Electrochemical Reduction of NO on ZnO and In_2O_3 Semiconductor Electrodes in Aqueous K_2SO_4 Solutions

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NO was efficiently reduced on ZnO and In_2O_3 of n-type semiconductor electrodes in aqueous solutions. Harmless N_2 was obtained as a main reduction product. Current-potential curves on the ZnO and In_2O_3 electrodes under NO were quite similar to those under N_2O. It is proposed that the NO reduction on the ZnO and In_2O_3 electrodes proceeds via the redox mechanism in which oxygen vacancies formed by the electrochemical reduction on the electrode surface play an important role.

Activation of NO is of interest from the view points of catalyses and emission control. Thermal catalytic reduction of NO by reducing reagents such as NH_3, CO, and hydrocarbons has extensively been studied for a long time.[1] On the other hand, the number of reports on the electrochemical reduction of NO is not so large.[2-8] Moreover, in most studies on the electrochemical NO reduction, platinum has been employed as an electrode material in acidic solutions. In contrast, oxide electrodes have hardly been used for this reaction. Unique electrocatalyses of the oxide electrodes will be expected because the oxides often possess various properties for thermal catalyses. The authors have reported the electrochemical reduction of N_2O on oxide semiconductor electrodes such as ZnO and In_2O_3.[9,10] The reduction product of N_2O is only N_2. In the case of the electrochemical NO reduction, however, some reduction products such as N_2, N_2O, and NH_3 are obtained. The selectivity of the reduction products can be argued. Therefore, NO reduction is an interesting system for studying catalyses on electrode surfaces as well as CO_2 reduction.[11-13]

This paper reports the efficient reduction of NO on ZnO and In_2O_3 of n-type semiconductor electrodes. The mechanism of the surface reaction on the electrodes is discussed by comparison of the electrochemical reduction of NO with that of N_2O reported previously.

Sintered polycrystalline ZnO (Kanto Chemical, purity; 99.0%), In_2O_3 (Kanto Chemical, purity; 99.9%), and In^{3+}-doped ZnO electrodes were prepared by heating pressed disks of the powder at 1370 K for 10 h in air using an alumina crucible. An ordinary H-type cell where catholytes were separated from anolytes with Nafion 417^R was employed. The electrolyte was an aqueous K_2SO_4 solution (0.3 mol dm^{-3}). A Pt black plate and Ag I AgCl I KCl (sat.) were used as counter and reference electrodes, respectively. The electrode potentials are noted with respect to the Ag I AgCl I KCl (sat.) reference electrode. The electrolyses were carried out with agitation galvanostatically using a potentiostat-galvanostat (Hokuto; model HZ3000) after current-potential curve measurements under Ar and NO. Ar and NO (purity: 99%) gases were used without further purification. Gaseous products were determined using gas chromatography. MS5A column, TCD detector, and Ar carrier were used for H_2 and N_2 analyses and PPQ column, TCD detector and He carrier were employed for N_2O analyses. The amount of NH_3 formed was determined by the Indophenol method[14] using a spectrometer (JASCO; Ubest V-570).

Figure 1 shows the current-potential curves of ZnO electrodes under Ar and NO in aqueous K_2SO_4 solutions. Under NO, the cathodic current arose at -1.0 V and a characteristic reduction wave was observed around -1.4 V during sweeping negatively. Figure 2 shows the current-potential curves of In_2O_3 electrodes under Ar and NO. The characteristic difference between Ar and NO condition as seen for ZnO electrodes was not observed for

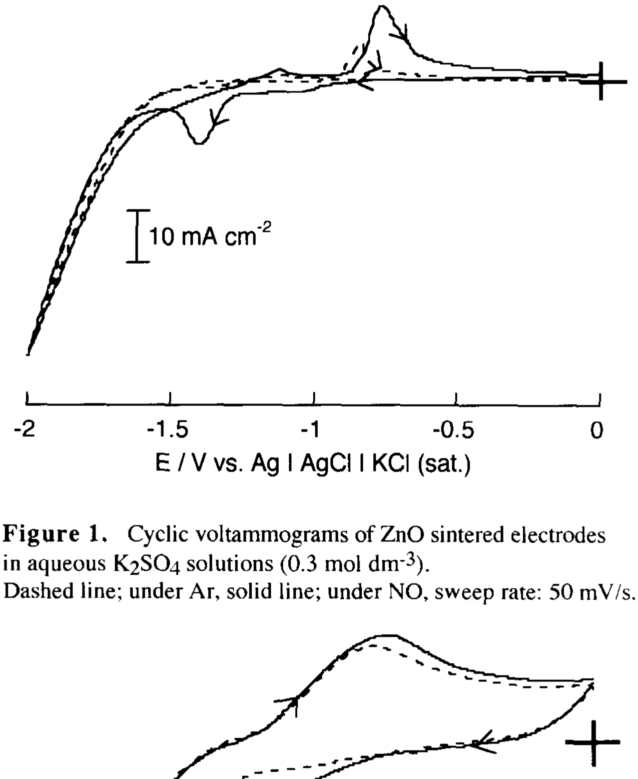

Figure 1. Cyclic voltammograms of ZnO sintered electrodes in aqueous K_2SO_4 solutions (0.3 mol dm^{-3}).
Dashed line; under Ar, solid line; under NO, sweep rate: 50 mV/s.

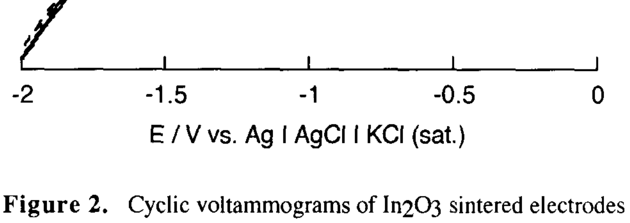

Figure 2. Cyclic voltammograms of In_2O_3 sintered electrodes in aqueous K_2SO_4 solutions (0.3 mol dm^{-3}).
Dashed line; under Ar, solid line; under NO, sweep rate: 50 mV/s.

Table 1. Efficiencies of electrochemical reduction of NO on oxide semiconductor electrodes at 13 mA cm^{-2} in aqueous K_2SO_4 solutions at 300 K

Electrode	Potential / V[a]	Faradaic efficiency / %				
		N_2O	N_2	NH_3	H_2	Total
ZnO	-1.65 → -1.55	11	53	27	2	93
In_2O_3	-0.96 → -1.43	6	77	13	2	98
In^{3+}(1mol%)-ZnO	-1.3 → -1.5	17	73	22	6	118

[a] vs. an Ag I AgCl I KCl-sat. reference electrode. Charge passed: 130C.

the In_2O_3 electrode although the cathodic current in the region between -0.8 and -1.5 V under NO was slightly larger than that under Ar. The behavior on the current-potential curves on the ZnO and In_2O_3 under NO was quite similar to that under N_2O.[9] This result suggests that the active site on the electrode surface for the NO reduction may be the same as that for the N_2O reduction. The current-potential curves of ZnO and In_2O_3 electrodes are divided into two regions at ca. -1.6 V. Steep curves of the cathodic current are observed at the region more negative than ca. -1.6 V while the curves with gentle slopes are obtained at less negative than -ca. -1.6 V. At the latter region, the increase in cathodic currents under NO is observed compared with that under Ar for ZnO and In_2O_3 electrodes. The electrode surfaces are reduced more or less at this potential region. These observations suggest that the active site may be an oxygen vacancy .

Table 1 shows the efficiencies of electrochemical reduction of NO on ZnO, In_2O_3, and In^{3+}(1 mol%)-doped ZnO electrodes at 13 mA cm^{-2} of a constant current density in aqueous K_2SO_4 solutions. NO was reduced with high Faradaic efficiencies. The main reduction product was harmless N_2 rather than NH_3. H_2 formation which should compete with the NO reduction in aqueous solutions was negligible. Electrode potentials of ZnO and In^{3+}(1 mol%)-doped ZnO electrodes were stable during electrolyses. In contrast, the electrode potential of In_2O_3 drastically changed from -0.96 V to -1.43 V at the initial stage of electrolyses. In this process, the In_2O_3 electrode is probably reduced to form oxides with low oxidation numbers such as In_2O. The electrochemical reduction of NO might proceed on such a surface.

The electrochemical reduction of NO has mainly been conducted on Pt electrodes in acidic aqueous solutions so far.[2-4,6-8] In these cases, NH_3, NH_2OH and N_2O have been obtained as main reduction products, depending on the electrolysis condition. It is noteworthy that, in the present study, N_2 was efficiently formed by using some oxide semiconductor electrodes which have not been employed for this reaction.

Two paths can mainly be considered for the electrochemical NO reduction as follows.

$$NO \xrightarrow{2e^-,\,2H^+} N_2O \xrightarrow{2e^-,\,2H^+} N_2 \qquad (1)$$

$$NO \xrightarrow{5e^-,\,5H^+} NH_3 \qquad (2)$$

The path (1) is a reduction reaction accompanied with the N-N bond formation. The path (2) is a hydrogenation reaction. The main product was N_2 on ZnO, In_2O_3, and In^{3+}(1 mol%)-doped ZnO electrodes showing that the main reaction might proceed via the path (1). It has been reported that an oxygen vacancy plays an important role for the adsorption and activation of NO molecules on oxide surfaces such as ZnO in gas phase.[15] When reducible oxide electrodes with an n-type semiconductor characteristic such as ZnO and In_2O_3 are polarized negatively, oxygen vacancies can be formed by the partial reduction.

$$-M-O-M- + 2H^+ + 2e^- \rightarrow -M-\_\_-M- + H_2O \qquad (3)$$

__: Oxygen vacancy

If the oxygen vacancy works as the active site for the NO reduction, a deoxygen reaction shown in the path (4) is favorable to hydrogenation. In this path, the oxide surfaces are reoxidized by NO.

$$2NO + -M-\_\_-M- \rightarrow N_2O + -M-O-M- \qquad (4)$$

N_2O formed in the path (4) can subsequently be reduced by the same mechanism (path (5)).

$$N_2O + -M-\_\_-M- \rightarrow N_2 + -M-O-M- \qquad (5)$$

It has been reported that the electrochemical N_2O reduction efficiently proceeds on ZnO, In_2O_3, and In^{3+}(1 mol%)-doped ZnO electrodes in an aqueous solution.[9,10] The highly efficiency for the electrochemical reduction of NO and selective formation of N_2 rather than NH_3 are thought to be due to the redox mechanism accompanied with oxygen vacancies formed by electrochemical reduction of the n-type semiconductor oxide electrode surfaces via paths (3)-(5).

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