Bull. Chem. Soc. Jpn., ***69***, *2159—2162 (1996)*

Electrochemical Reduction of N_2O on Gas-Diffusion Electrodes

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(Received December 28, 1995)

The electrochemical reduction of N_2O to N_2 on gas-diffusion electrodes (GDEs) modified by Pt and Ni electrocatalysts at room temperature was studied. The Faradaic efficiency for the reduction of N_2O was 100%, even for a low concentration of N_2O gas at a low current density. When 0.6 mmol of N_2O was electrolyzed, 99.7% of the N_2O was decomposed at a constant current density of 6.4 $\mathrm{mA\,cm^{-2}}$. The Faradaic efficiency of N_2O reduction was increased by using pulse electrolysis.

Among nitrogen oxides, dinitrogen oxide (N_2O), which is mainly emitted from soils,[1—3] is relatively stable under ambient conditions. The lifetime of N_2O in the atmosphere is estimated to be 150 years. It is known that N_2O produces a greenhouse effect. The concentration of N_2O in the air is lower than that of CO_2, which is the main component of the greenhouse effect gases. The greenhouse effect due to N_2O (per molecule) is 206-times stronger than that of CO_2.[4,5] The elimination process of N_2O has never been much studied, though it is needed. It is not kinetically easy to decompose N_2O into N_2 and O_2 at low temperatures, even in the presence of catalysts. Oxygen is hardly released into the gas phase by decomposition at low temperatures, because of the adsorption of oxygen species on the catalyst surface.[6] Therefore, the decomposition of N_2O into N_2 and O_2 at room temperature is important from both industrial and academic view points.

Furuya et al. have studied the electrochemical reduction of N_2O using a GDE based on the idea of a H_2–N_2O fuel cell.[7,8] They showed that the current efficiency of N_2O reduction could reach 100%. Since this study was carried out by electrolysis in a flow system, it is considered that they showed the property of electrochemical N_2O reduction when the concentration of N_2O is relatively high.

In order to eliminate N_2O in the atmosphere, it is important to decompose the low concentration of N_2O. However, the electrochemical reduction of low-concentration N_2O has never been studied. It is also important to investigate the change in the absolute amount of N_2O in N_2O reduction as well as the current efficiency. In the present study, the electrochemical reduction of N_2O under 1 atm on GDEs modified by Pt and Ni electrocatalysts was investigated in detail.

Experimental

Preparation of the Gas-Diffusion Electrode (GDE). Pt GDE and GDE without a catalyst were purchased from Tanaka Kikinzoku Kogyo. The Pt GDE comprised two layers made from PTFE (Polytetrafluoro ethylene) and carbon black; one was a catalyst layer containing Pt catalyst; the other was a gas-diffusion layer. The amount of incorporated Pt catalyst in the catalyst layer was 0.56 $\mathrm{mg\,cm^{-2}}$, and the apparent surface area of the GDE was 0.8 $\mathrm{cm^2}$. The process for preparing the Ni GDE was as following: a 0.1 mL of $Ni(NO_3)_2$ methanol solution (0.16 $\mathrm{mol\,dm^{-3}}$) was impregnated into the catalyst layer of the GDE without using a metal catalyst (1.5 cm×1.5 cm). The amount of incorporated Ni catalyst (calculated from the amount of the solution) was 0.42 $\mathrm{mg\,cm^{-2}}$. After desiccating the GDE in air, it was reduced in an H_2 atmosphere at 533 K for 1 h.

Electrolyses and Analysis of the Products. A schematic diagram of the apparatus for the electrolyses is shown in Fig. 1. An aqueous electrolyte of 1.0 $\mathrm{mol\,dm^{-3}}$ KOH, prepared from reagent-grade chemicals and distilled water (Wako Pure Chemical Industries Ltd.), was purified by pre-electrolysis using a Pt black cathode for more than 15 h to eliminate any heavy-metal impurities. Pt and Ni GDEs were used as the working electrode. A Ag/AgCl/saturated

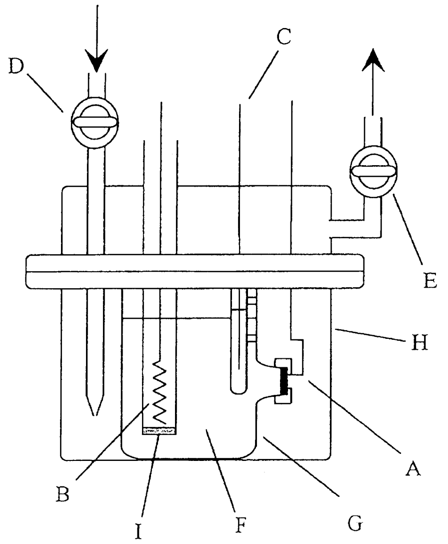

Fig. 1. Schematic diagram of the electrolysis apparatus: (A) working electrode (GDE), (B) counter electrode (Pt), (C) reference electrode (Ag/AgCl), (D) gas inlet, (E) gas outlet, (F) electrolyte, (G) inner cell, (H) outer cell, (I) glass filter.

KCl electrode and a Pt wire were used as a reference electrode and a counter electrode, respectively. In the case of electrolyses under a low concentration of N_2O, a given amount of N_2O was added into the cell after the cell had been substituted with Ar by bubbling for 20 min. The electrolyses were carried out galvanostatically using a potentiostat/galvanostat (Hokuto HA-501) connected in series with a coulomb/amperehour meter (Hokuto HF-201) at 25 °C under 1 atm. The electrode potential of the GDE was measured and corrected with an IR-compensation instrument (Hokuto HI-203). For pulsed electrolyses, an electrical pulse was imposed on the working electrode using an arbitrary function generator (Hokuto HB-105). The form of the electrical pulse was (ON : OFF) = (5 s : 5 s), (5 s : 10 s), and (5 s : 20 s) in the present experiments. The electrolysis products and N_2O in the gas phase were quantitatively analyzed by a gas chromatograph (Ohkura GC-802) equipped with a thermal conduction detector (TCD). The following columns were employed for the analysis: a molecular sieve (MS) 13 X and Porapak Q for N_2 and N_2O, an active carbon for H_2. The electrode reactions of N_2O reduction proposed by Johnson et al. are as follows:[9]

$$\text{Cathode}: N_2O + H_2O + 2e^- \rightarrow N_2 + 2OH^-, \qquad (1)$$

$$\text{Anode}: 2OH^- \rightarrow 1/2O_2 + H_2O + 2e^-. \qquad (2)$$

Equation 1 shows that N_2O is reduced by 2 electrons and decomposed to N_2. Thus, the faradaic efficiency of N_2O reduction can be determined based on the faradaic efficiency of N_2 formation using Eq. 1. No analysis of the liquid phase was conducted.

Results and Discussion

Current–Potential (*I–E*) Curve. Figure 2 shows the *I–E* curve obtained for a Pt GDE under 1 atm of N_2O and Ar. As shown in this Figure, the cathodic current due to hydrogen evolution by the reduction of H_2O under an Ar atmosphere starts to increase at −0.8 V (vs. Ag/AgCl), while that under N_2O increases drastically at −0.4 V. The intensity increase in the cathodic current depends on the presence of N_2O. This result shows that N_2O reduction occurs at a more positive potential than does H_2O reduction. In the case of GDE without a metal catalyst, no change was observed in the *I–E* curve upon the introducing N_2O, compared with that under an Ar atmosphere. This indicates that N_2O is not reduced on GDE without a Pt catalyst (i.e. on carbon). The above results show that Pt is an effective catalyst for N_2O reduction.

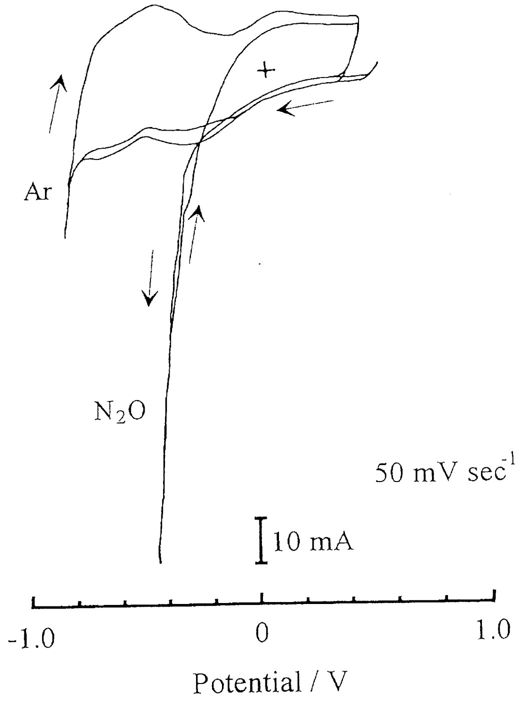

Fig. 2. Cyclic voltammograms obtained on Pt GDE in 1 mol dm^{-3} KOH aqueous solution under 1 atm of Ar and N_2O. Scan rate: 50 mV s^{-1}.

N_2O Reduction on Pt and Ni GDEs. Table 1 shows the faradaic efficiencies of the reduction products formed on GDEs. As shown in this Table, in the cases of Pt and Ni GDEs, N_2O is reduced to N_2 at high faradaic efficiencies. The faradaic efficiencies of N_2 formation on Pt and Ni GDEs at a constant current density of 6.4 mA cm^{-2} under 1.0 mol% of N_2O, are 84.7 and 77.1%, respectively. In the case of GDE without a metal catalyst, hydrogen formed by the reduction of H_2O is the predominant reduction product, and the faradaic efficiency of N_2 is only 1.9%. These results show that N_2O is reduced to N_2, catalyzed by Pt and Ni electrocatalysts.

The current-density dependence of the faradaic efficiencies for N_2O reduction (i.e. N_2 formation) and H_2 formation at a concentration of 1 mol% of N_2O using Pt GDE are shown in Fig. 3. The faradaic efficiency for N_2O reduction increases with decreasing the current density, while that for H_2 formation decreases (Fig. 3). N_2O is reduced to N_2 at a Faradaic efficiency of 100% at a smaller current density than 1.3 mA cm^{-2}. The faradaic efficiency for N_2O reduction decreases and approaches nearly 20% for current densities greater than 25 mA cm^{-2}.

Figure 4 shows the dependence of the Faradaic efficiencies for N_2O reduction and H_2 formation on the initial concentration of N_2O in electrolyses with a constant current density of 127 mA cm^{-2} using Pt and Ni GDEs. In the case of Pt GDE, the Faradaic efficiency for N_2O reduction reaches 100% at a concentration larger than 15 mol% of N_2O; however, it decreases rapidly with decreasing the initial concentration of N_2O at less than 10 mol% of N_2O (4% at 1 mol% of N_2O). In the case of Ni GDE, the initial concentration dependence is similar to that using Pt GDE. The faradaic efficiency for N_2O reduction is about 100% for an initial N_2O concentration

Table 1. Faradaic Efficiencies of Reduction Products Formed on GDEs

	$[N_2O]$	j	E[a]	Q	Faradaic efficiency/%		
Catalyst	mol %	mA cm^{-2}	V	C	N_2	H_2	Total
—	17	25.5	−1.48	70	1.9	97.0	98.9
Ni	1.0	6.4	−1.2	30	84.7	30.1	114.8
Ni	1.0	25.5	−1.3	30	31.2	71.2	102.4
Pt	1.0	6.4	−0.71	30	77.1	23.1	100.2
Pt	1.0	12.7	−0.88	30	45.4	51.6	97.0

a) The electrode potential were corrected with an IR compensation instrument (vs. Ag/AgCl).

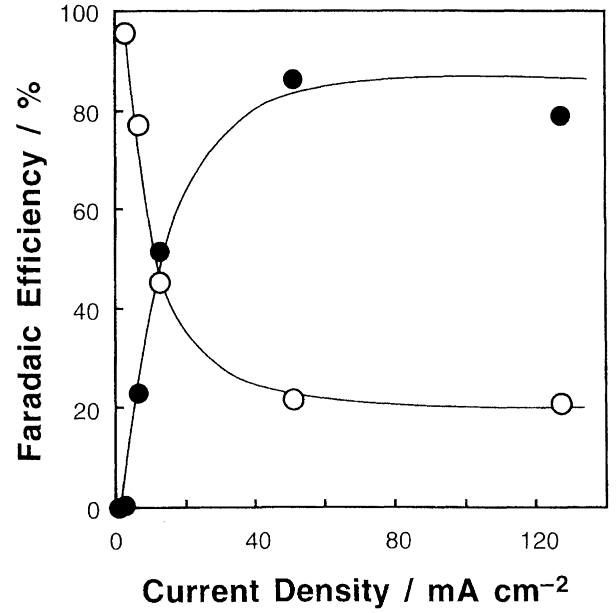

Fig. 3. The current density dependence of faradaic efficiencies of N_2 and H_2 formed on a Pt GDE in 1 mol dm^{-3} KOH aqueous solution for 30 C: (○) N_2; (●) H_2. Initial concentration of N_2O: 1 mol%.

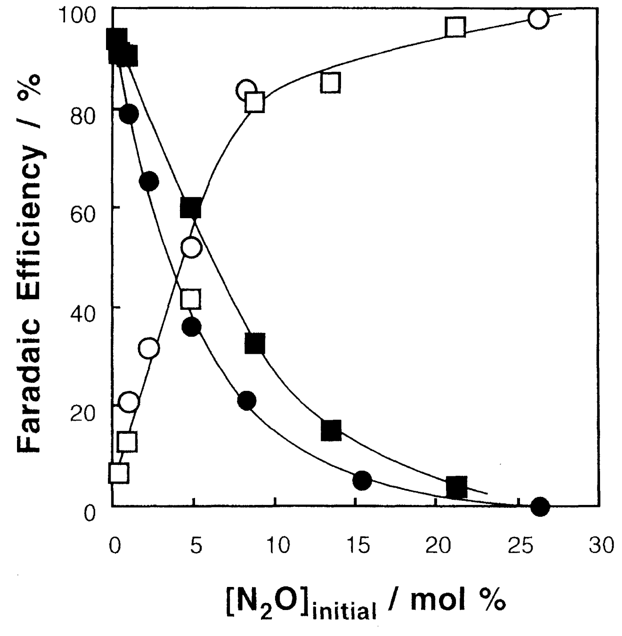

Fig. 4. Dependence of faradaic efficiencies of N_2 and H_2 formed on Pt and Ni GDEs on the initial concentration of N_2O: (○) N_2–Pt GDE; (●) H_2–Pt GDE; (□) N_2–Ni GDE; (■) H_2–Ni GDE.

larger than 20 mol% of N_2O; however, it decreases rapidly at less than 10 mol% of N_2O and becomes 13% at 1 mol% of N_2O. As shown in Fig. 4, the Faradaic efficiencies of the reduction products depend strongly on the initial concentration of N_2O and the current density. This results show that the Faradaic efficiencies for the reduction products depend on the amount of N_2O molecules which reach the surface of the catalyst per unit time. In other words, it shows that the diffusion and adsorption of N_2O to the surface of the catalyst is the rate-determining step of the reaction.

Figure 5 shows Tafel plots for N_2O reduction and H_2 formation on Pt and Ni GDEs at 1 mol% of N_2O. The partial current density for N_2O reduction on Pt GDE is larger than that on Ni GDE at all potential conditions. However, the partial current density for H_2 formation on Pt GDE also exceeds that on Ni GDE. This result suggests that since the surface area of the Pt catalyst used in this experiment was larger than that of Ni catalyst, the activity of the electrode reactions of a Pt catalyst was larger than that of a Ni catalyst in this experiment. The maximum partial current density for N_2O reduction at a 1 mol% of N_2O concentration in this electrode potential range on Pt and Ni GDEs was 27 and 14 mA cm^{-2}, respectively.

Change in the Absolute Amount of N_2O at Galvanostatic Electrolyses. Figure 6 shows the change in the absolute amount of N_2O against the passed charge at galvanostatic electrolyses of 6.4 and 64 mA cm^{-2} using Pt GDE. The initial amount of N_2O was 0.6 mmol. The broken line indicates the change in the amount of N_2O in the case of 100% of the Faradaic efficiency of N_2O reduction. As shown in this figure, the amount of N_2O decreased to half the initial amount (0.3 mmol) for the passage of 150 C at a current density of 64 mA cm^{-2}, and decreased to 15% of the initial amount (0.09 mmol) for the passage of 150 C at 6.4 mA cm^{-2}. Moreover, the amount of N_2O decreased to 0.3% (0.002 mmol) for the passage of 300 C at 6.4 mA cm^{-2}. It is shown in this experiment that 99.7% of the initial amount of N_2O could be decomposed. The result of Fig. 6 indicates that the efficiency of the decomposition of N_2O depends on the current density, and that a highly efficient decomposition is possible

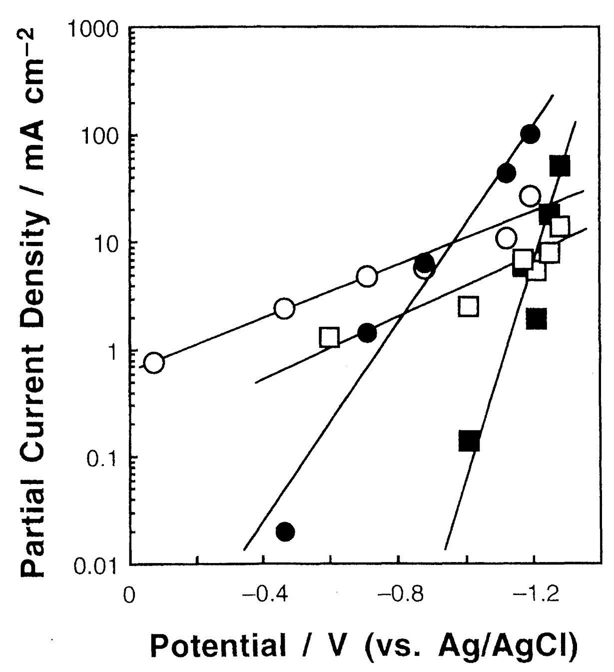

Fig. 5. Tafel plots of N_2 and H_2 formations on Pt and Ni GDEs in 1 mol dm^{-3} KOH: (○) N_2–Pt GDE; (●) H_2–Pt GDE; (□) N_2–Ni GDE; (■) H_2–Ni GDE.

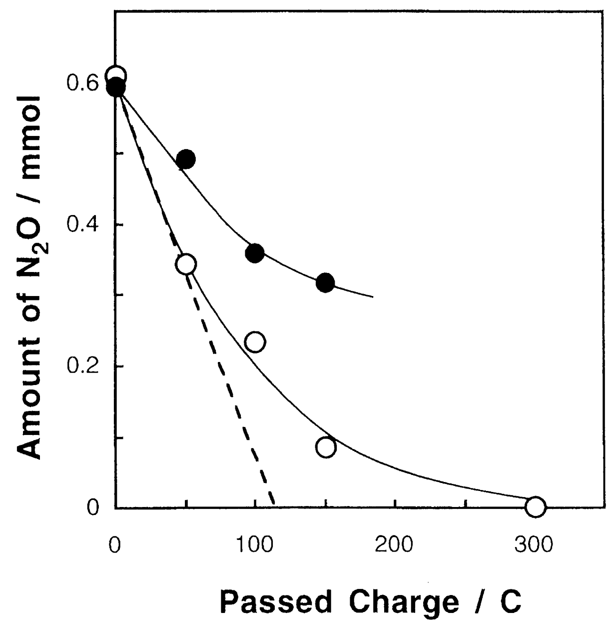

Fig. 6. Relationship between the amount of N_2O and the passed charge in galvanostatic electroreduction of N_2O using Pt GDE: (●) 64 mA cm^{-2}; (○) 6.4 mA cm^{-2}. Initial amount of N_2O: 0.6 mmol (4%).

at a smaller current density for the same passed charge.

Pulse Electrolysis. Figure 7 shows the amount of N_2O against the passed charge and the effect of pulsed electrolysis. Pulse electrolysis was carried out at a current density of 64 mA cm^{-2}. The broken line indicates the change in the amount of N_2O in the case of 100% of the Faradaic efficiency of N_2O reduction. The inset in Fig. 7 shows the form of the applied pulse. As shown in Fig. 7, in the case of the pulse form of (ON : OFF)=(5 s : 5 s), no effect of the pulse electrolysis was observed. However, it becomes effective when the OFF time becomes long, i.e. (ON : OFF)=(5 s : 10 s) and (5 s : 20 s). When an excess amount of electrons is supplied from electrocatalyst in the case of a large current density, the Faradaic efficiency of N_2O reduction would be decreased because of a mass-transfer limitation and adsorption limitation to the catalyst of an N_2O molecule. In this case, H_2O (or H^+) is reduced to H_2 on the electrocatalyst instead of N_2O. If a small amount of electrons is supplied after a sufficient amount of N_2O is supplied and adsorbed to the catalyst, the Faradaic efficiency of N_2O reduction would increase, since H_2O reduction does not proceed. Since the Faradaic efficiency of N_2O reduction is increased by using pulse electrolysis, it can be concluded that the diffusion and adsorption of N_2O to the electrocatalyst is the rate-determining step of N_2O reduction in the low-concentration range of N_2O.

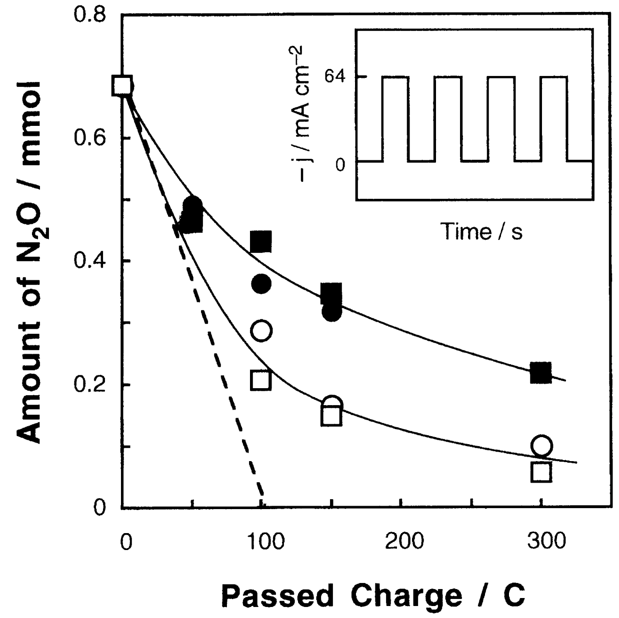

Fig. 7. Relationship between the amount of N_2O and the passed charge in pulsed electroreduction of N_2O using Pt GDE in 1 mol dm^{-3} KOH: (●) no pulse; (■) on 5 s : off 5 s; (○) on 5 s : off 10 s; (□) on 5 s : off 20 s. Initial amount of N_2O: 0.6 mmol (4%). Current density: 64 mA cm^{-2}.

Conclusions

N_2O could be reduced to N_2 in the electrolyses using Pt and Ni GDEs. It was found for the first time that N_2O is reduced on a Ni electrocatalyst. The Faradaic efficiency of N_2O reduction was 100% under the conditions of low current density and/or high N_2O concentration. It is indicated for the first time that the Faradaic efficiency of N_2O reduction increased by using pulse electrolysis. The Faradaic efficiency of N_2O reduction decreased when the current density was large and/or the N_2O concentration was low, because of the mass-transfer limitation and adsorption limitation of N_2O.

This work was supported by a Grant-in-Aid for Scientific Research No. 416307 from the Ministry of Education, Science and Culture.

References

1) K. A. Brice, A. E. J. Eggleton, and S. A. Penkett, *Nature*, **268**, 127 (1977).

2) J. R. Freney, O. T. Denmead, and J. R. Simpson, *Nature*, **273**, 531 (1978).

3) J. M. Bremner and A. M. Blackmer, *Science*, **199**, 295 (1978).

4) R. E. Dicknson and R. J. Cicerone, *Nature*, **319**, 109 (1986).

5) M. H. Thiemens and W. C. Trogler, *Science*, **251**, 932 (1991).

6) A. Kudo and T. Sakata, *Chem. Lett.*, **1992**, 2381.

7) N. Furuya and H. Yoshida, *J. Electroanal. Chem.*, **303**, 271 (1991).

8) N. Furuya and K. Murase, *Pro. -Electrochem. Soc.*, **93-18**, 203 (1993).

9) K. Johnson and D. T. Sawyer, *J. Electroanal. Chem.*, **49**, 95 (1974).