Two-Dimensional Distribution of Ground-State NO Density by LIF Technique in DC Needle-to-Plate Positive Streamer Coronas During NO Removal Processing

Seiji Kanazawa, *Member, IEEE*, Takeshi Ito, Yasuyuki Shuto, Toshikazu Ohkubo, *Member, IEEE*, Yukiharu Nomoto, *Member, IEEE*, and Jerzy Mizeraczyk

***Abstract*—Two-dimensional distribution of the ground-state NO molecules density was investigated using laser-induced fluorescence (LIF) technique in a dc positive streamer corona reactor (needle-to-plate electrode geometry) during NO removal from a flue gas simulator (NO/air). NO density in the corona discharge reactor was monitored under the steady-state dc corona discharge condition. It was found that NO molecules density decreased due to the corona discharge processing not only in the discharging region but also in the upstream vicinity of the discharge.**

***Index Terms*—DC positive streamer corona, ground-state NO molecule, laser-induced fluorescence, NO removal.**

I. Introduction

CORONA discharge plasma processing for NO_x removal has been studied both numerically using plasma-chemistry models and experimentally (e.g., [1] and [2]). However, there is still a lack of fundamental data to develop the model of the plasma-chemistry processes, which would satisfactorily describe NO_x removal from flue gases. In order to develop the proper model for further numerical simulation, it is important to understand the discharge-induced chemical reactions occurring during NO_x removal in the plasma reactor. The understanding of the processes occurring in the corona discharges is indispensable for improving the efficiency of NO_x removal. However, in most experimental investigations on NO_x removal by the nonthermal plasmas, NO concentration has been measured using conventional NO_x monitors based on chemi-luminescence, infrared absorption, or potentiostatic electrolysis, placed at the outlet of the reactor. Such measurements did not provide information on the concentration and distribution of NO molecules in the reactor and, in particular, in the discharge region. Therefore, they are not very informative with respect to the corresponding plasma-chemistry kinetics in the discharge.

The diagnostic method based on the laser-induced fluorescence (LIF) is very useful for *in-situ* detection of various species, such as radicals and molecules in electrical discharges and plasma devices. The potential of LIF method based on a tunable UV laser for diagnostics of transient discharges has already been proved experimentally by Ershov and Borysow [3], who investigated time transient density of OH radicals in pulsed discharges. Using LIF method, Coogan and Sappey [4] have imaged the distribution of the OH radicals within the silent discharge plasma reactor. Recently, Ono and Oda [5], [6] observed spatial and temporal distribution of OH radicals in various kinds of pulsed discharges, while Hazama *et al.* [7], Roth and Gundersen [8], and Tochikubo and Watanabe [9] have studied the behavior of NO molecules in a pulsed corona discharge by LIF technique. Recently, Fresnet *et al.* [10], also using LIF technique, measured NO concentration after a single-pulse discharge. The results obtained by these authors concerned the NO behavior during the post-discharge time interval in either the single transient discharge or low-repetition pulsed discharges in the electrode arrangement with gaps shorter than 1 cm.

In this paper, results of the LIF measurement of the two-dimensional distribution of the ground-state NO molecules in a steady-state high-repetition (about several kilohertz) dc corona discharge between a 3-cm-gap electrode arrangement (needle-to-plate) are presented.

II. Experimental Apparatus and Methods

The laser-induced fluorescence on the NO $(A^2\Sigma^+(v' = 0) \leftarrow X^2\Pi(v'' = 0))$ transition at 226 nm [11] was chosen for the monitoring of the ground-state NO molecules, which are dominant molecules in NO_x. The schematic diagram of the experimental apparatus is shown in Fig. 1. The laser pulses from an XeF excimer laser (Lambda Physik, COMPex 150, tuned at 351 nm) pumped a dye laser (Lambda Physik, SCANmate) with Coumarin 47 as a dye that generated a laser beam of a wavelength tuned around 450 nm. A BBO crystal (BaB_2O_4) pumped by the tuned dye laser beam produced the second harmonic radiation of a wavelength correspondingly tuned around 226 nm. The 226-nm UV laser beam of energy of 0.8–2

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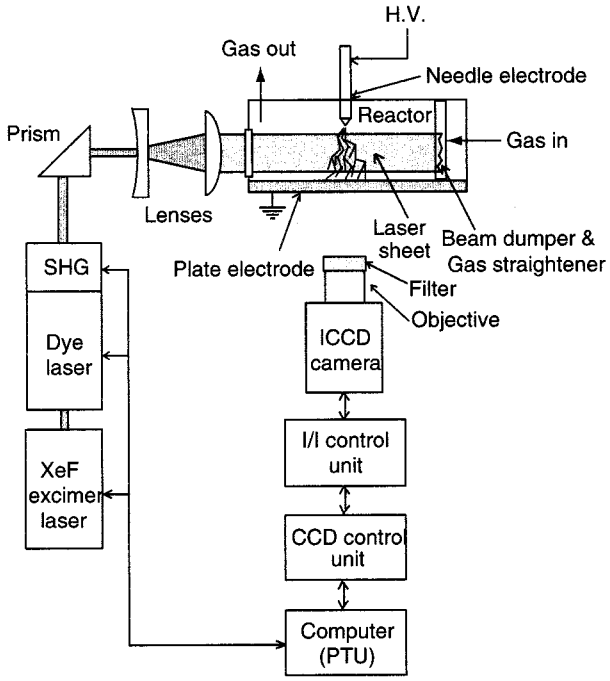

Fig. 1. Schematic diagram of the experimental apparatus.

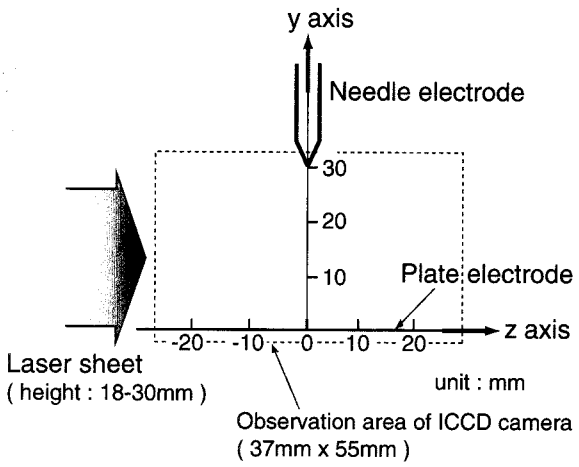

Fig. 2. Cross section of the discharge gap. Observation area of the ICCD camera is indicated by the dashed rectangle.

mJ and duration of about 20 ns was transformed into the form of the so-called laser sheet (width of 1 mm, height of about 30 mm) by lenses. The laser sheet passed between the electrodes in the reactor. The LIF signal emitted at 90° to the laser sheet was imaged onto an intensifier-gated charge-coupled device (ICCD) camera (LaVision, Flame Star II) and two-dimensional distribution of NO molecules density in the discharging area was recorded, and then processed by a computer. The area of the LIF measurement is illustrated in Fig. 2.

The reactor was an acrylic box (100 mm × 125 mm × 700 mm) in which quartz windows were mounted for the transmission of the laser pulses and the LIF signal detection. To minimize the scattered light, the laser pulses were absorbed in beam dumper plates with small holes placed at the rear of the reactor (Fig. 1). A conventional needle electrode was used as the stressed electrode. It was made of a brass rod (6 mm in diameter), the end of which had a tapered profile with the tip of a radius of curvature of 0.5 mm. The grounded electrode was a stainless-steel plate. The distance between the electrodes was 30 mm. DC high voltage with positive polarity was applied through a 10-MΩ resistor to the stressed electrode. In general, corona discharges have several modes depending on the experimental conditions. In this experiment, the streamer coronas were generated and used for NO removal, because the streamer coronas are more effective for NO removal than the glow coronas.

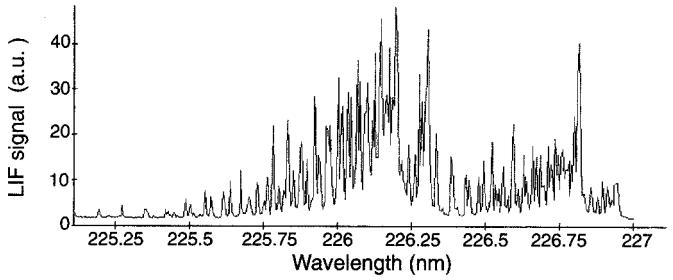

Fig. 3. LIF spectrum of NO molecule without discharge. Operating gas: NO (300 ppm)/air.

NO (200 ppm)/air mixture flowed along the reactor with a flow rate of 1 L/min, which corresponds to an average flow velocity of 2 mm/s. Concentrations of NO and NO_2 molecules at the inlet and outlet of the reactor were measured using an NO_x monitor (Hodakatest, Testo 33). This allowed the calibration of the LIF signal in an absolute unit of NO concentration, i.e., in parts per million. The experiment was carried out at room temperature and atmospheric pressure.

III. Experimental Results and Discussion

A. NO Detection and Calibration of NO LIF Signal

In order to determine the laser wavelength for NO LIF measurement, the laser was scanned through $(A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0))$ transitions in the range of 225–227 nm with a stepwidth of 2.5 pm. The laser line width given by the LIF system manufacturer was about 3 pm. The typical LIF spectrum of NO molecules measured in NO/air without discharge is shown in Fig. 3. In all the further LIF measurements presented in this paper, the laser wavelength related to the strongest peak in the NO LIF spectrum was used in order to obtain an intensive NO LIF signal. The so-called "scan peak finding" routine of the LIF system was repeatedly used to determine precisely the laser wavelength at the peak. In this procedure, the laser was scanned in the vicinity of the objective peak with a stepwidth of 0.5 pm and the wavelength at the peak ($\lambda = 226.198$ nm) was used for NO LIF measurement.

The calibration between NO LIF signal and NO concentration was carried out without discharge, when NO/air mixture with known concentrations of NO molecules flowed through the reactor. Fig. 4 shows the dependence of the NO LIF signal, observed by the laser beam with the wavelength at the strongest peak in the NO LIF, on NO concentration in the NO/air mixture. Typical fluctuation of the signal peak value due to the possible variations of wavelength and intensity of the laser pulse was in the range ±15%. A linear relationship between NO LIF intensity and NO concentration was observed up to NO concen-

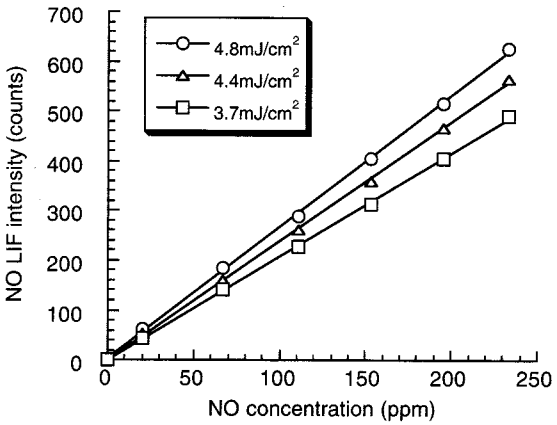

Fig. 4. Calibration curve: NO LIF intensity versus NO concentration. The legend indicates the energy density of the laser sheet pulses.

tration of about 250 ppm. This linear relationship was then used for determining NO concentration in the reactor and expressing it in an absolute unit (parts per million).

B. Interference of the Light Emitted by the Regular and Laser-Induced Streamers With LIF Signal

The dc streamer corona discharge employed in this experiment is a train of streamers occurring almost regularly with a relatively high repetition rate (about 2–7 kHz). The light emitted by the streamers can interfere with the LIF measurements of NO concentration around the discharge zone because the LIF signal is weaker than the discharge emission. In the case of a repetition rate of 5 kHz, for example, the time interval between the regular streamer is 200 μs and the typical streamer duration is about 350 ns, while we confirmed that the LIF signal appeared almost immediately after the laser pulse and lasted for about 30 ns. Therefore, the probability of coincidence of the regular streamer and LIF signal is still low, although the streamer repetition rate in the present dc corona discharge is much higher than in the pulsed coronas used in the previous investigations [7]–[10].

As another possibility of an interference, the LIF measurements can be hindered by streamers induced by the UV laser sheet pulses passing the electrode gap because they appear shortly after the laser pulses and the light emitted by them can overlap the LIF signal. We also confirmed the laser-induced streamers usually started after a time delay (about 35–300 ns after the laser pulse, depending on the position of the laser sheet in the gap) and lasted for about 350 ns [12]. Due to it, no overlapping of the LIF signal and the light emitted by the induced streamer occurred, and separate recording of the LIF signal was possible in the dc corona discharge at an appropriate adjusting of the recording delay and exposure time of the ICCD camera.

C. Two-Dimensional Distribution of NO Molecules

Fig. 5(a)–(c) shows two-dimensional distributions of NO concentration around the electrode gap during dc corona discharge processing of a dry NO (200 ppm)/air mixture at the gas flow rate of 1 L/min. The intensity of the images shown in Fig. 5 corresponds to NO concentration. The dc corona discharge was started after the NO concentration in the reactor reached a steady state. Fig. 5(a) is an image at the start of the discharge ($t = 0$ min.), indicating that the inside of the reactor is uniformly polluted with NO. Fig. 5(b) and (c) shows the images at 2 and 4 min after starting the corona discharge, respectively. They represent the typical images as a time elapsed in the high-repetition (about several kilohertz) dc streamer corona discharge.

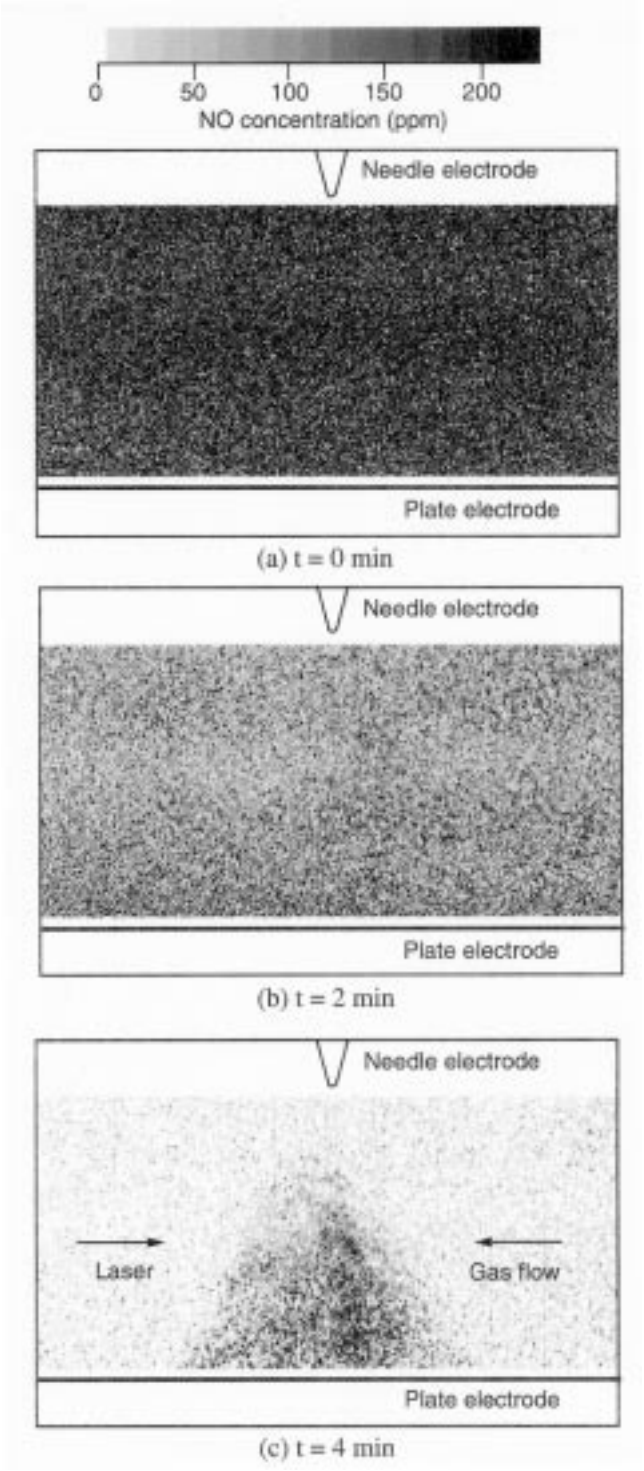

Fig. 5. Operational time evolution of the NO LIF images during the streamer corona discharge. The intensity of the images corresponds to NO concentration. Time $t = 0$ min and $t = 4$ min indicate the start of the discharge and the steady state, respectively. Operating gas: NO (200 ppm)/air,; gas flow rate: 1 L/min; applied voltage: 21 kV.

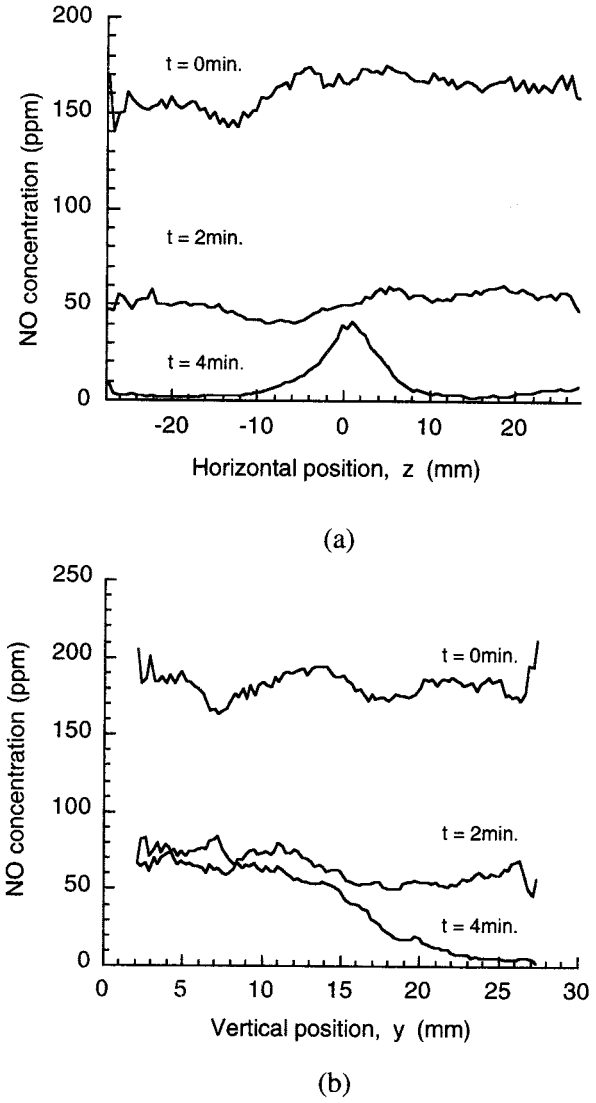

Fig. 6. Spatial NO distribution for various operational times. (a) Horizontal profile (z direction) at $y = 17$ mm. (b) Vertical profile (y direction) at $z = 0$ mm. $y = 0$ and $y = 30$ mm indicate the position of the plate and needle electrodes, respectively (see Fig. 2). Operating gas: NO (200 ppm)/air; gas flow rate: 1 L/min; applied voltage: 21 kV.

This was an essential difference to the previous investigations [7]–[10] in which the LIF monitoring of NO molecules was carried out either after the single transient discharge or between two discharge pulses with a relatively long interval between them (low-repetition pulsed discharges, e.g., 10 Hz). The discharge volume was approximately a cone with a base radius of 15 mm. The NO LIF signal became weaker compared to that before the discharge. This indicated a decrease of NO concentration, i.e., NO removal from the processed gas mixture. In particular, the NO concentration decrease was observed not only in the discharge region and downstream region of the reactor, but also in the upstream vicinity of the discharge region during the discharge. After about 4 min, a steady state was established (8 min is the residence time of the operating gas in the reactor) and, practically, NO molecules were found only in the region below the needle electrode [Fig. 5(c)]. However, their concentration there was much lower than their initial concentration (at $t = 0$ min).

Fig. 6(a) and (b) shows time-dependent distributions of NO concentration along the gas flow direction and along the needle-to-plate direction, respectively. They correspond to the time evolution of NO concentration in the reactor shown in Fig. 5. The concentration of NO molecules is given in parts per million, based on the calibration curves presented in Fig. 4.

We consider the observed removal of NO to be a result of oxidation NO to NO_2 through the reactions [2]

$$NO + O + M \rightarrow NO_2 + M \quad (1)$$

$$NO + O_3 \rightarrow NO_2 + O_2. \quad (2)$$

This was confirmed by the increase of NO_2 concentration at the reactor outlet, measured by the NO_x monitor. The reason for the astonishing decrease of the concentration of NO molecules in the upstream vicinity of the discharge region is not clear at this moment. In another experiment on the velocity field in the present reactor [13], [14], we found that the strong secondary flow (ionic wind) from the stressed electrode toward both the upstream and downstream directions of the main flow occurs. This may suggest that the electrohydrodynamic (EHD) flow is capable of transporting long-living active species (e.g., O_3) from the discharge region into the upstream direction, where they may oxidize NO molecules in the reaction (2). The reaction (2) is known to be the most efficient path of NO removal in the chemical reactions occurring after the streamer pulse, in the time interval when the other active species, such as O, N, HO_2, and OH have already disappeared [15]. Recently, Spaan *et al.* suggested [16] that the direct photodissociation of NO molecules played an important role for NO decomposition in the vicinity of the discharge region in dielectric barrier discharges. This effect was not clarified at this stage of our experiment.

IV. Conclusion

The measurements of two-dimensional NO concentration in the positive dc streamer corona discharges occurring between the needle and plate electrodes using LIF diagnostic technique were carried out.

The results can be summarized as follows.

1) In the positive dc corona discharges, corona streamers are induced by UV laser sheet pulses shot into the electrode gap for NO removal. However, the separate monitoring of the LIF signal and the light emitted by the laser-induced streamer is possible, if an appropriate adjusting of the recording delay and exposure time of the ICCD camera is set.
2) Two-dimensional concentrations of the ground-state NO molecules between the electrodes in the positive dc corona discharges were measured. The results showed an efficient removal of NO molecules from the operating gas by streamer corona discharges. In the steady-state condition, the concentration of NO molecules decreased not only in the discharge and downstream regions of the reactor, but also in the upstream vicinity of the discharge region. To clarify this phenomenon more investigation is needed.

It was found that the process of NO removal by streamer corona discharges can occur not only in the paths of the corona streamers or in their vicinity, but also in the upstream region of

the flue gas flow. This has to be taken into account when modeling the kinetics of plasma-chemistry processing of NO_x removal by the corona discharges and designing the reactors.

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