

# Synthesis of Ammonia through Direct Chemical Reactions between an Atmospheric Nitrogen Plasma Jet and a Liquid

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Fundamental chemical reactions between an atmospheric nitrogen plasma jet and water or a water/ethanol solution have been investigated. When the nitrogen plasma jet was injected directly into pure water, active nitrogen species produced nitric acid and ammonia through fatal reactions with H<sub>2</sub>O. The interaction between nitrogen plasma and a liquid mixture of pure water and ethanol produced NH<sub>4</sub><sup>+</sup> ions effectively. These experimental results clearly show that the active nitrogen species in the pulsed-discharge atmospheric plasma can interact strongly with materials in solution to extract oxygen or hydrogen from them and add atomic nitrogen to them.

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Although ammonia (NH<sub>3</sub>) is currently synthesized from nitrogen (N<sub>2</sub>) and hydrogen (H<sub>2</sub>) at high temperature (500°C) and high pressure (above 200 atm) with iron catalysts, a biological nitrogen-fixation system can operate under mild conditions [1–4]. A few research groups reported nonbiological catalytic reduction of nitrogen to ammonia at ambient temperature and pressure with catalysts including metal centers [5–9]. On the other hand, some studies have reported the production of NH<sub>3</sub> from nitrogen and hydrogen using non-equilibrium plasmas at low pressure [10–14], or atmospheric pressure [15, 16]. Active nitrogen species in plasmas such as N, N<sub>2</sub><sup>+</sup> and N<sub>2</sub><sup>\*</sup> play an important role in ammonia synthesis in which no catalysis is necessary. We recently confirmed that high-density atomic nitrogen can be produced using an atmospheric nitrogen plasma jet pumped by the pulsed-discharge [17]. In pulsed-discharge plasmas, the active nitrogen species can be easily produced, although the energy required to excite them is relatively high in gaseous species.

Many chemical materials have been compounded through chemical reactions in the liquid phase. However, some chemical materials require the introduction of atomic nitrogen to obtain useful functions. In the present study, direct interactions between atmospheric nitrogen plasmas and solutions were systematically investigated. We achieved the non-catalytic reduction of nitrogen to ammonia through the interactions between an atmospheric nitrogen plasma jet and liquid water with or without ethanol.

Figure 1 shows a schematic diagram of the experimental apparatus. The present facility consists of an atmospheric plasma jet, a glass container and a water-cooled

glass tower. The plasma jet device is an atmospheric-pressure plasma jet source (Plasmatreat Openair PFW10). The repetition rate of the discharge is 16 kHz. The working gas of the plasma jet was nitrogen, and the mass flow rate was set to 30 L/min. The input power was 300 W. The glass container is made of Pyrex glass. One hundred milliliters of deionized water or a solution was placed in the glass container. The top of the plasma jet nozzle was set at the same position as the water's surface. The nitrogen gas was allowed to flow for 1 min to purge residual air from the container, and then the plasma jet discharge was started. The pH value of the water was measured using a pH meter (Horiba Ltd. F-22) after each operation.

As the first step, the interactions between nitrogen

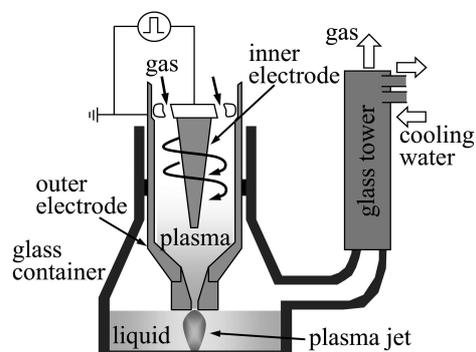


Fig. 1 Schematic diagram of experimental apparatus. Facility consists of an atmospheric plasma jet, a glass container and a water-cooled glass tower. Water or solution was placed in the glass container. The top of plasma jet nozzle was set at the same position as the water's surface.

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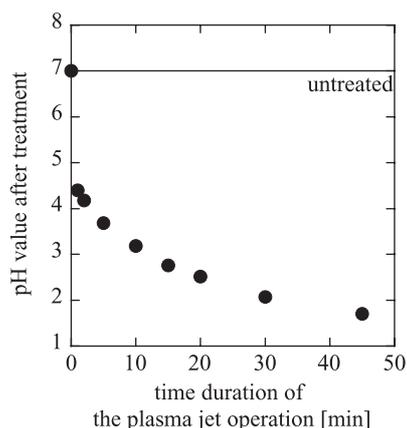


Fig. 2 Dependence of pH value after treatment on treatment time.

plasma and pure water were investigated. The atmospheric nitrogen plasma jet was injected directly into the deionized water. The treatment time was varied from 1 min to 45 min, and the pH value was measured after each treatment.

The dependence of the pH value on the treatment time is shown in Fig. 2. The pH value decreased with increasing treatment time and was not saturated at the longest duration of plasma jet operation. After 5 min of operation, the quantity of water decreased from 100 mL to 91 mL, and the pH value reached 3.7, i.e., the liquid became strongly acidic. The water treated for 5 min was analyzed using ion chromatography. The result is shown in entry (a) of Table 1. This treated water contained  $\text{NO}_3^-$  ions at a high concentration of 0.687 mmol/L. Note that  $\text{NH}_4^+$  ions are also included in the treated water at a concentration of 0.2 mmol/L. These results show that  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were produced through fatal reactions with  $\text{H}_2\text{O}$ .

If the water contains appropriate materials, including reactive hydrogen atoms, the efficiency of  $\text{NH}_3$  production is expected to greatly increase. Ethanol, which has hydrogen atoms in the form of C-H and O-H, is a good candidate for hydrogen carrier. We investigated the interaction between nitrogen plasma and a 20 vol% aqueous ethanol solution (100 mL) consisting of deionized water and ethanol. After 5 min of plasma jet operation, the quantity of the solution decreased to 80 mL. The treated solution is weakly basic, with a pH of 7.45.

The treated solution was also analyzed using ion chromatography. The results are shown in entry (b) of Table 1.

The treated solution contained  $\text{NH}_4^+$  ions at a high concentration of 3.2 mmol/L, which corresponds to an ammonia production rate of 0.064 mmol/min. The present production rate is higher than that observed in Ref. 16 (0.04 mmol/min). Obviously,  $\text{NH}_4^+$  ions have been produced effectively through the interactions between nitrogen plasma and ethanol. This indicates that the active nitrogen species have reacted with hydrogen in ethanol to synthesize  $\text{NH}_4^+$ . The production rate of ammonia tends to increase with increasing of ethanol concentration and saturates with a concentrated aqueous ethanol solution. On the other hand, the concentration of  $\text{NO}_3^-$  ions was only 0.008 mmol/L. The treated solution also contained  $\text{NO}_2^-$  ions at a low concentration of 0.11 mmol/L.

To double-check the presence of  $\text{NH}_3$  in the treated solution, we analyzed the solution using  $^{15}\text{N}$  NMR spectroscopy (JEOL, JNM-ECA500, 50 MHz) method. Because  $\text{NH}_3$  is volatile, the solution was reacted with 2 mol/L hydrochloric acid. If  $\text{NH}_3$  is present in the solution, we can obtain  $\text{NH}_4\text{Cl}$ , which is hard to volatilize. The solution was evaporated to obtain a solid sample. The remaining materials were dissolved into dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ) for  $^{15}\text{N}$  NMR analysis. The  $^{15}\text{N}$  NMR spectrum of this sample solution is shown in Fig. 3(a). Two signals appear at 22.4 ppm and 245.4 ppm in the  $^{15}\text{N}$  NMR spectrum. Figure 3(c) shows the  $^{15}\text{N}$  NMR spectrum of formamide in DMSO- $d_6$  as the standard of the abscissa, the position of which corresponds to 108.0 ppm. Figure 3(b) shows the  $^{15}\text{N}$  NMR spectrum of commercially available  $\text{NH}_4\text{Cl}$  in DMSO- $d_6$ , which includes the signal at 24.5 ppm. The position of this signal agrees well with that at 22.4 ppm for the treated solution. The signal at 245.4 ppm could not be assigned.

The reason why the chemical reaction of nitrogen plasma with pure water differs from that with aqueous ethanol solution is the following. For pure water, both the oxidation and reduction of nitrogen are caused by the reaction of active nitrogen species (e.g. atomic nitrogen and excited molecular nitrogen) with  $\text{H}_2\text{O}$  and  $\bullet\text{OH}$ .  $\text{NO}_3^-$  is generated through progress of oxidation of nitrogen and  $\text{NH}_4^+$  is produced by progress of reduction of nitrogen. The quantities of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  produced are of the same order (Table 1). These results show that the oxidation and reduction of nitrogen occur equally in pure water. In contrast, in the aqueous ethanol solution, the presence of ethanol as a hydrogen donor makes the reduction of nitrogen a more facile reaction than its oxidation [18]. The

Table 1 Results of ion chromatography analysis of treated solutions.

Solutions	$\text{NH}_4^+$ [mmol/L]	$\text{NO}_2^-$ [mmol/L]	$\text{NO}_3^-$ [mmol/L]
(a) Water	0.2	0.00	0.687
(b) 20 vol% aqueous ethanol solution	3.2	0.11	0.008

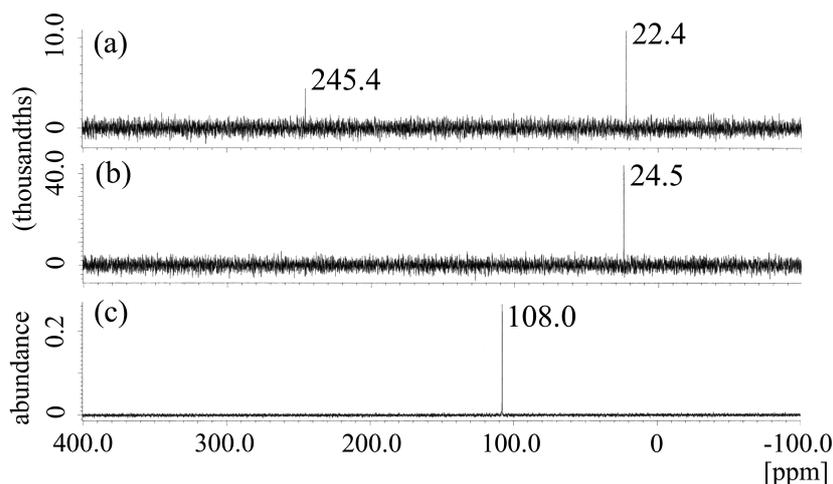


Fig. 3  $^{15}\text{N}$  NMR spectra (DMSO- $d_6$ ) of (a) treated solution, (b) commercially available  $\text{NH}_4\text{Cl}$ , and (c)  $\text{HCONH}_2$ .

abstraction of hydrogen from the carbon atom bonded to the hydroxyl group of ethanol is easy as compared with the abstraction of water. Therefore,  $\text{NH}_4^+$  is produced in larger quantities than in pure water, and the oxidation of nitrogen is suppressed by the progression of the reductive reaction. We also confirmed this trend in other aqueous alcohol solutions (methanol and isopropyl alcohol).

We have investigated fundamental chemical reactions between an atmospheric nitrogen plasma jet and water or a water/ethanol solution. When the nitrogen plasma jet was injected directly into pure water, the active nitrogen species produced nitric acid and ammonia through fatal reactions with  $\text{H}_2\text{O}$ . The interaction between nitrogen plasma and a liquid mixture of pure water and ethanol produced  $\text{NH}_4^+$  ions effectively. These experimental results clearly show that the active nitrogen species in a pulsed-discharge atmospheric plasma can interact strongly with materials in solution to extract oxygen or hydrogen from them and add atomic nitrogen to them. In many cases, the reactions of organic compounds, such as the chemical conversion of functional groups, are usually conducted in solution. Therefore, the method described in this paper is expected to be highly useful for applications to organic reactions.

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