Spatio-temporal profile of atomic oxygen in a 1 kHz repetition atmospheric-pressure plasma jet in He–O₂–H₂O mixture

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Abstract
Atomic oxygen (O) is one of the essential reactive species in plasma oxidation processes. We investigated the behavior of atomic oxygen in a 1 kHz-repetition pulsed plasma jet in atmospheric-pressure He/O₂/H₂O mixture. By two-photon absorption laser-induced fluorescence, the spatio-temporal profiles of O density were measured under various conditions. In the dry ([H₂O] ⩽ 100 ppm) condition, the rate of O production did not depend on the [O₂] fraction in the range of [O₂] = 275–8600 ppm. The analysis of the O-production rate indicates that the atomic oxygen in this plasma jet arises from electron-impact dissociation and quenching of O(¹D), similar to the O-production mechanism in radio-frequency plasma jet. The dependence of O-production in each discharge pulse (∆[O]) on the discharge energy E_d and [O₂] in the plasma region at dry condition is formulated as

\[ \frac{\Delta [O] (\text{cm}^{-3})}{E_d (\text{mJ})} = 1.3 \times 10^{15} \times \left\{ 1 - \exp(-1.85 \times 10^{-17} [O_2](\text{cm}^{-3})) \right\}. \]

The decay rate of atomic oxygen was not explained by self-recombination or ozone-generation reactions; it was consistent with the reaction rate of O + OH → O₂ + H at [OH] = 2 \times 10^{13} \text{ cm}^{-3}. This result suggests that the small amount of [OH] with 10^{13} \text{ cm}^{-3} density is more responsible for O behavior than [O₂] with large fraction of 10^{15} \text{ cm}^{-3}. We conducted a chemical reaction simulation considering the measured results of [O] and [OH] production, resulting in good agreement with the spatial distribution of [O]. Chemical reaction analysis revealed that the cyclic reproduction of OH via chain reaction with O and O₂ is important, therefore a small amount of OH catalytically consumes atomic oxygen with two-order higher density.

Keywords: atomic oxygen, atmospheric pressure pulsed plasma jet, TALIF

(Some figures may appear in colour only in the online journal)
1. Introduction

An atmospheric-pressure plasma jet (APPJ) has high chemical reactivity with low-temperature, and it has been investigated for applications such as biomedical treatment [1–4] and surface modification [5–8]. Among the types of APPJ, low-frequency (up to 100 kHz) helium (He) APPJ is considered to produce radicals with lower temperature [9–11] than radio-frequency (RF) driven APPJ [12–14]. Thus, it is more suitable for treatment of heat-sensitive targets including living organisms.

Helium APPJ is generally produced by applying a high voltage between two electrodes wrapped on a dielectric tube, and the plasma flows out of the tube into the ambient air. Hereafter, we refer to the area between the two wrapped electrodes as the ‘plasma region’, and the luminous region outside the electrodes as the ‘plasma plume’. Several studies have reported on the measurement of reactive species in He-APPJ such as He metastable (He*) [15, 16], OH [17, 18], O [19, 20], O₂(a‘Δ) [21, 22], and O₃ [23], as these species play major roles in the chemical treatment by the plasma jet. In the previous studies, the reactive species were mostly measured in the plasma plume, and not in the plasma region. This is because the behavior of the reactive species in the plume is more important in evaluating the flux on the target. However, some studies have shown that the reactive species in the upstream plasma region can affect the density of the reactive species in the plume [22, 24]. Therefore, the behavior of reactive species in the plasma region is also worth clarifying. Ono and Tokuhiro investigated the behavior of OH from the upstream plasma to the downstream plume in repetitive pulsed He-APPJ [25], revealing the production and loss processes of OH and the dependence of the OH density on the discharge energy and repetition frequency.

Atomic oxygen (O) is one of the most important radicals in oxidation processes using APPJ. Previous studies have reported on the behavior of O in RF-plasma jets [26–28], whereas the behavior of atomic oxygen in kHz-repetition pulsed He-APPJ has not been clarified. In this study, we investigated the production and loss mechanism, spatio-temporal distribution for the entire region of the plasma and the plume, and the dependence on discharge energy and O₂ fraction of atomic oxygen in kHz-repetition pulsed APPJ in He/O₂/H₂O mixture.

2. Experiments

2.1. Two-photon absorption laser-induced fluorescence (TALIF) measurement of atomic oxygen

Ground state atomic oxygen O(2p³ ³P) was measured by TALIF technique [29–33]. Energy levels related to TALIF of O(2p³ ³P) are represented in figure 1. A 225.6 nm laser excites the ground state O to O(2p³ ³P) state via two-photon absorption, and an 844.6 nm fluorescence corresponding to 2p³ ³P → 2p³ ³S transition is observed as a signal. The TALIF signal Sₚ is integrated over time, volume, and wavelength, and expressed in terms of the O(2p³ ³P) density n₀ and laser intensity I as below:

\[
S_\text{F} \propto A_F \Gamma \sigma^{(2)} \int F \, dt, \tag{1}
\]

where \(A_F\), \(\Gamma\), and \(\sigma^{(2)}\) are the emission coefficient of the observed fluorescence, total deexcitation rate of the excited state, and two-photon absorption cross section, respectively. Hereafter, the word ‘atomic oxygen’ refers to the ground state O(2p³ ³P).

The absolute density of atomic oxygen was calibrated by TALIF of xenon (Xe) [34–38]. A standard gas of Xe(1%)/N₂ was used as the reference, and a 224.2 nm laser excited the ground state Xe to 6p’ [3/2]₁ state, after which an 834.7 nm fluorescence was observed. The absolute value of n₀ is estimated by

\[
n_{\text{Xe}} f_J = \frac{C_{\text{Xe}}}{C_\text{O}} \frac{a_{\text{Xe}}}{a_\text{O}} \frac{\sigma_{\text{Xe}}^{(2)}}{\sigma_{\text{O}}^{(2)}} \frac{\nu_{\text{Xe}}^2}{\nu_{\text{O}}^2} \frac{S_{\text{F}-\text{O}}/E_{\text{L}-\text{Xe}}}{S_{\text{F}-\text{Xe}}/E_{\text{L}-\text{Xe}}}, \tag{2}
\]

Here, \(a_X, E_{\text{L}-X},\) and \(C_X\) in equation (2) represent the branching ratio, laser energy per pulse, and fluorescence collection efficiency including the optics, bandpass filters, and detector, respectively, related with species \(X\). The branching ratio \(a\) is expressed in terms of the quenching coefficient \(k_i\) of collider species \(M_i\) as

\[
a = \frac{A_F}{\Gamma} = \frac{A_F}{A_e + \sum_i k_i[M_i]}, \tag{3}
\]

where \(A_e\) is the total radiative decay rate of the excited state. The ratio \(A_F/A_e\) is 1 for O (2p³ ³P) [34, 37] and 0.733 for Xe (6p’ [3/2]₁) [37, 39]. The parameter \(f_J\) is the fine structure distribution factor of the ground state O (2p³ ³P, \(J = 0, 1, 2\)),

\[
f_J = \frac{(2J + 1) \exp(-U_J/k_BT_g)}{\sum_{J=0,1,2}(2J + 1) \exp(-U_J/k_BT_g)}, \tag{4}
\]

where \(U_J\) represents the internal energy of each state. In this study, \(J = 2\) and gas temperature \(T_g = 300\) K were used. The
The spatio-temporal profiles of atomic oxygen were measured by TALIF at different \( z \) and \( \tau \). Figure 3 illustrates the

cylindrical lens with 200 mm focal length. Fluorescence was detected by a photomultiplier tube (R13456, Hamamatsu), and the stray light of the excitation laser was blocked by optical band-pass and high-pass filters (FF01-840/12-25 and FF01-300/LP-25, Semrock). The fluorescence from the excited O was collected by collimating and focusing lenses positioned perpendicularly to both the laser axis and quartz tube axis. The laser beam’s horizontal width was 1 mm, and the estimated laser beam waist size in the vertical direction was approximately 5–10 \( \mu \)m. Therefore, the observed volume \( V_0 \) was 1 (laser beam width) \( \times \) 4 (quartz inner diameter) \( \times \) 0.005–0.01 (laser beam height) mm\(^3\). The time-averaged laser energy was measured by a laser power meter (PowerMAX-USB PM3, Coherent). An excitation laser pulse was delayed from a discharge pulse using a delay generator (DG535, Stanford Research Systems), and the time evolution of the TALIF signal after a discharge pulse was measured by changing the time delay \( \tau \). The experimental TALIF signals and laser energies were averaged over 512 shots at each measurement condition. The TALIF signal was compensated using the signals at off-resonant of TALIF excitation and without laser irradiation.

### Table 1. Coefficients used for the absolute density calibration.

| Species | O       | Xe     |
|---------|---------|--------|
| Emission coefficient \( A_p (10^7 \text{ s}^{-1}) \) | 2.88 \[34\] | 2.45 \[34\] |
| Quenching coefficient \( k \) | O: 0.82 \[29\] | Xe: 3.7 \[32\] |
|          \( (10^{-10} \text{ cm}^3\text{s}^{-1}) \) | O\(_2\): 9.4 \[34\] | N\(_2\): 5.1 \[32\] |
|          | H\(_2\)O: 49 \[40\] | He: 0.017 \[34\] |
| Two-photon absorption cross section \( \sigma^{(2)} \) | \( (10^{-32} \text{ cm}^4) \) | 2.66 \[41\] | 4.94 \[34\] |

Coefficient values in equation (2) used in this study are summarized in table 1. The Xe-TALIF signal dependences on the reference gas pressure and the laser energy were investigated before the calibration, and the signal was saturated at the reference gas pressure of approximately 30 kPa and the laser energy of 0.2 mJ. The calibration was conducted under the condition where \( S_{Xe} \) was proportional to the partial pressure of Xe and \( E_\text{L} \). Therefore, the three-body quenching of excited Xe \[37\] and the Xe-TALIF saturation against laser energy were both negligible.

#### 2.2. Experimental settings

The experimental apparatus is presented in figure 2. A mixture of O\(_2\)/H\(_2\)O/He was supplied to a synthesized quartz tube with inner and outer diameters of 4 and 6 mm, and pulsed plasma jet was generated by applying a 1 kHz repetitive high voltage pulse between the two electrodes wrapped on the quartz tube. The applied voltage had a rectangular form with a duration of approximately 800 ns and a peak height of \( V(0–10 \text{ variable}) \) (kV). The applied voltage and current were measured by a high-voltage probe (P6015A, Tektronix) and a current transformer (CT: model 2877, Pearson), respectively. The two electrodes were 10 mm wide and placed 20 mm apart. The total gas flow rate was controlled to be 1 SLM by mass flow controllers, and the volume fraction of O\(_2\) and H\(_2\)O were measured by a zirconia oxygen analyzer (OX400, Yokogawa) and a dew point transmitter (TK-100, Tekhne), respectively. Humidity was not completely eliminated owing to the small amount of gas transmission through the tube and the attached water molecules inside the gas tube. To control the gas composition accurately, the plasma jet plume was shielded from the ambient air by the quartz tube. A grounded electrode was wrapped at the end of the quartz tube to stabilize the plasma plume. The \( z \)-axis was defined along the quartz tube as represented in figure 2. The inter-electrode region of \( 0 \leq z \leq 20 \text{ mm} \) was the plasma area, whereas the downstream of \( z \geq 30 \text{ mm} \) was regarded as the plasma plume.

An Nd:YAG (355 nm)-pumped pulsed dye laser (Scanmate 2C400, Lambda Physik) generated a 451.2 nm beam, which was converted to a 225.6 nm beam by second-harmonic generation. The laser pulse duration \( \tau_p \) was 20 ns. The 225.6 nm laser was introduced to the observed area, and the beam was vertically focused into a sheet shape on the plasma jet by a
schematic concept of atomic oxygen production and decay between the repetitive discharge pulses. The production of atomic oxygen by each discharge pulse is defined as $\Delta [O]$, and $z$ can be converted as $z = vt$ using the gas flow velocity $v$. Atomic oxygen is produced by each discharge and consumed during the afterglow phase, and the following discharge pulse superimposes $\Delta [O]$ to the residual O density.

### 2.3. Simulation of O behavior

To analyze the spatio-temporal behavior of atomic oxygen, a simple simulation with zero-dimensional time-dependent model was used. The major scheme of the simulation was similar to that used by Ono and Tokuhiro [25]. The simulation was conducted assuming a laminar flow of the working gas in the quartz tube. A radially uniform flow velocity $v$ was assumed in the calculations for simplicity, while the actual flow velocity in the quartz tube has a radially parabolic profile of Hagen–Poiseuille flow.

The simulation in this study differs from that in [25] in terms of the considered reactions and the radical profiles. We considered O, O$_3$, OH, H, HO$_2$, H$_2$O$_2$, He, O$_2$, H$_2$O, and H$_2$ in the simulation. The time evolution of the densities $[P_i(t)]$ of the considered species $P_i$ was calculated by solving the rate equations of the reactions listed in table 2. The calculated temporal profile $[P_i(t)]$ was then converted into a spatial profile $[P_i(z)]$ using the relation $z = vt$, with $v = 1.35$ m/s. The simulation started at $t = 0$ ms, and the radicals O, OH, and H were increased at the discharge timing for simplicity.

### 3. Results and discussion

#### 3.1. Linear plots for the ozone interference evaluation

The linearity of the TALIF signal against squared laser energy was checked. In ozone (O$_3$) rich condition, the 226 nm laser induces photo-fragmentation of ozone, which leads to additional production of atomic oxygen as

\[
O_3 + h\nu \rightarrow O_2 + O^1D, \tag{5}
\]

\[
O^1D + M \rightarrow O + M. \tag{6}
\]

The photo-fragmentation-originated atomic oxygen results in the additional TALIF signal (ozone interference) as [59]

\[
S_F = \eta_0 n_O E_L^{-2} + \eta_z n_z E_L^{-3}, \tag{7}
\]

where $n_z$ is the ozone density and $\eta_0$, $\eta_z$ are the proportionality factors for atomic oxygen and ozone, respectively. Figure 4 represents TALIF signals against the squared laser energy at $[O_2] = 1800$ ppm, $[H_2O] = 100$ ppm, $V = 10$ kV, $z = 10$ mm (center of the powered electrodes), $\tau = \pm 2$ ms (immediately before and after each discharge pulses). The plots in figure 4 demonstrate the linearity of $S_F$ against $E_L^{-2}$, indicating that the ozone interference is negligible in this study when $E_L \leq 0.3$ mJ. The following results are obtained with the laser energy below 0.2 mJ.

#### 3.2. Atomic oxygen behavior at the plasma region

Atomic oxygen behavior in the plasma region ($0 < z < 20$ mm) is discussed in this section. Figure 5 represents the time evolution of atomic oxygen density at the dry condition ($[H_2O] \leq 100$ ppm) at $V = 10$ kV, $z = 10$ mm with different O$_2$ densities. Atomic oxygen is produced within several microseconds after the discharge, and thereafter decreased until the next discharge.

#### 3.2.1. Production phase of atomic oxygen

The atomic oxygen production process can be evaluated by the analysis of the production phase of $0 < \tau < 10$ ms. Waskoenig et al. estimated the main process of atomic oxygen production in RF-plasma jet as electron-impact dissociation and quenching of excited atomic oxygen [26], while the atomic oxygen production process in 1 kHz-plasma jet may be different owing to different electron density and temperature. Figure 6 represents the relative O density in the production phase at various $[O_2]$ normalized by maximum and minimum $[O]$ in the range of $-5 < \tau < 10$ ms. The normalized voltage waveform is also plotted in figure 6 to show the timing of $\tau = 0$ s. The O density at $[O_2] = 275$ ppm at close to the discharge ($\tau < 2$ ms) is...
Table 2. Considered reactions and their rate coefficients at 298 K. The ratios for R4, R6, R10–R14, and R23 are branching ratios. Refer to [43] for calculation of $k$ for three-body reactions.

| Reactions | $k$ (cm$^3$ s$^{-1}$) | References |
|-----------|----------------------|------------|
| (R1) O + O$_2$ + M $\rightarrow$ O$_3$ + M | $3.4 \times 10^{-34}$[He] | [44] |
| (R2) O + O + M $\rightarrow$ O$_2$ + M | $1 \times 10^{-33}$[He] | [45] |
| (R3) O + O$_3$ $\rightarrow$ O$_2$ + O | $8.0 \times 10^{-15}$ | [43] |
| (R4) O($^1$D) + O$_2$ $\rightarrow$ O + O$_2$(X, a, b) | $4.0 \times 10^{-11}$ (15:5:80) | [43] |
| (R5) O($^1$D) + O $\rightarrow$ O + O | $2.5 \times 10^{-12}$ | [46] |
| (R6) O($^1$D) + O$_3$ $\rightarrow$ O$_2$ + O$_2$, O$_2$ + O + O | $2.4 \times 10^{-10}$ (1:1) | [43] |
| (R7) O($^1$D) + H$_2$O $\rightarrow$ OH + OH | $2.1 \times 10^{-10}$ | [43] |
| (R8) O($^1$D) + H$_2$ $\rightarrow$ OH + H | $1.2 \times 10^{-10}$ | [43] |
| (R9) O($^1$D) + He $\rightarrow$ O + He | $1.0 \times 10^{-13}$ | [47] |
| (R10) O$_2$(b) + He $\rightarrow$ O$_2$(a) + He | $1 \times 10^{-17}$ | [44] |
| (R11) O$_2$(b) + O$_3$ $\rightarrow$ O$_2$ + O$_2$, O$_2$ + O$_3$ | $2.2 \times 10^{-11}$ (7:3) | [43, 48] |
| (R12) O$_2$(b) + O $\rightarrow$ O$_2$(X, a) + O | $8.0 \times 10^{-14}$ (1:9) | [43, 49] |
| (R13) O$_2$(b) + H$_2$O $\rightarrow$ O$_2$(X, a) + H$_2$O | $4.6 \times 10^{-12}$ (1:9) | [43, 49] |
| (R14) O$_2$(b) + O$_3$ $\rightarrow$ O$_2$(X, a) + O$_2$ | $4.1 \times 10^{-17}$ (1:9) | [43, 49] |
| (R15) O$_2$(a) + O$_3$ $\rightarrow$ O$_2$ + O$_2$ + O | $3.8 \times 10^{-15}$ | [43] |
| (R16) O$_2$(a) + He $\rightarrow$ O$_2$ + He | $8.0 \times 10^{-21}$ | [50] |
| (R17) O$_2$(a) + O$_3$ $\rightarrow$ O$_2$ + O$_2$ | $1.6 \times 10^{-18}$ | [43] |
| (R18) O$_2$(a) + O $\rightarrow$ O$_2$ + O | $1.6 \times 10^{-16}$ | [51] |
| (R19) O$_2$(a) + O$_3$ $\rightarrow$ O$_2$(b) + O$_2$ | $1.9 \times 10^{-17}$ | [52] |
| (R20) O$_2$(a) + H$_2$O $\rightarrow$ O$_2$ + H$_2$O | $5 \times 10^{-18}$ | [43] |
| (R21) OH + O $\rightarrow$ O$_2$ + H | $3.5 \times 10^{-11}$ | [43] |
| (R22) H + O$_2$ + M $\rightarrow$ HO$_2$ + M | $k_0 = 2.0 \times 10^{-32}$[He] ($F_r = 0.51$) | [53] |
| | $k_0 = 3.1 \times 10^{-32}$[O$_2$] ($F_r = 0.50$) | [43] |
| | $k_0 = 3.3 \times 10^{-31}$[H$_2$O] ($F_r = 0.81$) | [53] |
| | $k_\infty = 9.5 \times 10^{-11}$ | [43] |
| (R23) HO$_2$ + O $\rightarrow$ OH + O$_2$ | $5.8 \times 10^{-11}$ | [43] |
| (R24) OH + HO$_2$ $\rightarrow$ H$_2$O + O$_2$ | $1.1 \times 10^{-10}$ | [43] |
| (R25) H + O$_3$ $\rightarrow$ OH + O$_2$ | $2.7 \times 10^{-11}$ | [54] |
| (R26) H + HO$_2$ $\rightarrow$ OH + OH, H$_2$ + O$_2$, H$_2$O + O | $8.0 \times 10^{-11}$ (90:7:3) | [43] |
| (R27) H + OH + M $\rightarrow$ H$_2$O + M | $2.6 \times 10^{-31}$[He] | [53] |
| | $6.8 \times 10^{-31}$[O$_2$] | [53] |
| | $4.3 \times 10^{-30}$[H$_2$O] | [53] |
| (R28) OH + OH $\rightarrow$ H$_2$O + O | $1.5 \times 10^{-12}$ | [43] |
| (R29) OH + OH + M $\rightarrow$ H$_2$O$_2$ + M | $k_0 = 3.7 \times 10^{-31}$[He] | [43, 55] |
| | $k_0 = 1.4 \times 10^{-30}$[O$_2$] | [43, 55] |
| | $k_0 = 4.5 \times 10^{-30}$[H$_2$O] | [43, 55] |
| | $k_\infty = 3.9 \times 10^{-11}$ ($F_r = 0.43$) | [43] |
| (R30) OH + H$_2$O$_2$ $\rightarrow$ H$_2$O + HO$_2$ | $1.7 \times 10^{-12}$ | [43] |
| (R31) OH + O$_3$ $\rightarrow$ HO$_2$ + O$_2$ | $7.3 \times 10^{-14}$ | [43] |
| (R32) HO$_2$ + HO$_2$ $\rightarrow$ H$_2$O$_2$ + O$_2$ | $1.6 \times 10^{-12}$ | [43] |
| (R33) HO$_2$ + HO$_2$ + M $\rightarrow$ H$_2$O$_2$ + O$_2$ + M | $2 \times 10^{-32}$[He] | [56] |
| | $4.5 \times 10^{-32}$[O$_2$] | [43] |
| (R34) HO$_2$ + O$_3$ $\rightarrow$ OH + 2O$_2$ | $2.0 \times 10^{-15}$ | [43] |
| (R35) O + H$_2$O$_2$ $\rightarrow$ OH + HO$_2$ | $1.7 \times 10^{-15}$ | [43] |
| (R36) H + H + M $\rightarrow$ H$_2$ + M | $6.0 \times 10^{-33}$[He] | [53] |
| | $9.1 \times 10^{-33}$[O$_2$] | [57] |
| | $9.3 \times 10^{-32}$[H$_2$O] | [58] |
| (R37) OH + H$_2$ $\rightarrow$ H$_2$O$_2$ + H | $6.7 \times 10^{-15}$ | [43] |
| (R38) H + H$_2$O$_2$ $\rightarrow$ OH + H$_2$O | $4.1 \times 10^{-14}$ | [54] |

aData for M = He are unavailable. Data for M = Ar are used instead.

b Data for M = O$_2$ are unavailable. Data for M = N$_2$ are used instead.

c Multiplied by $\{1 + 2.3 \times 10^{-18}[H_2O]\}$. 


Figure 4. Linearity of TALIF signal against squared laser energy at immediately before and after the discharges.

Figure 5. Time evolution of atomic oxygen at various [O₂] at the center of plasma region.

Figure 6. Time evolution of normalized O density in the production phase.

We can discuss the atomic oxygen production processes in terms of the time constant of increase in [O]. Atomic oxygen production in He–O₂ mixture arises from O₂ dissociation by electron-impact or collision with excited helium (He⁺ or He*). The reactions that can contribute to the atomic oxygen production are listed in table 3. Here, the time constants \( \tau_R \) of primary reactions are calculated as

\[
\tau_R = (k_R [M])^{-1},
\]

where \( k_R \) and [M] are the reaction coefficient and the collider (O₂ or He) density, respectively. The quenching of O(1D), RP2, follows the O(1D) production by the electron-impact dissociation RP1, and thus the atomic oxygen production by RP1 and RP2 are both electronic dissociation-originated.

As for the excited-He-originated O production, the charge transfer reaction RP3 leads to additional O production via RP4. However, if the excited-He-originated production of atomic oxygen was dominant in the afterglow, the time constant of O production should depend on [O₂], under the assumption that the excited He density is constant regardless of [O₂]. Figure 6 exhibits that the atomic oxygen production is completed within 4 \( \mu s \) after discharges regardless of [O₂], which is shorter than the time constant of RP4 at [O₂] = 275 ppm. Furthermore, Norberg et al simulated the He⁺ density as two or three orders of magnitude lower than the electron or O density in He–O₂ (0.2%) negatively pulsed plasma jet at 5–500 kHz repetition [60], which can hardly contribute to O production. Therefore we can conclude that the atomic oxygen production does not arise from RP3 to RP4. The Helium metastable He* also has the potential to produce atomic oxygen via RP5 and RP6, whereas we cannot evaluate the O production via RP6 because O₂⁺ density is not clarified. Naidis simulated the He⁺ density as \( 1–6 \times 10^{12} \text{ cm}^{-3} \) in a He–H₂O plasma jet at 8.4 kHz repetition [61], and Cadot et al measured the He⁺ density as \( 0.4–3 \times 10^{13} \text{ cm}^{-3} \) in a pure He 700 ns-pulsed plasma jet at 20 kHz repetition [62]. These orders of density should not contribute to produce atomic oxygen in the order of \( 10^{15} \text{ cm}^{-3} \), similar to He⁺. As a consequence, the atomic oxygen in the low-frequency APPJ should be produced by electron-impact dissociation and the following quenching of O(1D), similar to the O-production in the RF-plasma jet [26].

3.2.2. Decay phase of atomic oxygen. The decay of atomic oxygen normalized by the maximum density is represented in figure 7. Figure 7 exhibits similar decay rates for [O₂] = 275 and 1050 ppm, while that at [O₂] = 8600 ppm is slightly faster than the others. The average gas flow velocity \( v \) in the tube is 1.35 m s⁻¹, and thus the gas refreshing time is
Table 3. Reactions related with atomic oxygen production.

| Reaction | Rate coefficient at 300 K | Time constant at [O₂] = 275 ppm | Time constant at [O₂] = 8600 ppm |
|----------|---------------------------|---------------------------------|----------------------------------|
| RP1 c + O₂ → c + O + O(1D) | Depends on electron energy | — | — |
| RP2 O(1D) + M → O + M | He: 1 × 10⁻¹³ cm³ s⁻¹ [47] | 0.41 µs | 0.41 µs |
| | O₂: 4.0 × 10⁻¹¹ cm³ s⁻¹ [43] | 3.9 µs | 1.02 µs |
| RP3 He⁺ + O₂ → He + O⁺ + O | 1.1 × 10⁻⁹ cm³ s⁻¹ [44] | 147 ns | 4 ns |
| RP4 O⁺ + O₂ → O₂⁺ + O | 2 × 10⁻¹¹ cm³ s⁻¹ [44] | 7.9 µs | 0.23 µs |
| RP5 He⁺ + O₂ → O₂⁺ + He + c | 2.54 × 10⁻¹⁶ cm³ s⁻¹ [44] | 620 ns | 18 ns |
| RP6 O₂⁺ + O₂ → O₂ + O + O | 1 × 10⁻⁹ cm³ s⁻¹ [60] | — | — |

![Normalized O density](image)

**Figure 7.** Decay of normalized atomic oxygen in plasma region under dry condition.

10 mm/1.35 m s⁻¹ = 7.41 ms, indicating that the atomic oxygen decay in 1 ms range is due to chemical reactions.

Main reactions in the O-decay phase are listed in table 4. Here, the time constants of RD1 are the half-life values of secondary reaction

\[ \tau_{RD1} = (2 k_{RD1} [M] n_{0-O})^{-1} \]  

where \( n_{0-O} \) is the atomic oxygen density immediately after the discharge. The values of \( n_{0-O} \) are estimated from the results of [O₂] variation in section 3.3.2. The half-life values of RD2 are calculated as that of primary reactions,

\[ \tau_{RD2} = \frac{\ln 2}{k_{RD2} [M] [O₂]} \]

where [M] is [O₂] or [He]. Time constants in table 4 indicate that reaction of RD2 with He as the third body has a consistent time constant with the experimental decay at [O₂] = 8600 ppm, whereas reactions RD1 and RD2 do not agree with the decay at [O₂] = 275 or 1050 ppm in figure 7. Reactions RD3 and RD4 could contribute to atomic oxygen consumption owing to their large rate coefficients, but He⁺ and He⁺ are unlikely to remain in the time scale of hundreds of microseconds (e.g. the lifetime of He⁺ and He⁺ are calculated to be 16 ns and 8.5 µs considering the rate of He⁺/He⁺ + 2He → He⁺/He₂⁺ + He [64]). Furthermore, He⁺ and He⁺ have two-order lower density than that of atomic oxygen (as described in section 3.2.1), which should not contribute to the O-decay. The same consideration applies to molecular ions He₂⁺ or metastables He₂⁺. Therefore RD1–RD4 are not supposed to be main factors of the atomic-oxygen decay in [O₂] \( \leq 1000 \) ppm.

A candidate of the main decay path of atomic oxygen is a reaction with OH radicals produced by contaminant H₂O, RD5,

\[ O + OH → O₂ + H. \] (RD5)

The half-life value of O due to RD5 is 1.00 ms when [OH] is 2.0 \times 10^{15} \text{ cm}⁻³. This value of the OH density is derived from measurements in similar condition (1 kHz repetitive rectangular pulsed voltage, 10 kV-peak, He/O₂/H₂O mixture, [H₂O] = 100 ppm, [O₂] = 1200 ppm. Figure 13 in [25]). Although this rough estimation of the time constant may not be accurate as it is on the assumption of the constant OH density, reaction RD5 is qualitatively consistent with the O-decay rate in figure 7, considering that the OH half-life value is in the order of 1 ms [25]. The assumption of a constant OH density is proved to be appropriate in section 3.4.2, considering a cyclic reproduction process.

Figure 8 depicts the normalized [O] decay with the variation of [H₂O] at [O₂] = 1000 ppm, V = 10 kV. In figure 8, increasing [H₂O] drastically accelerated the [O] decay compared to figure 7, indicating the contribution of water-originated particles on the decay of atomic oxygen. The aforementioned discussion leads to an important feature that the several ppm of OH predominates the decay of atomic oxygen, rather than several thousand ppm of O₂. In section 3.4.2, we discuss the reason why OH with 10^{15} \text{ cm}⁻³ density can affect the behavior of O with 10^{15} \text{ cm}⁻³ density.

3.3. Dependence of O production on the discharge condition

In this section, the dependence of atomic oxygen production in each discharge pulse, ∆[O], in the plasma region (z = 10 mm) on the discharge condition is discussed.

3.3.1. Dependence on the applied voltage and discharge energy. Dependence of ∆[O] in the discharge area (z = 10 mm) on the applied voltage and discharge energy at dry
Table 4. Reactions related with atomic oxygen decrease.

| Reaction | Rate coefficient at 298 K | Half-life value at [O2] = 275 ppm | Half-life value at [O2] = 8600 ppm |
|----------|--------------------------|-----------------------------------|-----------------------------------|
| RD1      | He: $1 \times 10^{-33}$ cm$^6$ s$^{-1}$ [45] | 230 ms                           | 3.0 ms                             |
|          | O: $2.57 \times 10^{-34}$ cm$^6$ s$^{-1}$ [45] | 3400 s                           | 1.3 s                              |
| RD2      | He: $3.4 \times 10^{-34}$ cm$^6$ s$^{-1}$ [44] | 13 ms                            | 390 s                              |
|          | O: $6.0 \times 10^{-34}$ cm$^6$ s$^{-1}$ [43] | 29 s                             | 24 ms                              |
| RD3      | He$^+$ + O → He + O$^+$ + e | 2.5 $\times 10^{-10}$ cm$^3$ s$^{-1}$ [44, 63] |                                    |
| RD4      | He$^+$ + O → He + O$^+$ | 5 $\times 10^{-11}$ cm$^3$ s$^{-1}$ [44] |                                    |
| RD5      | O + OH → O$_2$ + H | 3.5 $\times 10^{-13}$ cm$^3$ s$^{-1}$ [43] |                                    |

3.3.2. Dependence on O$_2$ fraction. Dependence of $\Delta$[O] on the [O$_2$] fraction of working gas was also investigated. The current waveforms for [O$_2$] = 110–8600 ppm are depicted in figure 11. Increasing [O$_2$] resulted in faster current rise and higher peak current in the range of [O$_2$] = 110–2000 ppm, whereas the current rising rate stayed constant when [O$_2$] exceeded 2000 ppm. The discharge energy against [O$_2$] fraction at $V = 10$ kV is plotted in figure 12, which exhibits a flat dependence of discharge energy on [O$_2$] fraction.

The energy-normalized O-production $\Delta$[O]/$E_d$ against [O$_2$] fraction under dry condition ([H$_2$O] $\leq$ 100 ppm) at $V = 10$ kV, $z = 10$ mm is represented in figure 13. Figure 13 exhibits a steep increase in $\Delta$[O]/$E_d$ against [O$_2$] in the range of [O$_2$] $<$ 2000 ppm, whereas $\Delta$[O]/$E_d$ is saturated for [O$_2$] $>$ 2000 ppm. The reason for this saturation is not clear, but one...
of the probable reasons is the balance between the electron-impact dissociation frequency and the number of electrons exceeding the energy threshold of \( \text{O}_2 \) dissociation. The frequency of electron-impact dissociation increases when \([\text{O}_2]\) increases, whereas the mean electron energy decreases due to rotational/vibrational \( \text{O}_2 \) excitation, leading to lower number of electrons contributing to \( \text{O}_2 \) dissociation. Enhancement of electron attachment by increasing \([\text{O}_2]\) can cause a decrease in the electron density, which also leads to a similar effect of suppression of \( \text{O}_2 \) dissociation. As a consequence of these opposing effects, atomic oxygen production can be saturated against \([\text{O}_2]\).

From the fitted line in figure 13, \([\text{O}_2]\) dependence of \( \Delta [\text{O}] / E_d \) is formulated as

\[
\frac{\Delta [\text{O}]}{E_d} = 1.3 \times 10^{15} \times \left\{ 1 - \exp(-1.85 \times 10^{-17} [\text{O}_2]) \right\},
\]

where the units of \( \Delta [\text{O}] / E_d \) and \([\text{O}_2]\) are \((\text{cm}^{-3} \cdot \text{mJ}^{-1})\) and \((\text{cm}^{-3})\), respectively. When we assume the proportionality of \( \Delta [\text{O}] \) against \( E_d \) as represented in figure 10 for the entire range of \([\text{O}_2] = 110–8600 \text{ ppm}\), we can calculate the atomic oxygen production in the plasma region using equation (12) as a function of \( E_d \) and \([\text{O}_2]\).

The typical \( \text{O} \) densities in the previous studies of pulsed DBD or RF plasma jets in atmospheric pressure are represented in table 5. Here, SED in table 5 is the specific energy density: SED = (dissipation power)/(flow rate). As represented in table 5, the dissociation rate of \( \text{O}_2 \) in this study is between those of DBD and RF plasma jets, although a simple comparison is difficult owing to different gas compositions and SED.

3.4. Spatial distribution of \( \text{O} \) density in the downstream of the plasma jet

Considering the application of the plasma jet, the axial distribution of \( [\text{O}] \) in the downstream of the plasma region \((z > 30 \text{ mm})\) is also important. In this section, we analyze the spatial distribution of \([\text{O}]\).

3.4.1. Estimation of \( \text{O} \) density profile by chemical reaction simulation

Figure 14 represents the spatial distribution of \([\text{O}]\) at \([\text{O}_2] = 1000 \text{ ppm}, [\text{H}_2\text{O}] = 90 \text{ ppm}, V = 10 \text{ kV}\). Here, \([\text{O}]_b\) and \([\text{O}]_p\) in figure 14 represent \([\text{O}]\) at \( \tau = -2 \mu\text{s} \) and \( 4 \mu\text{s} \), respectively. To estimate the \([\text{O}]\) behavior at the non-measured points, we conducted a chemical reaction simulation considering multiple chemical species, as described in section 2.3. The saw-toothed lines in figure 14 represent the simulated \([\text{O}]\) profiles. One simulation was conducted using the \( \Delta [\text{OH}] \) profile obtained with the same power source and plasma-jet geometry under similar conditions \(([\text{O}_2] = 1200 \text{ ppm}, [\text{H}_2\text{O}] = 100 \text{ ppm}, 1 \text{ SLM flow rate, } V = 10 \text{kV, figure 13 in [25]})\). The profile of \( \Delta [\text{OH}] \) at the discharge timing \( t_d \) was also estimated.
The chain reactions of R21–R23 reproduction of OH, which was consumed by reaction R21. Reaction R23 contributes to the O-decay cannot be attributed to a single equivalent effect of the absence of R21 (O

This indicates that the O-decay cannot be attributed to a single equivalent effect of the absence of R21 or R23. The important feature in figure 3.4.2. Analysis of dominant reactions in the decay of atomic oxygen.

by interpolating the measured results in [25]. The other line is the simulated result with ∆[OH] = 0. The simulation with the ∆[OH] profile exhibits good agreement with the experimental results, indicating that the simulation using measured ∆[O] and ∆[OH] can reproduce the atomic oxygen behavior with a certain accuracy. By contrast, the simulation without OH shows the [O] distribution different from the experiments, owing to significantly slower decay of atomic oxygen between discharges. These results demonstrate the necessity of considering the ∆[OH] distribution to calculate O behavior, indicating the validity of discussion in section 3.2.2, which emphasizes the importance of O consumption by OH.

3.4.2. Analysis of dominant reactions in the decay of atomic oxygen.

In this section, we discuss the reason why OH with 10^{13} \text{cm}^{-3} density can affect the decay of O with 10^{15} \text{cm}^{-3}. Figure 15 depicts the experimental results at [O_2] = 1000 ppm, [H_2] = 90 ppm, V = 10 kV and the simulated results omitting either R21 or R23. The important feature in figure 15 is that the absence of R23 (O + HO_2 → O_2 + OH) results in the equivalent effect of the absence of R21 (O + OH → O_2 + H). This indicates that the O-decay cannot be attributed to a single reaction of either R21 or R23. Reaction R23 contributes to the reproduction of OH, which was consumed by reaction R21. The chain reactions of R21–R23

O + OH → O_2 + H, \quad (R21)

H + O_2 + M → HO_2 + M, \quad (R22)

cyclically reproduces OH with continuous consumption of atomic oxygen (see figure 16). Therefore, OH reduces atomic oxygen without substantial decrease of itself, like a catalyst. This is why the small amount of OH affects the decay of atomic oxygen with the two-order higher density. This cyclic reproduction of OH is also referred in the literatures considering the OH behavior in the streamer discharge [65, 69].

The profiles of [O] and [OH] simulated by full reactions under the same condition as that in figure 15 are represented in figure 17. The density of OH decays immediately after OH production by each discharge (seen as the positive spikes), and thereafter gradually increases or remains constant due to the cyclic reproduction. By contrast, O density has monotonic decreases between discharges. The relatively constant profile of [OH] supports the consideration that OH catalytically consumes atomic oxygen.

3.5. Dependence of O density distribution on the gas composition

Figure 18 illustrates the spatial profiles of [O]_p and [O]_b with the variation of [O_2] under dry condition at V = 10 kV. Atomic oxygen density at [O_2] = 240 ppm, z > 70 mm was not measured because of low signal-to-noise ratio. The measured [O]_b and [O]_p at [O_2] = 8600 ppm had flat profiles at z > 40 mm. However, at the condition of large [O_2] in the plume, [O_3]
is supposed to be significantly high, and the TALIF for [O] would not be correct owing to large ozone interference (see equation (7)). Therefore, the data at [O] = 8600 ppm for z > 40 mm are omitted in figure 18. We confirmed the linearity of $S_{E_2} - S_T$ in the plasma region as shown in figure 4, but did not measure in the plume. The O density at $[O] \leq 1000$ ppm in the plume should not be affected by the ozone interference, because of low O$_3$ density. In figure 18, similar decay rates of [O] against z (slope of z-[O]) in the plume at different $[O_2]$ can be seen.

Axial profiles of [O] at different humidity at $[O_2] = 1000$ ppm and $V = 10$ kV are represented in figure 19. In contrast to figure 18, the humidity of the working gas strongly affected the z-[O] slope in the plume. This different z-[O] slope can be attributed to the decrease of atomic oxygen production $\Delta [O]$ owing to an electron energy suppression by increasing H$_2$O. Another possible factor of the increase in the z-[O] slope is the acceleration of the temporal O decay due to increased OH, H, and HO$_2$, therefore this factor is evaluated. According to a previous report using the same experimental equipment, the slope of z-[OH] is not different between $[H_2O] = 100$ and 1000 ppm (figure 11 in [25]). Under the assumption that the spatial distribution of $\Delta [OH]$ at $[H_2O] = 400$ ppm is simply tripled without changing the shape of that at $[H_2O] = 100$ ppm, a chemical simulation for $[O_2] = 1000$ ppm, $[H_2O] = 400$ ppm was conducted. Figure 19 includes the simulated results; the simulations considered $\Delta [OH]$ (and $\Delta [H]$) distribution as the
same or triple of that at [H$_2$O] = 100 ppm, [O$_2$] = 1200 ppm in literature [25]. The simulated results indicate that the increase in OH leads to only the amplified width of saw-tooth, without changing the slope of $z$-[O]. Therefore, we can conclude that the change in the $z$-[O] slope does not arise from the increase in OH and H; the decrease in $\Delta$[O] is responsible for the increased $z$-[O] slope.

4. Conclusion

We investigated the behavior of atomic oxygen by TALIF in a 1 kHz-repetition pulsed plasma jet in atmospheric-pressure He/O$_2$/H$_2$O mixture. In the dry ([H$_2$O] $\leq$ 100 ppm) condition, the rate of O production did not depend on the [O$_2$] fraction in the range of [O$_2$] = 275–8600 ppm. The analysis of the O-production rate indicates that the atomic oxygen in this plasma jet arises from electron-impact dissociation and quenching of O([D]), similar to the O-production mechanism in RF-plasma jet. The dependence of O production in each discharge pulse ($\Delta$[O]) on the discharge energy $E_d$ and [O$_2$] in the plasma region at dry condition is formulated as $[\Delta$[O]$]$/[cm$^3$]$/E_d$[mJ]$ = 1.3 \times 10^{15} \times \{1 - \exp(-1.85 \times 10^{-17}[O_2]$][cm$^{-3}$]$\}$. The decay rate of atomic oxygen was not explained by self-recombination or ozone-generation reactions; it was consistent with the reaction rate of O + OH $\rightarrow$ O$_2$ + H at [OH] = 2 $\times$ 10$^{13}$ cm$^{-3}$. This result suggests that the small amount of [OH] with 10$^{13}$ cm$^{-3}$ density is more responsible for O behavior than [O$_2$] with large fraction of 10$^{15}$ cm$^{-3}$. We conducted a chemical reaction simulation considering the measured results of [O] and [OH] production, resulting in good agreement with the spatial distribution of [O]. Chemical reaction analysis revealed that the cyclic reproduction of OH via chain reaction with O and O$_2$ is important, therefore a small amount of OH catalytically consumes atomic oxygen with two-order higher density. Humidity in the working gas affected the decay rate of [O] against increasing distance $z$ from the plasma region. This increase in the decay rate of $z$-[O] slope is attributed to $\Delta$[O] suppression rather than the acceleration of O consumption.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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