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CHEMICAL ACTIVATION OF THE HIGH VOLTAGE PULSED, COLD ATMOSPHERIC PLASMA JETS

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Abstract. Chemical activation of the high voltage pulsed, cold atmospheric plasma jets is performed by introducing a low quantity of oxygen into the main flow of helium or argon. This article presents the influence of the oxygen over the intensity of the plasma jet current. Using optical emission spectroscopy we can demonstrate that there is an optimal value of the oxygen concentration that maximizes the plasma chemical activity.

Key words: cold atmospheric plasma jets, chemical activation, high voltage pulses.

1. INTRODUCTION

At present the production and applications of cold plasmas are strongly developed areas of research all over the world.

In most cases, cold atmospheric plasmas are produced by electric discharges in inert gases (helium, argon). The voltages used are high alternative or pulsed voltages. There are a few situations where continuous voltages are used [1]. Alternative voltages may have frequencies of tens of kHz [2–5] or may be radiofrequency [6, 7] or ultra high frequency voltages [8]. The amplitudes of these voltages are of hundreds-thousands of V.

When high voltage pulses are used for producing cold atmospheric plasma jets (as in the case presented in this article), they have amplitudes of tens of kV, durations of tens-hundreds of ns and repetition frequencies of hundreds-thousands of pulses per second (pps) [9–12].

The plasma jets produced in pure helium or argon have a low chemical activity, thus being inappropriate for certain applications (e.g. biomedical applications, food/surface treatment applications). Their chemical activation is necessary, this implying that some chemically active species such as: oxygen atoms, OH radicals, nitrogen atoms, NO radicals, nitrogen ions, helium/argon excited atoms, etc. exist in the plasma jet.

The most important chemically active species are oxygen atoms and OH radicals. That is why the introduction of the oxygen in the discharge area is of greatest importance to chemical activation.

When obtaining chemically active species, the electrons obtained from electric discharges have the essential contribution. The collisions between the energized electrons and the heavy particles result in enhanced levels of excitation, dissociation, and ionization, i.e. enhanced plasma chemistry.

The most important chemical activation reactions are as follows:

$$O_2 + e \rightarrow O + O + e . \tag{1}$$

Reactions with water/nitrogen molecules from the air crossed by the plasma jet:

$$H_2O + e \rightarrow OH + H + e , \tag{2}$$

$$N_2 + e \rightarrow N + N + e. \tag{3}$$

Penning ionization reaction:

$$He\,(2\,^3S) + N_2 \rightarrow He + N_2^+ + e. \tag{4}$$

Charge transfer reaction:

$$He_2^+ + N_2 \rightarrow N_2^+ + He + He. \tag{5}$$

It has been recently demonstrated that narrow voltage pulses are favorable for enhanced plasma chemistry [13–16].

Introducing the oxygen in the discharge area implies finding a solution to the following problem: the concentration of the oxygen must be sufficiently low in order not to excessively disturb the electric discharge, but sufficiently high for a strong chemical activation of the plasma jet. That is why the final result of the experiments outlined in this article is determining optimal oxygen concentrations in the helium/argon plasmas in view of some applications in fields such as biomedicine, food or surface treatment.

2. EXPERIMENTAL SETUP

This article presents the research regarding the chemical activation of the high voltage pulsed cold plasma jets generated at atmospheric pressure with syringe-type structures. The high voltage pulses are applied between the needle-electrode positioned inside a dielectric cylinder and a metal ring placed on the exterior of this cylinder. The electrical characteristics of such a device have been presented in [17]. In order to obtain electric discharges at atmospheric pressure, an inert gas (helium, argon) is introduced in the cylinder. Electric discharges are obtained with voltage pulses of the type presented in Fig. 1. The amplitudes of the high voltage pulses used in the research presented here were of 15–20 kV.

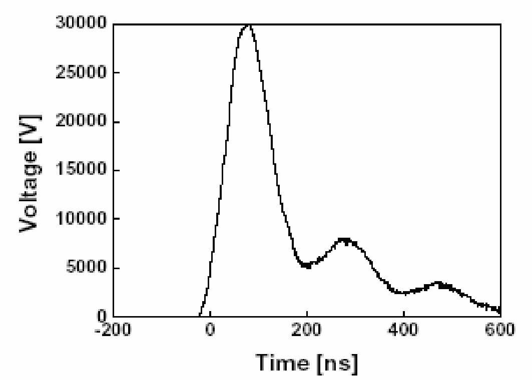

Fig. 1 – High voltage pulse, obtained with the high voltage repetitive pulser.

For chemical activation, oxygen is the chemically active gas introduced in the inert gas jet. The introduction of the oxygen results in a decrease of the current of the discharge plasma. If the oxygen concentration is too high, the discharge may stop and the plasma jet could disappear. Therefore the oxygen concentrations in the mostly inert gas must be of a few percents at most.

From a high pressure cylinder the oxygen passes first through a pressure reductor. Further on, the flow is adjusted using a flowmeter into a range of 0–100 ml/min or 0–500 ml/min, depending on the type of the apparatus. Flowmeters from Aalborg, USA have been purchased. Considering the flow of the mostly inert gas is of a few liters per minute, these flowmeters allow for a fine adjustment of the oxygen concentrations within a range of 0–3%; this range covers the most probable optimal concentrations.

Plasma jets obtained using a new type of device, shown in Fig. 2, have been analyzed. This device replaces old devices, made using medical syringes [17]. The advantage of the new structure is that it allows for flexibility during the modification of various geometrical parameters. The device shown in Fig. 2 is made out of an insulating material cylinder, with an inner/outer diameter of 16/18 mm. The piston made of Teflon is placed in this cylinder. A medical syringe needle with the inner/outer diameter of 1.2/1.6 mm passes through the center of this piston. The needle is the high voltage electrode. At the same time the needle works as the device, which introduces the chemical activation gas (oxygen, in this case) in the discharge area. The mostly inert gas (He/Ar), facilitating the occurrence of electric discharges at atmospheric pressure is introduced through an orifice in the lateral wall of the dielectric cylinder. The lower end of the dielectric cylinder is covered with a Teflon lid. The exit channel of the plasma jet is positioned at the center of this lid. The inner diameter of the exit channel is of 1.5 mm. A metal ring working as the mass electrode of the device is stuck onto the outer part of the lid. The discharges within the cylinder are similar to the dielectric barrier discharges. The inert gas (helium, argon) flow pushes the discharge plasma out, forming the plasma jet.

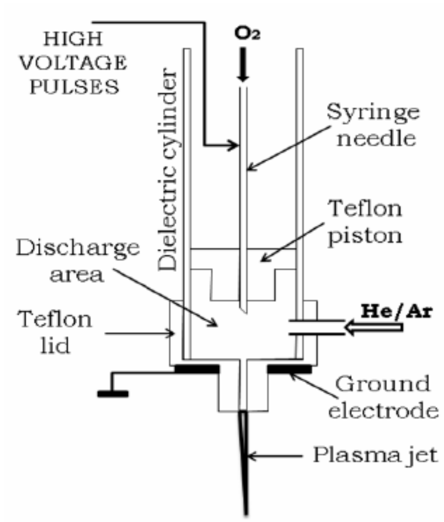

Fig. 2 – Drawing of the device for generating high voltage pulsed, cold atmospheric plasma jets.

The measuring procedure for the current along the plasma jet has been described in [17].

For spectral analysis, a high resolution (0.75 nm FWHM) optical fiber spectrometer connected to a computer running SpectraSuite is used: HR4000 (Ocean Optics Inc. – USA).

3. EXPERIMENTAL RESULTS

Once the concentration of the oxygen introduced in the discharge area is rising, the plasma jet current is getting lower and lower. Fig. 3 shows the currents of the plasma jet at a distance of 1 cm and 2 cm respectively from the exit outlet, for various oxygen concentrations, from 0.2 % up to 2 %. The helium flow is 4 l/min. The explanation of this phenomenon lies in the fact that the introduction of an electro-negative gas (such as oxygen) in the inert gas produces a reduction of the electron density and, as a result, a reduction of the electric conductivity.

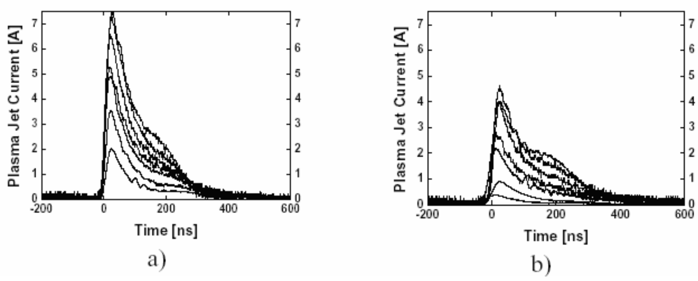

Fig. 3 – The current of the plasma jet at a distance of 1 cm (a) and 2 cm (b) from the exit outlet, for various concentrations of oxygen in helium (He – 4 l/min). From the most intense to the weakest current, the oxygen concentrations are: 0.2 %; 0.4 %; 0.6 %; 0.8 %; 1 %; 1.5 %; 2 % respectively.

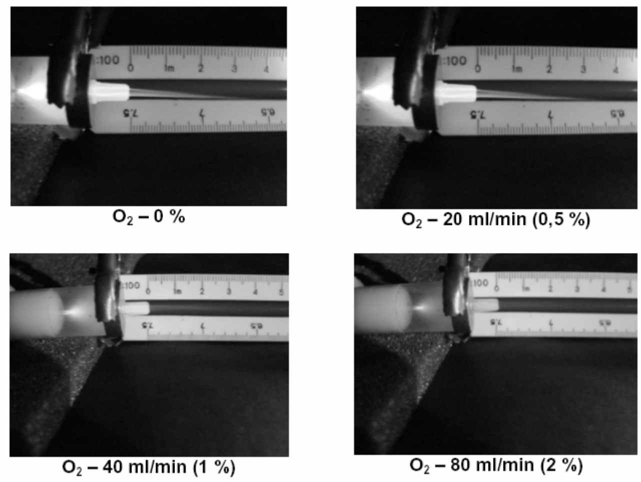

Fig. 4 – Oxygen chemical activation (He – 4 l/min). Discharge between electrodes, and plasma jet for various concentrations of oxygen in helium. Chemical activation of the high voltage pulsed, cold atmospheric plasma jets

These results are also confirmed by the visual aspect of the plasma jet. Fig. 4 shows the discharge within the dielectric cylinder and the plasma jet, for oxygen concentrations from 0% up to 2%. It is observed that while the oxygen concentration is rising, the discharge within the cylinder is getting weaker and weaker, and the outer plasma jet is less and less luminous, and shorter and shorter. The plasma jet disappears completely at an oxygen concentration of around 3 %.

The experimental observations presented above are according to the optical emission spectra at 1 mm downstream of the nozzle exit.

A first observation with reference to the helium (Fig. 5) and argon (Fig. 6) plasma spectra is that emission lines in 200–300 mm range are very weak. This means that ultraviolet photons do not constitute an active species in such plasmas. This is the conclusion reached by other authors as well [18, 19].

Fig. 5 shows the emission spectra of the high voltage pulsed, cold atmospheric plasma jets, with helium working gas, for various concentrations of oxygen introduced for the chemical activation of the plasma. The helium flow was 5 l/min, the amplitude of the voltage between the electrodes was of 20 kV, and the pulse repetition frequency – 100 pps.

The helium 587 nm line and the atomic oxygen 777 nm line are present in all the situations shown in Fig. 5. The nitrogen lines from the air crossed by the plasma jet are obvious in the 337–406 nm spectral zone, at oxygen concentrations of up to 0.5 %.

In general, the increase of the oxygen concentration in the discharge area leads to lower intensity spectral lines. The explanation lies in the decrease of the plasma jet current when the oxygen concentration increases.

From the plasma chemical reactivity point of view, the intensity of the 777 nm line of the atomic oxygen is relevant. In Fig. 5a we can notice that though no oxygen is introduced in the discharge area, the intensity of the atomic oxygen line is nevertheless of 13,000 units. In this case, the atomic oxygen is due to the interaction of the electrons produced by the electric discharge with the air crossed by the plasma jet. The intensity of the atomic oxygen line increases to 27,500 units when oxygen of 0.5% concentration is introduced in the discharge area (Fig. 5b). However the 777 nm line intensities drop to 14,000, 9,200 and 5,600 units respectively at oxygen concentrations of 1, 1.5, 2 %.

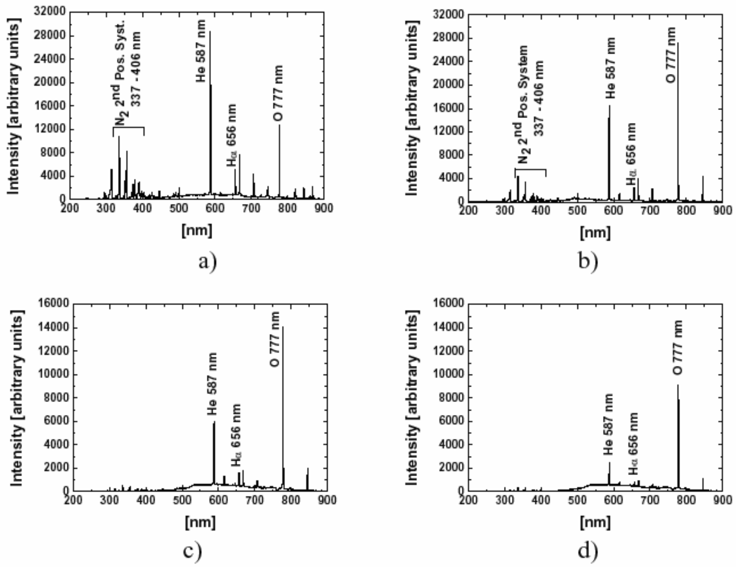

Fig. 5 – Emission spectra of the helium plasma jets (5 l/min), for various values of the concentration of the oxygen introduced in the discharge area: a) 0 %; b) 0.5 %; c) 1 %; d) 1.5 %.

One more thing to observe, especially at the spectra shown in Fig. 5a, 5b, is the presence of the H_α (656 nm) line, a result of the collision between the water molecules and electrons ((2) reaction in the Introduction). This spectral line demonstrates the presence of OH radicals, an extremely active chemical species, in the plasma jet.

The conclusion of these experiments is that the maximum chemical activity of the helium plasma jet is obtained upon the introduction of oxygen with a concentration of 0.5% in the discharge area.

The emission spectra of the argon plasma jets (Fig. 6) show that most spectral lines belong to argon-excited atoms. The nitrogen lines in the air crossed by the plasma jet are very weak in this case, as opposed to the helium plasma spectra. The explanation lies in the fact that most electrons in the discharge area interact with the argon atoms and oxygen molecules.

The emission spectra shown in Fig. 6 are obtained with concentrations of oxygen in argon of 0, 0.5, 1, 1.5 %. The argon flow was of 2 l/min. The amplitude of the voltage between the electrodes was of 20 kV, and the pulse repetition frequency – 100 pps. The spectral lines from the 650–950 nm range are presented below; this range includes all the lines emitted in the UV-visible range by the argon plasma jet. The spectral lines emitted by the argon-excited atoms correspond to the 4p – 4s transitions in the Paschen notation [6]. Thus emission lines with wavelengths of: 696.5, 706.7, 714.7, 727.3, 738.4, 750.4, 763.5, 772.4, 794.8, 801.5, 811.5, 826.5, 842.5, 852.1 nm are present. The most intense lines are 763.5 nm ($2p_6-1s_5$) and 811.5 nm ($2p_9-1s_5$) lines.

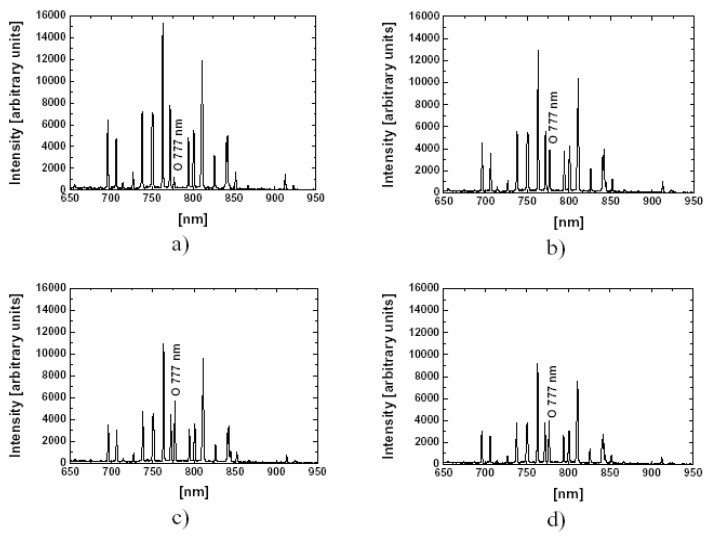

Fig. 6 – Emission spectra of the argon plasma jets (2 l/min), for various values of the concentration of the oxygen introduced in the discharge area: a) 0 %; b) 0.5 %; c) 1 %; d) 1.5 %.

The spectra in Fig. 6 include the atomic oxygen 777 nm line which highlights the chemical activity of the plasma jet. The intensity of this line is minimal at 0% oxygen concentration, which corresponds to the theory that says that the interaction of the electrons with the air from the environment is very weak with argon plasma jets.

The intensity of the atomic oxygen 777 nm line is maximal at 1% concentration of oxygen in argon. The further increase of the oxygen concentration has as result the decrease of the number of oxygen atoms. The result is that in the experimental conditions shown here, the optimal oxygen concentration from the plasma chemical activity point of view is of 1%.

The future perspective of our research is using cold atmospheric plasma jets in the biomedical field, at decontaminating thermo-sensitive food products and in surface treatments.

The first results of the treatment of certain skin tumor cells of mouse (B16 type cells) have been obtained. The treatment aims to maximize the number of the cells in apoptosis (slow death) and to minimize the number of the cells in necrosis (rapid death that has as result the inflammation of the tissue and further development of the tumor [20, 21]). Fig. 7a shows five B16 tumor cells. Fig. 7b and Fig. 7c show two B16 tumor cells in apoptosis after 1 minute-treatment with 1 % oxygen chemically activated helium plasma.

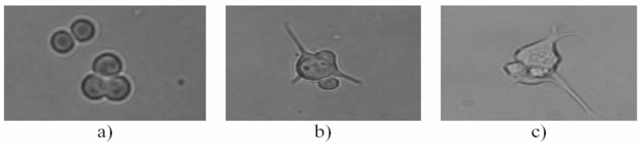

Fig. 7 – a) Five skin tumor cells of mouse (B16 type cells); b), c) two B16 tumor cells in apoptosis after 1 minute-treatment with 1 % oxygen chemically activated helium plasma.

4. CONCLUSIONS

High voltage pulsed, cold atmospheric pressure plasma jets have been chemically activated by introducing low concentrated oxygen in the main flow of helium or argon. The helium-argon flows were in the 1–5 l/min range, and the flows of the oxygen introduced in the electric discharge area were of up to 100 ml/min.

Using optical emission spectroscopy it has been demonstrated that the most important chemically active species in the plasma jet are oxygen atoms and OH radicals.

There is an optimal value of the oxygen concentration introduced in the electric discharge area; this value maximizes the chemical activity of the plasma: 0.5 % oxygen in helium and 1 % oxygen in argon.

Chemically active cold plasmas, which have been obtained, will be further used in biomedical applications, in research regarding the decontamination of thermo-sensitive food products, as well as in surface treatment.

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REFERENCES

1. D. Dudek, N. Bibinov, J. Engemann, P. Awakowicz, *Direct current plasma jet needle source*, J. Phys. D: Appl. Phys., **40** 7367 7371 (2007).
2. Xianhui Zhang, Maojin Li, Rouli Zhou, Kecheng Feng, and Size Yang, *Ablation of liver cancer cells in vitro by a plasma needle*, Appl. Phys. Lett., **93**, 021502 (2008).
3. Xin Pei Lu, Zhong He Jiang, Qing Xiong, Zhi Yuan Tang, Xi Wei Hu, Yuan Pan, *An 11 m long atmospheric pressure cold plasma plume for applications of plasma medicine*, Appl. Phys. Lett., **92**, 081502 (2008).
4. Qiu-Yue Nie, Chun-Sheng Ren, De-Zhen Wang, Jia-Liang Zhang, *A simple cold Ar plasma jet generated with a floating electrode at atmospheric pressure*, Appl. Phys. Lett., **93**, 011503 (2008).
5. Gui-Min Xu, Yue Ma, Guan-Jun Zhang, *DBD Plasma Jet in Atmospheric Pressure Argon*, IEEE Trans. Plasma Sci., **36**, *4*, 1352–1353 (2008).
6. V. Leveille, S. Coulombe, *Design and preliminary characterization of a miniature pulsed RF APGD torch with downstream injection of the source of reactive species*, Plasma Sources Sci. Technol., **14,** 467 476 (2005).
7. Dan Bee Kim, J. K. Rhee, B. Gweon, S. Y. Moon, W. Choe, *Comparative study of atmospheric pressure low and radio frequency microjet plasmas produced in a single electrode configuration*, Appl. Phys. Lett., **91**, 151502 (2007).
8. D. Mariotti, *Nonequilibrium and effect of gas mixtures in an atmospheric microplasma*, Appl. Phys. Lett., **92**, 151505 (2008).
9. M. Kuchenbecker, N. Bibinov, A. Kaemlimg, D. Wandke, P. Awakowicz, W. Viol, *Characterization of DBD plasma source for biomedical applications*, J. Phys. D: Appl. Phys., **42**, 045212 (10pp) (2009).
10. Xin Pei Lu, Tao Ye, Ying Guang Cao, Zi Yong Sun, Qing Xiong, Zhi Yuan Tang, Zhi Lan Xiong, Jing Hu, Zhong He Jiang, Yuan Pan, *The roles of the various plasma agents in the inactivation of bacteria*, J. Appl. Phys., **104**, 053309 (2008).
11. X. Lu, M. Laroussi, *Dynamics of an atmospheric pressure plasma plume generated by submicrosecond voltage pulses*, J. Appl. Phys., **100**, 063302 (2006).
12. B. L. Sands, Biswa N. Ganguly, Kunihide Tachibana, *A streamer-like atmospheric pressure plasma jet*, Appl. Phys. Lett., **92**, 151503 (2008).
13. J. L. Walsh, M. G. Kong, *Room-temperature atmospheric argon plasma jet sustained with submicrosecond high-voltage pulses*, Appl. Phys. Lett., **91**, 221502 (2007).
14. X. Lu, M. Laroussi, *Electron density and temperature measurement of an atmospheric pressure plasma by millimeter wave interferometer*, Appl. Phys. Lett., **92**, 051501 (2008).
15. Xin Pei Lu, Zhong He Jiang, Qing Xiong, Zhi Yuan Tang, Yuan Pan, *A single electrode room-temperature plasma jet device for biomedical applications*, Appl. Phys. Lett., **92**, 151504 (2008).
16. J. L. Walsh, M. G. Kong, *Room-temperature atmospheric argon plasma jet sustained with submicrosecond high-voltage pulses*, Appl. Phys. Lett., **91**, 221502 (2007).

17. N. Georgescu, *High voltage pulsed,cold atmospheric plasma jets: electrical characterization*, Romanian Reports in Physics, **60**, 4, 1025–1032 (2008).
18. M. Laroussi, X. Lu, *Room-temperature atmospheric pressure plasma plume for biomedical applications*, Appl. Phys. Lett, **87**, 113902 (2005).
19. Gui-Bing Zhao, Morris D. Argyle, Maciej Radosz, *Optical emission study of nonthermal plasma confirms reaction mechanisms involving neutral rather than charged species*, J. Appl. Phys., **101**, 033303 (2007).
20. T. L. Whiteside, *The tumor microenvironment and its role in promoting tumor growth*, Oncogene, **27**, 5904–5912 (2008).
21. T. J. Stewart, S. I. Abrams, *How tumor escape mass destruction*, Oncogene, **27**, 5894–5903 (2008).