LIF Observation of Ground-State OH Radicals in DC Nozzle-to-Plane Positive Streamer Corona

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Abstract: In this study, the planar LIF detection of the hydroxyl (OH) radicals was performed in a nozzle-to-plane electrode system having an electrode gap of 30 mm during the steady-state positive streamer corona discharge at atmospheric pressure. For monitoring the ground-state OH radicals, OH transition at 282 nm was used. The two-dimensional OH distribution in the DC corona discharge in air/H_2O/Ar mixture was measured. The time relationship between the regular streamer coronas, laser pulse, OH fluorescence and laser-induced streamer was measured. The time course of OH radicals between the successive streamers was measured for the evaluation of OH dynamics during the steady-state positive streamer corona discharge. The two-dimensional OH distribution in the DC corona discharge was observed. The obtained results showed that the ground-state OH radical were generated mainly in the filamentary part of the streamers. It was found that LIF detectable amount of ground-state OH radicals stayed in the region where streamers propagate during the steady-state DC positive streamer coronas.

Introduction

Streamer coronas at atmospheric pressure play an important role in the non-thermal plasma processing of harmful gases. The streamer coronas generate radicals e.g. hydroxyl (OH) radicals, which enhance the plasma chemical reactions in the reactor. The direct study of the streamer-induced plasma chemical processes in non-thermal plasma reactors is of great importance. Laser-induced fluorescence (LIF) is a useful diagnostic method for *in-situ* observation of the phenomena during the non-thermal plasma processing of gaseous pollutants. The LIF has been already employed by us (*1, 2*) and others (*3-6*) for studying NO molecule processing in various non-thermal plasma reactors.

The LIF method for measuring the concentration of a given gaseous species consists in the excitation of this species using a laser radiation and in measuring the intensities of the fluorescence induced by the laser radiation. Usually the laser induced fluorescence comprises the emission of several spectral lines which are characteristic for the given species.

Recently, several researchers succeeded in measuring the OH radicals using LIF technique in the pulsed corona discharges (*7-9*). However, there are still no experimental data of OH radicals concentration in the DC corona discharges. This is mainly due to difficulties in the synchronization of the DC corona streamers, LIF signals and observation time. The DC positive corona discharge consists of more or less regular self-repetitive current pulses (streamers) with a pulse duration up to several hundred nanoseconds and repetition frequency in the range of 1 to 100 kHz. When the DC voltage is high enough, the inception probability of each DC corona current pulse is one. However, the inception time-lag of the DC corona current pulse usually fluctuates. On the other hand, OH radicals lifetime is short (up to 1 ms), and to perform the LIF measurement of OH synchronization of laser excitation and LIF signal recording with DC corona streamers is necessary.

In this study, the planar LIF detection of the hydroxyl radicals (OH) was performed in a nozzle-to-plane electrode system having an electrode gap of 30 mm during the steady-state positive streamer corona discharge at atmospheric pressure. For monitoring the ground-state OH radicals, OH transition at 282 nm (1-0 band) was used.

One of the purposes of the present paper is to make clear whether DC streamer corona generate OH radicals or not. A second purpose is to observe the state of OH radicals during steady-state positive streamer corona discharge if OH radicals are generated.

Experimental Set-up

The schematic diagram of the experimental apparatus is shown in Figure 1. In order to observe the ground-state of OH radicals in the reactor using

Keywords: DC corona discharge, streamers, LIF, OH radicals
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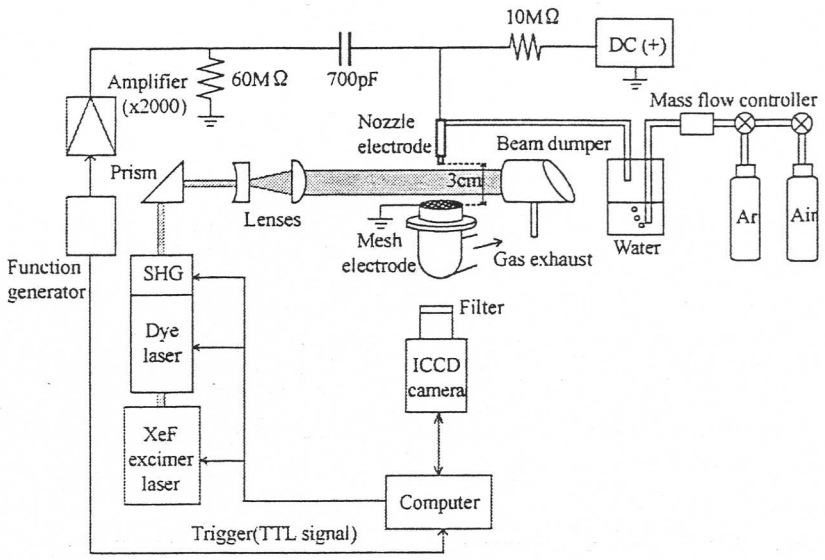

Figure 1. Schematic diagram of the experimental setp-up.

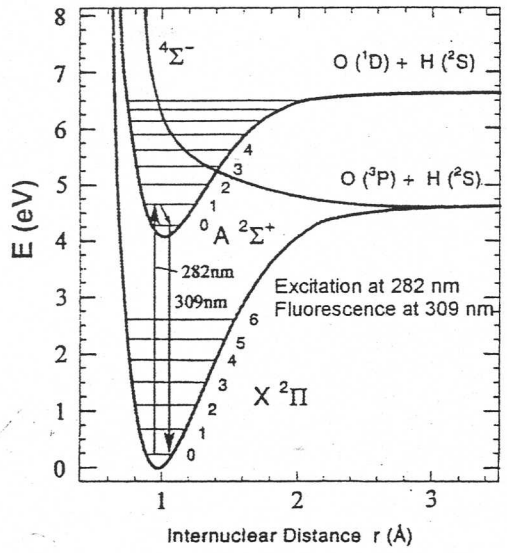

Figure 2. Energy level diagram of OH.

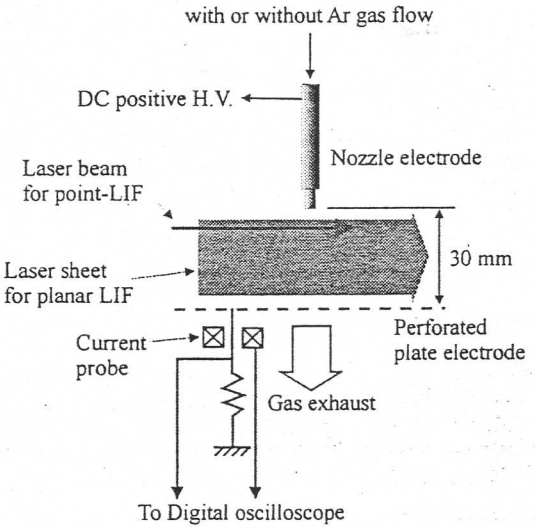

Figure 3. Schematic diagram of the discharging region and incident laser beam for LIF measurement.

LIF technique, OH [$A^2\Sigma+(v'=1) \leftarrow X^2\Pi(v''=0)$] system at 282 nm was used (Figure 2). A frequency-doubled-dye laser system was used for the LIF measurement. 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 153 as a dye that generated a laser beam of a wavelength tuned around 564 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 282 nm (energy: ~2.5 mJ, duration: 20 ns as FWHM). The 282 nm laser beam with a diameter of 2 mm passed between the electrodes as shown in Figure 3. Excitation of OH was achieved via the $Q_1(1)+Q_{21}(1)$ line (281.92 nm). This transition was chosen due to the strongest fluorescence signal. LIF signal emitted at 90 degree to the laser beam was focused onto the entrance slit of a 25 cm monochromator (Nikon, P-250) through a lens. The LIF signal at around 309 nm [$A^2\Sigma+(v'=0) \rightarrow X^2\Pi(v''=0)$] was detected by a photomultiplier tube (PMT). The PMT signal was sent to a digital oscilloscope through a preamplifier. In order to observe two-dimensional (2-D) OH profile, a laser beam was formed into the laser sheet (1 mm-width and 25 mm-height) and a gated ICCD camera (LaVision, Flame Star II) was used instead of the monochromator system. To remove the scattered laser light, the narrow optical filter centered at 310 nm was attached to the lens of the ICCD camera.

A stainless-steel pipe with a nozzle (1.0 mm in inner diameter, 1.5 mm in outer diameter) was used

as the stressed electrode. An additional gas (argon) could be supplied to the discharge zone through the nozzle. The plane electrode (100 mm in square) was a brass plate with an array of holes (1.5 mm in diameter) perforated to allow the gas exhaust. Averaged air flow velocity due to this suction was 1.1 m/s in the gap. DC high voltage with positive polarity was applied through a 10 MΩ resistor to the nozzle electrode. To synchronize the DC corona discharge with the LIF system DC + pulsed high voltage system was used. The DC high voltage with a positive polarity was applied through a 10 MΩ resistor to the nozzle electrode and was set below the corona onset voltage (7 – 15 kV). The additional voltage pulses (6–10 kV) produced from a generator + amplifier system was applied through the 700 pF capacitor. The DC corona streamers appeared only during the voltage pulse. The duration (50-100 μs) of the voltage pulse was chosen to obtain only one streamer per voltage pulse.

The DC positive corona discharge was realized in open air with and without additional gas flow. The discharge current pulse was measured using a current probe (Pearson Electronics, 2877). Also the potential across a resistor connected between the plane electrode and the ground was measured. The laser pulse was monitored using a PIN photodiode placed at 2.6 m in advance of the discharge zone. A time relationship between discharge current and the laser pulse was measured by another oscilloscope. In Figure 4 the voltage-current characteristics of DC positive corona discharge in air (Figure 4a) and in air/Ar mixture (Figure 4b) are presented. The measurements were carried out with and without time synchronization between the discharge and laser pulse. In the case of measurement without synchronization a laser pulse is irradiated at random between the discharge current pulses (in this case only DC voltage was supplied). The time relationship between the discharge current pulses, laser pulse, and LIF signal were described in detail elsewhere (*10, 11*). The experiment was carried out at room temperature under atmospheric pressure. The concentration of water in the room was estimated to be in the range of 1-2 vol. %.

Results and Discussion

During the investigations of OH radicals production in DC corona discharge the following measurements were performed:

- emission spectra of DC corona discharge for air and air/Ar mixtures and various discharge voltage,

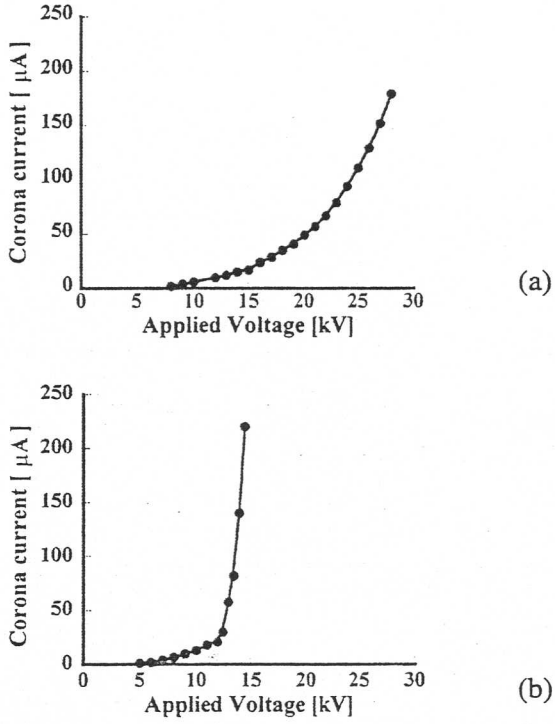

Figure 4. Voltage-current characteristics for discharge in air (a) and air with 3% Ar admixture (b).

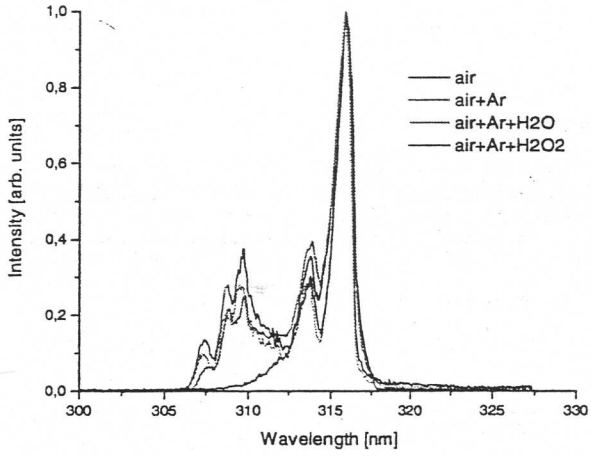

Figure 5. Emission spectrum of DC streamer corona discharge in air/Ar/H_2O/H_2O_2 mixtures.

- 2D-LIF of OH radicals of DC corona discharge for air and air/Ar mixtures and various discharge voltage, with corona streamer-laser pulse synchronization,
- point-LIF of OH radicals of DC corona discharge for air and air/Ar mixtures and various discharge voltage,
- comparison of OH LIF spectra from DC corona discharge and methane burner (known source of OH radicals).

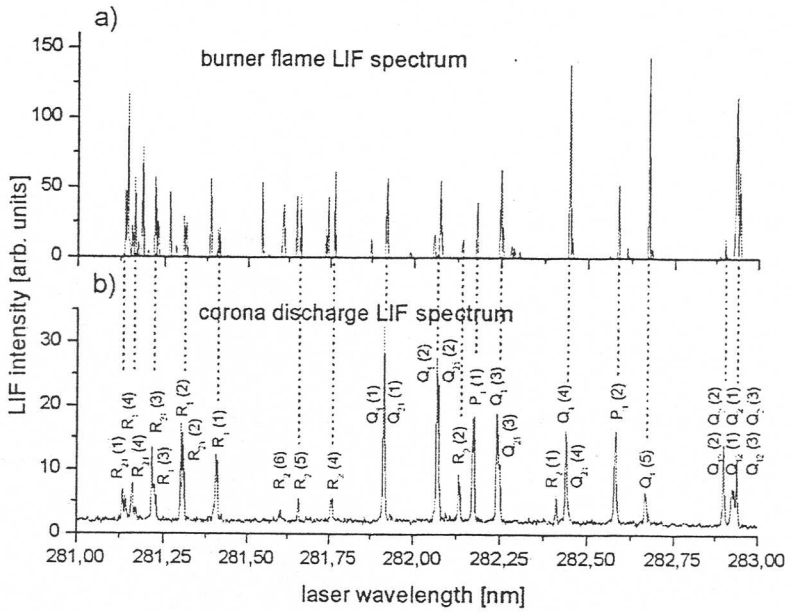

Figure 6. LIF spectrum of OH (OH in the ground level) a) combustion using a burner, b) DC streamer corona discharge in air + 3% Ar. DC voltage of 10 kV + pulse of 7 kV and 60 μs, additional flow air/Ar/H_2O of 0.3 L/min, ICCD gate of 100 μs.

The spontaneous emission of OH molecules (around 308 nm) was present in the spectra of DC corona discharge only when the admixture of Ar was added to the discharge. The example of emission spectra of DC corona discharge is presented in Figure 5. In the 300-330 nm spectral range only N_2 lines (2^{nd} positive band) were detected. When the small admixture (3%) of Ar was introduced into the discharge, the OH emission around 308 nm appeared. Addition of H_2O or H_2O_2 increased slightly the OH emission. Similar optical emission characteristics were observed in dielectric barrier discharges by Z. Falkenstein (*12*).

Also the 2D-LIF measurements confirmed that the OH radicals are generated only when Ar admixture is added to the discharge.

To be sure that observed LIF signal came from OH, the LIF spectrum of DC corona discharge was compared with OH LIF spectrum of methane burner which is well known source of OH (Figure 6).

When Ar is present in the DC corona discharge the shape of the streamers changes. In Figure 7 the comparison of DC corona streamers in air (Figure 7a) and air/Ar mixture (Figure 7b) is presented. In air streamers are composed of many branches and occupies much more space than filamentary type of streamers in air/Ar discharge.

Figure 7c and d show two-dimensional images of OH LIF during the DC streamer corona discharge. The two-dimensional LIF images were taken using DC+pulse voltage supply system, e.g. when discharge was synchronized with laser pulse. When the

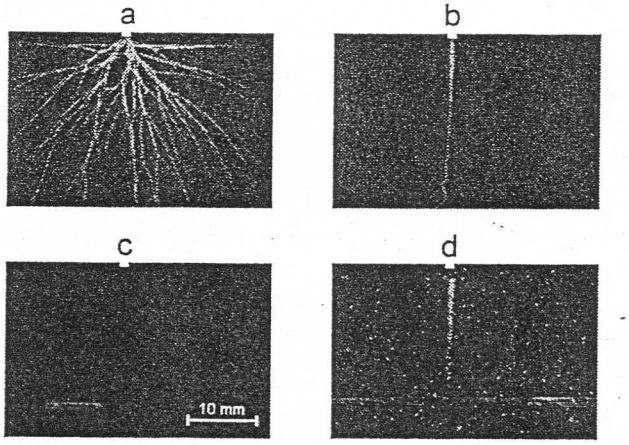

Figure 7. Images of DC corona streamers and OH 2D-LIF for discharge in air (a, c) and in air/Ar mixture (b, d). DC voltage of 10 kV + pulse of 7 kV and 60 μs, ICCD gate of 100 μs.

discharge was realized in air (Figure 7c) there was no LIF signal visible, even with the highest gain of ICCD camera. When the additional flow of air/Ar mixture was introduced through the nozzle electrode into the discharge, the OH LIF signal was detected. It can be seen that OH LIF signal comes mainly from the streamer region and it seems to be a little wider than the streamer. However, when comparing the vertical and horizontal profiles of streamer emission and OH LIF signal averaged of 100 captured images one can observe that OH LIF signal comes from within the streamer volume. These suggest that OH radicals generation occurred inside the streamer.

The averaged current densities underneath the nozzle electrode were about 0.6 μA/mm^2 at 26 kV for

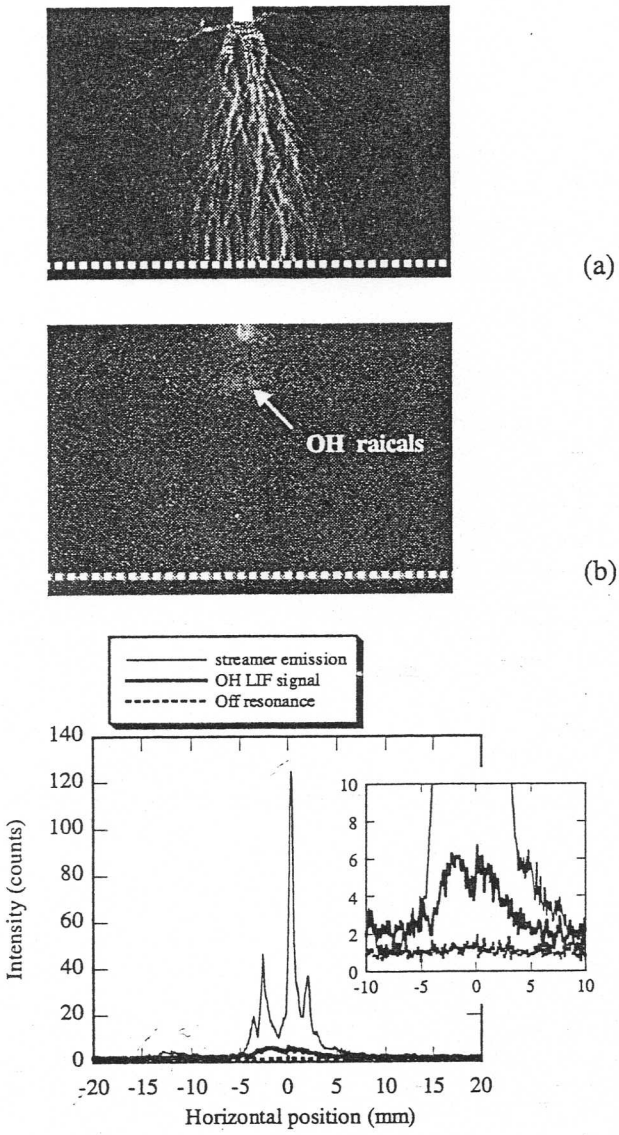

Figure 8. Comparison of streamer and point-LIF images in open air. The applied voltage is 29 kV and corona current is 190 μA. (a) streamer emission observed by the ICCD camera with gate time of 900 ms; b) OH LIF near the tip of the stressed electrode (ICCD gate of 100 ns); (c) horizontal profile for both streamer emission and OH LIF. The profile obtained at the laser wavelength of off resonance is also shown.

the discharge without Ar injection and about 4.7 μA/mm^2 at 13kV for the discharge with Ar injection, respectively. The averaged streamers repetition frequency increases up to 5.1 kHz at 11 kV when Ar is present in the discharge. The averaged time interval between two consecutive streamers is about 500 ms for the discharge without Ar gas flow and 200 ms for the discharge with Ar gas flow. Therefore, the OH radicals produced in the one streamer may be still present in the discharge region when the next streamers occur. Moreover, OH LIF signal is highly dispersed in the case of the discharge without Ar gas flow through the nozzle. There are many factors which should be considered concerning to the fluctuation of LIF signals: fluctuation of laser energy, collisional quenching, discharge instability such as fluctuation of the current pulses respect to the time interval and amplitude, branching of the streamers, spatial relationship between the laser and streamers, and electrohydrodynamic (EHD) flow effect. Especially, the discharge characteristics are much different depending on the gas composition existed in the gap. In the case of Ar injection, it is considered that not only the energetic electrons but also metastable Ar atoms contribute to generate OH radicals through the dissociation of H_2O. In air the streamers are composed of many branches and occupy much more space than filamentary type of discharge in the case of Ar injection. When the discharge was realized in open air, the LIF signal is much weaker and it is insufficient for single-shot 2D imaging of OH radicals. Therefore, to detect OH radicals in DC positive corona discharge we applied point-LIF measurement method based on no time synchronization between the streamer and laser pulse. If we average the signals, the steady-state measurement of OH LIF is possible. The, laser beam, which was not expanded to the sheet, was used. In order to increase SN ratio of the image, the image shown in Figure 8 (b) is an average of 50 captured images. Although the streamer emission and LIF images taken separately, it can be seen that OH LIF signal comes mainly from the streamer region as shown in Figure 8 (c).

Conclusions

The OH radicals generation in DC streamer corona discharge was examined using the LIF technique. The results are summarized as follows:

- Emission spectra of DC streamer corona discharge in air (with 1-2 vol. % of water) showed no OH emission,
- Presence of Ar in the discharge resulted in OH emission,
- OH 2D-LIF signal was obtained only when Ar was present in the discharge,
- OH point-LIF signal was obtained in discharge in air for steady-state measurement,
- OH LIF signal came from the streamer volume.

Since the both spontaneous emission and 2D-LIF signal of OH was not detected in the DC streamer corona discharge in air and only the point-LIF could apply to the measurement of OH radicals stayed in the steady-state DC streamer coronas in air suggests

that there is extremely low concentration of OH radicals (in the ground-state or excited) in such discharge. This is very interesting result, since many researchers consider the OH radicals play important role in chemical processes in the DC corona discharge and use the OH radicals for modeling the reactions in such discharge.

On the other hand when the Ar is present in the discharge both the OH emission and OH 2D-LIF signal was detected. The Ar addition change the shape of the corona streamer. In air streamers are composed of many branches and occupies much more space than filamentary type of streamers in air/Ar discharge. Also, the current density is much higher in case of air/Ar discharge. Moreover, the LIF results showed that the ground-state OH radicals are generated mainly in the filamentary part of the streamers. These suggest that for OH radicals generation high current density is needed. This hypothesis seems to be in agreement with results obtained by other researchers of OH LIF measurements in the pulsed corona discharge were the discharge current is up to three orders of magnitude higher than in the DC corona discharge case (e.g. *6-9*) and high concentration of OH is reported.

From the practical point of view, DC corona discharge with Ar addition is not attractive. Streamers occupy very small volume and gas treatment becomes inefficient. Thus, DC corona discharge should be used when OH is not necessary. When process which needs OH radicals is considered, the use of pulsed corona discharge should be preferred.

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Received for review March 3, 2006. Revised manuscript received March 8, 2006. Accepted March 8, 2006.