Cold atmospheric pressure plasma jets as sources of reactive oxygen species for biomedical applications

J.S. Sousa (*) [1,2], Q.Th. Algwari [1,3], L.J. Cox [1], L.M. Graham [1], J. Waskoenig [1], K. Niemi [1,4], D. O'Connell [1,4], T. Gans [1,4]

[1] *Centre for Plasma Physics, School of Maths & Physics, Queen's University Belfast, Belfast BT7 1NN, United Kingdom*
[2] *Laboratoire de Physique des Gaz et des Plasmas, CNRS and Université Paris-Sud, 91405 Orsay, France*
[3] *Electronic Department, College of Electronics Engineering, Mosul University, Mosul 41002, Iraq*
[4] *York Plasma Institute, Department of Physics, University of York, York YO10 5DD, United Kingdom*
(*) joao.santos-sousa@u-psud.fr

Absolute densities of the three main reactive oxygen species (ROS) – atomic oxygen (O), ozone (O_3), and singlet delta oxygen ($O_2(a^1\Delta_g)$) – created in two different atmospheric pressure plasma jets (a capacitively coupled radio-frequency-driven and a kilohertz-driven dielectric barrier discharge) were measured by different optical diagnostics. The influence of different parameters, such as gas flows and mixtures and power coupled to the plasmas, on the production of these ROS was investigated. The results show that the control of the operating conditions of the plasma jets enables the tailoring of their ROS composition. This provides scope to tune the plasma jets for desired applications, e.g., in biomedicine.

Atmospheric pressure non-thermal plasma jets (APPJs) have great technological potential, notably in biomedicine. The current interest in this type of atmospheric pressure discharges stems from the fact that they provide a means of delivering in open air, at ambient pressure and temperature, reactive plasma species (viz. radicals, positive or negative ions, electrons, UV radiation), and not only long-lived afterglow species, to a target located some centimeters away from the main discharge zone. This property opens up a host of new and interesting possibilities including, among others, extremely localized treatments (down to dimensions of living cells), 2D and 3D treatments (for cleaning and thin film deposition), production of nanomaterials, decontamination and biomedical applications. The understanding of the fundamental plasma chemistry is vital for the development and optimization of such plasma sources for applications. The aim of this work was to measure the reactive oxygen species content of two different APPJs, and explore their potential biomedical applications.

The first plasma jet design that was investigated is, as shown in Figure 1, composed of a cylindrical capillary dielectric tube (quartz) with inner diameter of 4 mm and outer diameter of 6 mm. Two external, 2 mm wide, tubular copper electrodes are assembled around the tube forming a dielectric barrier discharge type configuration. The distance between electrodes can be varied, being the electrode separation typically of few centimeters. The downstream electrode is driven at a pulse excitation frequency of tens of kHz (20–80 kHz) and high voltage (1–10 kV). An intense plasma forms inside the glass tube between the two electrodes, and a relatively long pulsed plasma plume of few centimeters emerges at both sides of the powered electrode (the one downstream), and propagate into free space in the gas channel. The length of the plume has been found to depend on the operational parameters (e.g. applied voltage, gas flow rate). These plumes, while continuous to the naked eye, consist in fact of a transient series of plasma pulses when imaged on a nanosecond time scale. The plasma pulses have a velocity much greater than the gas flow velocity, and are sustained through a streamer-like mechanism [1].

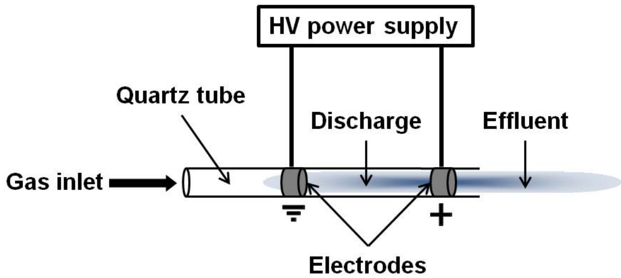

Fig. 1: Schematic of the kHz-driven atmospheric pressure plasma jet.

The second APPJ is a homogeneous glow discharge sustained between two parallel stainless steel plates – see Figure 2. One electrode is driven at 13.56 MHz by a RF broadband amplifier via an impedance matching network, while the other one is grounded. In this RF-driven APPJ, the electric field is perpendicular to the gas flow, and, thus, the effluent emitted from the plasma bulk into ambient air is charge-free [2]. The electrode spacing is of 1 mm, and quartz windows enclose the discharge region along the sides, providing optical access to the plasma volume. The core plasma channel has a cross section of 1 mm × 1 mm, over a length of 30 mm. Typical RF-generator powers applied through the matching network are 5–70 W, voltage amplitudes are several 100 V and total current amplitudes are in the range of 1–10 A. However, large stray capacitances within the matching network can be expected due to the small dimensions of the active plasma region within the RF-APPJ, which considerably reduce the amount of RF-power actually coupled into the plasma. The operational RF power range depends on the flow and feed gas composition.

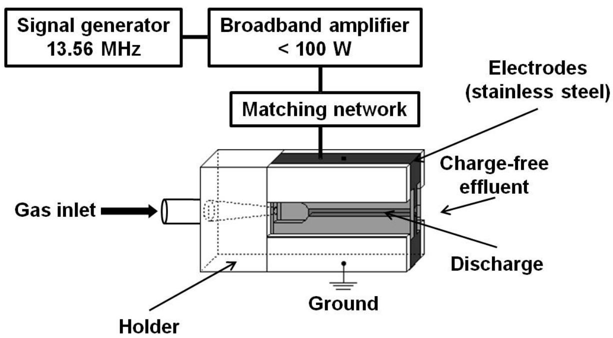

Fig. 2: Schematic of the RF-driven atmospheric pressure plasma jet.

In order to characterize both APPJs and determine, for instance, the deposited power, the gas temperature, and the reactive species density, several electrical and optical diagnostics were implemented (e.g. emission and absorption spectroscopy (from UV to IR), electrical measurements, fast imaging). The absolute densities of the three main reactive oxygen species (ROS) were measured through different optical diagnostics of the discharge volumes and effluent regions: atomic oxygen (O) inside the discharge by diagnostic based modeling [3], ozone (O_3) by ultra-violet optical absorption along the discharge channel [4], and the output of meta-stable singlet delta oxygen molecules ($O_2(a^1\Delta_g)$) by infra-red emission in a calibrated afterglow detection cell [5]. When operated in helium with small oxygen admixture (O_2 <2%), both APPJs efficiently produced high densities of these ROS (10^{14}–10^{16} cm^{-3}; cf. Figures 3 and 4) in the gas phase at low gas temperatures (300–350 K) [6]. Both these properties are essential for sensitive surface treatments in bio-medicine [7]. The effect of different parameters, such as gas flows and mixtures, and power coupled to the plasmas, on the production of these ROS by the two APPJs were studied. Our results show that the ROS density dependences on the oxygen admixture and deposited power are different in the two APPJs. These observed differences combined with complementary experiments regarding the use of different effluent geometries, allowed us to highlight the role of the charged species on the quenching of singlet delta oxygen.

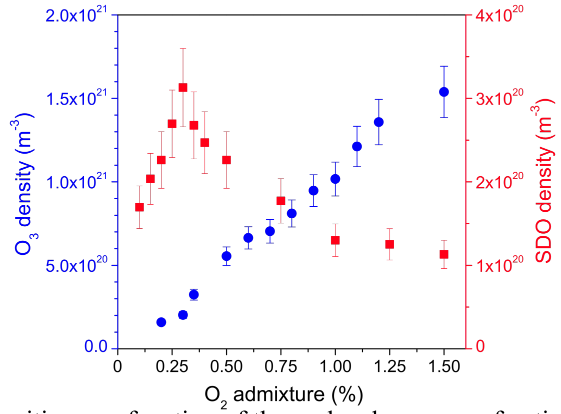

Fig. 3: $O_2(a^1\Delta_g)$ and O_3 densities as a function of the molecular oxygen fraction in the gas mixture (He/O_2). Plasma jet (kHz-APPJ) operation at 6 kV and 20 kHz, with a He flow of 2 slm.

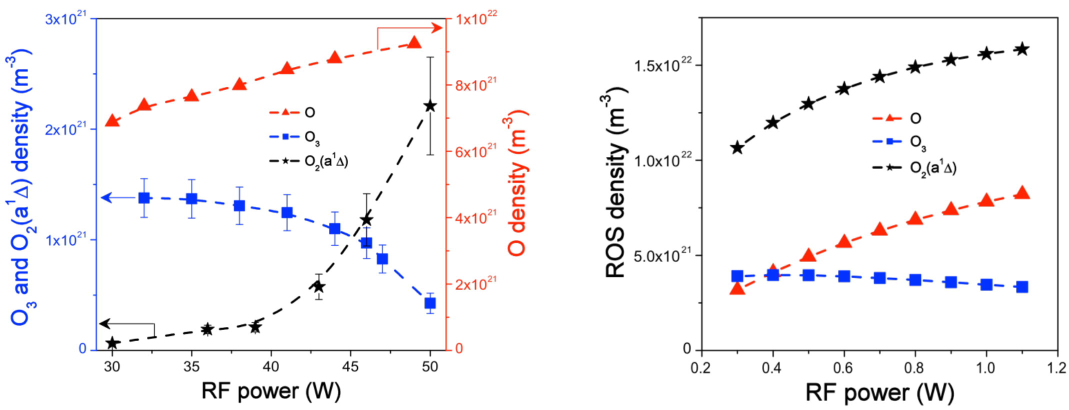

Fig. 4: Measured (left) and simulated (right) ROS densities as a function of RF generator power. Plama jet (RF-APPJ) operation with a He flow of 1 slm, and 0.5% of O_2 admixture.

The experimental results of the RF-APPJ were compared to a one-dimensional numerical simulation of the discharge, which includes a semi-kinetical treatment of the pronounced electron dynamics and the complex plasma chemistry (20 species and 184 reactions in total) [8]. Figure 4 shows the measured and simulated RF power dependencies of the ROS densities. The simulation yielded a good qualitative agreement with the measurements and a further understanding of the relevant production and destruction mechanisms for the different ROS inside the discharge. Particularly, the absolute values for atomic oxygen and ozone showed a better agreement, since the corresponding measurements were taken inside the discharge region. The quantitative disagreement for singlet delta oxygen confirmed its loss during transport in the afterglow before its detection. The numerical simulation further revealed the dominant production and destruction processes for the different ROS inside the discharge [8]. The formation of ROS could be described fairly accurately by only a few important plasma chemical reactions.

Furthermore, as exemplified in Figures 3 and 4, opposite trends for the different ROS densities within the operational range of each APPJ were also observed. Thus, the control of each APPJ operating conditions enables to tailor the ROS composition of the APPJs effluent towards different biomedical applications, from fundamental biochemical studies to therapeutic treatments, through sterilization and bio-decontamination. In order to improve the understanding of how plasma treatment can affect living tissues, and having in mind that the measured densities of the different ROS in the effluent of both APPJs could be directly correlated with modifications observed in biological materials after plasma treatment, biological experiments have been performed. The preliminary results are quite promising.

Acknowledgments

The authors thank V. Puech (LPGP, CNRS & UPS-11, Orsay, France) for providing the diagnostic setup for measuring the absolute singlet delta oxygen density. The numerical simulations were initially supported by Y. Sakiyama and D.B. Graves (University of California, Berkeley). The authors are grateful to M.J. Kushner (University of Michigan) for providing electron-impact cross-section data. The authors acknowledge support from the UK Engineering and Physical Sciences Research Council (EPSRC), through a Science and Innovation Award (Grant No. EP/D06337X/1) and a Career Acceleration Fellowship (Grant No. EP/H003797/1). Q.Th.A. acknowledges the financial support from the Iraqi Ministry of Higher Education. Two of the authors (L.J.C. and L.M.G.) are supported by the Northern Irish Department for Employment and Learning (DEL).

References

[1] B.L. Sands, B.N. Ganguly, K. Tachibana, *Appl. Phys. Lett.* **92** (2008) 151503.

[2] A. Schütze, J.Y. Jeong, S.E. Babayan, J. Park, G.S. Selwyn, R.F. Hicks, *IEEE Trans. Plasma. Sci.* **26** (1998) 1685.

[3] K. Niemi, S. Reuter, L.M. Graham, J. Waskoenig, N. Knake, V. Schulz-von der Gathen, T. Gans, *J. Phys. D: Appl. Phys.* **43** (2010) 124006.

[4] G. Cunge, D. Vempaire, M. Touzeau, N. Sadeghi, *Appl. Phys. Lett.* **91** (2007) 231503.

[5] J.S. Sousa, G. Bauville, B. Lacour, V. Puech, M. Touzeau, L.C. Pitchford, *Appl. Phys. Lett.* **93** (2008) 011502.

[6] J.S. Sousa, K. Niemi, L.J. Cox, Q. Algwari, T. Gans, D. O'Connell, *J. Appl. Phys.* **109** (2011) 123302.

[7] D. O'Connell, L.J. Cox, W.B. Hyland, S.J. McMahon, S. Reuter, W.G. Graham, T. Gans, F.J. Currell, *Appl. Phys. Lett.* **98** (2011) 043701.

[8] J. Waskoenig, K. Niemi, N. Knake, L.M. Graham, S. Reuter, V. Schulz-von der Gathen, T. Gans, *Plasma Sources Sci. Technol.* 19 (2010) 045018.