Nitrogen Fixation through the Plasma/Liquid Interfacial Reaction with Controlled Conditions of Each Phase as the Reaction Locus

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ABSTRACT

In the plasma/liquid (P/L) interfacial reaction, nitrogen fixation is performed on a water phase surface. In the P/L reaction, discharged nitrogen gas reacts with water molecules at the interface between the plasma gas phase and the water phase, followed by either a reduction reaction, ammonia production or oxidation reaction, nitric acid production. The production of nitric acid in the P/L reaction is influenced by the concentration of oxygen present in each gas phase and water phase, and the atomic nitrogen contained in the nitrogen plasma. For the reduction reaction at the P/L reaction locus, the water phase was modulated in order to make ammonia production dominant in nitrogen fixation. Ammonia is released into the gas phase under conditions of high water temperature and high pH. To obtain only ammonia using this reaction, it is necessary to incorporate a process for raising the temperature of the water. In the P/L reaction, only the ammonia gas can be obtained in one-step by using the rise in water temperature due to the discharged heat plasma gas. A reaction system was developed to control the water and the gas phase to enable high purity ammonia trapping as released by the gas phase.

Keywords : Ammonia, P/L Reaction, Activated Nitrogen Species

1. Introduction

Nitrogen fixation technology is important in many fields of industry, such as agriculture. The current task of nitrogen fixation technology is to reduce energy consumption and CO2 emissions. One method to do this is the on-site production of nitrogen fixation technology. Currently, nitrogen fixation is being studied in the fields of catalyst development, electrolytic synthesis, and discharge technology in order to perform on-site production with low energy consumption.

The P/L reaction requires only air, or nitrogen and water as raw materials and can perform nitrogen fixation via a one-step reaction at ambient temperature and normal pressure. It is expected that the P/L reaction can perform nitrogen fixation production on-site, since water that can be procured on the spot, without hydrogen production. The reaction field of the P/L reaction is a gas-liquid interface composed of the plasma gas phase and water phase. The outermost surface of the water phase is important for this reaction system. The P/L reaction performs a reduction reaction to generate ammonia, as the activated nitrogen species is important in the nitrogen plasma gas react with the hydrogen (H) of the water molecules. Additionally, the activated nitrogen species can react with oxygen (O) of the water molecule, inducing an oxidation reaction that produces nitric acid. Controlling the reduction and oxidation reaction pathways in the P/L reaction can be an industrially important new chemical process. Important factors to control the balance between the reduction and oxidation reaction, are the condition of the water phase and the state of activated nitrogen species in plasma gas generated by discharge. There are different species of activated nitrogen in the discharged nitrogen plasma including, atomic nitrogen (Natom), excited nitrogen molecule (N2), and nitrogen molecular ion (N2+). Each activated nitrogen species has a different lifetime and reactivity. Previous studies have suggested that by modulating activated nitrogen species in the gas phase the oxidation and reduction reaction pathways can be controlled. From our results under conditions of high Natom concentrations, Natom performed both oxidation reaction and reduction reactions due to the high reactivity. In this study, we constructed a system that increases the selectivity of ammonia production under conditions of numerous Natom. In order to obtain the high selectivity of ammonia, the one approach is to suppress nitric acid produced in the water phase. Active species of water molecules such as HO· and H· are generated through the activated nitrogen species reacts with water. Therefore, electron spin resonance (ESR) measurements were used to detect these active species of water molecules and clarify the reaction pathway of nitric acid. As a second approach to increase ammonia selectivity, we investigated the relationship between the pH of the water phase and the type of nitrogen compounds produced by the P/L reaction. It is well known that the ammonia stripping method, as a chemical engineering process, utilizes the pH change of the water phase. This is an effective method in which only ammonia is selectively released from the liquid into the gas phase, whereby a high-temperature vapor is brought into contact with a liquid containing a high concentration of ammonia. From the formula, NH4+ + OH− → H2O + NH3, it is important that the liquid is alkaline and that the water temperature is high. In the P/L reaction, the gas temperature is high due to the discharge, and the water temperature rises when the gas and water phase come into contact with each other. Therefore, the P/L reaction does not require temperature control of the water. It is expected that the P/L reaction can be tuned to recover only ammonia by only modulating the pH of the water phase. In this study, we propose a new on-site technology in which nitrogen fixation can be controlled freely by modulating...
the condition of the water phase according to the activated nitrogen species.

2. Experimental

2.1 Plasma/liquid interfacial reaction

P/L reaction consists of the plasma gas and water phase (Fig. 1a). The plasma gas phase was generated by discharge. The discharger used dielectric barrier discharge (DBD) (Fig. 1b). An AC voltage (5 kV, 20 kHz) was applied to a discharger through which high-purity nitrogen gas flowed to form a nitrogen plasma gas. N$_{atom}$, N$_2^*$ and N$_2^+$ were confirmed in a plasma emission spectrum (Fig. 2). The previous report have successfully determined N$_{atom}$ by vacuum ultraviolet (VUV) absorption at the wavelength of 120 nm.15 P/L reaction was performed under the condition that the density of N$_{atom}$ was enough. Nitrogen compounds produced by P/L reaction were measured by ion chromatography (SHIMADZU Co., HIC-NS). A Shim-pack IC-C4 column (SHIMADZU) was used for NH$_4^+$ detection and a Shim-pack IC-SA3 column (SHIMADZU) for NO$_2^-$ and NO$_3^-$ detection. The concentration of the produced ammonia in the pH adjustment water phase was determined by the indophenol blue method.

2.2 ESR measurements

H· and HO· produced by the P/L reaction were detected by the spin trap method. 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 0.2 M) was used as a radical scavenger. The magnetic field range for the measurement was 337 ± 10 mT. Measurements were performed with a time constant of 0.1 s and a modulation width of 0.2 mT. The distance between the outermost surface of the water phase and the discharge locus set at 40 mm. The P/L reaction was performed and then the water phase after the reaction was measured by ESR.

2.3 Altering the pH of the water phase

The pH change of the water phase was modulated with 1 M HCl and 1 M NaOH. Experiments were performed in a glove box under an anaerobic atmosphere (oxygen concentration 50–100 ppm, Fig. 1c). High purity nitrogen gas was introduced into the discharger, and the gas outlet of the discharger was set 10 mm above the water surface in the vertical direction. The distance between the discharge locus and the water surface was unified at 40 mm. A comparison was made under two conditions: 3 ml of ultrapure water (specific electrical resistance of deionized water ≥ 18.2 MΩ·cm$^{-1}$) in a petri dish made of PTFE with a diameter of 30 mm and 30 ml of ultrapure water in a petri dish made of PTFE with a diameter of 90 mm. The reaction time was 5 minutes.

2.4 Construction of the trap cell system for P/L reaction

The reactor cell and trap cell are connected by a 100 mm flow path (Fig. 1d). The gas outlet of the discharger was set inside the water phase in the reactor cell. For the convenience of measurement conditions, the distance between the gas outlet and the discharge locus was set at 60 mm. The P/L reaction time was 5 minutes. The experiment was performed with the reactor cell set to 10 ml of water and trap cell set to 20 ml of water. The solution in the reactor cell was 1 mM NaOH and the solution in the trap cell was 1 mM H$_2$SO$_4$. For comparison experiments, ultrapure water was used both the reactor cell and trap cell.

Figure 1. (a) Schematic illustration of P/L interfacial reaction. (b) Schematic illustration of the P/L reaction under atmospheric and anaerobic conditions. ESR measurement analysis of the radicals in the water phase produced by P/L reaction under atmospheric and anaerobic conditions. The P/L reaction due to pH change in the water phase was measured under anaerobic conditions. (c) Illustration of the reaction P/L reaction system with a trap cell.

Figure 2. N$_2$ plasma emission spectrum.
3. Results and Discussion

3.1 The relation between oxygen in the gas phase and P/L reaction

In order to confirm the influence of oxygen in the gas phase on the P/L reaction, the reaction was conducted under atmospheric and anaerobic (50–100 ppm) conditions (Fig. 1c). Figure 3 shows the nitrogen compounds produced when the P/L reaction was performed under both atmospheric and anaerobic conditions. Production amount of nitrogen compounds were the same regardless of the oxygen concentration in the gas phase. On the other hand, the production of NO₂⁻ and NO₃⁻ increased depending on the oxygen concentration in the gas phase (Fig. 3a). This suggested that oxygen and activated nitrogen species reacted in the gas phase. Natom reacted with oxygen (N· + O₂ → NO· + O·).¹⁸ There is also a reaction by which a by-product is generated by the reaction of Natom and oxygen (N₂ + O· → NO· + N⁻). The presence of oxygen in the gas phase results in an increased pathway for nitrate formation.

3.2 Increase in HO· by oxygen in the gas phase

After the P/L reaction under the same conditions, as in Fig. 1c, the H· and HO· signals content of the water phase was measured by ESR. Figure 4 shows a typical ESR signal obtained when plasma gas reacts with water. The HO· signal tended to increase as the oxygen concentration in the gas phase increased, suggesting that the production of HO· in the water phase is affected by the oxygen concentration in the gas phase. The increase in HO· may also increase the pathway of nitrate formation in the water phase. It is an oxidation reaction pathway in which Natom reacts with HO· (Natom + HO· → NOH). It was shown that the presence of oxygen in the gas phase promoted a pathway that could produce NO₃⁻ and NO₂⁻ in the water phase (Fig. 3a). Therefore, it is important to suppress oxygen in the gas phase since oxygen in the gas phase increases HO· production in the water phase.

3.3 Change in the P/L reaction due to the pH of the water phase

Here, we examine the control of the oxidation and reduction reaction pathway of the P/L reaction by changing the water phase conditions. These experiments were performed by changing the volume and the pH of the water phase. Figure 5a shows the nitrogen

Figure 3. Nitrogen compounds produced by the P/L reaction under (a) atmospheric and (b) anaerobic conditions.

Figure 4. ESR measurement of P/L reaction under atmospheric (green) and anaerobic (blue) conditions.

Figure 5. Relationship between nitrogen compounds produced by the P/L reaction when the water phase volume and pH of the water phase were changed. (a) water volume 3 ml, petri dish diameter 30 mm, and (b) water volume 30 ml, petri dish diameter 90 mm.
compounds produced by the P/L reaction with a water volume of 3 ml and changing pH. The amount of ammonia produced was clearly reduced under alkaline conditions. When the water volume was increased to 30 ml, the decrease in ammonia under alkaline conditions was suppressed (Fig. 5b). From this result, it is clear that ammonia evaporates into the gas phase more when smaller volumes of water are used. When low water volumes are used, the water temperature rises more due contact with the plasma gas, heated by the discharge. Ammonia easily dissolves in water when the water temperature is low, and as a result, ammonia is produced in the water phase when the water temperature is low, due to a high volume of water. The rise in water temperature was suppressed, which then suppressed the evaporation of ammonia. Furthermore, due to the higher pH and equilibrium relationship (NH₂⁺ + OH⁻ → H₂O + NH₃), the nitrogen is likely released into the gas phase as NH₃. Therefore, an effective method of recovering ammonia gas is to make the water phase alkaline and actively evaporate ammonia by the heat of discharged gas.

The relationship of pH to NO₂⁻ and NO₃⁻ showed a tendency for NO₃⁻ to increase under the acidic conditions.

3.4 Selective production of ammonia

Nitrogen compounds produced by the P/L reaction are released into the gas phase. A system was constructed to trap nitrogen compounds released into the gas phase (Fig. 1d). From the results shown in Figs. 3 and 4, it is necessary to suppress oxygen in the gas phase in order to suppress nitrate in the water phase. Therefore, the gas outlet of the discharger was placed into the water. Figure 6 shows detected nitrogen compounds in the reactor cell and trap cell. When both the reactor cell and the trap cell were ultrapure water, ammonia was present in both cells (Fig. 6a). The ammonia produced on the reactor cell side was released as ammonia gas. Therefore, ammonia presence was confirmed even in the trap cell. Alternatively, it is possible that activated nitrogen species, with a long-lifetime, reached the trap cell and that long-lived activated nitrogen species reacted with the water in the trap cell. On the other hand, NO₂⁻ and NO₃⁻ were hardly present in the water phase of the trap cell, and are less than 1/50 of the amount of ammonia production. Of the activated nitrogen species that reached the trap cell, the amount of N₃⁻ was very low. Therefore, the reaction of N₃⁻ + H₂O → NH + HO⁻ does not proceed in the trap cell. Since the amount of HO⁻ was low, it is likely that nitrate production was suppressed in the trap cell. Based on the results from the pH experiments (Fig. 5), alkaline conditions were used for the reactor cell, ensuring that nitrogen compounds were released into the gas phase and that these nitrogen compounds were trapped with an acidic aqueous solution (Fig. 6b). NO₂⁻ and NO₃⁻ were not measured due to the limitations of the technique in the pH range used for the trap cell. Compared to Fig. 6a, Fig. 6b detected more ammonia in the trap cell. This suggests that the ammonia concentration can be increased in the trap cell side by using the discharged gas heat to raise the temperature of the water phase and by changing the pH of the water phase.

4. Conclusions

To selectively control the oxidation and reduction reaction pathways in the P/L reaction, both the water phase and plasma gas phase were modulated. N₃⁻ in the nitrogen plasma gas is a highly reactive activated species. A reaction between N₃⁻ and oxygen increased nitrate in the water phase when oxygen was present in the gas phase. One way to increase the selectivity of ammonia in the water phase is to decrease the oxidation reaction (NO₂⁻ and NO₃⁻ generation) by suppressing oxygen in the gas phase. Another effective way of increasing ammonia selectivity is by controlling the water phase conditions. The temperature of the water can be increased through contact with the plasma gas so that only ammonia can be released into the gas phase under the high water phase pH. We have shown that it is possible to separate nitrogen compounds in one-step by controlling the water phase conditions in the P/L reaction.

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