Measurement of O and OH radicals produced by an atmospheric-pressure helium plasma jet nearby the surfaces

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Atmospheric-pressure helium plasma jets are getting much attention especially in plasma medical application filed. It is thought that active species play important role in the plasma processes and they are generated from the interaction between the plasma and molecules included in the ambient air and the discharge gas. O and OH radicals are recognized as important active species for plasma medical applications. However, their production mechanisms are not yet elucidated completely. In this study, density distributions of O and OH radicals in the vicinity of the surface were measured using laser induced fluorescence (LIF). When the helium plasma jet was generated by applying 10 kV_{pp} 8.4 kHz onto the quartz tube, O and OH density distribution varied depending on some parameters: helium flow rate, gas composition and water concentration on objective surface. Those results suggest production mechanisms of O and OH radicals in the plasma jet.

1. Introduction

Atmospheric-pressure helium plasma jet (APPJ) is one of the non-thermal plasmas that has low heat load [1]. This plasma is gathering much attention because of its high energy efficiency and extremely low heat load. These days, many biological researches have been done using this kind of plasma jet such as sterilization, cell activation and plasma cancer care [2]–[12]. In these plasma processes, active species generated by the plasma jet such as radicals or ions play important role. It is thought that this plasma can produce various active species by the reaction between the plasma and the ambient air. However, understanding of the production mechanism of active species or their density is still unclear, because primary mechanism of the plasma jet and behavior of active species become complicated in the air.

In this plasma jet, the interaction of air with plasma affects not only plasma propagation mechanism but production mechanism of active species. Therefore, to investigate primary mechanisms of this plasma jet, air-helium mixture ratio has to be considered.

O and OH radicals have high chemical reactivity that play important role in many plasma processes including biological plasma process. We previously measured two-dimensional distribution of OH radical in this plasma in the open-air region [13]. In a biological plasma process, the helium plasma jet usually extends toward the surface of object such as human skin or tissues. Thus, it is important to measure the active species density distribution in the vicinity of the surface to understand how they are provided into objects.

In this study, we measured O and OH radical density distribution nearby the surfaces using laser induced fluorescence (LIF) in some conditions.

2. Experimental setup

2-1. Atmospheric-pressure helium plasma jet

A Schematic diagram of the plasma jet is shown in Fig. 1. This shrinking plasma jet is generated by applying high voltage onto outer surface of the quartz tube. Usually, applied voltage is sinusoidal wave or pulsed waveform of ~10 kV, ~10 kHz. In this study, the sinusoidal high voltage was used to generate the plasma jet.

Although this plasma jet can be generated with only high-voltage electrode, in this study, the ground electrode on the quartz tube surface was used to stabilize the plasma. The widths of the two electrodes are 20 mm and they are separated by 20 mm each other. The distance between quartz tube terminus and the edge of the high voltage electrode was 50 mm. Previous studies showed that the length of the plasma jet varies depending on the applied voltage waveform, the helium gas flow rate, and the configuration of electrodes [14]–[18].

Fig.1. A schematic diagram of APPJ and LIF measurement.
2-2. Laser induced fluorescence (LIF)

2-2-1. LIF for OH radical

A tunable dye laser (Lambda Physik, Scanmate 2EC-400 LPY400) was used to excite the ground-state OH radicals. The laser pulse duration was approximately 10 ns and its wavelength was around 283 nm. The cross section of the laser beam was adjusted as 0.7 × 0.3 mm² using a slit. The OH fluorescence was detected on the r axis direction using an interference filter and a photomultiplier tube (PMT) as shown in Fig. 1. The measurement volume of LIF signal was set to 0.5 × 0.7 × 0.3 mm³ using a 0.5-mm slit in front of the PMT. The energy density of the laser beam was approximately 5 mJ/cm², monitored using a laser power meter. The laser oscillation frequency was 10 Hz, synchronizing with the discharge pulse. Thus, the LIF signal and OH density was averaged over 512 shots at the same post discharge timing. This measurement gives time-resolved OH density. Radial distribution of OH density was measured by moving the quartz tube along r axis with 0.50-mm step, as shown in Fig. 1. Simultaneously, air-helium mixture ratio along r axis was measured using the decay rate of the LIF signal of OH radical. The method to obtain OH absolute density and air-helium mixture ratio was shown in our previous research [13].

2-2-2. Two-photon absorption LIF

Two-photon absorption LIF (TALIF) is widely used for the measurement of O atoms. In this method, O atoms at ground state are excited by absorbing two photons. An energy diagram of O-TALIF is shown in Fig. 2. The laser wavelength was set at 226 nm to excite O(2p³P, J”=2) atom to O(3p³P) and 845 nm fluorescence (3p³P → 3s³S₀) was detected. When given that I_L is laser power and σ is cross section of photon, rate equation for O-TALIF is given as below:[19]:

\[
\dot{N}_1 = -\sigma I_L^2 N_1 \\
\dot{N}_2 = \sigma I_L^2 N_1 - (A + Q + \sigma_p I_L) N_2.
\]  

(1)

In equation (1), N₁ is O(2p³P) density, N₂ is O(3p³P) density and A and Q are spontaneous coefficient and quenching coefficient, respectively.

Therefore, TALIF signal intensity \(I_{TALIF}\) is given as

\[
I_{TALIF} = c \int_0^\tau N_2 \, dt = \frac{\sigma I_L^2}{Q} N_1^0 \tau ,
\]

(2)
where, \( c \) is light velocity and \( r \) is laser pulse width. In the effluent of an atmospheric-pressure helium plasma jet, air-helium mixture ratio is different at each position. The air-helium mixture ratio can be obtained by \( \text{OH-LIF} \) in our previous study [13]. Thus, quenching coefficient was corrected at each position. Quenching coefficients are shown in Table I [20].

A schematic diagram of \( \text{O-TALIF} \) is shown in Fig.3. In this study, laser beam was point-focused using spherical quartz lens of \( f = 100 \) mm. The laser energy in this study was set within the range where \( I_{	ext{TALIF}} \) does not saturate. In TALIF measurement, \( I_{	ext{TALIF}} \) is theoretically in proportion to \( I_c^2 \). Fig. 4 shows the relation between \( I_{	ext{TALIF}} \) and \( I_c \). Fig. 4 shows that laser \( I_{	ext{TALIF}} \) is in proportion to \( I_c^{2.03} \), that is, \( I_{	ext{TALIF}} \) does not saturate in this study. Meanwhile, the difference of \( I_c \) was corrected in every measurement. The discharge condition was the same as in \( \text{OH-LIF} \). O atom is said that it plays very important role in plasma medicine [21, 22]. The helium plasma jet is often generated by adding a little portion of \( \text{O}_2 \) to the discharge gas for efficient generation of O atoms. Our previous measurement result has shown that 0.5 % of additional \( \text{O}_2 \) is the most efficient composition for producing O atom, corresponding to simulation by Park et. al [23]. Thus we added 0.5 % of \( \text{O}_2 \) to the discharge gas in addition to helium as the discharge gas.

![Fig. 5. (a) An ICCD image of the plasma extending to the grass surface. (b) A shadowgraph image of helium flow in the vicinity of the surface.](image)

![Fig. 6. OH radial distribution nearby the wet/dry surface](image)

![Fig. 7. O density radial distribution nearby the surface in helium and He/O\(_2\) plasma jet.](image)

### 3. Results

Oh et al. reported that when the plasma jet extends toward the Polystyrene surface, helium gas flew along the surface [24]. Fig. 5 (a) and Fig. 5 (b) show the plasma jet propagation and helium flow in the vicinity of glass surface. From those images, there can be seen that helium gas flows along the surface and the plasma propagates with the gas flow. As shown in Fig. 5(b), helium flows with laminar flow along the surface; contrary it flows with turbulence above the surface. It is known that plasma bullet, microscopic propagation of the plasma jet, can propagate in the laminar flow. In addition, Karakas et al. reported that about 50 per cent of helium in the discharge gas is required for the propagation of the helium plasma jet [25]. Therefore, it is estimated that the plasma can propagate only along the surface where helium gas flows as laminar flow with high concentration of helium.

Moreover, we also measured the OH density distribution in the vicinity of the wet surface. To demonstrate human skin, we used melamine sponge absorbed pure water. Fig. 6 shows the result for wet sponge and dry glass surface.

The maximum OH density nearby the wet and dry surface were \( 1.0 \times 10^{13} \) cm\(^{-3} \) (approx. 0.4 ppm) and \( 2.3 \times 10^{13} \) cm\(^{-3} \) (approx. 1.0 ppm), respectively.

Fig. 7 shows O radical density radial distribution in the vicinity of grass surface. When the discharge gas was consisted of only helium, O radical can be measured in \( r < 1.25 \) mm. On the other hand, O radical can be measured in \( r < 2.25 \) mm. In He/O\(_2\) (0.5 %) plasma jet, the maximum density was four times as large as in helium plasma.

As Fig. 5 (a) shows, the plasma jet propagates along the surface wider than 4 mm, the diameter of the quartz tube, with helium surface flow. Thus it is
thought that O radical is generated only in the centre of the plasma jet when the discharge gas is helium. Contrary, O radical can be measured within larger area in He/O$_2$ plasma than in helium plasma.

4. Conclusion
Firstly, OH density radial distribution in the vicinity of wet and dry surface was measured using LIF. The maximum density of OH radical was located on $r = 1.5 \sim 2.0$ mm in some experimental conditions. This result varies from our previous study when the plasma jet extends to open-air region. The maximum OH density was 0.4 ppm in the vicinity of dry surface and 1.0 ppm of wet surface, respectively. It was also measured that when the plasma jet extends toward the surface, helium gas flows along the surface and the plasma jet propagates along the surface at the same time. Those results suggest that OH radical is produced by the dissociation of H$_2$O that adheres on or evaporates from the surface in an atmospheric-pressure helium plasma jet. In addition, OH radicals produced in the plasma upstream region are transported by helium flow in which OH radical life time is prolonged.

Secondly, O radicals can be measured in the luminous area of the plasma jet, where $r < 2.50$ mm in contrast to OH-LIF. When the discharge gas was consisted of 99.5 % of helium and 0.5 % of O$_2$, O density was at maximum. And the maximum O density in He/O$_2$ (5%) plasma was four times larger than in helium plasma. And when the plasma jet extended toward the surface, O density was at maximum at $r = 0$ mm. These results suggest that both O and OH radicals are generated through the dissociation of molecules in the discharge gas and to produce the active species efficiently, additional gas to helium is significantly important.

5. References