Surface Dielectric Barrier Discharge characterization based on mass spectrometry diagnostic techniques

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Non-thermal plasmas in atmospheric air have been proposed as a tool aimed to various applications, including air purification, food packaging, textile finishing and new materials development, owing to its capacity to generate highly reactive species under ambient conditions. Surface Dielectric Barrier Discharges (SDBD) are particularly promising because the plasma state is almost two-dimensional and confined to region facing the dielectric surface, with only indirect interactions with the surrounding gas-phase or with the to be exposed surfaces aimed for functionalization. One key aspect is the generation of reactive oxygen and nitrogen species (RONS), which play a fundamental role in oxidative processes. The relative concentrations of these species determine the overall oxidative potential of the plasma and its effectiveness in biological and chemical applications. Therefore, the accurate identification and quantification of these species are essential for any optimization strategy to enhance the efficiency of the plasma. Mass spectroscopy could be used to gain insight into such gas-phase composition. Our mass-spectrometer (HPR60 by Hiden) in particular, with its ability to change the electron energy in an extended range (namely 4-150 eV), their intensity (about four decades between 0.2 to 2000 uA) and the electrical optics (so that it is able to collect native positive and negative ions from the discharge region), could aim to a comprehensive characterization of plasma gas-phase [1]. Here we present results of an experimental campaign aimed to this.

Mass spectroscopy of atmospheric pressure plasmas was performed using an home-made SDBD configuration based on an hollow cylinder quartz tube (external diameter 60 mm, height 190 mm, thickness 3 mm). Inside the cylinder a stained copper tape was glued (thickness 0.2 mm) for an height of 160 mm, leaving about 15 mm uncovered at each edge. This prevent discharges inside the cylinder. On the outer surface the electrode is made of a stainless steel grid with rhomboidal holes (M-Metall R8, 8x4 mm, thickness 0.8 mm), with the same height and corresponding to the internal one. This is connected with the HV supply, whereas the outer grid is connected to ground. A HV voltage probe (Tektronix P6015A, bandwidth 75 MHz) can be used to measure the voltage applied to the inner electrode, whereas in the circuit connection to ground a shunt resistance (R=5Ω), a suitable capacitor (0.15 μF) or a current probe

(Tektronix CT1, bandwidth 1 GHz) can be inserted to record the electrical current or the charge flowing in the discharges with a large bandwidth oscilloscope (Agilent MSO8104A, 1 GHz bandwidth, 4 GSample/s rate). The total capacitance of the SDBD was 162 pF. An home-made (from the Electronic Engineering Department, University of Bologna) HV supply was used. The supply drives with a DC voltage two MOSFET with their drain pins connected at the two ends of a transformer primary coil, with a push-pull circuit configuration. The secondary coil is coupled to our electrode system, so the supply provides tunable trains of HV sinusoidal signals (frequency range 18-55 kHz, amplitude up to 6/8 kV depending from the frequency) with a pre-fixed duty-cycle. The DC primary circuit voltage and current are monitored to measure also the total power consumed by the system.

The core instrumentation used in this study is the Hiden HPR-60 quadrupole mass spectrometer. It samples plasma gas-phase through an orifice (diameter 100 μm) drilled at the center of a stainless steel disk (diameter 200 mm). The orifice position correspond to one of the rhomboidal mesh holes. Inside the disk two skimmer cones (apertures 300 and 700 μm) allows transport of species in a supersonic jet environment minimizing interactions with background species and walls, but maintaining a differential pumping that reduces the pressure in three stages until the entrance of the spectrometer. A RF quadrupole analyzer allows to scan masses up to 1000 amu. A tunable extraction optics electrode system could discriminate charged from neutral particles, as well as optimizing detection efficiency, together with a triple filter. A 45° electrostatic sector energy analyser controls the ion transmission uniformity efficiency and the energy resolution. The electron ionizing beam for neutrals detection could be controlled both in intensity and energy. Finally a secondary electron multiplier detector is used to measure collected ions, with 7 decades range and 24 bit resolution [1].

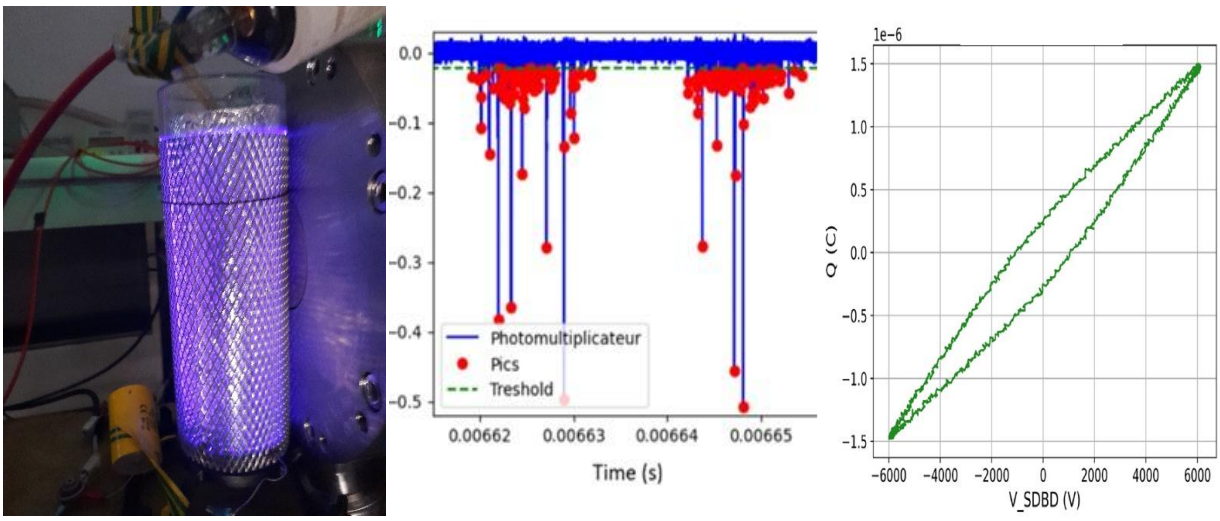

Fig.1 – A picture of the discharge setup (a) together with the pattern of light emission (b) and charge transport (c).

Fig.1 collects some characteristics of the discharges. They fills uniformly the holes in the mesh, happening in two strokes for each AC voltage cycle. It is clear that the plasma gas-phase is the results of some hundred thousand repetitions of these, averaging the single event and the rest periods [3-5]. Fig.2 reports some observations of the plasma gas-phase, in particular the formation of ozone and nitrogen oxides. In the experimental conditions selected here, the build-up of a distinct plasma state is reached immediately after the break-down (within 1") and a transition is reported between an ozone dominated to a NO with a time-scale of about 55". This phenomenon was observed in some DBD experiments, as well as predicted by some scheme of chemical kinetics modelling [6]. We also report a minor formation of NO_2 oxide, whereas an upper limit on the concentrations of other species could be put, such as N_2O (not very tight, due to superimposed CO_2 background), NO_3 and N_2O_5. We could also exclude substantial amounts of other minority species arising from the air humidity (O_2H, HNO_x as sometimes reported in modelling. However it is clear that a quantitative measurements of the concentrations will be crucial to fully test such theoretical approaches and pin down their parameters and assumptions. The figure also reports the signal dependence from the electron energy, clearly demonstrating the advantage of our instrument capabilities.

Fig.3 collects the electron impact energy dependence for the production of nitrogen and oxygen ions from the gas-phase before and during the discharge. In plasma, a small amount of ions are collected from low energy electrons below the ionization threshold. Their source is some population of excited molecules which have a lower ionization energy respect to ground state ones (some metastables states being the most probable to contribute) [6]. A quantitative evaluation of their concentration and the possible identification of the excited states is actively pursued but requires some more efforts in the data taking and plasma stabilization for longer periods.

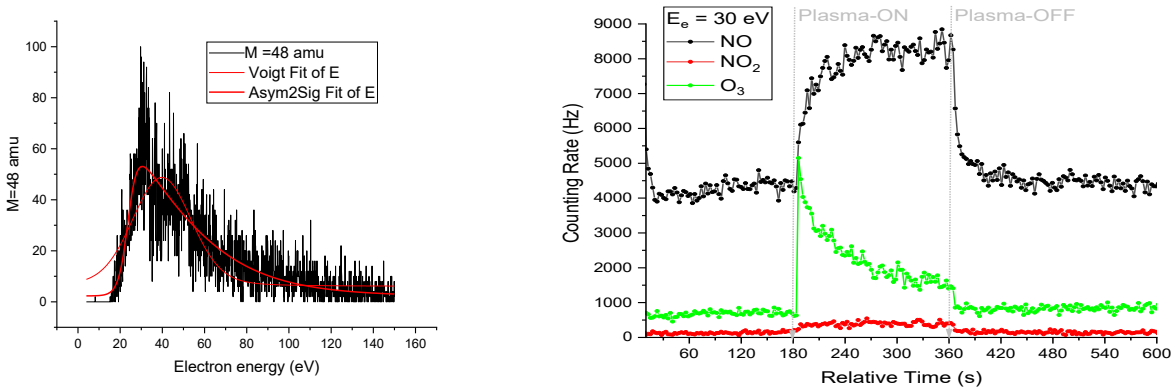

Fig.2 – Neutral molecules sampled out of the discharge (b) together with the ionization pattern of O3 (a).

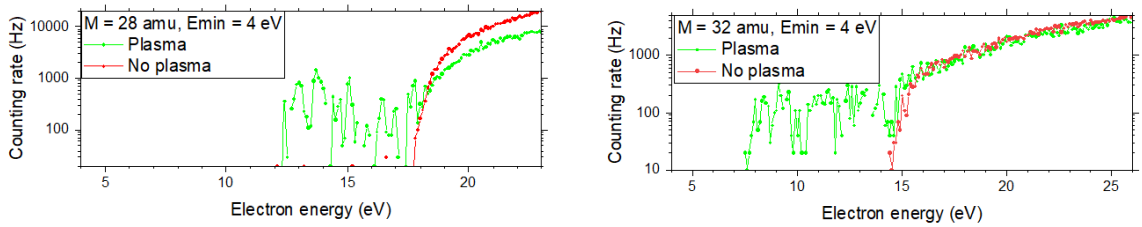

Fig.3 – Electron energy dependence of the ionization to (a) M=28 (N_2^+) and (b) M=32 (O_2^+) .

Fig.4 collects the electron impact energy dependence for the production of nitrogen and oxygen atomic ions from the gas-phase before and during the discharge. In atmospheric air they are produced only from dissociative ionization from their parent molecules. In plasma, a small amount of ionized nitrogen atoms are collected from low energy electrons below the dissociative ionization threshold. The absence or relatively weaker concentration of oxygen atoms contrasts with their readily appearance in the optical emission spectra [7] and their expected in modelling [6]. However it is also expected that O atoms are much more reactive than N ones, so they could be already consumed before reaching the spectrometer. Again a quantitative evaluation of their concentration requires some more efforts from us.

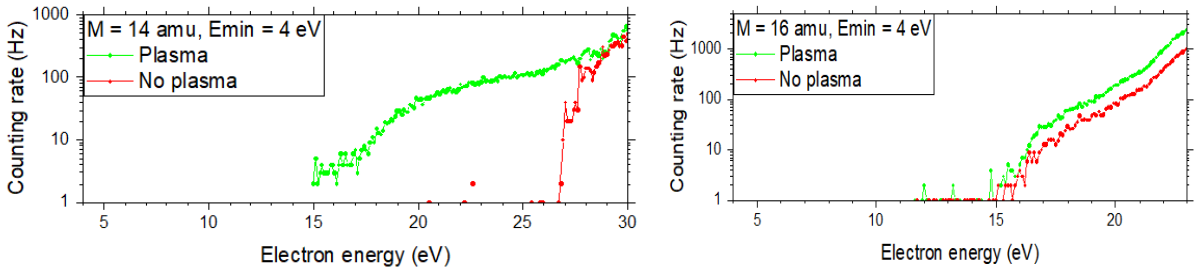

Fig.4 – Electron energy dependence of the ionization to (a) M=14 (N^+) and (b) M=16 (O^+) .

Acknowledgments

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