Spectroscopic Measurement of Radical in Non-equilibrium Plasma

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Abstract

The concentration of atomic N radical, produced by non-equilibrium discharge, at atmospheric pressure, was measured. Probe technique was combined with resonance absorption spectroscopy (RAS)[1] to acquire suitable absorbance. Loss of N radical in the probe was estimated theoretically. The results showed that this technique is available for the measurement of N radical concentration range up to about 100 ppm at room temperature and atmospheric pressure.

1. Introduction

Non-equilibrium atmospheric discharge is now expected as an effective technique for the pollution control. Various discharge methods have been developed to various gas contents, and gas phase reactions were estimated with the final products. Some of them are now applied to industries.

Fig. 1 Plate type SPCP

Surface induced plasma chemical process (SPCP)[2] is a kind of surface discharge. It consists of film isolator, a plate electrode and wire electrodes. Alumina plate as isolator puts between these electrodes. An example of plate type SPCP is shown in Fig. 1. A small pulsed plasma is produced over the surface of the wire electrode side. This system already has been applied to ozone production system and energy efficiency of about 40% is achieved[3]. SPCP has been also applied to NOx reduction[4,5] and fluorocarbon decomposition[6] in research works. However, there still remains the big problem of energy efficiency to produce the active species by discharge. Significant improvement of energy efficiency is required for the breakthrough of
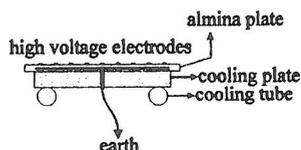
this technology.

Researches and developments in this category have been carried out mainly from the view point of electrical side. Studies from chemical point of view have not been done so much. It is because of difficulties of the measurements of active species in atmospheric pressure plasma.

Our previous works[5] have indicated that N radical plays an important role in NOx reduction. In this works, we tried to measure the concentration of N radical in atmospheric pressure N_2 by RAS in order to obtain the basic knowledge on the improvement of the energy efficiency. The probe technique which was combined with RAS was used to obtain the distribution of N radical into the SPCP reactor.

2. Experimental apparatus

Measurement system consisted of a probe, an absorption cell,, a resonance lamp, a detector, a needle valve and a vacuum pump (Fig. 2).

The sampling probe consisted of a stainless tube combined with a polymer tube. The stainless tube was 60 mm in length and 0.25 mm in inner diameter. Polymer tube was 10 mm in length and 0.25 mm in inner diameter. The tubes were combined with thermosetting resin film so that the polymer side came to plasma area.

Fig. 2 Scheme of absorption part of measurement system

Through the probe, discharge gas was introduced into pressure-reduced absorption cell by pressure difference. The pressure in absorption cell was controlled with the needle valve and monitored with a semiconductor pressure gauge. The resonance light which transmitted through the absorption cell was formed by microwave plasma (1% N_2 in He; total pressure was between 3 and 5 Torr). The spaces of microwave plasma, absorption cell and the monochrometer were separated by MgF_2 windows. Distance between
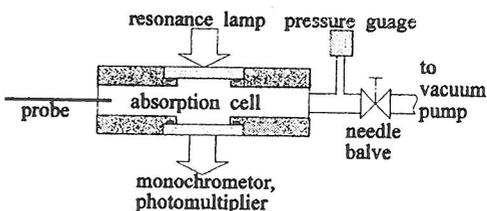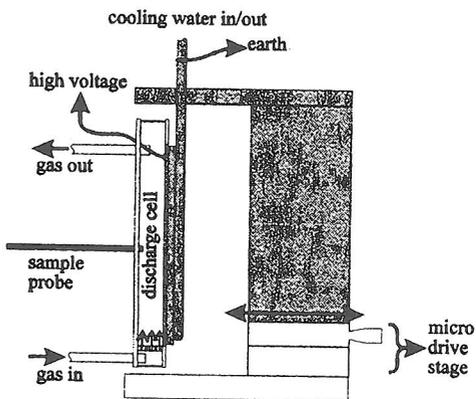
Fig. 3 Scheme of discharge cell stage

two MgF$_2$ windows, which was optical path length of absorption, was 23 mm.

Discharge system consisted of a discharge cell stage and a power supply. Discharge cell stage is shown in Fig. 3. Discharge cell, where the discharge plasma was formed by SPCP, was movable to the probe by using micro drive stage. The discharge cell consisted of SPCP plate and polymer-coated pasteboard, both 80 mm in width, and 160 mm in height. The distance between the SPCP plate and the polymer-coated panel was 20 mm.

N$_2$ gas was introduced into the bottom of the discharge cell, though honeycomb block made of Teflon. Then N$_2$ gas flowed throughout the discharge cell and exited from the upper part. From the center of polymer-coated pasteboard, probe was inserted into the discharge cell vertically toward the SPCP plate.

In all experiments, 99.9999% qualified pure N$_2$ and He (Nihhon-Sanso, S class gas) were used.

Using this system, N radical distributions over the plate type SPCP were measured. The effect of discharge voltage, discharge gas flow rate and distance between SPCP plate and measurement position on the N radical concentration were investigated.

3. Results and Discussions

3.1. Correlation between absorbance and concentration

We calculated the loss ratio of N radical in the probe under the following assumptions:

1. Pressure gradient in probe was estimated on Newton's law.

2. N radical recombination both in gas phase and on wall surface were taken into consideration.

3. N radical recombination in gas phase was regarded as three bodies reaction proceeds as:

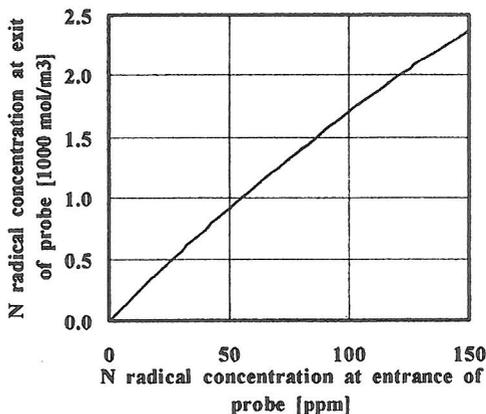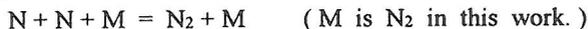$$N + N + M = N_2 + M \quad (M \text{ is } N_2 \text{ in this work. })$$

Fig. 4 Calculated correlation between concentrations of entrance of the probe and of exit of probe

Probe is 70 mm in length, 0.25 mm of inner diameter.

Pressure in absorption cell is 100 Torr.

4. Rate of N radical recombination on the wall was determined by N radical's diffusion to the surface of the wall.

We used 5.5×15 [$cm^6 mol^{-2} s^{-1}$] [7] as the recombination rate constant of N radical in gas phase, 0.2 [cm^2/s] as N radical diffusion coefficient in N_2 [8] and 18.0 [μPas] as viscosity of N_2. Results of this calculation at the condition, at which experiments in this work was carried out, is shown in Fig. 4.

Judging from Fig. 4, it is clear that correlation of concentrations of N radical at the entrance of probe and at the exit of probe is linear, in the range up to 100 ppm.

In previous works[5], we know that N radical produced from the tube type SPCP is about several 10 ppm. We supposed that plate type SPCP production of N radical is at the same level so that this probe can be used in measurement for N radical distribution over SPCP plate.

3.2. Effect of discharge voltage and gas flow rate

As SPCP's plasma area is very localized only nearby the discharge surface, N radical is also produced very near the surface. As N radical is probably deactivated during the diffusion from the surface, as well as bulk, one needed to know and to control the diffusion process of N radical in order to improve the energy efficiency for the production of N radical. In order to examine the diffusion process of N radical in detail, we selected a plate type SPCP where N radical distribution can be easily measured compared with the tube type SPCP.

With this system, we changed 3 parameters : discharge voltage, gas flow rate and distance between the entrance of probe and SPCP surface. Thus we obtained influences of discharge voltage and gas flow rate, on distribution of N radical over plate type SPCP. Results are shown in Fig. 5 and Fig. 6.

In 3.1., it is indicated that N radical concentration at the exit of the probe is proportional to that at the entrance of the probe. On the other hand, according to Lambert-Beer's law, light transmitting ratio and concentration of absorbent is expressed as :

$$-\log(I / I_0) \propto l \cdot C \qquad (1)$$

In equation (1), I/I_0 is transmittans of resonance light. l is optical pass length. C is concentration of absorption substances. Lambert-Beer's law means that logarithm of transmittans was proportional to the concentration of absorption substances. From equation (1) and result of 3.1., it was indicated

that log(I/I_0) was proportional to the N radical's concentration at the entrance of the probe.

In Fig. 5, concentration of N radical is very high nearby the SPCP plate, and decreases as the distance from the SPCP plate increases at any discharge voltage. Then in the area further than 8 mm from the SPCP plate, concentration gradients become flat. Effect of discharge voltage is positive. It is due to increase of electrons, or electron energy.

Fig. 6 shows effect of gas flow rate. It is clearly observed that increase of flow rate brings about higher concentration near the SPCP plate and steeper concentration gradient. Because the total N radical production is production of the flow rate and the concentration, the effect of flow rate on energy efficiency of N radical production is more than first order. (Change of discharge power was not observed during the experiments in Fig. 6.)

An increase of N radical concentration with an increase of gas flow rate can be explained as follows:

It is easily imaged that increase of flow rate brings about consequently increase of

the concentration in plasma area and electron density. As the result, the production rate of N radical in the plasma area is increased with as increase of flow rate. On the other hand, an increase of N concentration gradient can be easily explained by a dependence of a gas diffusion film as the Reynolds number becomes higher with the flow rate increase.
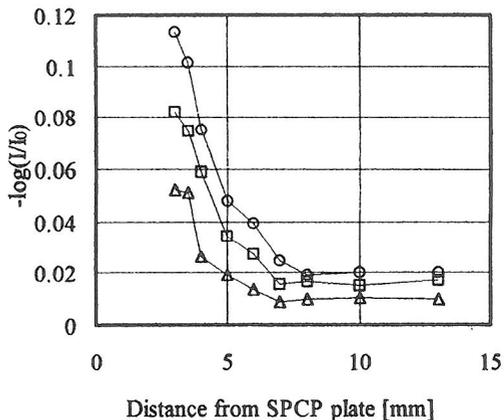
Fig. 5 N radical distribution over SPCP plate
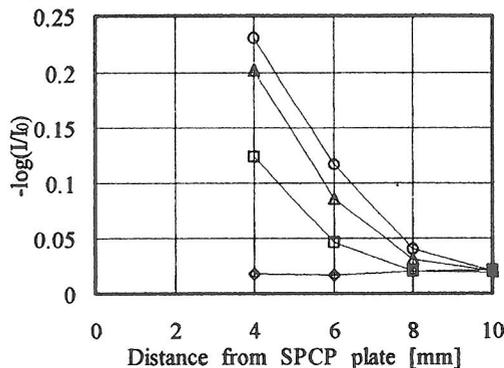Flow rate of discharge gas : 2.35 [Nl/min]

—△— 8kV   —□— 10kV   —○— 12kV

Fig. 6 N radical distribution over SPCP plate
Effect of gas flow rate
Discharge voltage : 10kV

—◇— 2[Nl/min]   —□— 4[Nl/min]
—△— 6[Nl/min]   —○— 8[Nl/min]

4. Conclusion

We developed a probe technique for measurements of very short lifetime substance in order to know N radical production process in high pressure non-equilibrium plasma. The following results were obtained.

1) Very sharp concentration distribution of N radical was observed near the discharge surface.

2) The level of N radical in the whole zone was increased. with an increase of the discharge voltage.

3) The level and gradient of N radical concentration increased with an increase of gas flow rate.

In summary, this study showed that the probe technique combined with the resonance absorption spectroscopy can be applied to measurements of radical in high pressure non-equilibrium plasma field.

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