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DEMS Study of NO_2^- Reduction on Pt(100) Electrode in Alkaline Solution

Yunzhi GAO, Hideaki KITA,* and Hideshi HATTORI
Division of Material Science, Graduate School of Environmental Earth Science, Hokkaido University, North 10, West 5, Kita-ku, Sapporo 060

Newly developed "one point touch" DEMS (Differential Electrochemical Mass Spectrometer) was applied to a small Pt single crystal electrode of ca. 0.1 cm^2 and succeeded to follow the electrode reactions of NO_2^- in situ, together with voltammogram at a potential sweep of 2-10 mVs^{-1}. It was confirmed that NO_2^- is reduced to NH_3 at Pt(100) in 0.2-0.5 V (RHE). NH_3 is oxidized exclusively to N_2 around 0.6 V (RHE).

Nitrogen Oxides have received deep concerns from a point of view of the environmental pollution. Many works have been reported on the electrochemical reduction of nitrogen oxides,1) e.g., NO_2^- and NO_3^- at platinized platinum electrode in alkaline medium,2) NO_3^- and NO_2^- at Pt and Ni in concentrated NaOH,3) and NO at platinum black gas diffusion electrodes.4) However, the work on the single crystal electrode is very few. We reported that the electrochemical reduction of nitrogen oxides is markedly structure-sensitive. For example, NO_2^- is sensitively reduced on Pt(100) in alkaline solution but not on Pt(111) and Pt(110) in a potential range of 0.2-0.5 V.5)

The present work aims to detect the product of the NO_2^- reduction on Pt(100) in alkaline solution by the newly developed " one point touch " DEMS which is applicable to a small electrode with a high sensitivity.6)

The mass spectrometer (MS) used was a quadrupole instrument (Anelva AQA-200) in which a microchannel plate was installed. It was controlled by a personal computer (NEC-9801 RA) and provided with eight channels for the simultaneous observation of various products. The microchannel plate was polarized at 650 V, which improved the single-to-noise ratio significantly. The emission current was kept at 2.0 mA. The gas inlet was a pin-hole of several μ m in diameter located at the center of the hemispherical end of a thick glass tube. The pin-hole was covered with Teflon film of less than 50 μm in thickness. The glass tube was fused vertically in a standard three-compartment cell and the bottom was connected to the vacuum system of the MS. The electrode in the dipping mode was in contact with the top of the gas-inlet system at the center of the electrode surface. Gaseous reactants and products were sampled through the pin-hole. Because of the point contact with the electrode surface, the area of the electrode effective for the sampling is extremely small and the solution thickness between the electrode surface and the top of the gas inlet will be a few micrometers. The pressure inside the MS was ca. 7×10^{-5} Pa under working conditions.

The Pt(100) electrode was prepared by Clavilier's method.7) Before each measurement, the electrode was annealed in a gas-O_2 flame for a few seconds and its surface state was checked by recording a cyclic voltammogram (CV) in blank solution.

The electrolyte solution was Ar-saturated Na_3PO_4 (0.2 M, pH=13) with 2mM $NaNO_2$ or 5 mM NH_3.

The CV and the corresponding Mass current (MSCV) were observed with a sweep rate of 2 or 10 mVs^{-1}. Potentials were referred to RHE (the reversible hydrogen electrode in the blank solution).

Figure 1 shows the CV at a sweep rate of 2 mVs^{-1} and the corresponding MSCV with respect to N_2. The CV (Fig.1a) reveals a large reduction current around 0.32-0.35 V in both negative- and positive-going scans (P_1). The occurrence of the reduction current even in the positive-going scan and a large amount of the charge consumed in the process of P_1, exceeding 70 $mCcm^{-2}$, indicate that the reduction current is due to the reduction of the bulk nitrite ion and not the adsorbed species. In addition, the positive-going scan reveals an oxidation peak around 0.6 V(P_2). In the previous work,[5)] we concluded the formation of NH_3 from NO_2^- from a chemical analysis after a prolonged electrolysis at 0.32 V and the reoxidation of NH_3 at P_2. However, the product of the NH_3 oxidation was unknown. The MSCV(Fig.1b) clearly shows that the oxidation product is N_2 in correspondence with P_2 of CV in the positive-going scan. In any other range of the potential scan, N_2 was not detected. Hence, N_2 cannot be the candidate for the NO_2^- reduction.

Since the present MS is provided with seven channels, other species of m/e=2 (H_2), 16(NH_3), 28(N_2), 30(NO), 44(N_2O), 46(NO_2) and 40(Ar) were examined simultaneously to obtain the information about the reduction and oxidation products of NO_2^-. Results were shown in Fig.2 where the MS currents were recorded against time, 0 to 1000 sec, corresponding to one potential cycle from 0 to 1.0 V and then from 1.0 to 0 V with a sweep rate of 2 mVs^{-1}. Mass signal due to H_2 is clearly noticed around 0 mV, showing the hydrogen evolution. Mass signal of Ar shows a depression at ca. 0.6 V in the positive-going scan. This depression is due to the dilution of Ar in the sampling gas by the N_2 formation. Mass signals of m/e = 15 (not shown in Fig.2) and 16, corresponding to NH_3 did not change in the entire potential range studied in both positive- and nagative-going scans. The absence of the signal change will be discussed shortly after. None of other possible products of N_2O, NO, and NO_2 were detected as shown at the bottom of Fig.2 with an enlarged scale of the MS current. Thus, N_2O and NO are excluded from the reduction products and NO_2 from the oxidation product, respectively.

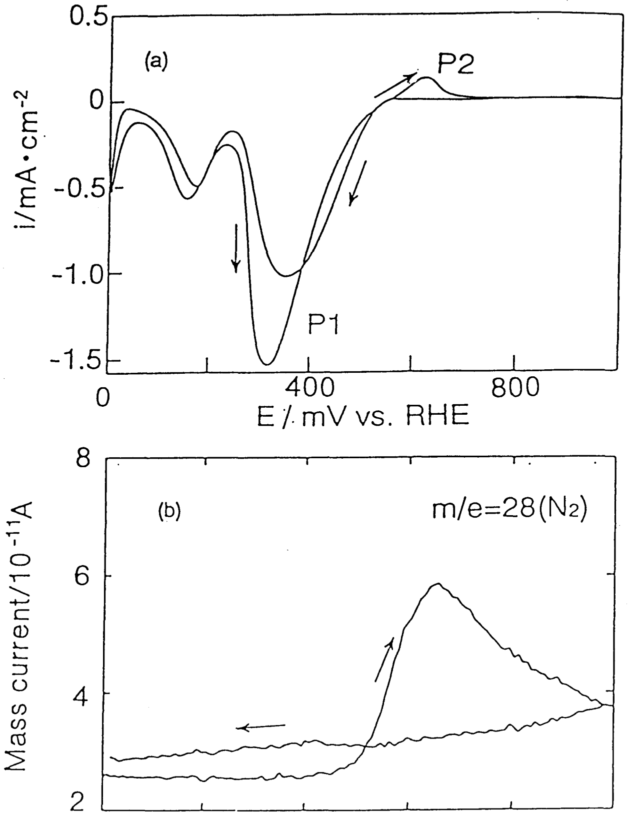

Fig.1. Cyclic voltammogram (a) and corresponding Mass current of N_2 (b) at Pt(100) in 0.2M Na_3PO_4 + 2 mM NO_2^-. Sweep rate, 2 mVs^{-1}.

In our previous study,[5)] we concluded the formation of NH_3 in P_1 and expected in the present study an appearance of the Mass signal of NH_3, since the solution is alkaline (pH=13) enough for ammonia to be present in a molecular form (pKa of NH_3 = 9.23). No appearance of the

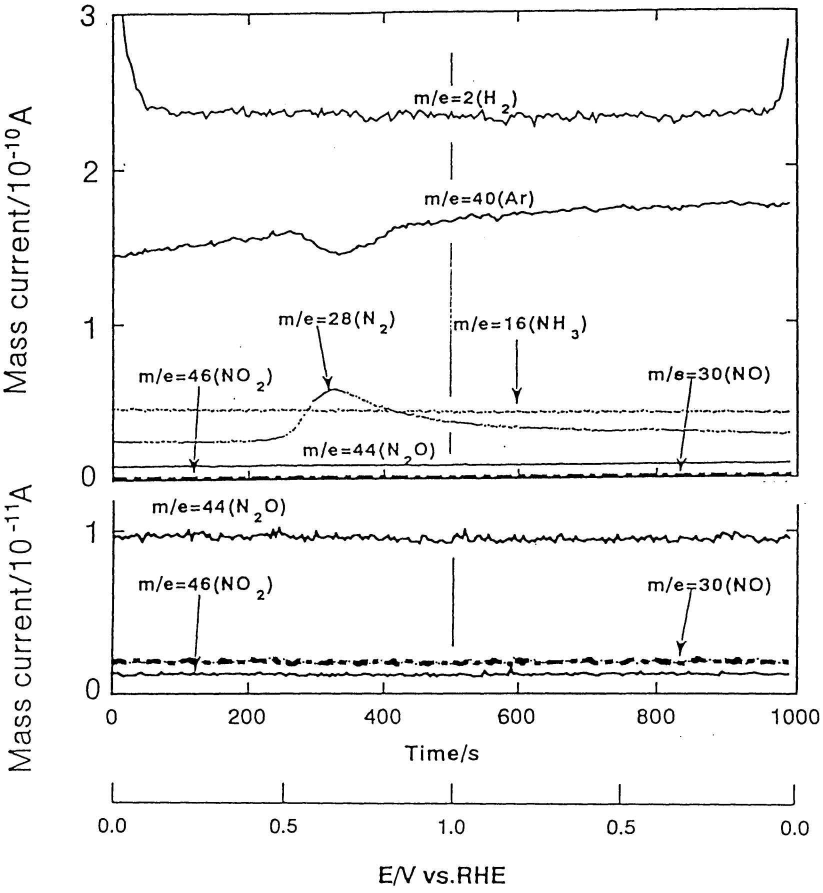

Fig.2. Mass currents vs. potential observed simultaneously with CV on Pt(100) in 0.2 M Na_3PO_4 + 2 mM NO_2^-. Sweep rate, 2 mVs^{-1}.

NH_3 signal must be attributed to its large solubility (ca. 500 in the volume ratio in 1 M NaOH) and hence its stability in aqueous solution.

Then, an amount of 5 mM NH_3 was intentionally added to the blank solution of 0.2M Na_3PO_4 to examine the effects of NH_3 on CV and MSCV. In this case, NO_2^- is absent in the solution. Results are shown in Fig.3. The CV reveals the clear oxidation peak in agreement with P_2 of Fig. 1a in the positive-going scan and no other peaks. The MSCV responds accordingly and shows the N_2 signal in the positive-going scan.

The comparison of Figs.1 and 3 confirms that in the positive-going scan, NO_2^- is reduced to NH_3 in P_1 and then the product of NH_3 is oxidized to N_2 in P_2.

$$P_1: NO_2^- + 5H_2O + 6e^- \rightarrow NH_3 + 7OH^-$$

$$P_2: NH_3 + 3OH^- \rightarrow 1/2N_2 + 3H_2O + 3e^-$$

The above reaction scheme will expect a ratio of 2:1 for P_1:P_2 in the peak size from the difference in the number of electrons concerned. However, as seen from Fig.1a, P_2 appears much smaller than P_1. The product of NH_3 will be taken to dissolve and diffuse away into the solution. In 5 mM NH_3 solution, P_2 (Fig.3a) appears much larger than P_2 in 2 mM NO_2^- solution (Fig.1a). However, the corresponding MS signal in 5 mM NH_3 (Fig 3b) is much smaller (ca. a fourth) than in 2 mM NO_2^- (Fig.1b). The smaller MS signal in 5 mM NH_3 will be explained as follows. The P_1 area of Fig.1a gives ca. 70 mC cm^{-2} (positive-going scan) which corresponds to ca. 120 mM NH_3 by assuming 10 μm thickness for the thin solution layer between the electrode surface and the sampling tip. This concentration is much higher (ca. 40 times) than 5 mM NH_3 and then will give rise to a larger N_2 Mass signal. However, it must be mentioned that the effective concentration will be not so much high because of the diffusion of NH_3 into the bulk solution.

The results obtained at a sweep rate of 10 mVs^{-1} reproduce the above results and are not presented.

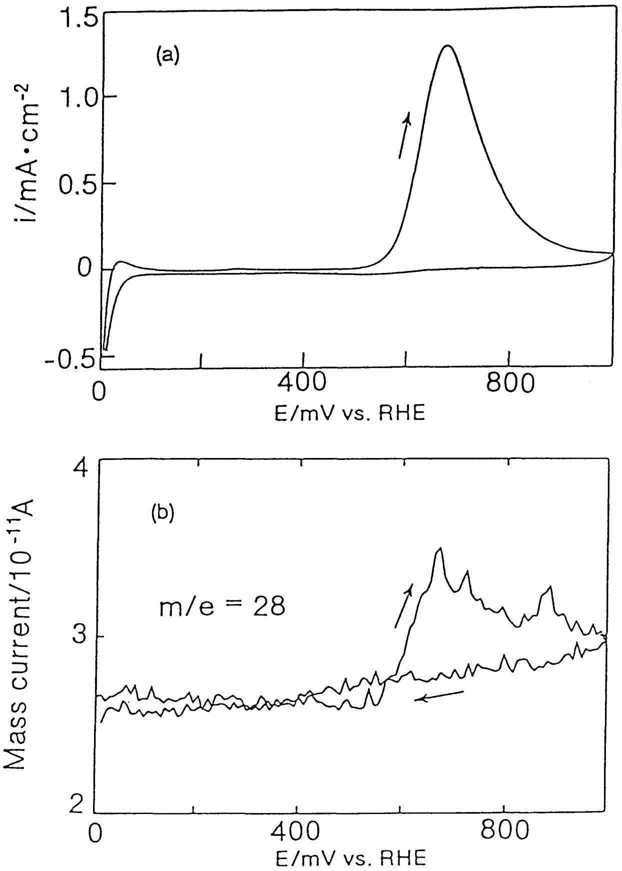

Fig.3. Cyclic voltammogram (a) and corresponding Mass current of N_2 (b) at Pt(100) in 0.2M Na_3PO_4 + 5 mM NH_3. Sweep rate, 2 mVs^{-1}.

In summary, the present study confirms the previous conclusion for the electrochemical behavior of NO_2^- on Pt(100) in alkaline solution. To be stressed is that the present DEMS provides an useful method to obtain the in-situ information about reaction products of small quantity in real-time together with CV. This method eliminates complex and time-consuming procedures required for the usual, chemical detection of products.

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