Multiple (eight) plasma bullets in helium atmospheric pressure plasma jet and the role of nitrogen

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As many as eight multiple plasma bullets produced at atmospheric pressure were observed in one voltage period in a capillary helium dielectric barrier plasma jet. We found that the number of the bullets strongly depends on the nitrogen fraction added to the helium supply gas. Using optical emission spectroscopy and ionization rate calculation, this study demonstrates that nitrogen gas plays an important role in the generation and dynamics of multiple plasma bullets through Penning ionization of nitrogen by helium metastables. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4833638]

Not only for a variety of practical applications but also for scientific understanding, non-thermal atmospheric pressure plasmas have been generated in a number of different ways with various voltage waveforms and frequencies ranging from ac (60 Hz) to microwave, or in a short pulse mode with many different geometries.¹ Among them, atmospheric pressure non-thermal plasma jets have especially been under intensive investigation aiming at recent bio-medical applications, such as wound healing, sterilization, and cancer therapy. In producing the cold jet plasmas, tens of kHz low driving frequencies are favored; they are generally combined with dielectric barriers at atmospheric pressure. In these plasmas, a streamer-like plasma cloud or plasma bullet generated in the vicinity of the powered electrode and propagating toward the ground electrode or into the ambient air with typically a few tens of km/s speed is often observed.² Over the years, active research has been underway on the plasma bullet with different electrode configurations, source geometry, and operation conditions, including gas flow rates and voltage waveforms.³,4 Many studies have been performed with various diagnostic tools in order to explain the bullet mechanism and dynamics.⁵,6 In particular, with the help of the fast intensified charge-coupled device (ICCD) camera, studies based on the plasma bullet image became possible, and it was found that the plasma bullet was generated along the discharge channel immediately after high voltage application. That atmospheric pressure plasma jet appearing as a continuous luminous plasma column has been regarded as the afterimage of “one” fast traveling plasma bullet until a second and/or third plasma bullet during a half voltage cycle was discovered.⁷

This paper reports the generation of as many as eight multiple bullets formed in plasma with a helium-nitrogen mixed gas inside a dielectric capillary tube. The plasma bullets were characterized by electrical and optical diagnostics, including ICCD camera images. In addition, in order to gain a qualitative understanding of the phenomenon of multiple bullet generation, we measured the nitrogen molecular emission spectra and calculated the ionization reaction rates related to the discharge plasma based on possible reactions.

The experimental set up for plasma generation is illustrated in Fig. 1(a). A helium gas with a purity of 99.999% was introduced at a constant flow rate of 1 standard liter per minute (slpm) to a fused silica tube with an inner diameter of 1 mm. The electrodes wrapped around the tubing downstream and upstream were used as the powered electrode and the ground electrode, respectively, and their separation was 15 mm. The plasma was generated at 50 kHz with a 3.7 kV bipolar square waveform voltage source (P6015A) and a current probe (Pearson 4100). The discharge voltage and current were measured by a voltage probe (Tektronix P6015A) and a current probe (Pearson 4100).

Figure 1(b) presents an ICCD image of the multiple plasma bullets propagating from the powered electrode (left) to the ground electrode (right) with 25 ns between the two consecutive images. At more than 4 standard cubic centimeter per minute (sccm) nitrogen addition to the helium supply gas, the multiple plasma bullets begin to appear, and as many eight bullets were produced at a 6 sccm N₂ addition. For the sake of better spatial and temporal resolution for each bullet and a quantitative study, we reduced the number of plasma bullets to four by changing the operating conditions. Furthermore, the role of nitrogen in multiple plasma bullet generation was investigated by supplying different amounts of N₂ to the He carrier gas. The introduction of the nitrogen contained in the ambient air to the plasma jet was reduced by locating the powered electrode 15 mm away from the end of the dielectric tubing, as depicted in Fig. 1(a).

Shown in Fig. 2(a) are sequential ICCD images of the bullets generated at different N₂ concentrations with a constant He gas flow rate (1 slpm) and a constant applied voltage (3.7 kV peak) with 25 ns time intervals. When the N₂ was added at less than 4.5 sccm, a single plasma bullet proceeded from the vicinity of the powered electrode to the ground...
electrode during the positive voltage period. When N₂ was added at greater than 6 sccm, more bullets were successively generated after the first bullet, clearly demonstrating that nitrogen plays a crucial role in multiple bullet generation. It is also observed that the starting point of the first bullet for the added N₂ cases is delayed by up to 250 ns compared to when no N₂ gas was added (i.e., 0 sccm case). It is noted that each of the plasma bullet images shown in Fig. 2(a) is an accumulation of 720 single shot ICCD images at the same corresponding moment in time for improvement of image quality. A single shot was exactly consistent with the accumulated image. Presented in Fig. 2(b) is the discharge current signal as a function of time in one positive voltage period. Two distinct current spikes are clearly seen in the 6.5 sccm case, which is another strong evidence of multiple bullets. It is noteworthy that only two current peaks were measured because the third bullet did not reach the electrode as depicted in Fig. 2(a).

The position and instantaneous speeds of the first bullets at different N₂ additions are plotted in Figs. 3(a) and 3(b), respectively, using the plasma images in Fig. 2(a). The average speed of the first bullet is about 31 km/s regardless of the N₂ concentration and the number of plasma bullets. The figures confirm that the general behavior of the first bullets is about the same. Figures 3(c) and 3(d) show the position and speed of the four bullets case. As depicted in the last picture of Fig. 2(a), the first two bullets reach the ground electrode, whereas during the observation time, the third and the fourth bullets do not. The mean speeds of the bullets are 30.8, 24.4, 13.0, and 10.8 km/s for the first, second, third, and fourth bullets, respectively. In general, the plasma bullet, especially the first bullet, is generated by a breakdown around the powered electrode by the intense electric field. Because bullet propagation is associated with a strong electric field and generation of charged particles, active species, and UV photons at remote locations, the successive breakdown near the powered electrode can occur by the presence of sufficiently high electric field and/or abundant electrons. Therefore, the electric field and electron density after the first plasma bullet generation would be smaller than the initial ignition, and thus, the speed of the successive bullets would decrease as depicted in Fig. 3(d).

In this study, we focused on the role of nitrogen impurities in multiple plasma bullet generation. As shown in Fig. 4, the dominant optical plasma emission spectra become significantly different as the N₂ gas is introduced into the helium discharge at 0 to 6.5 sccm. In the 0 sccm case, i.e., with helium only supplied, He I (706 nm), OH (306.4 nm system, A₂ R侯–X₂ P侯), and O I (777 nm) emissions are dominant with negligible N₂ and N₂⁺ spectra originating from the ambient air. In comparison, when 6.5 sccm N₂ was added to the 1 slpm He gas, N₂ SPS (Second Positive System, C²Πu–B²Πg) and N₂⁺ FNS (First Negative System, B²Σ⁺ u–X²Σ⁺ g) emissions are significantly enhanced.
molecular bands became dominant. In order to investigate the role of nitrogen, nitrogen was included in the He related reactions. The calculation of the ionization reaction rate was obtained from the following reactions:\textsuperscript{8–11}

\begin{align}
He + e \rightarrow He^* + e, & \quad k_1 = f(E/N), \\
He^* + N_2 \rightarrow He + N_2^+ + e, & \quad k_2 = 7.6 \times 10^{-11} \text{ cm}^3\text{s}^{-1} \\
He^* + He + N_2 \rightarrow 2He + N_2^+ + e, & \quad k_3 = 3.3 \times 10^{-30} \text{ cm}^6\text{s}^{-1} \\
He^* + He + He \rightarrow He_2^+ + He, & \quad k_4 = 1.9 \times 10^{-34} \text{ cm}^6\text{s}^{-1} \\
He^* + He + O_2 \rightarrow \text{products}, & \quad k_5 = 9 \times 10^{-30} \text{ cm}^6\text{s}^{-1}
\end{align}

\begin{align}
\frac{d[He^*]}{dt} = k_1[He][e] - \{k_2[He^*][N_2] + k_3[He^*][He][N_2] + k_4[He^*][He][He] + k_5[He^*][He][O_2] + k_6[He^*][O_2] \\
+ k_7[He^*][He][N_2] + k_8[He^*][N_2]\},
\end{align}

where the square bracket $[Q]$ indicates the number density of the species $Q$. In steady state ($d[dt = 0$), the Penning ionization reaction rate derived from $f_P[e] = k_2[He^*][He^*] + k_3[He^*][He][N_2][He^*]$ is expressed as a function of $E/N$, $[He]$, and $[N_2]$, and $k_j$ ($j = 1, \ldots, 8$) as

\begin{align}
f_P = k_4[He] \times \left\{ \frac{k_2[N_2] + k_3[He][N_2]}{k_2[N_2] + k_3[He][N_2] + k_4[He]^2 + k_5[He][O_2] + k_6[O_2] + k_7[He][N_2] + k_8[N_2]} \right\}.
\end{align}

Since the electrode bias voltage and discharge gap for the experiment were 3.7 kV and 15 mm, respectively, the reduced electric field $E/N$ in air is approximately 10 Td. At the front of the plasma bullet, however, the local electric field induced by the plasma bullet head is known to be about 4–7 times higher than the external electric field in the air discharge gap.\textsuperscript{12} Therefore, we used 60 Td in our calculation. In addition, the quenching reactions of He* (Eqs. (5) and (6)) by 0.1% air impurities in helium gas were taken into account due to air diffusion into the tube.

To make a quantitative comparison, the rates of electron impact ionization of He (Eq. (10)) and N$_2$ (Eq. (9)) as well as the rate of Penning ionization of N$_2$ by He* Eqs. (2) and (3) were compared under different N$_2$ concentrations. The result is shown in Fig. 5 where the sum of the Penning ionization rate ($f_P$) and the electron impact ionization rate ($f_{He}$) of N$_2$ is denoted as the blue curve and the electron impact ionization rate ($f_{He}$) is plotted as the red curve, respectively. The N$_2$ fraction in the abscissa is given as the N$_2$ flow rate with respect to the He flow rate as a percentage. As shown in the figure, ($f_P + f_{N2}$) > $f_{He}$ at [N$_2$]/[He] > 0.5%. These results indicate that electron production from N$_2$ can be significant beyond a certain N$_2$ concentration. This result is generally consistent with our experiment in which the multiple bullets begin to appear above a 4.5 sccm N$_2$ flow rate mixed with a 1 slpm He flow as shown in Fig. 2. Furthermore, our plasma was not maintained at [N$_2$]/[He] > 1%, which is also consistent with the large drop of both ($f_P + f_{N2}$) and $f_{He}$.

As the external electric field is applied, electrons start to drift toward the anode and impact ionization occurs, which brings about expansion of the ionization region toward the anode. Due to the charge separation by the electron drift, however, the field strength in the expanding ionization region becomes reduced, which results in ionization stop. This is the first (primary) plasma bullet.\textsuperscript{13,14} The numerical simulation performed by Naidis (see Fig. 4 of Ref. 15) demonstrated that the electric field can be maintained as high as 30 kV/cm even far behind the bullet head. By considering the differences in the simulation condition (8 kV anode voltage, pure He, larger jet radius, metal surface as the anode etc) compared to our experimental condition (3.7 kV anode voltage, gas mixing, smaller jet radius, dielectric wall between the anode and the plasma, etc), the electric field near the anode may be lower than the value for He breakdown. Figure 5 indicates that $f_P$ can be comparable to $f_{He}$ at an appropriate N$_2$ fraction. We believe that these additionally produced electrons via Penning ionization behind the bullet head may increase the electric field near the anode above the electric field strength for He.
breakdown, resulting in the generation of the subsequent bullets.

In summary, as many as eight plasma bullets were experimentally observed in one half cycle of the voltage waveform by adding a small amount of nitrogen to the helium supply gas in atmospheric pressure jet plasma. By analyzing the time evolution of the plasma photographs, discharge current waveforms, and optical emission spectra, we found that additional electrons produced by the Penning ionization of nitrogen molecules play a crucial role in generating subsequent bullets. In addition, a calculation of the ionization rates demonstrates that electron production from N$_2$, especially Penning ionization, can be more significant than that due to electron impact ionization of He at [N$_2$]/[He] > 0.5%, which is consistent with our experimental result.

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