Electrochemical Reduction of NO, NO₂⁻, and NO₃⁻ using Prussian Blue Film-coated Electrode

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Electrocatalytic activities of a glassy carbon electrode coated with the Prussian blue film (PB|GC) toward reduction of NO, NO₂⁻, and NO₃⁻ have been tested. Cyclic voltammetry of the PB|GC electrode taken in a solution containing NO₂⁻ revealed that a redox reaction due to Prussian blue/Prussian white exhibited catalytic activities for electrochemical reduction of the substrate. Electrolysis of the NO₂⁻ solution with the PB|GC electrode at -1.1 V vs. Ag|AgCl gave NH₃ production. The amount of NH₃ production increased with a decrease in solution pH, indicating that NO species generated from NO₂⁻ in acidic solution was a reaction substrate. The NH₃ production was also obtained by electrolysis of a solution containing NO₃⁻. The electrolysis of a NO gas-saturated solution using the PB|GC electrode produced NH₃, as expected, and current efficiencies larger than 98% were obtained at different pH. If NO gas was introduced into the cell during the electrolysis, the constant rate of NH₃ production was kept for 5 h.

Key Words : NO Reduction, NO₃⁻ Reduction, Prussian Blue, Modified Electrode

1 Introduction

NO in air, NO₂⁻ and NO₃⁻ dissolved in aqueous solution are known as environmental pollutants and technologies for removing these compounds are required. In the electrochemical field, several kinds of devices allowing detection and quantitative analysis of these species have been fabricated,¹⁻⁶⁾ but there are very few studies on electrochemical conversion of these species aiming their elimination.^{7,8)} It has been already found that some materials, such as metal complexes^{9,10-11)} and noble metals,^{2-5,7)} exhibit high catalytic activities toward reduction of the above-mentioned species to ammonia. However, their instability and/or high price are inappropriate for fabricating practical elimination devices. Recently, an interesting report was published regarding electrochemical detection of NO in aqueous solution using an electrode modified with the Prussian blue (PB) film.¹²⁾ As well known, electrochemical properties of the PB-modified electrodes were extensively studied by Itaya, *et al.* in relation to their electrochromic properties.¹³⁻¹⁶⁾ The modification of PB on an electrode can be easily made by electrochemical reduction of a solution containing FeCl₃ and K₃Fe(CN)₆, both of which are economical compounds.

According to the literature,¹²⁾ the PB film possesses catalytic activities for both electrochemical reduction and oxidation of NO. However, the electrolyte solution used was relatively complicated, that is, acidic solution containing NO₂⁻. Since nitrite dissolved in aqueous solution is present in an equilibrium state, which is given by¹⁷⁾

This was used for generation of NO in the electrolyte so-

lution.

The present study was initiated with two purposes; one is confirmation of species which can be really reduced by catalytic activities of the PB film and the other is study on stability of the PB-modified electrode for the electrocatalytic reactions. As will be shown, the PB-modified electrode possesses high catalytic activities and high stability for electrochemical reduction of NO to NH₃, allowing us to consider this electrode as a candidate for the electrode used for elimination of pollutants.

2 Experimental

Compounds including NaNO₃, NaNO₂, K₃[Fe(CN)₆] and FeCl₃ are of reagent grade and used without any specific purification. Water used was purified by a Milli-Q ultrapure system. NO gas was generated by dropping 1 mol dm⁻³ H₂SO₄ solution onto NaNO₂ powder. The generated gas was passed through a column containing NaOH pellets in order to remove water and impurities and stocked in a Teflon gas bag.

A glassy carbon (GC) plate purchased from Tokai Carbon Co. Ltd. was used as an electrode substrate and its surface was polished with 1.0 and 0.3 μm alumina powder prior to use. The GC electrodes having areas of 0.5 cm² and 4.5 cm² were used for cyclic voltammetry and controlled potential electrolysis, respectively. An Ag|AgCl in saturated KCl solution and a Pt foil were used as reference and counter electrodes, respectively. All electrode potentials given in this paper are those respected to this reference electrode.

Modification of the PB film on the GC electrode was conducted by polarizing the electrode at 0.6 V vs. Ag|AgCl for 1 min in aqueous solution containing 0.1 mol dm⁻³ KCl, 0.01 mol dm⁻³ K₃[Fe(CN)₆] and 0.01 mol

Fig. 1 Cyclic voltammogram the PB|GC electrode taken at 0.1 V s^{-1} in N_2 -saturated 0.1 mol dm^{-3} KCl solution (pH 1.3).

dm^{-3} FeCl_3 , pH of which was adjusted to 2.0 by addition of 0.1 mol dm^{-3} HCl. After the polarization, the electrode was washed with water and moved to 0.1 mol dm^{-3} KCl solution (pH 2.0). Then, the electrode potential was cycled 15 times at 0.1 V s^{-1} between 0.6 and -0.2 V vs. Ag|AgCl to remove uncoordinated Fe^{3+} and $\text{Fe}(\text{CN})_6^{3-}$ in the PB film.¹³⁾

Controlled potential electrolysis was carried out using an H-type electrolyte cell, of which working electrode and counter electrode compartments were separated by a Nafion® membrane. The working electrode compartment was capped with a silicon rubber stopper, which equipped with the working electrode, the reference electrode, and a short glass tube. The latest one was sealed with a rubber septum that was used as inlet and outlet of gas exchange and a mouth for exploitation of gas and electrolyte solution to be analyzed.

Cyclic voltammetry was conducted using an ALS electrochemical analyzer (CHI 701). In case of controlled potential electrolysis, Hokuto Denko potentiostat (HAVF 501) was used and the products were analyzed by a Yanagimoto gas chromatography (G-2800). For analyzing NH_3 , small portion of electrolyte solution was exploited from the electrolyte cell and 1 mol dm^{-3} NaOH solution ($10 \mu\text{l}$) was added to the sample solution just before injecting it into the gas chromatography. This procedure converted NH_4^+ to free NH_3 even for acidic electrolyte solution.

3 Results and Discussion

3.1 Electrochemical reduction conducted using aqueous solution containing NO_2^-

Figure 1 shows cyclic voltammogram of the PB|GC electrode taken at 0.1 V s^{-1} in N_2 -saturated 0.1 mol dm^{-3} KCl solution, pH of which was adjusted to 1.3 by 0.1 mol dm^{-3} HCl solution. Two redox couples are seen and the couple appeared at more negative potential and that at more positive potential can be assigned to redox reac-

Fig. 2 Cyclic voltammogram of the PB|GC electrode taken at 0.1 V s^{-1} in N_2 -saturated 0.1 mol dm^{-3} KCl solution (pH 1.3) in the absence (a) and the presence (b) of 0.05 mol dm^{-3} KNO_2 .

tions of PB/Prussian white (PW) and Prussian yellow (PY)/PB, respectively. Their equations are given by^{13,16)}

When 0.05 mol dm^{-3} KNO_2 was added to the electrolyte solution, changes in voltammograms shown in Fig. 2 were observed. These voltammograms were taken at potential ranges between 0.6 and -1.3 V where the redox couple due to PB/PW appeared. In the voltammogram (a) taken in the absence of KNO_2 , increase in cathodic currents was seen at potentials negative than -0.8 V , indicating reduction of H_2O to H_2 at this electrode. Addition of NO_2^- caused disappearance of the anodic wave and increase in cathodic currents, suggesting that electrochemical reduction took place with catalysis of PW on the electrode.

In order to know the electrochemical reaction catalyzed by PW, the electrolysis was made by polarization of the PB|GC electrode at -1.1 V and products were analyzed by a gas chromatograph. The product definitely detected was NH_3 and plots of its amount as a function of electrolysis time gave the results shown in Fig. 3. In this figure, the results obtained for a bare GC electrode are also shown. The PB|GC electrode polarized at -1.1 V produced NH_3 with a constant reaction rate, whereas the bare GC electrode gave no product.

3.2 Electrochemical reduction of NO_2^- and NO_3^-

To obtain further information about the electrochemical reaction using the PB|GC electrode, electrolysis experiments were conducted under different conditions. In case of the solution containing NO_2^- , solution pH and NO_2^- concentration were changed. The experiments us-

Fig. 3 NH_3 production obtained by electrolysis of N_2 -saturated 0.1 mol dm^{-3} KCl / 0.05 mol dm^{-3} KNO_2 using PB|GC electrode (a) and bare GC electrode (b).

Table 1 Production of NH_3 obtained by electrolysis of 0.1 mol dm^{-3} KCl solution containing KNO_2 or KNO_3 using the PB|GC electrode at -1.1 V for 60 min.

Reaction substrate	pH	Concentration of NH_3 (mmol dm^{-3})
0.01 mol dm^{-3} KNO_2	1.3	3.8
0.05 mol dm^{-3} KNO_2	1.3	8.5
0.1 mol dm^{-3} KNO_2	1.3	9.0
0.05 mol dm^{-3} KNO_2	7.0	1.8
0.05 mol dm^{-3} KNO_2	9.0	0
0.05 mol dm^{-3} KNO_3	1.3	2.6
0.05 mol dm^{-3} KNO_3	7.0	0

ing the solution containing NO_3^- were also carried out. The amounts of NH_3 obtained by electrolysis for 60 min are summarized in Table 1.

Amount of NH_3 produced from NO_2^- solution increased with an increase in NO_2^- concentration from 0.01 to 0.05 mol dm^{-3} , but further increase did not give definite effects. The reaction was largely inactivated with an increase in solution pH. The electrochemical reactions of NO_2^- and NO to NH_3 are given by

Their standard potentials are $+0.90 \text{ V}$ vs. NHE and $+0.84 \text{ V}$ vs. NHE, respectively.¹⁸⁾ In the electrolyte solution at pH 7.0, the equilibrium potential (E_{eq}) of $\text{NO}_2^-/\text{NH}_3$ is $+0.42 \text{ V}$ vs. NHE and that of NO/NH_3 is $+0.43 \text{ V}$ vs. NHE. The $E_{1/2}$ potential estimated from the PW/PB redox couple shown in Fig. 1 was $+0.17 \text{ V}$ vs. Ag/AgCl , which corresponds to ca. $+0.37 \text{ V}$ vs. NHE. Since the redox potential of eq. (2) is independent to pH and more negative than the E_{eq} of eq. (4) and (5) even at pH 7, the pH-dependence of E_{eq} might not be the sole reason for explaining large inactivation of the reaction caused by the increase in the solution pH.

Fig. 4 NH_3 production obtained by electrolysis of NO -saturated 0.05 mol dm^{-3} KCl solution (pH 1.3 (a), 7.0 (b), and 9.0 (c)) at -1.1 V vs. Ag/AgCl using the PB|GC electrode.

The equilibrium constant (K) of eq. (1) is defined as

$$K = \frac{a_{\text{NO}_2^-}^3}{a_{\text{NO}}^2 a_{\text{NO}_3^-} a_{\text{OH}^-}^2} \quad (6)$$

where a_x is activity of substance x . The K value was determined to be $1.1 \times 10^{20} \text{ mol}^{-2} \text{ dm}^6$.¹⁷⁾ Computation of eq. (6) using 0.05 mol dm^{-3} as the initial $a_{\text{NO}_2^-}$ value gave $0.0331 \text{ mol dm}^{-3}$ and $0.00068 \text{ mol dm}^{-3}$ as a_{NO} values under the equilibrium condition at pH = 1.3 and 7.0, respectively. The decrease in the reaction substrate by a factor of 1/50 can be regarded as the main reason that caused inactivation of the reaction with a decrease in pH. It can, therefore, be concluded that the main species which is reduced by the PB|GC electrode in KNO_2 solution is not NO_2^- but NO generated by the reaction (1) in the electrolyte solution.

It is noticed that the electrolysis experiment using KNO_3 solution also gave NH_3 as a product and its amount largely depended on the solution pH. In many cases of electrochemical reduction of NO_3^- , NO_2^- was obtained as an intermediate or final product by the following reaction.⁷⁻¹⁰⁾

Unfortunately, NO_2^- could not be detected in this study, but if the reaction (7) occurred by using the PB|GC electrode, NH_3 production from KNO_3 solution at pH 1.3 would be explained by assuming that NO was generated after the reaction (7) and it became the reaction substrate.

3. 3 Electrochemical reduction of NO gas

The electrolysis experiments were carried out using NO gas-saturated 0.1 mol dm^{-3} KCl solution at pH = 1.3, 7.0, and 9.0. As shown in Fig. 4, amount of NH_3 increased linearly with electrolysis time for all cases. The decrease in NH_3 production with an increase in solution

Fig. 5 NH_3 production obtained by electrolysis using the PB|GC electrode at -1.1 V vs. Ag|AgCl in 0.1 mol dm^{-3} KCl solution (pH 1.3) while introducing NO gas to the cell at *ca.* $0.5 \text{ mdm}^3 \text{ min}^{-1}$. The NO introduction was stopped at 60 min electrolysis (a) and restarted at 120 min (b).

pH was also observed, but magnitude of the pH effects was much less than the case of the NO_2^- solution. As a matter of fact, significant amount of NH_3 was produced even at pH = 9.0. The pH effects observed would be partially due to decrease in NO concentration in the solution because of the equilibrium reaction given by eq. (1). In this case, however, since gas phase in the cell was 100% NO, continuous supply of the reaction substrate from the gas phase to the electrolyte solution would suppress the pH effects.

The quantity of electricity consumed by the electrolysis using the solution at pH 1.3 was 48.1 C for 60 min where amount of NH_3 was $8.2 \text{ mmol dm}^{-3} \times 12.0 \text{ mdm}^3$ (volume of solution) = $98.4 \times 10^{-6} \text{ mol}$. Based on the reaction given by eq. (5), the current efficiency was estimated to be as high as 98.7%. The efficiencies larger than 98% were also obtained for the electrolysis at pH 7.0 and 9.0, indicating high catalytic activities of PW toward NO reduction.

Stability test of the PB|GC was carried out by the electrolysis while introducing NO gas in the working electrode compartment of the cell at *ca.* $0.5 \text{ mdm}^3 \text{ min}^{-1}$. The time course of NH_3 production is shown in Fig. 5. After the initial 60 min, introduction of NO was stopped for 60 min, and then NO flow was initiated again. The NH_3 amount increased linearly, but quit of NO flow caused gradual decrease in the production rate. The restart of NO introduction recovered NH_3 production and its rate was essentially the same as the initial value and was not varied for 5 h. The obtained results indicated clearly the PB film on the electrode was very stable.

4 Conclusion

The present study has clarified that the Prussian blue film modified on the GC electrode possesses high catalytic activities for electrochemical reduction of NO. The film is able to induce catalytic reduction of NO_3^- , too.

The latter thing is the fact that was discovered for the first time in this study. As mentioned in the introductory remarks, the main purpose of this study was confirmation of an ability to use of the PB films for removing pollutants of nitrogen oxides. The results of the stability tests shown in Fig. 5 allows us to have a conclusion that the PB film possesses desired properties for the purpose. However, there are another pollutants belonging to nitrogen oxides, such as N_2O , NO_2 , N_2O_3 , and N_2O_4 . Studies on the catalytic activities of PB toward these species should become the next subject.

Another matter to be consider is significance of remove of pollutants by electrochemical means although the reduction of NO by the PB|GC electrode occurred with the efficiency larger than 98%. The first problem is that the devices will have relatively complex structures, which might prevent their wide utilization. Use of expensive electric energy should become second problem especially if the devises would be used in industries. Fortunately, the Prussian blue is originally powder material, which can be chemically prepared. This implies that the PB can be used as a solid catalyst with an appropriate reducing agent. With these matters in mind, we expect development of new technology that is capable of removing NOx pollutants using the economic material of Prussian blue.

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