Electroreduction of nitric oxide to ammonia at chemically modified electrodes

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The electroreduction of NO has been studied using various modified electrodes with the mediators including cobalt phthalocyanine(CoPc) and a redox polymer. Selective conversion of NO into ammonia was obtained at a CoPc-coated glassy carbon electrode with a maximum selectivity of 92.3%. A similar result was obtained with a Pc-coated electrode, but the yield of ammonia was not so high as with the CoPc-coated electrode. A bright platinum as well as Fe(II)-poly(4-vinylpyridine) film-coated nesa glass was less active for the NO conversion into ammonia.

1. Introduction

The problem of the removal of nitric oxide from effluent gases is an important one. Various methods including heterogenous reduction by H_2, CO or NH_3 taking place at elevated temperatures under high pressures have been proposed [1–4]. The conversion of NO in mild conditions (almost at room temperature and atmospheric pressure) has been given attention recently. This technique usually employs a reducing agent with a homogeneous catalyst [5–7], or electric energy in the absence [8–10] or presence [11–16] of a homogeneous catalyst. In these methods, attention has mainly been devoted to the conversion of NO into innocuous species. However, it will be of industrial significance if NO can be selectively converted to a valuable compound, e.g. NH_3, since ammonia is a nitrogen source in fertilizers. Langer and Pate [17] have studied the electrogenerative reduction of nitric oxide, and found that ammonia tends to be favoured at low potentials, and the addition of carbon monoxide leads to the selective formation of hydroxylamine. However, the selectivity for NH_3 formation was less than 70% under the most favourable conditions. In previous work, the electrochemical reduction of NO to NH_3 was very selective (more than 90%) at platinum in the dark [15], and p-gallium arsenide irradiated with visible light [16] in the presence of a metal chelate complex as a homogeneous catalyst. These results show the industrial possibility of converting noxious nitric oxide in an effluent gas into ammonia at room temperature and atmospheric pressure. The present work was undertaken in order to obtain a higher efficiency of the conversion of NO to NH_3 by using various modified electrodes.

Chemically modified electrodes have been investigated for many purposes. The application as an electrocatalyst would be most attractive, and almost all catalytic modified electrodes are composed of immobile redox mediators which act to stimulate the charge-transfer between the electrode and the species in solution. Modification with phthalocyanines [18–20] and redox polymers [21, 22] has been actively studied from the standpoint of their electrochemical characterization or application to electrochemical processes (mostly the reduction of oxygen molecules). In the present work, various modified electrodes with mediators including phthalocyanine and redox polymer have been applied to the electroreduction of NO into NH_3. The modified electrode with the cobalt phthalocyanine film supported on a glassy carbon substrate was most effective for the NO reduction.

2. Experimental details

Four different types of electrode were used: bright platinum, nesa glass coated with Fe(II)-poly(4-vinylpyridine) (PVP) film, glassy carbon

substrates coated with cobalt phthalocyanine (CoPc) and with phthalocyanine (Pc). A grade GC-20 glassy carbon electrode ($15 \, mm \, \phi \times 50 \, mm$) was supplied by Tokai Electrode Manufacturing. The electrode was covered with epoxy resin adhesive at $70°C$ and was inserted into a cylindrical Teflon plug leaving one flat edge exposed. The surface area of the glassy carbon electrode was $1.76 \, cm^2$. The electrode surface was first polished with a series of emery papers of increasing fineness. After this electrode had been washed with 7 M ($mol \, dm^{-3}$) aqueous ammonia, it was immersed for 1 min in ethanolic 5% sodium hydroxide solution and washed carefully with distilled water. The CoPc and Pc materials were supported on the glassy carbon substrates in the following way: CoPc and Pc solutions were prepared by dissolving 0.01 mmol of CoPc and Pc in acetone to give $10 \, cm^3$, and a portion of this solution was evaporated onto the surface of the electrode. The average concentration of CoPc or Pc was calculated from the amount of solution taken for evaporation. The electrode was subsequently washed with doubly distilled water prior to use. An Fe(II)–PVP film was coated on a nesa glass electrode of $1.5 \, cm^2$ area by the following method. The PVP was supplied from Koei Kagaku Co., and its average molecular weight was about 1.4×10^5. Solutions containing PVP were prepared by mixing an aqueous Fe^{2+} solution (pH 3) and a methanolic solution of PVP. The coating of Fe(II)–PVP film was prepared by micropippeting an aliquot of the PVP solution onto the nesa glass electrode and allowing the solvent to evaporate. The platinum electrode was a bright platinum disc of $0.28 \, cm^2$ surface area.

The supporting electrolytes used were:

0.1 M citric acid + 0.2 M phosphate and

0.1 M citric acid + 0.1 M hydrochloric acid.

The NO gas was a mixture of NO and N_2 gases (1 : 99 vol ratio) and it was dissolved into the above solutions by bubbling at a flow rate of $100 \, cm^3 \, min^{-1}$ for 1 h in a $1 \, dm^3$ storage vessel. The concentration of absorbed NO was determined by the colourimetric method described below. In order to obtain an enhancement of NO solubility, ethylenediaminetetraacetate (EDTA) was sometimes added to the supporting electrolytes. To remove possible N_2O and NO_2 impurities

the NO, prior to being bubbled through the storage vessel, was passed through two wash bottles containing 5 M NaOH.

A $50 \, cm^3$ portion of the working solution was transferred to the electrolytic cell in which the electrochemical measurements were performed with a potentiostat with a potential programmer. The counter electrode was a platinum foil of $5 \, cm^2$ area and the reference electrode a saturated calomel electrode. The concentration of NO dissolved into solution was determined by colourimetric analysis using a Kjedahl apparatus. The absorbance of the solution was measured at 625 nm by means of a double beam spectrophotometer (Hitachi Model 100-50). The determination of NH_3 was performed in the same way as described above, and that of NH_2OH and N_2H_4 by methods described elsewhere [23]. The amount of N_2O was measured with a JEOL gas chromatograph (JGC-1100) using a molecular sieve 5 A column and a thermal conductivity, t.c.d., detector; however, significant amounts of N_2O were not detected.

3. Results and discussion

Cyclic voltammograms of NO at four different electrodes are shown in Fig. 1. Fig. 1a is the curve obtained at the bright platinum electrode in the phosphate–citric acid solution containing 3 mM Fe(II) EDTA. Two cathodic and one anodic waves were obtained with apparent $E_{1/2}$ values of $-0.15, -0.55$ and -0.2 V, respectively. The waves at -0.15 and -0.2 V are due to the oxidation and reduction of Fe(II) EDTA, and the wave at -0.55 V is caused by the electrochemical reduction of NO. Figs. 1b and 1c were obtained at glassy carbon electrodes coated with CoPc and Pc, respectively, in the citric acid–hydrochloric acid solution of pH 2. A distinct peak is seen at about -0.8 V with the CoPc-coated electrode, but with the Pc-coated electrode a cathodic wave is observed at $E_{1/2} = -0.85$ V. At a nesa glass electrode coated with Fe(II)–PVP film (Fig. 1d) the wave due to the NO reduction is observed at about -1.0 V, but the magnitude is very small. Among the four electrodes, the CoPc-coated electrode gives the best separation of the wave due to the NO reduction from that due to hydrogen evolution. In all cases the electrochemical reduction of NO is irreversible.
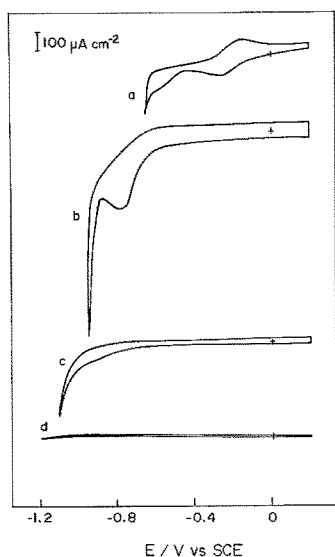
Fig. 1. Cyclic voltamograms of NO at (a) Pt electrode in the phosphate–citric acid solution of pH 6 with 3 mM Fe(II) EDTA, (b) glassy carbon coated with CoPc in the citric acid–hydrochloric acid solution of pH 2, (c) with Pc in the same condition as (b), and (d) nesa glass coated with Fe(II)–PVP film in the phosphate–citric acid solution of pH 7. Potential scan rate: 60 mV s^{-1}.

In the cyclic voltamograms of NO at the CoPc-coated electrode shown in Fig. 2, NO was continuously bubbled through the solution, and the bubbling was interrupted only for the duration of a cyclic voltametry experiment. The amount of
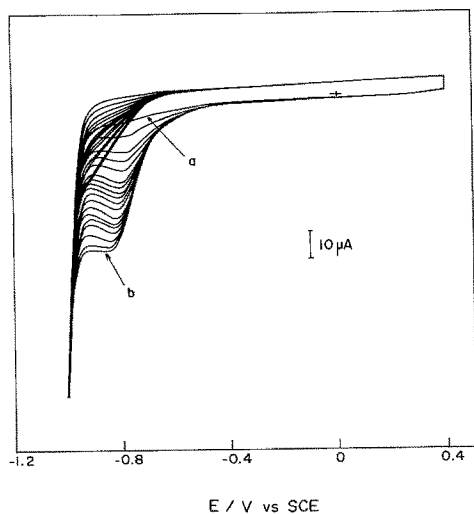

Fig. 2. Cyclic voltamograms of NO at the CoPc-coated electrode in the phosphate–citric acid solution of pH 3. Bubbling time of NO into solution is from (a) 0 to (b) 320 min at a flow rate of 10 cm^3 min^{-1}. Potential scan rate: 60 mV s^{-1}. Amount of CoPc: 1.06 × 10^{-5} mol cm^{-2}.

CoPc was 1.06 × 10^{-5} mol cm^{-2}, and the i–E curves were monitored over 320 min. The current due to the NO reduction increases with the bubbling time, due to an increase in dissolved NO. The CoPc-coated electrode was capable of reducing NO without any deactivation in aqueous solution. Except for Fig. 2, all solutions used here were prepared by bubbling NO for 1 h in the storage vessel, and the concentration of dissolved NO is not high because of the low solubility of NO in aqueous solution. Hence, as shown later the concentration of the reduction product, NH$_3$ hardly exceeded 40 μM; however, it is possible to obtain higher concentrations of NH$_3$ if electrolysis is carried out in the solution bubbled continuously with NO in the same way as shown in Fig. 2.

The effect of the amounts of CoPc and Pc coated on glassy carbon electrodes on the i–E curves is shown in Fig. 3, where CoPc and Pc films were varied from 3.5 × 10^{-6} to 3.1 × 10^{-5} mol cm^{-2}, and from 3.5 × 10^{-6} to 2.8 × 10^{-5} mol cm^{-2}, respectively. The cathodic peak due to NO reduction at the CoPc-coated electrode increases as the CoPc film thickens, but the peak
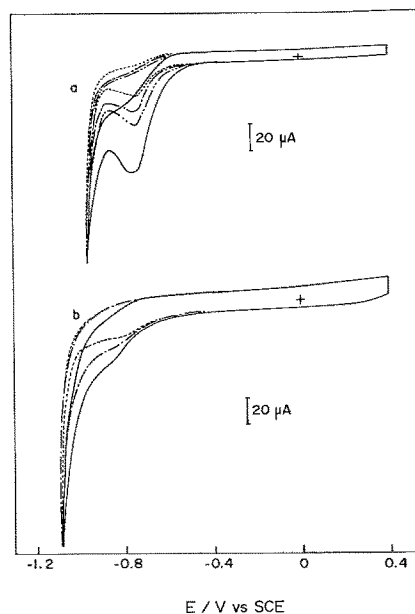

Fig. 3. Cyclic voltamograms of NO at (a) CoPc-coated electrode, the amount of CoPc: - - - - - 3.5 × 10^{-6}; — - - 6.9 × 10^{-6}; - - - - 1.0 × 10^{-5}; —— - 3.1 × 10^{-5} mol cm^{-2}, and (b) Pc-coated electrode, the amount of Pc: — - - 3.5 × 10^{-6}; —— - 1.7 × 10^{-5}; - - - - - 2.8 × 10^{-5} mol cm^{-2} in the citric acid–hydrochloric acid solution of pH 2. Potential scan rate: 60 mV s^{-1}.
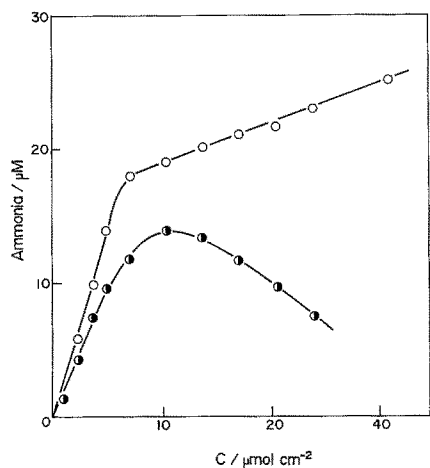
Fig. 4. Relationship between ammonia produced and the amounts of CoPc – ○ and Pc – ◑ coated on a glassy carbon. Applied potential: − 1.2 V; Time: 3 h; pH: 2.
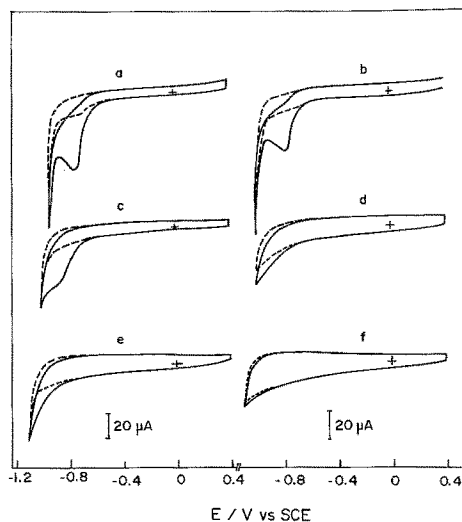

Fig. 5. Cyclic voltamograms of NO at a glassy carbon-supported CoPc electrode at pH. (a) 2, (b) 3, (c) 4, (d) 5, (e) 6, and (f) 7. Potential scan rate: 60 mV s⁻¹; the amount of CoPc: 1.06×10^{-5} mol cm⁻². —— – with and - - - - – without NO.

potential is independent of the CoPc amount. The corresponding wave at the Pc-coated electrode is not very distinct, and the reduction current decreased with increasing the Pc amount beyond 2.8×10^{-5} mol cm⁻². The influence of the Fe(II)–PVP amount on the i–E curve was negligibly small.

In Fig. 4, the concentrations of ammonia produced in the electrolysis at − 1.2 V using CoPc- and Pc-coated electrodes are shown vs CoPc and Pc amounts. As seen from this figure, the NH₃ concentration vs CoPc plot gives a linear line with an inflection point at CoPc = 6.8×10^{-6} mol cm⁻². However, the Pc-coated electrode gives a maximum concentration of NH₃ at Pc = 1.1×10^{-5} mol cm⁻². At the CoPc-coated electrode, however, such a drop of the NH₃ concentration is not observed. The decrease of NH₃ may be due to the low conductivity of the Pc film, but the CoPc film would be more conductive because of the coordination of the cobalt atom to Pc. The appearance of the inflection point with the CoPc-coated electrode is presumably attributable to the change of the rate-determining step of the electrode reaction: i.e. in the range of Pc $< 6.8 \times 10^{-6}$ mol cm⁻² the NO reduction is controlled by the rate of the charge-transfer reaction, but at thicker CoPc films ($> 6.8 \times 10^{-6}$ mol cm⁻²) the rate is increasingly controlled by the diffusion of reduction products to the bulk solution.

Fig. 5 shows i–E curves obtained at the CoPc-coated electrode in citric acid–hydrochloric acid solutions of various pHs. A distinct peak due to

NO reduction appears at pH = 2 and 3, but it becomes obscure with further increase of pH. The change in the i–E curve caused by pH change is naturally related to the concentrations of the reaction products obtained in the electrolysis at a constant potential. The quantitative results for ammonia were plotted vs pH in Fig. 6 where the electrolysis was carried out at − 1.2 V for 3 h using CoPc- and Pc-coated electrodes. As seen from this
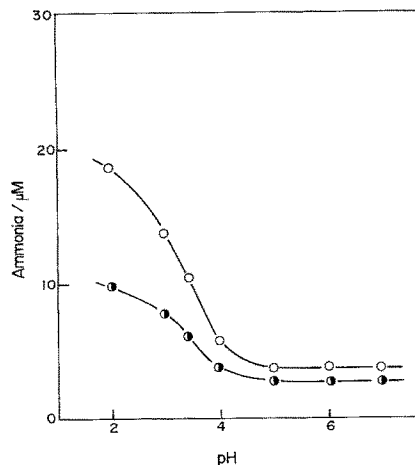

Fig. 6. Relationship between ammonia produced and pH at CoPc – ○ and Pc – ◑ electrodes. The amounts of CoPc and Pc: 1.06×10^{-5} mol cm⁻²; applied potential: − 1.2 V; polarization time: 3 h.
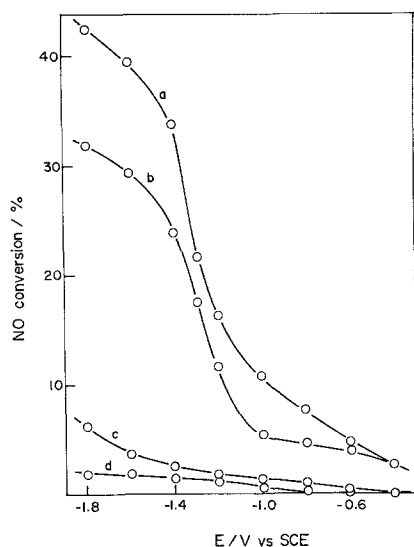
Fig. 7. Relationship between NO conversion (%) into ammonia and electrolysis potential. (a) CoPc- and (b) Pc-coated glassy carbon in the citric acid–hydrochloric acid solutions of pH 2, (c) Pt in the phosphate–citric acid solution with 3 mM Fe(II) EDTA of pH 6, and (d) Fe(II)–PVP film-coated nesa glass in the phosphate–citric acid solution of pH 7. Polarization time: 3 h.

figure and the reduction mechanism proposed previously [15] (Reaction 1), the formation of ammonia is very sensitive to the concentration of protons.

$$NO + 6H^+ + 5e \rightleftharpoons NH_4^+ + H_2O \qquad (1)$$

Both electrodes give an abrupt increase of NH_3 at pH = 4.2, and operated satisfactorily in more acidic solutions. However, the situation in the electrolysis using platinum, and nesa glass coated with Fe(II)–PVP film is different in acidic solution. Reaction 1 is inhibited on both electrodes, because at the platinum electrode the hydrogen evolution becomes predominant over Reaction 1, and the Fe(II)–PVP film tends to be soluble. Hence these two electrodes are suitable for use for NO reduction in neutral or alkaline solution; however, this condition is unfavourable to Reaction 1.

In Fig. 7, the NO conversion efficiency to ammonia obtained using modified electrodes is plotted vs electrolysis potential. The conversion efficiency was calculated from the amount present in the electrolytic cell after a 3 h electrolysis and the initial amount of NO present before electrolysis. The solution pH was adjusted to the optimum value for each electrode. The NO conversion increases as the electrode potential shifts to less noble values, and this trend is conspicuous especially at the CoPc- and Pc-coated electrodes. The NO conversion to NH_3 is very low on other electrodes ($\leqslant 8\%$ on Pt and $\leqslant 2\%$ on Fe(II)–PVP film at -1.8 V). The main product was hydrogen

Table 1. Results of the quantitative analysis of the reaction products and the selectivity for NH_3 formation at (A) Pc (1.0 × 10⁻⁵ mol cm⁻²)- and (B) CoPc (1.06 × 10⁻⁵ mol cm⁻²)-coated electrodes in the citric acid–hydrochloric acid solution of pH 2

Applied potential (V vs SCE)		Reaction products (μmol dm⁻³)			Selectivity for NH_3 formation (%)
		NH_3	N_2H_4	NH_2OH	
− 0.4	A	1.3	0.135	5.33	19.3
	B	3.1	0.264	8.67	25.8
− 0.6	A	1.7	0.176	6.00	21.6
	B	7.2	0.320	6.67	50.7
− 0.8	A	2.2	0.128	5.33	28.7
	B	8.2	0.149	4.00	66.4
− 1.0	A	9.1	0.203	1.33	85.6
	B	11.2	0.298	5.33	66.6
− 1.2	A	10.1	0.236	4.00	70.5
	B	19.0	0.256	1.33	92.3
− 1.4	A	10.6	0.324	1.33	86.5
	B	19.8	0.426	3.33	84.1
− 1.6	A	12.7	0.258	6.00	67.0
	B	24.3	0.662	4.67	82.0
− 1.8	A	17.3	0.469	1.33	90.6
	B	28.6	0.810	4.00	85.6

molecules at Pt, and the Fe(II)–PVP film-coated nesa glass was hardly electroactive in this system. The CoPc-coated electrode gave a better performance for the conversion of NO to NH_3, although the current efficiency dropped considerably at very negative potentials: 63% at -1.0 V and 3.7% at -1.8 V.

Table 1 shows the results of the quantitative analysis of the reaction products and the selectivity for NH_3 formation at (A) Pc- and (B) CoPc-coated electrodes. On both electrodes, the amount of NH_3 produced increases with a shift of the electrolysis potential to more negative values. Such a tendency is apparent generally for N_2H_4 formation, but not for NH_2OH. Ammonia and hydrazine are both produced more favourably on the CoPc- than the Pc-coated electrode, but the dependency of NH_2OH formation on the identity of the electrode is not observed. The selectivity for NH_3 formation tends to increase with an increase of the electrolysis potential. A maximum selectivity (92.3%) is observed at -1.2 V for the CoPc-coated electrode, and (90.6%) at -1.8 V for the Pc-coated electrode. Direct electrochemical reduction of NO at a platinum electrode in 4 M H_2SO_4 gives hydroxylamine, ammonia and nitrous oxide with a comparable ratio as reaction products [9]. Nitrogen gas in addition to these products is observed in the electrogenerative reduction of NO [17]. Hence the high selectivity for NH_3 formation obtained in the present work may be attributed to the property of the electrode surface where electrons and protons can react with NO. It was difficult on both the platinum and the Fe(II)–PVP film-coated glass electrodes to obtain favourable conditions for NO reduction because hydrogen evolution and dissolution of the PVP film were involved at these electrodes in acidic solution. On the other hand the CoPc and Pc films are quite stable in acidic solution, and the hydrogen overpotentials are relatively high on these films. The coordination of the Co atom to phthalocyanine gives an increase of the electron density on the

d_{z^2} orbital which promotes a partial electron transfer to NO, which may lead to the enhancement of NH_3 production and its selectivity on the CoPc-coated electrode. Metalloporphyrin being similar in properties, would also be expected to give a high degree of NH_3 production and selectivity, and work to confirm this is in progress.

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