

Letter

Prussian White as a highly active molecular catalyst for proton reduction

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Abstract

Electrocatalytic H⁺ reduction was found with the polynuclear iron-cyanide complex called Prussian White (PW, K₄Fe₄[Fe^{II}(CN)₆]₃) coated on a Pt electrode. The PW-coated Pt produced much larger amounts of H₂ than a bare electrode even at the theoretical potential of H⁺/H₂. Its electrocatalytic activity exceeded the conventional Pt catalyst. © 1997 Elsevier Science B.V.

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1. Introduction

Proton reduction to produce H₂ is attracting attention in the fields of both basic science and researches in constructing new energy conversion systems. Particularly in the latter case, proton reduction is important in order to construct an artificial photosynthetic system capable of producing fuels from water and solar energy. Such a system should be composed of a molecule-based photoexcitation center and active catalyst sites (reduction and oxidation). In this regard, reduction and oxidation catalysts have been investigated [1–8]. As for the oxidation catalyst, we have found that trinuclear Ru complex called Ru-red shows high activity as a molecule-based catalyst [2]. As a catalyst for

H⁺ reduction to produce H₂, it has been reported that metal colloids or particles [4,5] such as Pt work as efficient catalysts. However, such metal catalysts usually need overpotential for H⁺ reduction. Hydrogenase [3] also possesses a catalytic activity for H⁺ reduction, but it is unstable against dioxygen. In these catalyst systems, reaction conditions are restricted so that they are not suited to apply to a molecule-based artificial photosynthetic system. As for H⁺ reduction catalysts, there have so far only been few molecular catalysts to produce H₂. Iron tetraphenylporphine (FeTPP) [6] worked as a molecular catalyst in nonaqueous solution for H⁺ reduction, but it was not used in water, and needs Hg electrode and much negative applied potentials. It is of importance to establish an active molecule-based catalyst for H⁺ reduction working in water and with lower overpotentials. We have now found that Prussian White (PW),

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which is a high molecular weight polynuclear iron complex with the repeating unit, $K_4Fe^{II}[Fe^{II}(CN)_6]_3$, efficiently catalyzes electrochemical H^+ reduction to produce H_2 as a molecular catalyst in water at almost theoretical potentials.

2. Experimental

The same volumes of a 20 mM potassium hexacyanoferrate(III) and a 20 mM iron(III) chloride aqueous solution were mixed to obtain a Fe^{III} – Fe^{III} complex (called Berlin Brown, BB; $Fe^{III}[Fe^{III}(CN)_6]$) solution [9]. The Fe^{III} – Fe^{II} complex called Prussian Blue (PB), which is the oxidized species of the PW, was electrodeposited onto a Pt plate electrode or a basal-plane pyrolytic graphite (BPG) electrode at +0.5 V (vs. Ag/AgCl) from the BB solution. The PB-coated Pt electrode was rinsed with water. The composition of the coated water-insoluble PB was reported by Itaya et al. [9] as $Fe_4^{III}[Fe^{II}(CN)_6]_3$. An electrochemical cell was equipped with the PB-coated working (effective area: ca. 1 cm²), a spiral Pt wire counter, and a silver–silver chloride (Ag/AgCl) reference electrode (a saturated KCl aqueous solution was employed as inner liquid). The potentiostatic electrolysis was carried out in a pH 1.35 aqueous solution containing 0.05 M potassium chloride electrolyte (KCl) for 1 h. The amount of H_2 produced was analyzed by a gas chromatograph (Shimadzu, GC-4CPT) with a molecular sieve 5Å column and argon carrier gas.

3. Results

Fig. 1a shows a typical cyclic voltammogram (CV) of the PB-coated Pt electrode in a pH 1.35 electrolyte solution. The electrochemistry of PB has been well characterized by various papers [9–11], and the PB-coated Pt showed reversible waves due to BB/PB and PB/PW couples at the potentials of $E_m = +0.86$ V (vs. Ag/AgCl) and +0.19 V, respectively (E_m shows the mid-

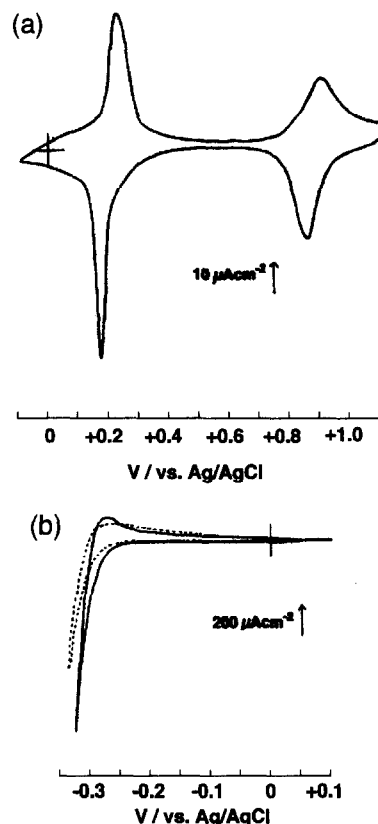


Fig. 1. Typical CV (scan rate, 20 mV s⁻¹) of the PB-coated Pt in a pH 1.35 aqueous solution containing 0.05 M KCl electrolyte (a). Results of the CV measurement (scan rate, 1 mV s⁻¹) in more negative potential regions for both the Pt/PW (solid line) and a bare Pt (dashed line) in the same electrolyte solution (b).

point potential of the anodic and the cathodic peaks in its cyclic voltammogram). The CVs measured on a more reductive scan are shown in Fig. 1b. Under these negative potentials the coated PB is present as a form of PW. Cathodic current increases from more positive potentials at the PW-coated Pt system than a bare Pt, and the current is much larger amount at the former electrode than at the latter one. This cathodic current is ascribed to H^+ reduction to produce H_2 (vide infra).

Fig. 2 shows the result of the potentiostatic electrolyses (1 h) at the PW-coated Pt electrode (denoted as Pt/PW) as well as at a bare Pt. The catalytic activity of the Pt/PW was remarkably higher than that of a bare Pt. The Pt/PW system could catalyze H^+ reduction even at the

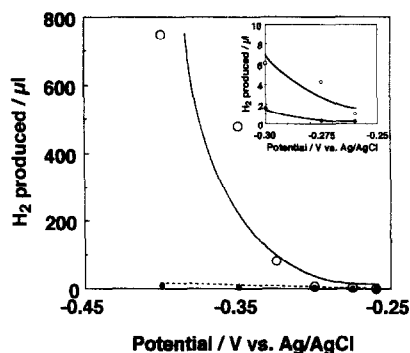


Fig. 2. H_2 production by the potentiostatic electrolyses (1 h) at a Pt/PW system (○) and a bare Pt system (●) in a pH 1.35 aqueous solution containing 0.05 M KCl electrolyte.

theoretical potential of H^+/H_2 (-0.274 V vs. Ag/AgCl in pH 1.35) without overpotential. The amount of the H_2 produced at the Pt/PW system was about 12 times as high as that of a bare Pt at -0.274 V. The amount of PW coated on the Pt electrode in Fig. 2 was estimated as 1.8×10^{-8} mol cm^{-2} from the CV, which corresponds to 0.12 μm thickness of the PW layer (the lattice constant of the PW is 1.02 nm as reported previously [9]). The turnover number (TN) of the PW unit cell for H_2 production was 1.7×10^3 h^{-1} at -0.4 V (Faradaic efficiency to produce H_2 exceeded 80%). The coated amount of the PW decreased only less than 10% after the electrolysis (1 h), so that the catalyst is stable during the electrolysis.

The catalytic activity of PW was investigated in relevant to its coated amount, and the results of the potentiostatic electrolyses are shown in Fig. 3. The amount of the H_2 produced increased linearly with the amount of the coated PW, showing that not only the PW surface but also the bulk PW is effective for H^+ reduction.

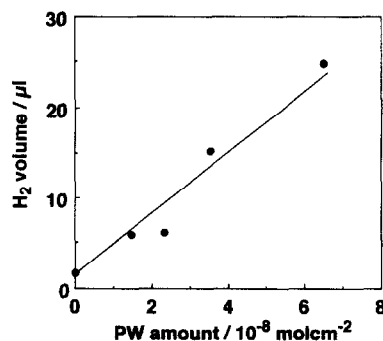


Fig. 3. Relationship between the amount of the H_2 produced and the coated amount of PW on a Pt electrode in the potentiostatic electrolyses (1 h) at -0.30 V (vs. Ag/AgCl) in a pH 1.35 aqueous solution containing 0.05 M KCl electrolyte.

The results show that the PW works as a molecular catalyst for H^+ reduction.

In a separated experiment, the steady current density (I) during the electrolysis was measured in various pH conditions (from 1.35 to 4.4). The plot of $\log I$ vs. pH showed the linear relationship, and the larger slope (1.5 times) was obtained in the Pt/PW system than in a bare Pt. This behaviour indicates that the catalysis by the Pt/PW system is unambiguously different from a bare Pt system, supporting that the PW works as a molecular catalyst.

The catalytic activity of PW was also much higher than that of Pt black deposited electrochemically onto a Pt electrode from PtCl_6^{4-} aqueous solution (denoted as Pt/Pt black). The TN of a Fe atom in the PW to produce H_2 is about 4 times higher than that of a Pt atom of the Pt black (e.g., the TN of Fe atom was 2.4×10^2 h^{-1} in the Pt/PW system and the TN of Pt atom 64 h^{-1} in the Pt/Pt black system, at -0.40 V vs. Ag/AgCl). The same electrolysis study was carried out by using a basal-plane

Table 1

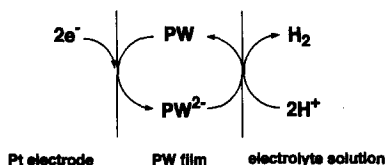
Electrocatalytic activity of Prussian White coated on a BPG electrode in comparison with a bare BPG electrode at -0.80 V vs. Ag/AgCl in a pH 1.35 aqueous solution (1 h) containing 0.05 M KCl

	Catalyst amount (mol cm^{-2})	Amount of H_2 produced (μl)	TN (h^{-1}) ^a
A bare BPG	—	0.23	—
PW-coated BPG	1.8×10^{-8}	6.35	6.7×10

^aThe value shows the turnover number to produce H_2 per unit cell of the PW.

pyrolytic graphite (BPG, effective area; 0.17 cm^2) electrode instead of Pt. The results are shown in Table 1. It was also found that the amount of the H_2 produced at the BPG/PW is much higher than at a bare BPG system.

Since the redox potential of PB/PW is $+0.19 \text{ V}$ vs. Ag/AgCl , PW would further be reduced to PW^{2-} in order to produce H_2 by H^+ reduction. It has been suggested recently that the cyanide ion in PB lattice can play a role as a H^+ transport site in acidic conditions by protonation of the cyanide ions [12]. It could be suggested that also in the present catalyst system the cyanide ions work as active sites for H^+ reduction probably by coordinating H^+ . Intermolecular electron transfer from the further reduced iron (i.e., PW^{2-}) to the cyanide ion may take place, and then two protons located on the adjacent cyanide sites would be reduced to H_2



Scheme 1. Electrocatalytic H^+ reduction in the Pt/PW system.

(Scheme 1). The study of the detailed mechanism is now underway.

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