Electron density measurements of atmospheric-pressure non-thermal N₂ plasma jet by Stark broadening and irradiance intensity methods

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An atmospheric-pressure non-thermal plasma jet excited by high frequency alternating current using nitrogen is developed and the electron density in the active region of this plasma jet is investigated by two different methods using optical emission spectroscopy, Stark broadening, and irradiance intensity method. The irradiance intensity method shows that the average electron density is about 10^{20}/m^3 which is slightly smaller than that by the Stark broadening method. However, the trend of the change in the electron density with input power obtained by these two methods is consistent. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4879033]

I. INTRODUCTION

Atmospheric pressure non-equilibrium plasmas (APNP) are widely used in biomedicine, waste water treatment, and surface modification¹–⁴ and many types of atmospheric plasma sources such as atmospheric glow discharge, dielectric barrier discharge, and atmospheric pressure plasma jets (APPJs) have been reported.⁵–⁹ Plasma diagnostics is crucial to the understanding of the discharge physics and optimization and the electron density is one of the most fundamental parameters in gas discharges. Typical methods to measure the electron density include the Langmuir probe, laser heterodyne interferometry, and laser Thomson scattering, as well as optical emission spectroscopy (OES).¹⁰–¹⁸ The probe method is not suitable for electron density measurement of non-thermal atmospheric-pressure plasmas because of the limited size of the discharge and strong collisional processes. The complicated and expensive laser system also limits the use of laser diagnostics in real applications. In contrast, OES is easy, convenient, and inexpensive and widely used in scientific and applied research.

Herein, two methods based on OES are employed to evaluate the electron density in the APPJ. The first technique analyzes Stark broadening of the hydrogen Balmer line (Hβ) by adding a small amount of hydrogen into the discharge gas. The Stark broadening spectroscopic method can only be used to measure ne exceeding 5.0 × 10¹³/cm³ because of the large pressure broadening superimposed by the Lorentzian shape.¹⁹ Particularly, Stark broadening is more restrictive than van der Waals broadening for a smaller electron density and so Stark broadening theories used in the diagnostics always have a lower limit of Hβ at around 1.0 × 10¹⁴/cm³.²⁰ In an atmospheric pressure air corona discharge, the Stark broadening method is also not suitable because no hydrogen emission lines are detected. The second method analyzes the emission spectra of nitrogen using numerical simulation by solving the Boltzmann’s equation (BE) to determine the electron density. Based on the irradiance intensity calibration, the absolute intensity of N₂(C-B,0-0) at 337.1 nm and N₂⁺(B-X,0-0) at 391.4 nm are used.²¹ Compared to the Stark broadening spectroscopic technique, the second method depends on the absolute emission intensity in lieu of the broadening mechanism and can calculate ne lower than 10¹⁷/cm³.²²,²³ In addition, nitrogen exists in air and the emission spectra can be acquired easily from the discharge.²⁴,²⁵ The discharge current is a function of the electron density and can be also used to determine the plasma parameters. Hence, the discharge current is measured to confirm the electron density calculated by the second method.

Since the emission intensity of the Hβ comes from the most intense part of the discharge, the electron density calculated from Stark broadening always represents the maximum value. While the irradiance intensity relies on the whole radiation power of the plasma, the average electron density can be obtained by considering the entire plasma volume. In this paper, in order to better understand the electron density range in the reactive region of APPJ, Stark broadening of Hβ and the irradiance intensity of excited nitrogen are employed to calculate the electron density of the active region with the aid of auxiliary models and the results are important to applications of APPJ such as biomedical ones.

II. EXPERIMENTAL AND CALCULATION DETAILS

A. Nitrogen plasma jet

Figure 1 depicts the schematic and diagnostic system of the atmospheric-pressure non-thermal AC plasma jet. A stainless steel cylinder with an external diameter of 14 mm and thickness of 3 mm is connected to ground as the outside electrode. The inner rod is composed of copper with a diameter of 2 mm. It is partially covered by a quartz tube to restrict the discharge to a small area. The active region is between the bare part of the inner copper rod and nozzle and the distance between the two electrodes is approximately

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2 mm. The diameter of the nozzle is about 4 mm. The plasma jet is excited by an AC power source which is a commercial transformer capable of providing continuous and tunable output voltages and frequencies. A Tektronix MSO 5104 digital oscilloscope equipped with a high voltage probe (Tektronix P6015A) and current probe (Tektronix P6021) is used to monitor the applied voltage and discharge current of the jet. Nitrogen as the working gas is injected into the chamber from the two gas inlets at a flow rate 1000 l/h controlled by the rotameter and the plasma jet forms the outside nozzle. The emission spectra are acquired on the AvaSpec-2048 spectrometer equipped with eight holographic gratings of 2400 lines/mm, a 10 μm wide slit, and a 5 μm long optical fiber. The instrumental broadening is about 0.11 nm measured by a mercury lamp.

In order to obtain the absolute OES intensity, the irradiance intensity is calibrated by AvaLight-DH-CAL on the AvaSpec-2048 spectrometer. The fiber of the spectrometer is directly connected to the calibration lamp which has the same size interface (SMA905) as the fiber for the calibration. With regard to the end emission spectra of the active region in Fig. 1, the measured images are focused onto the optical fiber through one quartz fused silica lens (50 mm in diameter and focal length of 100 mm) which is set on the axis 30 cm away from the end of the nozzle.

Figure 1 also shows the representative image of the non-thermal plasma jet at a total flow rate of 1000 l/h and discharge power of 22.7 W in nitrogen captured by a digital camera (Canon 5D Mark II) with an exposure time of 0.04 s. Because there is no insulation dielectric barrier between the two electrodes, the discharge channels are not steady and in fact random in the active region. Hence, the active region of the discharge is inhomogeneous. However, as shown in the inset in Fig. 1, the plasma jet of the afterglow out of the nozzle seems to be homogeneous and the length reaches 30 mm. Although the plasma of the afterglow appears to be bright and hot, the gas temperature of the plasma is only about 40–60 °C and the jet is touchable at 10 mm away from the nozzle.

B. H\textsubscript{β} Stark broadening

The specific spectral line of H\textsubscript{β} emitted spontaneously from the plasma is employed to estimate the electron density by analyzing the full-width at half-maximum (FWHM) in Stark broadening (Δ\textlambda:\textsubscript{S}). However, owing to fast collisions among particles in the atmospheric-pressure discharge, broadenings are apparent as several broadening mechanisms including Stark (caused by collisions among charged particles), Van der Waals (due to collisions of neutral particles), Doppler (effect of the thermal motion of emitting atoms), nature, and others exist in the emission line. Each mechanism can result in a shift in the energy levels of the emitting atoms and the relative importance of these broadenings is determined by the plasma conditions. Compared to other broadenings, resonance and natural broadening can be neglected in the atmospheric-pressure discharge with a moderate electron density and temperature. Doppler broadening \( \Delta \lambda_{D} \) is caused by the random thermal motion of the emitting atoms and depends on the gas temperature \( T_{g} \). The approximate formula of FWHM is shown below

\[
\Delta \lambda_{D} = 7.16 \times 10^{-7} \lambda_{0} \sqrt{\frac{T_{g}}{M}}
\]

where \( T_{g} \) is the temperature in Kelvin, \( M \) is the mass of the emitters in atomic mass units, and \( \lambda_{0} \) is the central wavelength of the line in nanometers. Concerning the spectral line of H\textsubscript{β} and by considering the \( \lambda_{0} \) (≈ 486 nm) and \( M = 1 \), \( \Delta \lambda_{D} \) can be simplified as \( \Delta \lambda_{D} = 3.48 \times 10^{-4} \sqrt{T_{g}} \). The instrumental broadening \( \Delta \lambda_{i} \) mentioned in part A and Doppler broadening are assumed to be Gaussian and the convolution
can be presented by a Gaussian function with the FWHM being

$$\Delta \lambda_G = \sqrt{\Delta \lambda_D^2 + \Delta \lambda_I^2}. \quad (2)$$

As the excited atoms interact with neutral ground state atoms of other species, Van der Waals broadening $\Delta \lambda_W$ is an important broadening mechanism in high pressure plasmas and the FWHM can be calculated by

$$\Delta \lambda_W (cm) = 8.2 \times 10^{-12} \lambda^2 (A(R^2))^{2/5} \left( \frac{T_g}{\mu} \right)^{3/10} N, \quad (3)$$

where $\lambda$ is the mean atomic polarizability of the neutral perturber, $\mu$ is the atom-perturbing reduced mass in atomic mass units, and $N$ is the neutral ground-state atom density in $cm^{-3}$. $(R^2)$ is the square difference of the mean coordinate vector of the radiating atom for the upper and lower levels. By considering the relationship of $N$ with pressure $P$ and temperature $T_g$, $\Delta \lambda_W$ can be simplified as $\Delta \lambda_W (nm) = 3.6 \times P/T_0^{0.7}$. Together with Stark broadening, they satisfy the Lorentz profiles and the convolution is also a Lorentz profile with the FWHM being

$$\Delta \lambda_L = \Delta \lambda_S + \Delta \lambda_W. \quad (4)$$

The convolution of the Gaussian profile and Lorentz profile is a Voigt profile and the FWHM can be described by

$$\Delta \lambda_V = \left[ \left( \frac{\Delta \lambda_L}{2} \right)^2 + \frac{\Delta \lambda_G^2}{2} \right]^{1/2} + \frac{\Delta \lambda_L}{2}. \quad (5)$$

According to the functions above and without considering either the temperature or perturbation masses, Stark broadening can be deduced and the FWHM of Stark broadening is related to the electron density by the following relationship:\textsuperscript{20}

$$\Delta \lambda_S = 4.8 \text{ nm} \times \left( \frac{n_e}{10^{17} \text{ m}^{-3}} \right)^{0.68116}, \quad (6)$$

where $n_e$ is the electron density in $m^{-3}$ and $\Delta \lambda_S$ is in nm. For a given gas temperature and gas density, the electron density $n_e$ can be obtained from the deduction of Stark broadening.

C. Absolute irradiance density of OES

The absolute irradiance density of OES and numerical simulation of the nitrogen-containing plasma are used to determine the electron density of the plasma. In the emission spectra, nitrogen emissions $N_2(C-B)$, $N_2^+(B-X)$, and $N_2^+(B-A)$ are the dominate radiative processes, and those high excited electronic states ($N_2(C)$, $N_2^+(B)$, and $N_2^+(B)$) can be excited by direct or step-wise electron impact (\textit{(7)}–\textit{(13)}) as follows:

\begin{align*}
N_2(X^1\Sigma_g^+) + e &\rightarrow N_2(C^3\Pi_u) + e, \quad (7) \\
N_2(X^1\Sigma_g^+) + e &\rightarrow N_2(A^1\Sigma_u^+) + e, \quad (8) \\
N_2(A^1\Sigma_u^+) + e &\rightarrow N_2(C^3\Pi_u) + e, \quad (9) \\
N_2(X^1\Sigma_g^+) + e &\rightarrow N_2(B^3\Pi_g) + e, \quad (10) \\
N_2(X^1\Sigma_g^+) + e &\rightarrow N_2^+(B^2\Sigma_u^+) + e, \quad (11) \\
N_2(A^3\Sigma_u^+) + e &\rightarrow N_2^+(X^2\Sigma_g^+) + 2e, \quad (12) \\
N_2^+(X^2\Sigma_g^+) + e &\rightarrow N_2^+(B^2\Sigma_u^+) + e. \quad (13)
\end{align*}

Apart from electron impact, the pooling reaction of the metastable state $N_2^+(A^3\Sigma_u^+)$ can contribute to the population of the excited states $N_2^+(B^2\Pi_g)$ and $N_2^+(C^3\Pi_u)$

\begin{align*}
N_2(A^3\Sigma_u^+) + N_2^+(A^3\Sigma_u^+) &\rightarrow N_2^+(C^3\Pi_u) + N_2^+(B^2\Pi_g) + N_2^+(X^2\Sigma_g^+), \quad (14) \\
N_2(A^3\Sigma_u^+) + N &\rightarrow N_2^+(X^2\Sigma_g^+) + N. \quad (15)
\end{align*}

$N_2(C-B)$ and $N_2^+(B-X)$ can be excited by direct electron impact excitation processes \textit{(7)} and \textit{(11)} and step-wise impact excitation processes \textit{(9)}, \textit{(13)}, and \textit{(14)}. However, considering the large rate constant of the pooling reaction \textit{(14)} and quenching reaction \textit{(15)} during collisions with nitrogen atoms, the steady-state density of metastable nitrogen is much smaller than that of the ground state and so we mainly consider the direct electron impact excitation of $N_2(C)$. With regard to $N_2^+(B)$, since most of the nitrogen molecular ions are in the ground state ($N_2^+(X)$), step-wise electron impact from $N_2^+(X)$ to $N_2^+(B)$ is also considered.

The electron density estimated by the radiance intensity of $N_2(C,B-0,0)$ and $N_2^+(B,X-0,0)$ is as follows:

\begin{align*}
I_{N_2^+} (C-B, 0-0) &= Q_{N_2^+} \cdot N_{N_2^+} \cdot k_{N_2^+} \cdot V_{\text{plasma}} \cdot n_e, \quad (16) \\
I_{N_2^+} (B-X, 0-0) &= Q_{N_2^+} \cdot N_{N_2^+} \cdot k_{N_2^+} \cdot N_{N_2^+} \cdot k_{N_2^+} \cdot V_{\text{plasma}} \cdot n_e, \quad (17)
\end{align*}

where $Q_{N_2^+}(C)$ and $Q_{N_2^+}(B)$ are the weights of $N_2(C,B-0,0)$ and $N_2^+(B,X-0,0)$ which can be found in other papers.\textsuperscript{21–23} $N_{N_2^+}$ and $N_{N_2^+}$ are the densities of $N_2^+(C)$ and $N_2^+(X)$ in the ground state at the given gas temperature and pressure, respectively. $k_{N_2^+}(C)$ and $k_{N_2^+}(B)$ are the excitation rate constants for $N_2(C)$ and $N_2^+(B)$ which are excited by direct electron impact excited from the ground state $N_2(X)$, respectively. $k_{N_2^+}^+(B)$ is the excitation rate constant of $N_2^+(B)$ which is excited by electron impact from $N_2^+(X^2\Sigma_g^+)$.

The excitation rate constants by electron impact, $k_{N_2^+}(C)$, $k_{N_2^+}(B)$, and $k_{N_2^+}^+(B)$, are determined by electron energy distribution function (EEDF ($f_E$)) and the excitation cross section $\sigma_{\text{exc}}$

$$k_{\text{exc}} = 4\pi \sqrt{2} \int_0^\infty f_E(E) \sqrt{\frac{2e}{m}} E \cdot \sigma_{\text{exc}}(E) dE, \quad (18)$$

where $e$ and $m$ are the elementary charge and electron mass, respectively. $E$ is the kinetic energy of electrons (in eV) and $f_E(E)$ is normalized to fulfill.
The relationship between $t$ions (20)–(22) and estimate the electron densities in independent curves of the electron densities based on functions (16) and (17) by solving the electron BE to obtain the electron transport coefficients and rate coefficients. Apart from the aforementioned main electronic state excitations (2)–(9), in order to obtain the accurate rate constants, vibrational excitations like $\text{N}_2^+ (\text{X} \Sigma^+_g)$ can be transformed to (20) and (21)

$$n_e = \frac{I_{N_2} (C - B, 0 - 0)}{Q_{N_2}(C) \cdot N_2 \cdot k_{N_2}(C) \cdot V_{\text{plasma}}},$$

(20)

$$n_e = \frac{I_{N_2^+} (B - X, 0 - 0)}{I_{N_2}(C - B, 0 - 0)} \cdot \frac{Q_{N_2}(C) \cdot N_2 \cdot k_{N_2}(C) - Q_{N_2}(B) \cdot N_2 \cdot k_{N_2}(B)}{Q_{N_2^+}(X) \cdot k_{N_2^+}(B)}.$$  

(21)

The average power dissipated into the plasma is calculated by the following formula:

$$P = \frac{1}{T} \int_0^T U(t) I(t) dt,$$

(23)

where $T$ is the discharge period and the average discharge power is about 22.7 W. Because the duration of current pulse is only tens of nanoseconds (inset in Fig. 2), the dissipated power is small and consequently, the gas temperature of this plasma jet is quite low.

### B. Gas temperature and electron density

OES is a common technique to determine plasma parameters such as the excited species, rotational temperature ($T_{\text{rot}}$), vibrational temperature ($T_{\text{vib}}$), and excitation temperature ($T_{\text{exc}}$). In the usual way, the rotational structures of the

![FIG. 2. Voltage and current waveforms of the discharge in nitrogen at a flow rate of 1000 l/h.](image)
nitrogen C-B (0–2) band from 365 to 381 nm are employed to estimate the gas temperature \( T_g \) by assuming that the gas temperature is equal to the rotational temperature. Comparing the spectrum calculated by Specair software\(^1\) to the experimental ones, a good fit is obtained at a rotational temperature of 1060 ± 50 K as shown in Fig. 3, indicating that the gas temperature in the active region of the plasma is much higher than that in the afterglow region.

Figure 4 presents the typical Voigt-function fitting of the H\(_b\) experimental profiles. As shown in Table I, by calculating the main broadenings at a gas temperature of 1060 K and pressure of 1 atm, Stark broadening is derived to be about 0.207 nm after deconvolution and the electron density is estimated to be about \( 9.9 \times 10^{20} \) m\(^{-3}\). After performing the irradiance intensity calibration, the absolute irradiance intensity of the emission spectra is measured and the absolute spectra for the vibrational band N\(_2\)(C-B) and N\(_2^+\)(B-X) in the nitrogen discharge shown in Fig. 5 are used to estimate the electron density of active region. The plasma in the active region is thin (0.2 mm) compared to the diameter (2 mm) and assumed to be the surface light source. The volume of the plasma in the active region is about \( 1.8 \times 10^{-9} \) m\(^3\) and the actual radiation area is about 0.24 cm\(^2\) considering the two radiation sides. According to the volume and radiation area, the photon density is calculated as shown in Fig. 5 and the corresponding irradiance is also shown on the right axis. By applying functions (20)–(22), the \( n_e \) distribution in a wide range of electric field \( E \) is shown in Fig. 6(a). The intersection of the three curves is not a single point and three points are found from the Fig. 6(b) due to the inaccuracy in the measured values and applied rate constants arising from the uncertainty of the data. There are three intersections, but they are very close and the average value is used to estimate the electron density. As shown in Fig. 6, at a flow rate of 1000 l/h and discharge power of 22.7 W in nitrogen, \( n_e \) is approximately \( 4.2 \times 10^{20} \) m\(^{-3}\) and the electric field E is about \( 10^6 \) V/m. The change in the electron density with the discharge power obtained by the two methods is shown in Fig. 7. By using the irradiance intensity method, the electron density increases from \( 3.0 \times 10^{20} \) m\(^{-3}\) to \( 5.6 \times 10^{20} \) m\(^{-3}\) when the input power increases from 18 to 28.2 W. However, the electron density obtained by the Stark broadening method increases from \( 6.5 \times 10^{20} \) m\(^{-3}\) to \( 1.5 \times 10^{21} \) m\(^{-3}\). As shown in Fig. 7, the electron density calculated by the Stark broadening method is two or three times of that derived by the irradiance intensity method but they exhibit the same trend as the input power increases. As shown in Fig. 4, Stark broadening of H\(_b\) line is not as smooth implying that the plasma in the active region may be non-uniform\(^3\) but on the other hand, the electron density estimated by Stark broadening should be the peak value of the electron density because the widest profile is usually recorded\(^3\) and so the electron density obtained by using Stark broadening is larger. The electron density obtained by the irradiance intensity method is the

**TABLE I.** FWHM for different broadenings at a gas temperature of 1060 K and pressure of 1 atm.

<table>
<thead>
<tr>
<th>Broadening</th>
<th>FWHM (nm)</th>
</tr>
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<tbody>
<tr>
<td>( \Delta \lambda_c )</td>
<td>0.11</td>
</tr>
<tr>
<td>( \Delta \lambda_D )</td>
<td>( 3.48 \times 10^{-4} \sqrt{T_g} \approx 0.011 )</td>
</tr>
<tr>
<td>( \Delta \lambda_W )</td>
<td>( 3.6 \times P/T_0^{0.7} \approx 0.027 )</td>
</tr>
<tr>
<td>( \Delta \lambda_S )</td>
<td>( 4.8 \text{ nm} \times (\frac{n_e}{10^{23} \text{ m}^{-3}})^{0.68116} \approx 0.207 )</td>
</tr>
</tbody>
</table>

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**FIG. 3.** Experimental and simulated spectra of the active region in the nitrogen discharge at a discharge power of 22.7 W and flow rate of 1000 l/h.

**FIG. 4.** Fit of Stark broadening of the active region in the nitrogen discharge at a discharge power of 22.7 W and flow rate of 1000 l/h.

**FIG. 5.** Irradiance intensity spectra of the active region in the nitrogen discharge.
average because the total irradiance intensity is measured from the plasma and divided by the plasma volume. This is the reason why the electron density computed by this method is smaller. Furthermore, the electrical current method is introduced in the irradiance intensity method and the value is reliable. On the one hand, Stark broadening is not the major broadening effect when the electron density is below \(1.0 \times 10^{14}/\text{cm}^3\) and hence, this method is not suitable for the electron density measurement of discharges with an electron density lower than the threshold value such as that in an atmospheric-pressure glow discharge. On the other hand, the irradiance intensity method which relies on the emission intensity can be used to estimate the electron density smaller than \(1.0 \times 10^{20}/\text{m}^3\). Moreover, the emission lines of nitrogen are easier to detect than those of \(\text{H}_2\), especially in a discharge in open air in which hydrogen cannot be added.

**IV. CONCLUSION**

The electron density of atmospheric-pressure non-equilibrium nitrogen plasma is studied by two methods. The Stark broadening method yields electron densities from \(6.5 \times 10^{20}/\text{m}^3\) to \(1.5 \times 10^{21}/\text{m}^3\) with discharge power from 18 to 28.2 W, whereas the irradiance intensity method shows value of \(3.0 \times 10^{20}/\text{m}^3\) to \(5.6 \times 10^{20}/\text{m}^3\). Although the electron density derived from Stark broadening is two or three times of that calculated by the irradiance intensity method, these two methods show the same trend with discharge power. It is because that the electron density obtained by Stark broadening is the maximum value in the plasma volume, whereas that derived by the irradiance intensity method is average value. When the electron density of the discharge is below a threshold of \(1.0 \times 10^{14}/\text{cm}^3\), the Stark broadening method is not suitable. In comparison, the irradiance intensity method is not limited because of the dependence on the emission intensity and so this method can be used to estimate the electron density in weak processes such as glow discharges and corona discharges.

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FIG. 6. Electron density calculated by applying functions \(20, 21\) and \(22\) in a wide range of electric field \(E\), and \(21\) in a local electric field \(E\).

FIG. 7. Change in the electron density with discharge power in the nitrogen discharge at a flow rate of 1000 l/h.