected by an aqueous polymer or detergent solution as well as by a polymer solid has been attempted.[11–13] However, their activity and stability are not enough to be used for a water photolysis system; moreover, because Pt is a rare and precious material, it is highly desirable to design and develop a new catalyst instead of Pt.

Based on these points of view, a few examples of molecular catalysts (e.g., cofacial metallo-porphyrin, and noble metal complex involving electropolymerized group, etc.) have been reported, especially by means of electrochemistry.[14–17] However, in these previous studies, the catalysis for H^+ reduction could take place only by applying much negative potentials; moreover, the activity was not high (turnover number, $\ll 100$ h^{-1}). We found molecule-based catalysts for H^+ reduction with much higher activity than that of a conventional Pt catalyst using molecular aggregates composed of a metal complex and a polymer membrane.[18,19] Molecular aggregates can often exhibit unique and active catalysis that can not be achieved by a homogeneous solution or by a neat catalyst[20] owing to the condensed phase bringing the reaction components into close proximity, as seen in biological systems. Therefore, employing of such a system is expected to open up a breakthrough for establishing a photosynthetic model.

Prussian Blue (PB) and its analogues have been extensively studied in view of basic science and applications to electrochromic devices,[21,22] biological sensors,[23] photoelectrochemical devices,[24,25] and electrocatalysts.[26–30] Such polynuclear cyanide complexes, where redox sites are close to each other within the cubic unit-cell structure, are also expected to be promising materials for constructing an efficient catalyst site. We have recently reported that iron(III) ruthenocyanide (Ruthenium Purple (RP); repeating unit cell, $Fe_4^{III}[Ru^{II}(CN)_6]_3$ (insoluble form) or $M^+Fe^{III}[Ru^{II}(CN)_6]^-$ (soluble form, M^+ represents a counter cation)) shows molecular catalysis dependent on the kind of electrolyte employed (Na^+, or K^+) when using the complex as a catalyst for evolving H_2.[31] Catalysis by neat RP successfully took place only in a Na^+ electrolyte solution. Since a reduced species capable of H^+ reduction catalysis is anionic, the catalysis can be associated with a charge compensation process influenced by the size of the cation employed. Comparing the size of the cation with the lattice channel (size of hydrated cation, Na^+ (0.36 nm) $>$ lattice cannel (0.35 nms) [22,32] $> K^+$ (0.24 nm) [33,34]), it appears that charge compensation during a redox reaction of the RP is less facile in Na^+ than in K^+. Therefore, it was concluded that, in the catalytically active redox state, the charge compensation takes place not only by Na^+ (a partially dehydrated ion) but also by H^+, by which the catalysis for H_2 evolution by neat RP is induced (i.e., a kinetically competitive access of both Na^+ and H^+ to the catalyst site needs to be allowed to bring about H_2 evolution; due to a facile transport of K^+, in its electrolyte solution H^+ cannot participate in compensating for the charge in any redox reaction of RP, so that no catalytic H_2 evolution is observed). When employing a polymer matrix to support RP, the redox reaction of the complex may be influenced kinetically, not only by the kinds of cation, but also by the cation transport process through the matrix. In that case the catalysis could be expected to be different from the neat system, even though a similar electrolyte solution is employed. In the present work, the preparation of RP in a Nafion membrane (Nf[RP]) was carried out, and its application as an electrocatalyst to reduce H^+ into H_2 was tried. The spectroscopic, voltammetric and electrocatalytic characteristics of the Nf[RP] will at first be mentioned compared with that of neat RP film. In addition, the factors that affect the overall kinetics in H_2 evolution will also be discussed in combination with electron-transfer analysis.

Experimental

A 5 wt% Nafion alcoholic solution and potassium hexacyanoruthenate ($K_4Ru(CN)_6$) were purchased from Aldrich Chemical Co., Ltd., and a glassy carbon (GC) (RA5-100) from Tokai Carbon Co., Ltd. The purest grade reagents were used without further purification.

Electrode modification to RP in a Nafion (Nf) film coated on a GC electrode was carried out as follows. A methanol solution containing 2.5 wt% Nf was first prepared, and a 6 μL portion of this solution was cast onto a GC electrode (effective area, ~0.2 cm^2), followed by solvent evaporation under air. The thickness of the Nf was estimated to be ~3 μm by considering the density of the Nf (2 $g\ cm^{-3}$).[35] The Nf-coated GC was dipped into deionized water for 30 min to improve its cation-exchange ability. The introduction of Fe^{3+} ion was carried out by casting a known amount of an acidic $Fe_2(SO_3)_3$ solution (1 mM) onto the Nf-coated GC (this operation was run under shaking), whereby water evaporation was simultaneously achieved under air. After washing the electrode with deionized water, the GC electrode coated with a Nf membrane containing Fe^{3+} was dipped into an acidic solution of $K_4Ru(CN)_6$ (1 mM) to form a Fe^{III}-Ru^{II} complex (under shaking for 1 day). The concentration of Fe^{III}-Ru^{II} complex in the matrix was controlled by the adsorbed amount of Fe^{3+}. In order to accomplish a complete complexation of the Fe^{III}-Ru^{II}, the modified electrode was polarized by applying a potential of +0.4 V (vs Ag/AgCl, in saturated KCl electrolyte solution (denoted as Ag/AgCl)) (passed charge, 4 mC) in a pH 1.5 HCl–KCl aqueous solution ($[K^+] = 0.01\ mol\ dm^{-3}$). The modified electrode was used for an electrochemical study after being dipped in deionized water for 1 day. The amount of the RP formed was estimated by measuring the coulometric curve during a potential scan from +0.6 V to −0.2 V (vs Ag/AgCl). A neat RP-coated GC electrode was also prepared as a reference.[36,37] An indium–tin oxide (ITO) electrode was also used instead of GC.

An electrochemical cell was equipped with a RP modified working electrode, a spiral Pt counter and a silver/silver chloride (Ag/AgCl) reference electrode soaked in a pH 1.5 HCl–KCl ($[K^+] = 0.01\ mol\ dm^{-3}$) aqueous solution. An electrochemical study was carried out using a potentiostat/galvanostat (HOKUTO DENKO, HA-301) equipped with a function generator (HOKUTO DENKO, HB-104), a coulometer (HOKUTO DENKO, HF-201) and a recorder (GRAPHTEC, WX4000). A typical potentiostatic electrolysis for H^+ reduction was run while stirring for 1 h under an argon atmosphere.

The visible-light absorption spectrum of the RP on an ITO electrode was measured using a Hitachi U-2010 spectrophotometer. The H_2 produced in the electrolysis was analyzed by a gas chromatograph (Shimadzu, GC-8A) with a molecular sieve 5Å-column and Ar carrier gas. The faradaic efficiency (%) for H_2 formation in the electrolysis always exceeded 80%.

Results and Discussion

Spectral Characteristics of RP Prepared in a Nf Membrane. Firstly, the visible-light absorption spectrum of RP prepared in a Nf membrane was measured in a pH 1.5 HCl aqueous solution containing KCl ($[K^+] = 0.01\ mol\ dm^{-3}$). The typical results are shown in Fig. 1 compared with that of neat RP. An absorption band due to an inter-valent charge transfer (IVCT) from Ru^{II} to Fe^{III} was observed at around 550–570 nm for both the Nf[RP] and the neat RP. Several examples of the spectrum for the neat RP were previously reported,[22,36,37] where the absorption maximum of their spectra was similar to the present one. However, it should be noted that spectrum (a) is somewhat broader than spectrum (b). As for a RP confined in a zeolite, a markedly broadened IVCT band has been reported, indicating an amorphous structure.[23] The spectrum (a) for the Nf[RP] probably suggests that a RP composed of a crystalline and an amorphous structure is synthesized in the polymer matrix.

Voltammetric Characteristics of RP Prepared in Nf Membrane in Comparison with the Neat Film. Figure 2 shows typical cyclic voltammograms (CV) at a GC electrode coated with a Nf membrane incorporating RP (denoted as GC/Nf[RP]) soaked in a pH 1.5 HCl–KCl aqueous solution compared with neat RP (denoted as GC/RP). In both systems, a redox couple of $Fe^{III/II}$ in RP was observed at around +0.2 V (vs

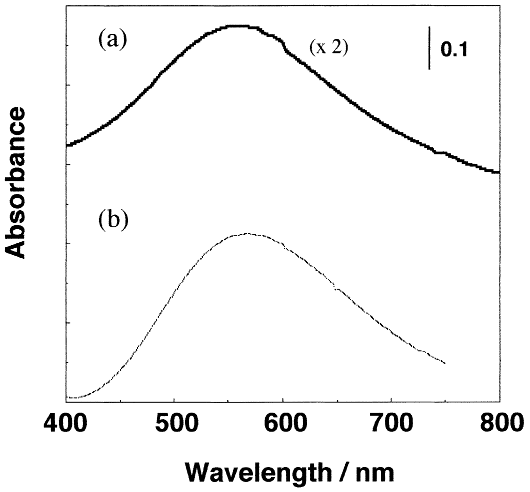

Fig. 1. Typical visible light absorption spectra of both Nf[RP] (a) and the neat RP (b) coated on ITO electrode. The spectral measurement was carried out in a pH 1.5 HCl–KCl solution ($[K^+] = 0.01\ mol\ dm^{-3}$).

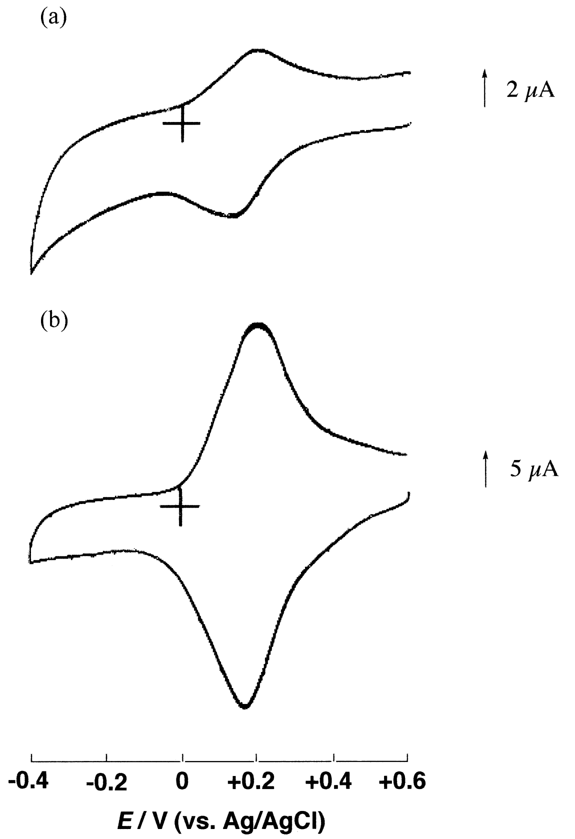

Fig. 2. Typical CVs at both GC/Nf[RP] (a) and GC/RP (b) in a pH 1.5 HCl–KCl solution ($[K^+] = 0.01$ mol dm^{-3}). scan rate: 20 mV s^{-1}, RP amounts: (a), 1.5×10^{-10} unit cell mol; (b), 1.2×10^{-9} unit cell mol.

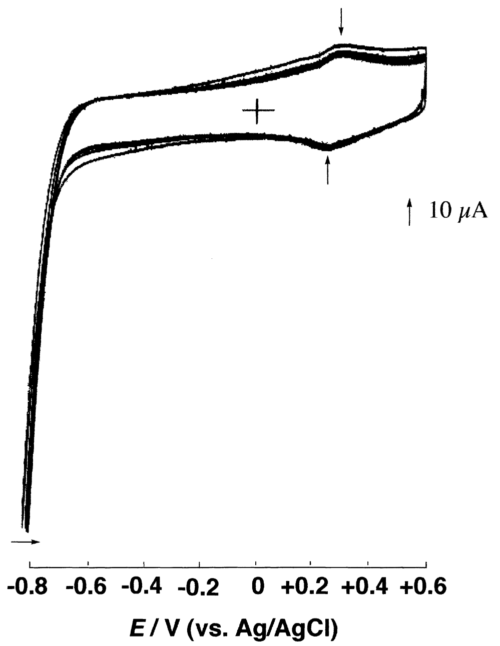

Fig. 3. CV at GC/Nf[RP] on more reductive scan in a pH 1.5 HCl–KCl solution ($[K^+] = 0.01$ mol dm^{-3}). scan rate, 20 mV s^{-1}; RP amounts, 6.3×10^{-10} unit cell mol.

Table 1. Typical Results of Potentiostatic Electrolysis at −0.90 V (vs Ag/AgCl)[a]

System	TN/h^{-1}	Reaction time/h
GC/Nf[RP][b]	9.0×10^5 [d]	1
GC/Nf[RP][c]	2.3×10^4 [d]	1
Pt plate (bare)	3.4×10^4	0.5
GC/RP	~0	1

a) The electrolysis was carried out in a pH ~1.5 HCl solution containing 0.01 mol dm^{-3} K^+. b) RP concentration in Nf membrane, 7.9×10^{-5} mol dm^{-3}. The RP concentration was represented by mole number of unit cells per membrane volume (~6.6×10^{-8} dm^{-3}). c) RP concentration in Nf membrane, 3.4×10^{-3} mol dm^{-3}. d) TN per an unit cell of both soluble and insoluble structures was estimated by subtracting the amount of H_2 at GC/Nf.

Ag/AgCl). However, the peak separation between the oxidation and reduction peaks was larger for the GC/Nf[RP], showing a slower kinetics of the electrode reaction than for the neat RP. Although the redox reaction involves an anionic structure (denoted as RP^-: $[Fe^{II}Ru^{II}(CN)_6]^{4-}$ for soluble form; $[Fe_4^{II}\{Ru^{II}(CN)_6\}_3]^{4-}$ for insoluble form), there is no occasion for change compensation by only H^+, since it has been reported that the redox reaction is blocked by H^+.[38] Therefore, in Fig. 2, K^+ essentially plays a roll to compensate the charges. The difference between GC/Nf[RP] and GC/RP concerning the voltammetric aspect is attributed to employing a polymer matrix in the former system. Different from the GC/RP system, the redox reaction in the GC/Nf[RP] system needs to involve a long-range transport of K^+ through the thick Nf membrane (~3 μm) in order to compensate for the charge (cf., the thickness of the neat film was estimated as ~0.04 μm considering both the coated amounts (1.2×10^{-9} unit cell mol) and the lattice constant of the RP (1.04 nm[22,32])). Figure 2(a) might show a kinetic irreversibility on the redox reaction, due to a slow transport of K^+ through the Nf. The details for the electron transport characteristics of the Nf[RP] are discussed later.

Electrocatalysis by Nf[RP] for Hydrogen Evolution. CV at GC/Nf[RP] was measured, including more negative potential regions, as shown in Fig. 3. The growth of cathodic currents due to the H^+ reduction was observed below ca. −0.6 V (the H_2 formation data is shown later in Table 1.), indicating that the RP acts as a catalyst for H^+ reduction. The steady appearance of a redox peak for the $Fe^{3+/2+}$ couple in a repeated CV scan could support that the charge compensation concerned in the redox reaction takes place by K^+. In a reference study, a remarkable growth of currents was not observed at a Nf-coated GC electrode. The characteristics of the molecular catalysis are discussed later.

Potentiostatic electrolysis at GC/Nf[RP] was carried out by applying a potential of −0.90 V (vs Ag/AgCl); the results are summarized in Table 1. This shows that an active electrocatalysis for H^+ reduction to form H_2 takes place at GC/Nf[RP], and that the turnover numbers (TN) of the RP repeating unit cell are extremely high. Furthermore, comparing the activity of Nf[RP] with a polycrystalline Pt plate, it was noteworthy that the TN of the RP is approximately comparable to that of Pt (assuming the closest-packed structure of Pt, the TN of a Pt atom was estimated by considering the number of Pt atoms exposed on the surface (6.5×10^{14} units ($\sim 1.1 \times 10^{-9}$ mol) per effective area (1 cm^2)). However, catalysis by neat RP was found not to take place for evolving H_2 when employing a similar electrolyte solution to the Nf[RP] system. This evidently indicates that the RP can exhibit catalysis by embedding it into the polymer matrix, especially in the presence of K^+.

Molecular catalysis for H^+ reduction by Nf[RP] is summarized as follows. The one-electron reduced RP (RP^-) is potentially unable to reduce H^+, since the formal potential of the $Fe^{III/II}$ ($\sim +0.2$ V vs Ag/AgCl) is much more positive than that of H^+/H_2 (~ -0.3 V vs Ag/AgCl). Therefore, it is essential that the complex is further reduced to a higher reduced state (postulated state, RP^{2-}) in order to catalyze H^+ reduction at the molecular level. In a Na^+ solution, an efficient molecular catalysis for H^+ reduction by neat RP was found to originate from the soluble structure (a typical activity (TN), 5.1×10^4 h^{-1}),[31] where two adjacent cyanide ions, located on both a lattice face and an inner lattice in the soluble species, were responsible for the catalysis. As has been indicated by the present authors,[39] a molecular catalysis for H^+ reduction should take place by the coordination of H^+ onto a catalyst prior to reduction. However, since all of the metal ions (Fe and Ru) in the soluble form are coordination-saturated, there would be no possibility that H^+ coordinates to the Fe or Ru site. The cyanide ion in the polynuclear complex could work as a H^+ coordination site, as was suggested in a previous report.[40] Therefore, in the most possible explanation for the catalysis, the cyanide ion can be expected to also function as a catalyst site by coordinating H^+. A similar catalysis to the neat RP is also suggested in the present Nf[RP] system.

It is currently recognized that cyanometallate films, such as RP, are composed of insoluble and soluble forms.[33,34] As for the electrode reaction of a composite RP, we have found that the redox reaction for $Fe^{III/II}$ in insoluble RP (the neat species) is kinetically irreversible when employing an electrolyte solution of Na^+.[31] This finding concerning the kinetic aspect was ascribed to the clear appearance of split redox peaks originating from both insoluble and soluble forms, where the insoluble form was kinetically distinct from the soluble one when measuring CVs with scan rates. However, in spite of a composite formation of RP, split peaks cannot be observed in the presence of K^+ (cf., the neat RP used in Fig. 2(b) was prepared by the same procedure as Ref. 31). As for the neat film, the voltammetric and electrocatalytic characteristics dependent on the kinds of electrolyte employed are essentially attributed to the intrinsic property of the alkaline metal ion (Na^+ or K^+). Comparing Na^+ with K^+, the hydration energy is larger in the former,[41] which results in the larger size of the hydrated Na^+ ion (vide supra). This is the reason that the participation of Na^+ during a redox reaction of RP is less facile, since a partially dehydrated ion is responsible for the charge compensation on cyanometallate.[33,34] In the case of K^+, the cation can facilely be participated in compensating the charge, even though its partial dehydration does not take place (vide supra). It is most possible that because only the cation (K^+) is involved in any redox state of the neat RP, the electrocatalysis for H^+ reduction could be found not to take place. However, as for the present Nf[RP] system, the electrode reaction involves a slow kinetic process, most probably due to a less-facile transport of K^+ thorough the polymer matrix; moreover, an electrocatalytic H_2 evolution evidently takes place even in the presence of K^+. The electrocatalysis by the Nf[RP] may be interpreted based on the same considerations as the neat system in the Na^+ solution (see introduction); in the Nf[RP] system, not only K^+ but also H^+, would be involved in the catalytically active redox state, which consequently results in electrocatalytic H_2 formation. It could be concluded that the RP can show electrocatalysis for H^+ reduction when the process involving charge compensation by alkali metal cation is slow.

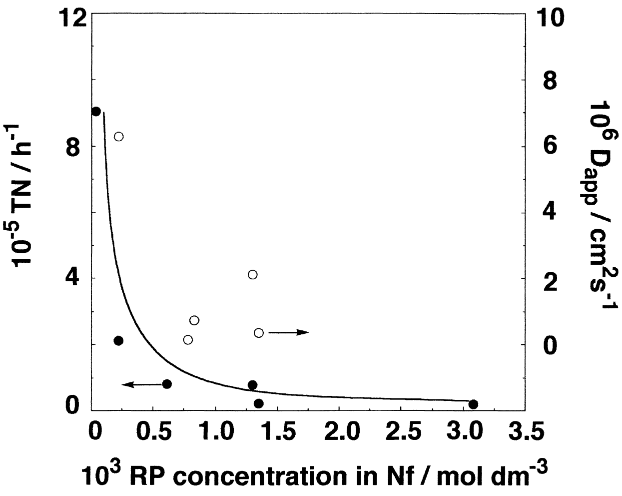

Fig. 4. Coated amount dependence of TN (●) and D_{app} (○) in a pH 1.5 HCl–KCl solution ($[K^+] = 0.01$ mol dm^{-3}). The RP concentration in Nf matrix was represented by the mole number of the RP unit cell per a volume of Nf membrane (6.6×10^{-8} dm^3). The chronoamperometry to obtain the j–$t^{-1/2}$ plot was carried out by stepping the potential from $+0.6$ V to -0.2 V. The potentiostatic electrolysis for H_2 formation was carried out at -0.90 V, and turnover number (TN) of a RP unit cell for the electrocatalytic H_2 formation was calculated by subtracting the amount of H_2 produced at a GC/Nf (blank).

Dependence of the Catalytic Activity for H_2 Evolution with Respect to the RP Amount in a Polymer Matrix, and the Electron Transport Features of Nf[RP]. In order to investigate the electrocatalysis characteristics, the potentiostatic electrolyses for H_2 formation were studied with respect to the RP amount in the Nf matrix; the results are shown in Fig. 4. It was found that the TN of a RP unit cell for H_2 formation remarkably decreased with the concentration, showing that the catalysis ability of a RP for H_2 formation is lowered by increasing the RP amount in the matrix.

Because the overall kinetics is often affected by electron propagation through the catalyst, a heterogeneous electrocatalysis by a functional molecule should be discussed in combination with its electron-transfer process. Therefore, potential-step chronoamperometry was carried out to analyze the electron-transfer process at GC/Nf[RP] according to Cottrell's equation (Eq. 1) based on a semi-infinite diffusion process,[42,43]

$$j = nFc(D_{app})^{1/2}/(\pi t)^{1/2}, \qquad (1)$$

where D_{app} (cm^2 s^{-1}) is the apparent diffusion coefficient of the electron, j (A cm^{-2}) is the current density, n is the number of electrons concerned in the process (4 per the RP unit cell) and F is Faraday's constant (9.65×10^4 C mol^{-1}). The concentration (c) was represented by the mole numbers of the RP unit cell per a volume of the Nf membrane (6.6×10^{-8} dm^{-3}). The electron propagation was studied by potential step from $+0.6$ V to -0.2 V. The relationship between j and $t^{-1/2}$ was linear and applicable to Cottrell's equation. From the slope, D_{app} was estimated as a function of the RP concentration (Fig. 4). The D_{app} of the electron propagation decreased with increasing the RP concentration. The D_{app} value is usually 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_{et}; this includes a term of concentration as a function).[44–46] If the electron transport by the RP takes place by a hopping mechanism, the D_{app} value should increase with the concentration. However, this is not the case; the present electron transfer must occur by physical diffusion of the redox center (RP). The preparation of PB in a Nf matrix has been reported,[47] where the iron-distribution profile across the membrane was studied by means of electron-probe microanalysis. The PB was mainly formed at only the solution/membrane interface (similar to the preparation concerning the present RP, the Fe^{2+} ion was at first adsorbed into the membrane and, subsequently, the Fe^{2+}-adsorbed Nf membrane was soaked into a $Fe(CN)_6{}^{3-}$ solution for forming the PB). Based on this reported knowledge, it is most probable that the RP would also be formed near to the solution/membrane interface, rather than at the membrane/electrode interface. This means that the RP prepared in the Nf matrix needs to move in the membrane for transferring the electrons by a physical diffusion mechanism. This electron-transport characteristic may also be supported by the visible spectrum of the Nf[RP] indicating the presence of an amorphous structure. We have experienced some examples concerning the downward dependence of D_{app} on the concentration in the electron reduction process.[18,19,39,48] The reason why the D_{app} value decreases with increasing the RP concentration could be ascribed to the effect that the diffusion of RP is prohibited by increasing the concentration. A further reduction of $[Fe^{II}[Ru^{II}(CN)_6]]^-$ (or $[Fe_4{}^{II}\{Ru^{II}(CN)_6\}_3)^{4-}$) could not be studied because electrocatalytic H^+ reduction takes place upon forming catalytically active species. However, since the RP exhibits molecular catalysis, probably without changing its fundamental structure, the electron-transfer mechanism could be similar to the reduction of Fe^{III} to Fe^{II}. Since the dependence of TN on the RP amounts is similar to D_{app}, the present catalysis would be dominated by the electron-transfer process.

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