TIME-RESOLVED MASS SPECTROMETRY OF POSITIVE IONS AND ICCD IMAGING OF ATMOSPHERIC PRESSURE PLASMA JET

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ABSTRACT

Nonequilibrium cold plasmas at atmospheric pressure are an ideal solution for treatment of an assortment of samples that cannot endure vacuum such as biological and medical materials. These kinds of plasmas contain molecular and atomic species that play a key role in modification of biological tissues and triggering of biological response. Accordingly, one needs to identify the species and determine their behaviour and concentration and to understand the mechanisms that bring these species to the surface of the sample. Here we will show results of the time-resolved mass spectrometry that provides us with information on composition and mechanisms within plasma.

1. INTRODUCTION

A rapid development of atmospheric nonequilibrium cold plasma led to the formation of various plasma sources that can be applicable in medicine and biology. Atmospheric pressure plasma jet (APPJ) is one of the most promising sources for that purpose. There are many variations of APPJ with different electrode types and geometries [1]–[3]. Different buffer gases, including some mixtures, are used for their operation [4]–[6]. They can operate in large range of excitation frequencies (from few tens of kHz up to MHz) with applied voltages ranging from few hundred up to few kV [7], [8], [9].

Due to the possible application of these sources it is necessary to characterise them in great detail in order to have better control of the desired treatments. One of the important diagnostic techniques of APPJ plasma that comes into contact with biological materials is mass spectrometry. Mass spectrometers can provide an information on the chemical composition of neutrals, positive and negative ions, and radicals created in the plasma [9][10]. It is already shown that concentrations of ROS and RNS radicals are essential for treatment of bio samples and modifications of materials [11]–[13].

Recently, time-resolved measurements of microscale atmospheric plasma jet were performed in order to explain propagation of plasma plume as it interacts in ambient air. ICCD fast imaging observation showed that the plasma effluent is not continuous but is composed of discrete packets of plasma moving at high speed the so-called “plasma bullets” [14]–[16]. The mechanism of the creation of the plasma bullet is associated with the propagation of the ionization front of a streamer but it still requires further studies and better understanding.

In this paper we shall present a set of time resolved measurements of positive ions originated from APPJ and we shall try to explain the correlation between time-resolved ion signals and propagation of the ionization front.

2. EXPERIMENTAL SETUP

We made APPJ body of a Pyrex glass tube with transparent polyester PET foil powered and grounded electrodes (15 mm wide) wrapped around it. Distance between electrodes was 15 mm. Operating excitation frequency was 80 kHz. Flow rate of the feeding gas (He) was kept constant at 5 slm.

Positive ions mass spectra were obtained by HIDEN HPR 60 mass spectrometer. In our measurements we have varied distances between the edge of the glass tube and HPR 60 orifice (15 mm, 25 mm and 30 mm). The applied voltage in all measurements was 10.4 kV.

In order to track in time the signal of detected ions we have synchronized spectrometer and

ICCD camera gating detector with the applied current and voltage signals. We did this by using a custom built comparator which generates TTL signal at the desired level of the current signal.

HPR 60 has 3 different stages in its pumping system and all measurements were done at pressures: the 1st stage $P_1=1.0x10^0$ Torr, the 2nd stage $P_2=2.5x10^{-5}$ Torr and the 3rd stage $P_3=4.2x10^{-7}$ Torr. We have grounded mass spectrometer orifice and also entrances to the second and third stage in order to prevent induction of the electric field within the mass spectrometer which would affect plasma ions. To make sure that the electric and time resolved ions signals are in sync we have performed the correction for time of flight inside the HPR 60 and its detector for every particular positive ion.

3. RESULTS

The most abundant ion species originated from APPJ (see *Fig. 1*) are N_2^+(36%), N^+(20%), O_2^+(18.5%) and O^+(16.8%). Apart from these an important role in plasma-cell interactions is played by NO^+, OH^+ and H^+.

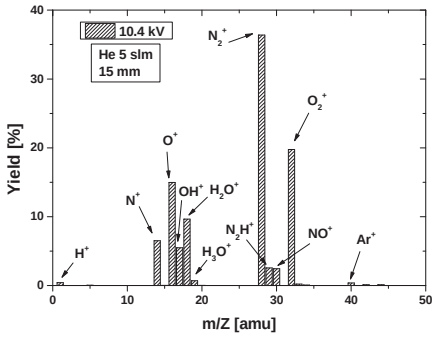

Fig. 1 Mass spectra for positive ions

ICCD camera was used to obtain time resolved images of APPJ positioned in front of the orifice of the mass energy analyzer. We could not use the time resolved emission recorded without the mass analyzer as its presence affected the development of the plasma. Images of plasma of plasma obtained during one period of 12.5 µs are shown in Figure 2. One may see that for the distance of 15 mm plasma is not forming one separate plasma package, but a series of plasma packages (*Fig. 2*, t=12 µs) followed by a constant plasma plume. For the longest distance (30 mm) in our experiments, plasma creates a single plasma package in the positive part of the voltage and current period. Images for distances 25 mm and 30 mm are not shown here due to the lack of space. Mass spectrometry results are presented for the distance of 15 mm unless stated otherwise. The triggering points for both ICCD camera and HPR 60 are shown on V-I waveforms.

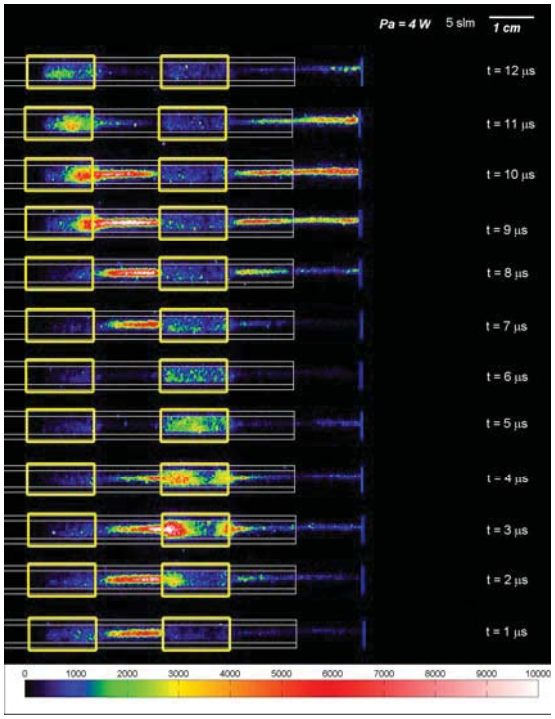

Fig. 2. ICCD images, 15 mm, 5 slm, 4 W

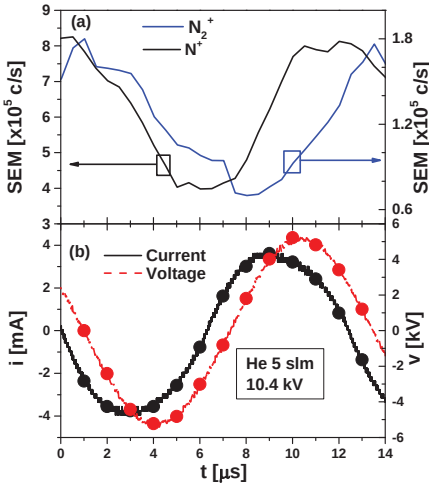

Fig. 3 Comparison of (a) time resolved N_2^+ and N^+ positive ions in sync with (b) current-voltage signals

Figure 3. shows signals of N_2^+ and N^+ positive ions (*Fig. 3(a)*) and waveforms of applied

voltage and current (*Fig. 3(b)*). We can see that signals for N_2^+ and N^+ ions are not in phase and that N^+ ion lags by almost 2 µs. At the same time both of these ions are out of phase with the current signal, N^+ being almost in the opposite phase with it.

As with nitrogen, O_2^+ and O^+ ions are slightly out of phase (*Fig. 4*). The difference with oxygen ions compared to nitrogen is that here maximum of O_2^+signal is lagging the O^+ signal. However, the width of the molecular signal is almost equal to the whole period of 12.5 µs and it has asymmetrical shape. It increases with time, reaches a plateau and then increases again to the maximum value. The position of the plateau corresponds to the maximum of O^+ signal (see *Fig. 4.*).

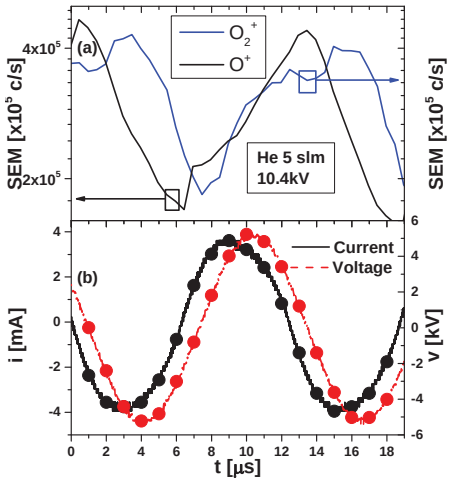

Fig. 4 Comparison of (a) time resolved O_2^+ and O^+ positive ions in sync with (b) current-voltage signals

Interesting point is that for all major ions that we have observed the recorded signals always have some base value and on that base value time resolved signals are superimposed. For example, in case of N_2^+ ion the base signal is around $4 \cdot 10^5$ c/s and for O_2^+ ion it is ~$2 \cdot 10^5$ c/s. The maximum of the signal obtained in time resolved measurements is only 2-2.5 times higher. On the other hand, signal for H^+ ions drops almost two orders of magnitude from its maximum values during one period. For larger distances between APPJ and HPR 60 drops almost to zero. This is probably caused by the small weight of hydrogen ions and therefore they can easily escape the plasma beam effluent.

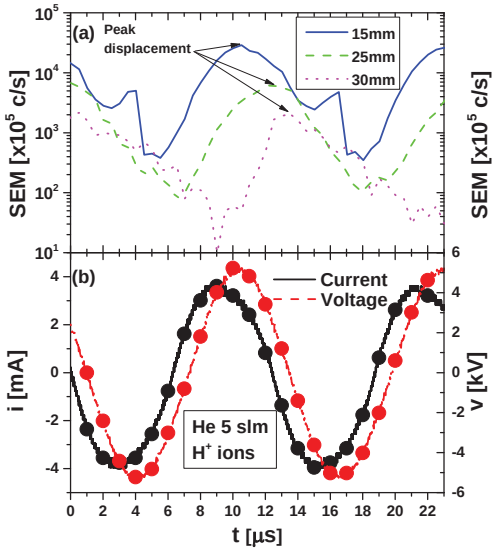

Fig. 5 Different APPJ position comparison for H^+ ions

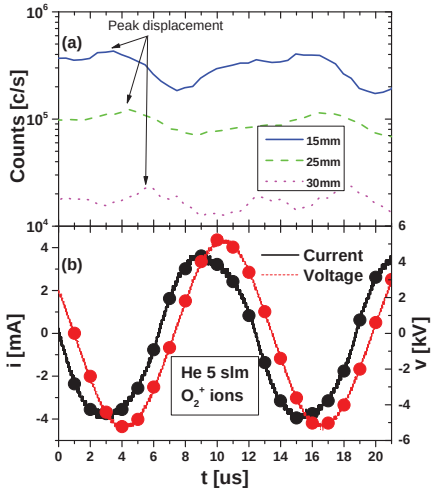

Fig. 6 Different APPJ position comparison for O_2^+ ions

The following figures (*Fig. 5*, *Fig. 6*) show the comparison of the H^+ and O_2^+ signal for three different distances of the plasma jet body from the mass spectrometer orifice. We can see that maximum intensities of the signals for both ionic species are lagging each other as the distance is varied. With the increase of the distance the maximum of the signal is obtained later in time. If we calculate the speed (4-5 km/s) of the plasma package from the data presented in Figs. 5. and 6. we can see that the speed is much lower than the speed of the plasma packages traveling in free air (15-20 km/s). The speed of plasma propagation was previously calculated by using

Andor ICCD fast imaging [17]. The speed of the plasma package in this case is more in agreement with the speed of plasma inside the electrodes.

4. CONCLUSION

We used HPR 60 mass energy analyser for time-resolved investigation of positive ions originated in APPJ. According to these temporal evolution measurements of ionic species it can be seen that variation of voltage and distance significantly affects the concentration and also the time of arrival of the ionic species.

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REFERENCES

[1] J. L. Walsh, F. Iza, N. B. Janson, V. J. Law, and M. G. Kong, "Three distinct modes in a cold atmospheric pressure plasma jet", J. Phys. D. Appl. Phys., **43**, no. 7, p. 75201, 2010.

[2] X. Lu and M. Laroussi, "Dynamics of an atmospheric pressure plasma plume generated by submicrosecond voltage pulses", J. Appl. Phys., **100**, no. 6, p. 63302, 2006.

[3] A. V Nastuta, I. Topala, and G. Popa, "ICCD Imaging of Atmospheric Pressure Plasma Jet Behavior in Different Electrode Configurations", IEEE Trans. Plasma Sci., **39**, no. 11, pp. 2310–2311, Nov. 2011.

[4] S. Reuter, J. Winter, a Schmidt-Bleker, D. Schroeder, H. Lange, N. Knake, V. Schulz-von der Gathen, and K.-D. Weltmann, "Atomic oxygen in a cold argon plasma jet: TALIF spectroscopy in ambient air with modelling and measurements of ambient species diffusion", Plasma Sources Sci. Technol., **21**, no. 2, p. 24005, Apr. 2012.

[5] N. Jiang, J. Yang, F. He, and Z. Cao, "Investigation of Helium Atmospheric Pressure Plasma Jet by Schlieren Visualization", IEEE Trans. Plasma Sci., **39**, no. 11, pp. 2284–2285, Nov. 2011.

[6] A. Sarani, A. Y. Nikiforov, and C. Leys, "Atmospheric-Pressure Plasma Jet in He / H 2 O Mixture", **39**, no. 11, pp. 2358–2359, 2011.

[7] Q. T. Algwari, C. O. Neill, and D. O. Connell, "Interactions between atmospheric pressure plasma jets", pp. 10–12, 2009.

[8] D. Maletić, M. Miletić, N. Puač, N. Selaković, and S. Lazović, "Plasma needle treatment of Staphylococcus Aureus (ATCC 25923) biofilms," **083037**, no. Atcc 25923, p. 83037, 2010.

[9] D. Maletić, N. Puač, S. Lazović, G. Malović, T. Gans, V. Schulz-von der Gathen, and Z. L. Petrović, "Detection of atomic oxygen and nitrogen created in a radio-frequency-driven micro-scale atmospheric pressure plasma jet using mass spectrometry", Plasma Phys. Control. Fusion, **54**, no. 12, p. 124046, Dec. 2012.

[10] G. Malovic, N. Puac, S. Lazovic, and Z. Petrovic, "Mass analysis of an atmospheric pressure plasma needle discharge", Plasma Sources Sci. Technol., **19**, no. 3, 2010.

[11] E. Stoffels, I. E. Kieft, R. E. J. Sladek, E. P. Van Der Laan, and M. Steinbuch, "Plasma needle for in vivo medical treatment : recent developments", **15**, pp. 169–180, 2006.

[12] S. Lazović, N. Puač, M. Miletić, D. Pavlica, M. Jovanović, D. Bugarski, S. Mojsilović, D. Maletić, G. Malović, P. Milenković, and Z. Petrović, "The effect of a plasma needle on bacteria in planktonic samples and on peripheral blood mesenchymal stem cells", New J. Phys., **12**, no. 8, p. 83037, 2010.

[13] N. Puac, Z. L. Petrovic, M. Radetic, and A. Djordjevic, "Low pressure RF capacitively coupled plasma reactor for modification of seeds, polymers and textile fabrics", Curr. Res. Adv. Mater. Process., **494**, pp. 291–296, 2005.

[14] N. Mericam-Bourdet, M. Laroussi, a Begum, and E. Karakas, "Experimental investigations of plasma bullets", J. Phys. D. Appl. Phys., **42**, no. 5, p. 55207, 2009.

[15] J. Jarrige, M. Laroussi, and E. Karakas, "Formation and dynamics of plasma bullets in a non-thermal plasma jet : influence of the high-voltage parameters", **065005**, 2010.

[16] M. Miletić, S. Mojsilović, I. Okić Đorđević, D. Maletić, N. Puač, S. Lazović, G. Malović, P. Milenković, Z. Lj Petrović, and D. Bugarski, "Effects of non-thermal atmospheric plasma on human periodontal ligament mesenchymal stem cells", J. Phys. D. Appl. Phys., **46**, no. 34, p. 345401, Aug. 2013.

[17] N. Puač, D. Maletić, S. Lazović, G. Malović, a. Orević, and Z. L. Petrović, "Time resolved optical emission images of an atmospheric pressure plasma jet with transparent electrodes", Appl. Phys. Lett., **101**, no. 2, p. 24103, 2012.