Ozone production in O_2 plasma at low pressure: surface or gas phase mechanism?

D. Marinov(*)[1], V. Guerra[2], O. Guaitella[1], A. Rousseau[1]

[1]*LPP, Ecole Polytechnique, UPMC, Université Paris Sud-11, CNRS, Palaiseau, France*
[2]*Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade Técnica de Lisboa, 1049-001 Lisboa, Portugal*
(*) daniil.marinov@lpp.polytechnique.fr

Ozone production in a pulsed O_2 DC discharge in silica reactor at pressures in the range 1.3-6.7 mbar was investigated. The comparison between UV absorption measurements of the ozone concentration and modelling results reveals that O_3 is formed in the gas phase reaction $O+O_2+O_2 \rightarrow O_3+O_2$ and indicates an important role of vibrationally excited ozone. Moreover, it demonstrates that O_3 production on the reactor walls plays only a minor role in the conditions of this study. Heterogeneous ozone formation was evidenced when high specific surface glass fibres were introduced in the reactor. It was found that the efficiency of ozone formation on the surface increases with increasing the pressure of O_2. At p=6.7 mbar ozone formation accounts for about 25% of the losses of atomic oxygen on the surface of the fibres.

Ozone production in low temperature O_2 containing plasmas is probably the most studied and the most commercialized plasma chemical process. A detailed understanding of the mechanisms of ozone formation in atmospheric pressure discharges in N_2/O_2 mixtures has been achieved in the second half of the 20th century. The ozone research was motivated by its importance for atmospheric chemistry [1] and due to the development of industrial ozonizers [2]. In low pressure (p~1 mbar) O_2 plasmas ozone production is usually neglected due to the low efficiency of the 3 body processes. Recently, it was suggested that ozone production from the surface recombination of oxygen atoms on the reactor walls $(O+O_2)_{wall} \rightarrow O_3$ (1) may represent an important source of O_3 in low pressure O_2 plasmas [3,4]. Authors in those papers find the probability γ_{O3} of the process (1) on silica surface (assuming a first order reaction) to be of the order of 10^{-3} and argue that it contributes substantially to the overall rate of surface losses of atomic oxygen. Both groups [3,4] worked with continuous discharges where ozone production was masked by a great number of loss processes. The aim of this work was to investigate the mechanisms of O_3 production in a pulsed DC discharge in O_2 in the pressure range of 1.3-6.5 mbar. The pulsed discharge technique allows time resolved measurements of O and O_3 kinetics and it is advantageous from the viewpoint of the modelling.

The experiments were performed in a cylindrical reactor of 60 cm full length and 2 cm inner diameter. The discharge current was in the range of 40-120 mA and the typical pulse duration was 0.5-2 ms. Ozone concentration was measured *in-situ* by broadband UV absorption using a deuterium lamp (OceanOptics DH-2000) and a spectrometer (ANDOR Shamrock 303i) coupled with an ICCD camera (ANDOR iStar). The lifetime of atomic oxygen in the postdischarge was measured by means of actinometry (argon used as an actinometer) with pulsed induced fluorescence re-excitation (PIF) [5]. Experiments were done either in a bare silica reactor or with an introduction of high specific surface glass fibres. The presence of the catalytic material inside the reactor led to an enhanced role of surface processes.

A self-consistent kinetic model of a pulsed DC discharge in O_2 and its afterglow was developed. The system of equations describing the time evolution of the heavy particles was coupled to the Boltzmann equation for the electrons. Vibrationally excited ozone O_3^* was found to be important, in accordance with [1-3], and was included in the model. The model uses as input the experimental value of the discharge current during the pulse. The rates of the most important processed were taken from the literature [1-3,6], whereas the surface loss probability of O atoms in the afterglow was chosen as to reproduce the PIF measured lifetime of O atoms.

Figure 1 shows ozone production as a function of afterglow time at different O_2 pressures. The injected energy was in the range E=0.14-0.22 J per pulse. One can see that the concentration of ozone in the post discharge increases by a factor of 30 with a 5 fold increase of the pressure. The characteristic time of ozone production decreases with increasing the pressure and it was found to be

in the range of 70-90 ms. On the same graph the result of the modelling for 6.7 mbar pressure is shown. One can see that both the absolute value and the time evolution of O_3 concentration are well reproduced by the model. It was found that the main ozone production mechanism is the 3 body gas phase reaction $O+O_2+O_2 \rightarrow O_3+O_2$. According to [1-3] about 2/3 of produced ozone is vibrationally excited with a preferential population of the asymmetric stretching mode. Model calculations reveal the key role of the excited ozone in the kinetics of O_3 formation. As the gas phase processes were found sufficient to reproduce the kinetics of O_3 at 6,7 mbar, no precise conclusion could be made regarding the surface formation of ozone for these conditions. One should note that the measured recombination probability of atomic oxygen at p=6.7 mbar was $\gamma_O=5\cdot10^{-4}$ and this value naturally sets the upper limit for γ_{O3}. Based on the present results we are not able to rule out the possibility of the surface production of ozone with $\gamma_{O3}\leq1\cdot10^{-4}$.

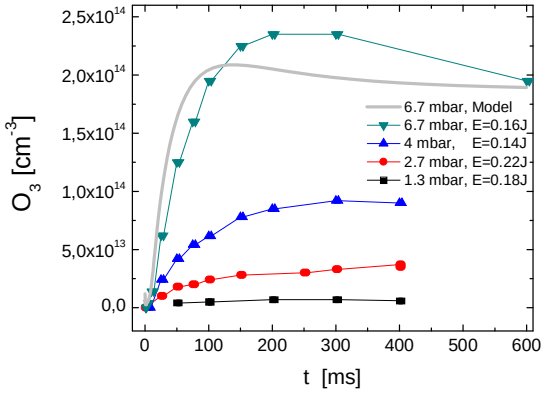

Fig. 1 : Ozone production in the afterglow of a pulsed DC discharge at different pressures. Bare tube. Energy input in the discharge was in the range E=0.14-0.22 J in the pulse.

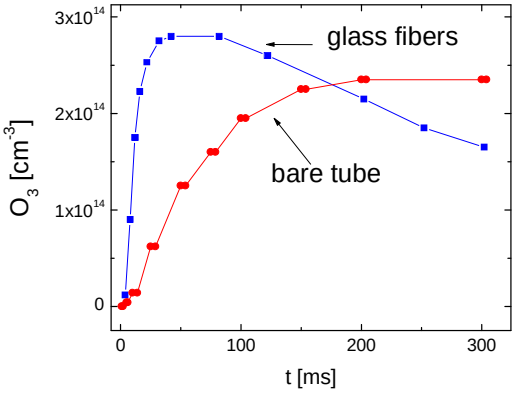

Fig. 2 : Ozone production in the afterglow of a pulsed DC discharge in bare tube and with glass fibres inserted in the reactor, p=6.7 mbar. Injected energy was kept constant E=0.16 J.

In order to enhance the role of surface processes, a tissue composed of glass fibres having a total surface area ~100 m^2 was introduced in the reactor. In figure 2 ozone productions with catalytic material and in bare tube is shown, O_2 pressure and injected energy were kept constant. One can note that the maximum O_3 concentration is almost identical in both cases. The lifetime of atomic oxygen and the characteristic production time of O_3 with the fibres are about 10 times shorted than in the bare reactor. This means that O atoms are rapidly lost on the catalytic surface and do not have enough time to produce ozone in the gas phase. Thus, the observed ozone is necessarily formed on the surface. Comparison between the calculated concentration of atomic oxygen at the end of the discharge pulse $[O]=1\cdot10^{15}$ cm^{-3} and the maximum measured concentration of ozone $[O_3]= 2.8\cdot10^{14}$ cm^{-3} shows that the production of ozone contributes to approximately 25% of the total surface losses of atomic oxygen. It was found that the surface O_3 production efficiency $\eta=[O_3]_{max}/[O]_{max}$ is directly proportional to the pressure of O_2 which indicates that ozone is produced in the recombination reaction with physisorbed O_2. The value of η depends also on the pre-treatment of the surface; it decreases by a factor of 4 when the fibres are calcinated at 600K or cleaned with a continuous O_2 discharge.

References

[1] W. Rawlins, G. Galedonia and R. Armstrong *J. Chem. Phys.* **87** (1987) 5209–21
[2] B. Eliasson, M. Hirth and U Kogelschatz *J. Phys. D: Appl. Phys.* **20** (1987) 1421-1437
[3] D. Lopaev, E. Malykhin and S. Zyryanov *J. Phys. D: Appl. Phys.* **44** (2011) 015202
[4] C. Janssen and B. Tuzson *J. Phys. Chem. A* **114** (2010) 9709–9719
[5] G. Cartry, X. Duten and A. Rousseau *Plasma Sources Sci. Technol.* **15** (2006) 479–488
[6] K. Kutasi, V. Guerra and P. A. Sá *J. Phys. D: Appl. Phys.* **43** (2010) 175201