*35th EPS Conference on Plasma Phys. Hersonissos, 9 - 13 June 2008 ECA Vol.**32D**, P-2.169 (2008)*

COMPARISON OF TOWNSEND DIELECTRIC BARRIER DISCHARGE IN N_2, N_2-O_2 AND N_2-N_2O: BEHAVIOUR AND DENSITY OF RADICALS

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1. Introduction

The goal of this work is to help in the understanding of the processes which control the transition from filamentary dielectric barrier discharge (DBD) to Townsend DBD (also noted APTD for Atmospheric Pressure Townsend Discharge). The approach consists in comparing the influence of the adding of rather similar additives on the stability of the N_2 APTD. These additives are O_2 and N_2O. According to the literature the maximum concentration allowing an APTD is only 400 ppm for O_2 [1] when it is more than 1200 ppm for N_2O.

In order to understand the mechanisms taking place in such processes, it is important to study the chemical kinetic occurring in the gas phase. To do so, Laser-Induced Fluorescence (LIF) has been developed here for the study of dielectric barrier discharges at atmospheric pressure. One photon LIF is used to measure the absolute concentration of NO and Two-photons Absorption LIF (TALIF) is used to measure [N] and [O] in N_2/O_2 and N_2/N_2O mixtures. A 0D model allows to determine the dominant reaction leading to N formation in N_2.

After a description of the electrical behaviour of the discharge in the two gas mixtures, the absolute density of atomic nitrogen N, atomic oxygen O and nitric oxide NO, in their ground state, are reported and discussed to try to understand the influence of reactive gases on DBD.

2. Experiment

The DBD reactor is a longitudinal flow one with a gas flow injection localized on one side of the discharge. The gas flow is laminar. Such a gas flow configuration allows the study of the chemical composition of the gas as a function of the equivalent gas residence time (t) in the discharge area and then the energy: E= power x t. The gas gap is 1 mm for the electrical study and 2 mm for the laser analyses. The power supply is a sinusoidal one allowing a separate adjustment of the voltage amplitude and frequency from 0 to $20kV_{pk-pk}$, and 0.5 to 20kHz respectively. The voltage applied to the electrodes is measured by means of a high voltage probe. The current is measured through a 50 Ω resistor in series with the electrodes. The discharge current and the voltage really applied to the gas are calculated from these two measurements [2].

Concerning the TALIF, the 2070Å nm excitation scheme is used to measure the $N(2p^3\ {}^4S_{3/2})$ atom (fluorescence between 742 and 747 nm). For $O(2p^4\ {}^3P_j)$ atom, 2255 Å laser wavelength is used and the fluorescence is observed at 844.6 nm. The absolute calibration is performed by TALIF in krypton for N and on xenon for O atoms[3,4]. For $NO(X^2\Pi)$, LIF has been achieved by the excitation of the (0,0) band at 225.16 nm and detection of (0,1) band at 236.3 nm. NO gas is used to calibrate the LIF signal.

Measurements are done for O_2 and N_2O concentrations in N_2 varying from 0 to 500 ppm and 2000 ppm respectively. The discharge power is varied from 1.5W/cm^3 to 3.5W/cm^3.

3. Results

3.1. Electrical behavior

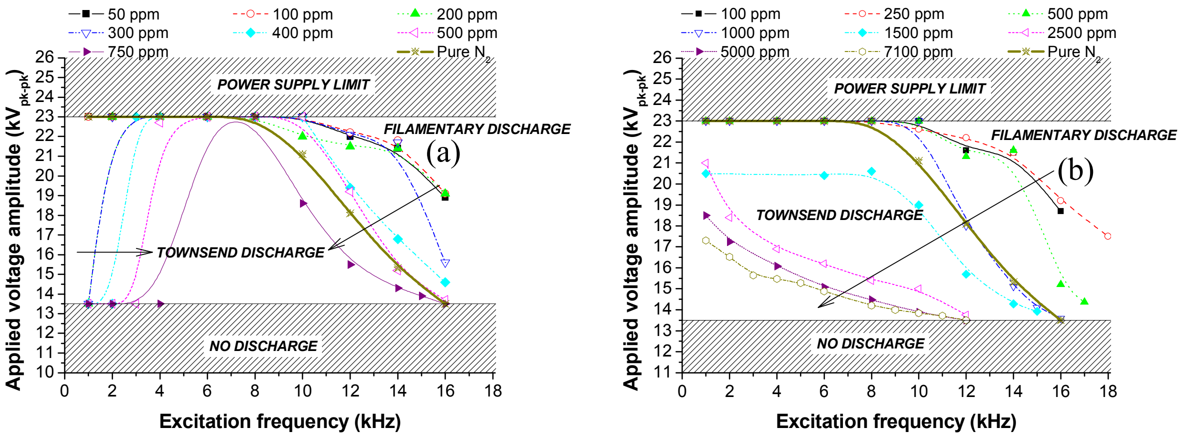

***Figure 1**: Working domains of the APTD for different concentrations of **a)** O_2 **b)** N_2O in N_2*

The Townsend discharge working domain, in terms of amplitude and frequency of the excitation determined for different concentration of N_2O and O_2 added to N_2, illustrates the influence of the nature of the additive on the APTD electrical behavior. At a given frequency, the working domain has two limits. The lower limit corresponds to the applied voltage required to extend the discharge over the entire electrode surface. The upper limit is either 23 kV$_{pk-pk}$, which is the maximum voltage used for these experiments (power supply limit) or the applied voltage at which instabilities appear on the discharge current and so which defines the transition to filamentary discharge.

In N_2/O_2 mixtures, the behavior is different for small and large amounts of O_2 (Figure 1a). For oxygen amounts lower than 200 ppm, the working domain is larger than in pure N_2, showing that a process compensates the increase of the nitrogen metastable quenching rate [5]. For higher concentrations, filamentary discharge can be observed at low frequency and the voltage limit at high frequency decreases as well. Thus, for 750 ppm of oxygen added in N_2, the working domain is especially reduced and centered around 8 kHz. The high frequency behaviour is very similar in N_2O and O_2: for amounts lower than 1000 ppm, the domain is larger than in pure N_2, showing that here also something compensates the nitrogen metastable destruction. Indeed, N_2O is also an efficient quencher of $N_2(A^3\Sigma_u^+)$ [6], and the reactive products generated by a N_2/N_2O discharge should not be really different from the ones produced by N_2/O_2 discharge. Actually, this is interesting to notice that the high frequency limit is similar in N_2/O_2 and N_2/N_2O mixtures for N_2O concentrations twice as large as in O_2 case. Then, the high frequency behaviour is controlled by the concentration of O atoms introduced in the discharge. Nevertheless, the low frequency behaviour is completely different for O_2 and N_2O mixtures: it is always possible to get a Townsend discharge at low power in N_2-N_2O mixtures for N_2O concentration lower than 1% and even in pure N_2O, with electrical characteristics (discharge current and gas voltage time dependence) very close to N_2 ones.

3.2. N, O and NO density

To try to understand these observations, N, O and NO absolute density in their ground state have been measured in an APTD for different amounts of N_2O and O_2 in N_2. Measurements are made as a function of the position along the gas flow (from the entrance to the exit of the discharge 17mm), of the power dissipated in the discharge and of the gas flow (1 to 4slm).

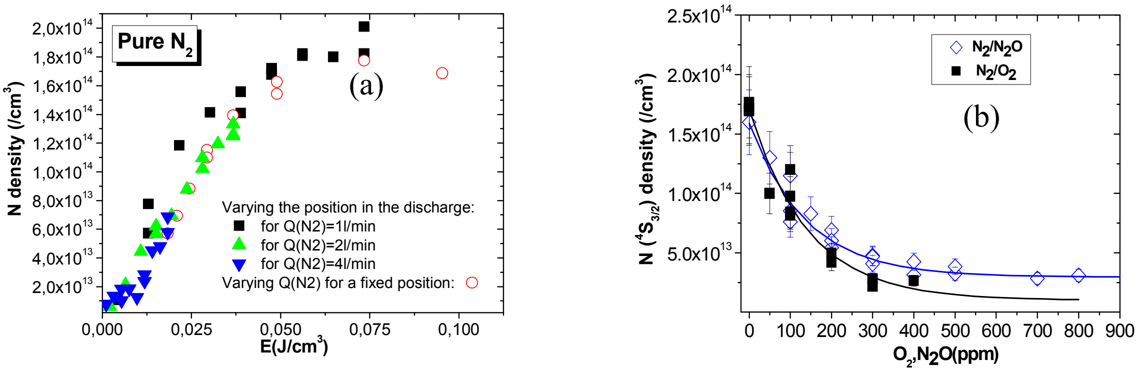

***Figure 2**: Absolute nitrogen atom density in an APTD **a)** in pure N_2 vs. energy dissipated in the discharge **b)** in N_2/N_2O and N_2/O_2 mixtures vs. N_2O and O_2 concentration for a fixed energy $E=73mJ/cm^3$*

The first results concern the $N(2p^3\ ^4S_{3/2})$ absolute density. The measurement sensitivity is $10^{13}cm^{-3}$. A reproducibility of 20% is reached including the error on krypton calibration.

As shown in figure 2a, for a given gas mixture, the N concentration increases following and exponential law: $N=N_0+A\exp(-E/E_0)$.

In pure N_2, the N maximum value, $(1.5 \pm 0.3)10^{14}cm^{-3}$, is reached for an energy of $E_0=18 \pm 2$ mJ/cm^3 which corresponds to 0.45 $kJmole^{-1}$ or 4.7 meV/N_2. In an APTD, the N density in the fundamental level slowly increases in agreement with its long lifetime. A 0D model has been developed [7] to determine the dominant mechanism of N creation and destruction. To obtain a N value of $10^{14}cm^{-3}$ the dissociative recombination of N_2^+ at the surface has to be taken into account and the ion temperature has to be higher than 10^3K to get the right balance between N_2^+ and N_4^+ ions.

When adding N_2O or O_2, as shown in figure 2b, the maximum value of $N(2P^3\ ^4S_{3/2})$ absolute density exponentially decreases with the concentration of N_2O or O_2. The variation is similar for the two added gases and the equivalent constant rate of the exponential law is around 46ppm.

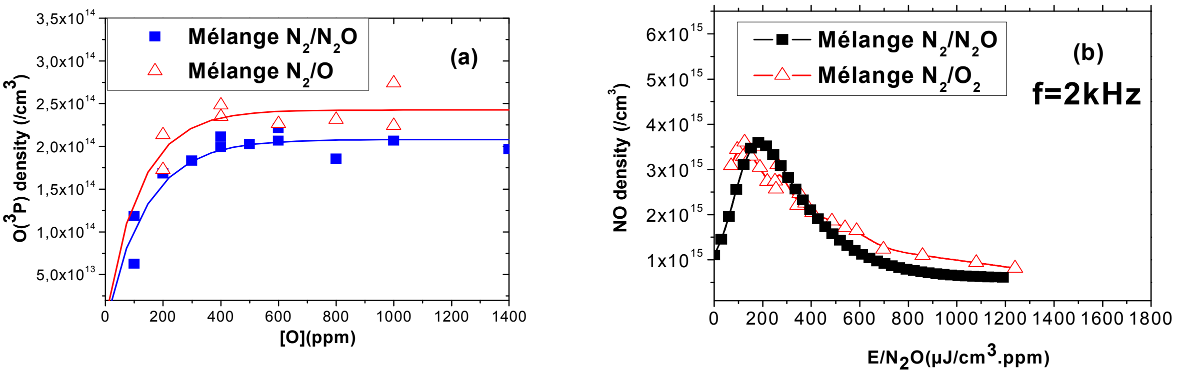

***Figure 3: a)** Absolute $O(2p^4\ ^3P_J)$ density as a function of the concentration of O atoms in the mixture ($[O]= [N_2O] = 2\ [O_2]$) for a fixed energy $E=73mJ/cm^3$ **b)** absolute $NO(X^2\Pi)$ density as a function of the energy injected in the gas per molecule of reactive gas added to N_2 for an excitation frequency of 2kHz*

The kinetic of the concentration of $O(2p^4\ ^3P_J)$ is a function of the energy. The O density is slightly higher in the case of O_2 and the value of 2.4 $10^{14}cm^{-3}$ is reached (Figure 3a). The variation as a function of the concentration of the added gas is two times higher in case of O_2 than in case of N_2O showing that the important parameter is the concentration of O atom added in the N_2:

$$[O\ (^3P)]= [O\ (^3P)_{max}](1-\exp([O]/\ [O]_0)) \qquad \text{with } [O]_0 = 130\text{ppm}$$

Even in pure nitrogen, $2.10^{14}cm^{-3}$ of $NO(X^2\Pi)$ can be detected. This is probably related to surface reaction of N atoms with oxygen atoms of the dielectrics in contact with the gas. The maximum value measured when oxygen compound is added is 30 times higher. One of the specificity of $NO(X^2\Pi)$ behaviour compared to that of N atoms is that the equivalency between the position and the residence time is not verified: a higher gas flow corresponds to a quicker is the kinetic of $NO(X^2\Pi)$ formation. The concentration of NO is a function of the energy and the number of reactive molecule added to nitrogen. For a given excitation frequency, all the results can be reported on one curve using the energy per N_2O or O_2 molecule as a parameter (figure 3b). For a 2 kHz excitation frequency, the maximum of NO is observed for 49eV/N_2O molecule and 35eV/O_2 molecule. When the excitation frequency is increased by a factor 3, the optimum energy is lower, 38eV/molecule for N_2O and 28eV/molecule for O_2.

4. Discussion and conclusion

Measurements of the density of N, O and NO confirm that products issued from N_2O and O_2 dissociation are rather similar. Then, the difference in the APTD stability observed in N_2/O_2 and N_2/N_2O mixtures has to be related to something else. A kinetic model of the chemistry occurring in the different gas mixtures will be very helpful. However, a possible explanation coherent with all the experimental results is that the negative ions play a dominant role.

According to the literature [1], in an APTD, attachment is negligible because of the low electronic density (10^8cm^{-3}). However in an APTD, the highest electronic density is reached between two discharges, when the electrical field value is low and then the attachment probability is high. A typical characteristic time for the reaction ($e+N_xO_y+M \rightarrow N_xO_y^- + M$) is between 19 and 190 µs for 100 ppm of N_xO_y. This time is comparable to the time between two discharges (about 100µs for a 2 kHz excitation). Then, attachment reduce the density of seed electrons except if detachment occurs previous to breakdown. The difference between the 2 mixtures is larger for low frequency excitation i.e. low power and then low dissociation of the N_2O or O_2. In these conditions electronic affinities which should be compared are those of O and O_2 (1.46eV and 0.44eV) and NO and N_2O (0.03eV and 0.24eV). According to these values we can assume that attachment is higher and detachment lower in N_2/O_2 mixtures inducing a decrease of the seed electrons and then a streamer breakdown.

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