Plasma chemistry in the effluent of a He/O₂ microplasma jet: the role of VUV photons

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RF-driven atmospheric-pressure plasma jets operated in He/O₂ gas mixtures are well known for their capability of producing high densities of reactive oxygen species (ROS) such as O, O₃ or O₂(a¹Δg) with densities of more than 10²¹ m⁻³. The ROS are effectively transported with the gas flow towards the surface, where they can inactivate for example bacteria. These sources are, therefore, in focus of many experimental and theoretical studies. Next to ROS, VUV photons are generated by the plasma as well. These photons have enough energy to dissociate or ionise molecular species in the effluent of the jet or at the surface. We have developed a specially designed plasma source, which allows us to investigate the role of these VUV photons in detail.

A microscale atmospheric-pressure plasma jet (μ-APPJ) source and its modifications are used in this study. The μ-APPJ has a very simple geometry. It is formed by two stainless steel electrodes (length 30 mm, thickness 1 mm) with a separation of 1 mm, and two glass plates, which are glued to the electrodes on the side and confine the inter electrode volume, cf. Fig. 1a). The well-controlled flow conditions without admixture of surrounding ambient atmosphere are maintained in this way. The plasma is generated in He gas flow of 1.4 standard liters per minute (slm) with small concentrations (<1.5 %) of O₂. A typical α-mode discharge is formed when a sinusoidal driving voltage with a root-mean-square value of 150-270 V (frequency 13.56 MHz) is applied to the electrodes.

This source has been described and studied in the past and quantitative measurements of O and O₃ densities as function of O₂ concentration, applied power, and distance to the jet are available [1-3]. Additionally, this jet geometry with He/O₂ gas mixture has been modeled and discussed in the literature [4-6].

Fig. 1: a) Photograph of the μ-APPJ source. b) Modified μ-APPJ source with two crossed channels after the nozzle, the so-called X-Jet. c) Schematic representation of the gas flows and photon flux in the channel structure during the study of the products of photochemical reactions of plasma generated photons (pink color) with neutral gas molecules (blue arrows).
The µ-APPJ can be modified allowing the separation of the effects of heavy reactive species and energetic photons. We call this modification an X-Jet. The nozzle of the µ-APPJ is extended in this case by two crossed channels as shown in Fig. 1b) and c). These channels are formed from glass and metal building blocks with 1 mm thickness, and fixed between two glass plates together with both electrodes. One channel is a direct extension of the inter-electrode region (direct channel) and the other channel (side channel) crosses the direct channel under a 45 degree 3 mm downstream of the end of the electrodes. Both channels have the same 1x1 mm² cross section. An additional He flow is applied to the side channel to divert particles in the plasma effluent from the direct channel into the side channel. This is possible, because the particle transport is controlled mainly by convection at atmospheric pressure and the flow velocities used. The diffusion is less important due to high collision rates. Contrary to particles, VUV and UV photons generated in the plasma can propagate further through the direct channel (also filled with He), cf. the scheme in Fig. 1c). More details about the X-Jet and its performance can be found elsewhere [7].

The X-Jet source allows studying the effect of reactive species without the presence of photons, the effect of photons without the presence of reactive species and also the combined effect of both components at the same time. It is very promising source especially for the study of the fundamental interaction mechanisms of plasma effluent with living cells or biological macromolecules. We have already studied the effects induced on E. coli and B. subtilis bacteria, plasmid DNA or proteins [7-9]. It has been found that the direct inactivation of E. coli bacteria by plasma generated photons is very slow compare to the effect of ROS. However, the reactive species generated in VUV photon-triggered photochemical reactions in the gas phase can contribute significantly to the inactivation.

The molecular beam mass spectrometry system described elsewhere [3] is used to study the possible neutral and charged photochemistry products. It has been checked that photodissociation of the ground state O₂ molecules is negligible under our conditions [8] and that the main photochemistry products are hydrogenated water cluster ions. Fig. 2 shows the typical positive ion spectrum detected directly after turning on the plasma.

![Fig. 2: The positive ion mass spectrum measured at the X-Jet direct channel. These ions are produced in the photochemistry reactions between plasma-generated VUV photons and water impurity in He gas.](image)

Water cluster ions with four and five water molecule are mainly detected when He or He with admixture of oxygen up to several percent is used in the side channel. The O₂⁺ ions are detected only at the level close to the detection limit of the mass spectrometer (less than 10 counts/s).

The water is present in the system as an impurity and its concentration varies with time. Fig. 3 shows the temporal variation of the signal for the mass-to-charge ratios of 73 and 91, which represents hydrogenated water cluster ions with four and five water molecules, respectively.
Fig. 3: The temporal evolution of the mass spectrometer signal for the mass-to-charge ratios of 73 and 91, which represents hydrogenated water cluster ions with four and five water molecules.

The measured signal decreases over time as the water impurity level decreases. Interestingly, the signal intensities do not decrease at the same rate. Clearly, the level of water impurity has to be well defined to obtain more detailed knowledge of the photochemical reactions in the plasma effluent. Measurements with controlled water vapor concentration are currently being performed and will be presented in the talk.

Additionally, two new modifications of the μ-APPJ source have been constructed as shown in Fig. 4. These sources will allow to identify the photochemistry products from the reaction of plasma generated photons with the reactive species in the plasma effluent (for example O₃). Also these results will be presented in the talk.

![Diagram](image)

Fig. 4: Two different modifications of the μ-APPJ source allowing measurement of a) generated reactive species including possible products of photochemistry reactions in the effluent, and d) reactive species with minimized effect of photochemistry reactions.

References


