On the use of pulsed Dielectric Barrier Discharges to control the gas-phase composition of atmospheric pressure air plasmas

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Abstract. We presents results obtained from the numerical simulation of the gas-phase chemical kinetics in atmospheric pressure air non-equilibrium plasmas. In particular we have addressed the effect of pulsed operation mode of a plane dielectric barrier discharge. It was conjectured that the large difference in the time scales involved in the fast dissociation of oxygen molecules in plasma and their subsequent reactions to produce ozone and nitrogen oxides, makes the presence of a continuously repeated plasma production unnecessary and a waste of electrical power and thus efficiency. In order to test such suggestion we have performed a numerical study of the composition and the temporal evolution of the gas-phase of atmospheric pressure air non-equilibrium plasmas. Comparison with experimental findings in a dielectric barrier discharge with an electrode configuration symmetrical and almost ideally plane is briefly addressed too, using plasma diagnostics to extract the properties of the single micro-discharges and a sensor to measure the concentration of ozone produced by the plasma.

1. Introduction

Dielectric Barrier Discharges (DBD) are a common source to produce non equilibrium plasmas at atmospheric pressure [1-3]. Limitation of the discharge current and of the gas heating at atmospheric pressure is achieved by the presence of an insulating material separating the two electrodes and avoiding a direct connection between them through the gas gap. Electrical breakdown will end up in delivering charge to the dielectric surface reducing the electric field and quenching the discharge. Near atmospheric pressure this produces narrow discharge filaments or streamers, reaching high electron density ($10^{12}$ to $10^{17}$ cm$^{-3}$) and very short lifetimes (few tens of ns) [1]. A steady state operation requires a somewhat regular repetition of such discharge events filling the gas gap and this is normally sustained by applying an oscillating voltage to one of the electrodes at kHz frequencies. The alternating voltage sweeps out the charge accumulated on the dielectric surfaces and a new streamer directed in the opposite direction could develop from the same location on the surface. It is worthy to point out that each of such discharges has a short duration with lapses of dead times between subsequent events. Moreover they could be considered as isolated also in space, since, at least in small gaps, they appear to be very thin (radius R ~ 100 µm [2]) while their average distance is much larger (a few mm, of the order of the gap width [1-2]).

Under steady state operation the local gas-phase composition is then controlled by both the nearby passage of one of the discharge paths (usually very fast) and by the quiet time intervals between subsequent such events. On a longer time scale diffusion both along and transverse to the discharge paths leads to mixing and uniformization of the gas-phase. The interplay between the two phases could be altered by delivering discharges in time bunches, using pulsed HV generators.
Our aim was to investigate the effect of a pulsed operation mode on the gas phase composition by using a model of the chemical kinetics of atmospheric pressure discharges suitable for the simulation of DBD devices [4-5].

Then we have implemented an experimental arrangement, mirroring as much as possible the model approximations, to compare actual results with the predictions of the simulations. In particular we have targeted the measure of the ozone concentration produced in the discharge gas-phase, since ozone is mainly formed much afterwards the discharge, mainly in gas phase reactions between neutrals, not directly affected by the discharge current evolution and charged particle dynamics [1,6].

There is wide interest in an efficient production of ozone for practical applications. Ozone is a strong oxidant and a potent disinfecting agent, long in use for water treatment [7-8]. A number of other uses have been found for ozone including food industries and medical application. Relatively low concentrations of ozone and short contact time are sufficient to inactivate bacteria, molds, yeasts, parasites, and viruses, for this reason it has been used with success to inactivate contaminants on meat, eggs, fish, fruits, vegetables, and dry foods [9-10]. In medicine ozone has been successfully applied for skin disinfection and for antimicrobial treatment on biological tissue, for example in active carious lesions [11-12].

The paper is organized as follows. At first we discuss the numerical simulation of the chemical kinetics in the gas-phase of a single air microdischarge. Then we implement a numerical study of pulsed operation in a DBD reactor, taking into account the effects of discharge repetition and of duty cycles on the evolution of the gas-phase composition. In particular we discuss how ozone production is affected by the parameters set in pulsed mode. Finally we present an experimental characterization of ozone production in a pulsed DBD reactor. Comparison with the prediction of the numerical study is discussed before conclusions are drawn in the ending section.

2. Chemical kinetics in an air microdischarge

As already stated, the discharge develops in a narrow current filament of some nanoseconds duration. They can be considered as isolated events in time and space. The first step in modelling is then to simulate the microdischarge formation. Some experimental observations [13-16] and several models [17-20] of streamer development and propagation exist by now. To make a somewhat rough summary, the overall picture looks similar in different kind of DBDs [4]. Streamer propagation is sustained by the electron avalanche multiplication in the strong field ahead of the streamer ($E_{\text{max}} \sim 5-15 \times 10^6 \text{ V/m}$) and it is very fast ($v \sim 10^5 - 10^6 \text{ m/s}$). After the streamer head reaches the dielectric barrier insulating the cathode, the channel allows the flow of a limited discharge current, which is rapidly quenched by the space charge accumulating at the dielectric surface [1]. The discharge body consists then of a thin channel of weakly ionized gas, almost quasineutral ($n^+ - n^- \sim 10^{13}-10^{15} \text{ cm}^{-3}$). At a fixed position along the streamer path, the electric field rises quickly as the streamer head is approaching and then decay almost as fast to the much smaller value it assumes in the streamer channel. It is worthy to point out that at high pressures electrons moves along the electric field at the drift velocity and almost instantaneously ($v_m^{-1} \sim 0.3 \text{ ps}$, $v_E^{-1} \sim 50 \text{ ps}$ [2]) reach a mean energy determined by the local amplitude of the field. On the other hand ions inertia keeps them almost frozen and substantially cold, that is at the set temperature. So the picture is one of an ionizing wave quickly propagating between the two dielectric surfaces, with the local charge density increasing as the wave passes by.

From the chemical kinetics point of view, the process can be seen as consisting of an almost instantaneous phase during which energetic electrons produce ions and atomic radicals, followed by a
phase in which electrons cool down almost instantaneously and reach the set temperature. Existing models could be used to predict the shape as well as the peak value of the electric field pulse during their propagation in the gas gap. However the dependence from the position along the streamer path is not large, apart from the region near the dielectric surface [17-18]. So we have neglected such differences and we have supposed uniformity along the streamer path. This was modeled as a thin cylinder, with a circular cross-section. The actual value of the radius could be considered as a free parameter of the simulation, but we have considered 100 µm as a reference [2]. The cylinder height, equal to the gas gap was chosen as 0.8 mm, since this matches the performed experiments. Another simplification was introduced to treat the ionizing wave. We assumed a square pulse shape of the electric field strength in the head of the streamer. The pulse is therefore characterized by the electric field amplitude \( E_{\text{max}} \) and by its time duration \( \tau_s \) (here 2 ns, based on the model in [17]). Although a little rough, such an approximation embodies all the relevant dynamics for our aims. It is worthy to point out that whether the electron density rises strongly, almost exponentially, during the ionizing wave passage, the total amount of radicals produced by electron impact happens to be largely independent from the time length \( \tau_s \) and from the initial electron density. Radical production level is set mainly by the actual value reached by the electron density at the end of the pulse [4,5]. So we have taken \( \tau_s \) fixed and we have treated the value reached by the electron density \( n_e \) at the end of the ionizing wave as the only relevant parameter of the simulation. As reference we considered a density of \( 10^{12} \text{ cm}^{-3} \) [17].

From a chemical engineering point of view, it means that the model can be formulated as a well-mixed reactor with cylindrical geometry [21]. The gas-phase composition in the reactor is determined by the chemical reactions among the reactive species and the transport processes. The concentration of the different N species in the gas phase only depends from time and could be calculated by integrating each balance equation for the density \( n_k \) of the \( k^{\text{th}} \) species

\[
\frac{dn_k}{dt} = \sum_{i<j=1}^{N} K(i + j \rightarrow k) n_i n_j - \sum_{i,j=1}^{N} K(k + i \rightarrow j) n_k n_i + \frac{D_k}{\Lambda_k} n_k
\]

where \( K \) are the reaction rates for the gas phase reactions including those involving electrons and ions, whereas \( D \) and \( \Lambda \) are the diffusion coefficient and length [22]. Within this approximation, the transverse profile of the concentration is described in terms of the normal mode dictated by the geometry. The coefficient \( \Lambda \) depends only on geometrical factors and on the sticking coefficient \( S \) of each chemical species. Using the assumed uniformity, diffusion along the streamer axis is neglected. Adsorption on the dielectric barrier could easily be included but, because of the much smaller extension of the streamer radius respect to the discharge gap, it turns out to be negligible. Balance equations containing all the processes described above form a system of coupled differential equations which has been integrated by using an adaptive Runge-Kutta routine [5]. The choice of species included in the model was based on existing experimental information based on emission spectroscopy or mass spectroscopy. A set of 10 neutral, 10 metastables and 9 charged species was included in this report. Rate constants for neutral gas-phase, charge exchange and ion recombination reactions have been taken from literature referenced in [4,5]. A cold plasma approximation is used. So reaction rates for ion as well as neutral species are evaluated at the set temperature, that is 300 K. Neutral rates depend also from the vibrational states of molecules [23,24]. This effect could be taken partially into account introducing a vibrational temperature and its effect on the reaction rates [4, 25]. In this preliminary work this effect was not addressed. Electron-impact reaction rates used in this study have
Figure 1. Temporal evolution of the gas phase composition during and after a microdischarge in dry air: neutrals (a), charges (b) and metastables (c) species concentration is reported (parameters: $T_e = 4$ eV, $n_e = 10^{12}$ cm$^{-3}$, $\tau_s = 2$ ns, $R_{str} = 100$ µm, $D_{gap} = 0.8$ mm).
been already discussed in our previous works too [4,5]. Rate constants have been evaluated assuming a Maxwellian energy distribution function for electron, described by a single parameter, their temperature $T_e$. This could be thought of as the mean electron energy, which is determined by the local electric field value by the Boltzmann equation [2]. In this way it is possible to make a direct comparison between this simulation and other existing ones or experimental data. We have considered as reference an electron temperature value of 4 eV [5]. A total of 410 reactions and 43 diffusion processes have been taken into account in the simulation.

At first we consider the evolution of a single discharge happening once. Neutral as well as charged species concentrations are displayed in a log-log scale as a function of time respectively in figure 1a for stable species, figure 1b for charged species and figure 1c for metastable neutral states. As expected, during the time length $\tau_s$ (2 ns) needed for streamer development mainly atomic N and O species are created, from electron impact-dissociation (the former more than the latter at such an electron temperature). Then a rather long evolution begins, where ozone is steadily formed until it reaches a concentration comparable to that of the atoms. Afterwards a fast decline in atomic oxygen is observed substituted by ozone as the main product in the gas phase. Overcoming happens after about 10 µs. The maximum density reached by ozone was about $10^{13}$ cm$^{-3}$ after about 30 µs. Then diffusion quickly removes the gas phase in a few milliseconds. Nitrogen oxides accumulates too, albeit at a somewhat slower rate, staying always minority in the gas-phase. On the other hand, the temporal dynamics of charged species seems to be faster than that of neutrals. This is due to the higher rates of ion-ion recombination and of electron attachment. All the charged species increase almost exponentially during the streamer development time (2 ns) and then the total charge density begins to decrease because of recombination. In presence of oxygen, after the pulse ends, when the electron temperature decreases less than 2 eV, electrons are quickly removed due to attachment processes. The $O_2^-$ is the majority negative ion and the overtake happens after just 15 ns. Positive charged species composition is mainly determined by charge exchange reactions on $N_2$ and $O_2$.

![Figure 2](image-url) Temporal evolution of the neutral gas phase composition in a microdischarge in dry air repeated at a fixed frequency (parameters: $T_e = 4$ eV, $n_e = 10^{12}$ cm$^{-3}$, $\tau_s = 2$ ns, $R_{str} = 100$ µm, $D_{gap} = 0.8$ mm, $\nu_{rep} = 40$ kHz).
They quickly remove atomic ions and leave $\text{O}_4^+$ as the majority ion. This change happens even faster than the removal of electrons. Later on positive and negative charged species density shows the same course: a power-law decrease in time (that is linear on the log-log plot) dictated by the ion-ion recombination process, followed by an exponential decay due to diffusion towards the dielectric surfaces. Excited atoms and molecules are produced during the passage of the ionization wave, just as ions and dissociated atoms. Most of them are quickly quenched by reactions in the gas-phase or radiative decay after the end of the ionization phase. Metastable atomic states start accumulating only after the production of a suitable amount of the parent atoms. Their lifetime is determined by the quenching reactions. The most lasting are metastable molecular oxygen states which accumulate in the gas phase discharge until diffusion starts removing all the discharge products. When a single discharge is repeated at a fixed frequency at some tens of kHz the interplay between the dissociation with subsequent production of oxygen atoms and the reactions in gas phase leading to the ozone formation are exposed. After a very small number of repetitions, in the order of ten, the gas phase reaches a steady composition during the times between each discharge. In particular an equilibrium between ozone produced in the post discharge phases and that removed by diffusion or destroyed in the discharges. The density of the same neutral species considered in figure 1a is displayed in a log-log scale as a function of time in figure 2 for a repetition frequency of 40 kHz, which corresponds to a 20 kHz HV oscillation in a symmetric DBD setup. Under such conditions ozone reaches a steady state concentration of about $5 \times 10^{13} \text{ cm}^{-3}$ (2 ppm) whereas atomic nitrogen and oxygen densities are about one tenth and nitrogen oxides below one hundredth. The main control parameter is whether the repetition period lies above the transition from atomic oxygen and ozone and below the diffusion loss time. By changing the repetition period it is possible to find an optimal frequency where the steady ozone concentration is maximal. However this does not constitute the best concentration achievable, since the continuous repetition of discharges leads to the destruction of part of the ozone formed during the post discharge times. Thus one is lead quite naturally to consider whether a pulsed operation mode could benefit for instance the ozone formation.

3. Ozone production in pulsed DBD

In order to investigate the effect of a pulsed operation mode on the gas phase composition we have to define better the device setup to be modeled. We conjectured a cylindrical gas gap such as the one between two symmetric insulated electrodes consisting in a couple of parallel planes. The ideal cylinder has diameter 35 mm and height 0.8 mm. A uniform electric field parallel to the cylinder axis is assumed in the whole gap. Discharge filaments, like those considered in the previous section, are supposed to happens with uniform probability at each position within the gap. The effective repetition rate is then determined not only by the period between subsequent active phases. It is determined by the average number of microdischarges during each active phase and by the ratio between the streamer volume and that of the whole gas gap. In a sense we consider all the microdischarges equal as for their plasma parameters and with a constant repetition rate at each position in the gap. Although a rough simplification of reality it does not overlook the relevant evolution of the discharge. Indeed a sort of uniformization of the gas gap composition is achieved in the experiments thanks to diffusion and the large number of microdischarges and cycles involved, despite each microdischarge shows a non-negligible variability in amplitude, duration and delay between subsequent events even considering only the same position [26]. Diffusion outside the gap due to radial transport was added to the simulation in a way completely mirroring the diffusion outside the streamer channel [22]. These
Simulations lead to results completely reproducing the evolution shown in figure 2. The gas gap reaches a steady composition with an equilibrium between diffusion outside the gap and production of ozone and other compounds due to the repeated discharge processes. Then ideal pulse operation is supposed, consisting in a number of equal active periods separated by quiet intervals. A duty cycle is determined, based on the duration of the on ($T_{on}$) and off ($T_{off}$) periods. The density of the neutral species in the gas-phase follows that already discussed for continuous operation. However during the pause periods ozone and nitrogen oxides accumulates while oxygen and nitrogen atoms are consumed. Equilibrium is reached in a few duty cycles, generally less than 10. The concentration reached by ozone at the end of the last pause period was estimated and displayed in figure 3 for two values of the active period. An enhancement of the ozone concentration, almost independent from the active phase duration, is predicted with a maximum for a pause period of several milliseconds.

![Figure 3](image)

**Figure 3.** Ozone concentration in the gas phase as a function of the duration of the plasma-off phases between active plasma pulses 450 and 1500 µs long (parameters: $T_e = 4$ eV, $n_e = 10^{12}$ cm$^{-3}$, $\tau_s = 2$ ns, $R_{sr} = 100$ µm, $D_{gap} = 0.8$ mm, $V_{rep} = 40$ kHz).

4. **Experimental study**

In order to draw a compelling comparison with the numerical simulation results we have prepared our experimental set-up so as to match as closely as possible the approximation made in the modeling. For instance the two electrodes for DBD have been made equal. Each of two stainless steel disks (diameter 35 mm, thickness 1.5 mm) has been inserted into a drilled Macor, a glass ceramic material (© Corning Inc.), cylindrical scaffold (diameter 40 mm, height 3.5 mm, dielectric constant $\varepsilon_r = 6.03$). Thus a dielectric barrier of 2 mm separates the electrode surface from the gas gap. Particular care was to them parallel and exactly corresponding. The discharge gap was fixed at 0.8 mm. The measured electrode capacitance was measured to be 8.30 pF, in good agreement with the result of the calculation using a 2D Laplacian electrostatic field solver (EStat 7.0 by Field precision LLC). Calculations show that the electric field is uniform in the gap within 10% and decreases outwards.

The DBD was operated into a cubic plexiglas box which was vented by blower to remove ozone after experiments. The upper electrode is connected through a HV cable to the secondary coil of a transformer, whose primary circuit is connected to a tunable power generator, providing the driving
high voltage for the discharge. We used a Laboratory Corona Station V20 by Tigres GmbH. This provide an alternating voltage whose frequency could be varied automatically between 18 and 50 kHz to provide a constant output power level or it can be fixed depending on the operating choices. In pulsed operation mode the supply provides a duty cycle where a HV oscillating signal, with an almost constant amplitude, is applied for a fixed time and is alternated by periods when no voltage, indeed a really low one, is applied to the electrodes. The switch-on phase could be very short, about 250 microseconds at minimum (which means about 10 oscillation cycles at 40 kHz), whereas the switch-off phase could be varied from such minimum up to 25 ms. Duty cycles as low as 1% could then be set. The HV signal, applied to the upper electrode was measured locally by a P6015A probe by Tektronix granted for a bandwidth of 75 MHz. The discharge current have been measured by means of Rogowskii coils. Details of this electrical measurements have been already discussed in literature [17]. In particular the number and amplitude of microdischarge events have been used as a guide for the choice of simulation parameters. In order to measure ozone production by our DBD we have employed an ozone sensor (OS-4 by KWJ Engineering Inc.) which was located at about 5 cm next to the electrode setup. The sensor is sensible in the 0.05-20 ppm range and was calibrated in factory, showing a typical accuracy below 20%. The instrument provides an output voltage signal proportional to the ozone concentration which was recorded and digitized with an acquisition rate of 1 Hz. In figure 4 a typical recorded time series is shown. After a brief delay, the signal reaches a stable plateau. The measure was taken by averaging 120 seconds data in the pulse, after the stabilization of the data. It is clear from figure 4 that the system reaches a steady state with a definite value of ozone concentration, stable for several minutes. After switching off the discharge, ozone removal is quite fast and the sensor is ready for a new measure in just a few tens of seconds. At first we have investigated the production of ozone by a continuously operated discharge. The steady state concentration of ozone was measured as a function of the power level. Ozone concentration is small at breakdown when only a limited number of microdischarges happens in the gap. It rises smoothly reaching a maximum at about 140 W power level, then starts decreasing. Although the HV amplitude keep rising and the frequency changes only slightly, ozone production is diminished.

![Figure 4](image.png)

**Figure 4.** Time series of the measured ozone concentration in the gas phase produced by a pulsed discharge (parameters: \( W = 120 \) W, \( T_{\text{on}} = 450 \) µs, \( T_{\text{off}} = 7.5 \) ms)
This behavior could be related to the heating of the gas-phase, which favors nitrogen oxide production versus ozone [3,5].

Then we have investigated the effect of a pulsed operation mode. A shrinking duty cycle was applied by maintaining constant the duration of the active phase and stretching the period of pause between two subsequent phases. This reduces progressively the total power absorbed by the discharge. Results are presented as a function of the pause duration in figure 5 for two values of the active phase duration. Even a small pause time is beneficial with a substantial increase in ozone concentration observed when pulse operation is applied. The increase continues up to reaching a maximum. The peak happens at a rather low value of the effective power ($W_{\text{eff}} = 16$ W, 17% duty cycle), much smaller than the most efficient power level needed in continuous mode. Further increasing the pause period leads to a decrease in the ozone concentration. The similarities with the simulation predictions are quite impressive. A throughout investigation of the operating parameters and setup dependencies are clearly needed for a more pointed comparison and it will be performed in future.

![Figure 5](image)

**Figure 5.** Ozone concentration in the gas phase as a function of the duration of the plasma-off phases between active plasma pulses 450 and 1500 µs long. Comparison with results from a continuous discharge is also shown.

5. Conclusions

We have performed a theoretical analysis of the evolution in the gas phase composition of a dielectric barrier discharge operating in a pulsed mode. In particular we have studied the production of ozone by the application of a fixed single microdischarge repetition rate and the application of suitable pause intervals to let the chemical kinetics evolve undisturbed. Indeed an enhanced concentration of ozone was predicted as the the duty cycle is lowered enough.

Finally we have modified a commercial reactor using its supply unit to drive pulsed DBD in an electrode setup the most similar to the model. Preliminary measurements of the ozone concentration shows a trend comparable to the predicted one. Ozone concentration achieved could be enhanced by pulsed operation with an optimal choice of the active and pause phase duration.
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References
[1] Kogelschatz U 2003 Plasma Chem. & Plasma Proc. 23 1
[2] Raizer Y P 1991 Gas Discharge Physics (Heidelberg: Springer)
[3] Becker K H, Kogelschatz U, Schoenbach K H and Barker R J 2005 Non-equilibrium air plasmas at atmospheric pressure (Bristol: Institute of Physics Publishing)
[4] Riccardi C and Barni R 2012 Chemical Kinetics in Air Plasmas at Atmospheric Pressure (Chemical Kinetics) ed V Patel (Rijeka, Croatia: Intech,) chapter 9 pp 185-202
[5] Barni R, Esena P and Riccardi C 2005 J. Appl. Phys. 97 073301
[6] Wei L S, Zhou J H, Wang Z H, Cen K F 2007 J. Plasma Phys. 73 427
[7] Laroussi M 2008 IEEE Transactions on plasma science 36 1612
[8] Hayes J, Kirf D, M. Garvey M and Rowan N 2013 J. Microbiol. Methods, 94, 325
[9] Kim J G, Yousef A E and Dave S 1999 J. Food Protection 62 1071
[10] Guzel-Seydim Z B, Greene A K and Seydim A C 2004 Food Sci.& Technol. 37 453
[11] Nogales C G, Ferrari P H, Kantorovich E O and Lage-Marques J 2008 J. Contemp. Dent. Practice 9 75
[12] Bocci V, Aldinucci C, Borrelli E, Corradeschi F, Diadori A, Fanetti G and Valacchi G 2001 Ozone Science & Engineering 23 207
[13] Hoder T, Brandenburg R, Basner R, Weltmann K-D, Kozlov K V and Wagner H-E 2010 J. Phys. D: Appl. Phys. 43 124009
[14] Luque A and Ebert U 2014 New J. Phys. 16 013039
[15] Ono R and Oda T 2006 J. Phys. D: Appl. Phys. 40 176
[16] Biganzoli I, Barni R, Riccardi C, Gurioli A and Pertile R 2013 Plasma Sources Sci. & Technol. 22 025009
[17] Kulikovsky A A 1998 Physical Review E.57 7066
[18] Braun D, Gibalov V I and Pietsch G J 1991 J. Phys. D: Appl. Phys. 24 564
[19] Papageorgiou L, Metaxas A C and Georgiou G E 2011 IEEE Trans. Plasma Science 39 2224
[20] Naidis G V 2005 J. Phys. D: Appl. Phys. 38 3889
[21] Benson S W 1982 Thermochemical Kinetics (New York: Wiley)
[22] Chanyon P J 1987 J. Appl. Phys. 62 1141
[23] Lopaev D V, Malykhin E M and Zyryanov S M 2011 J. Phys. D: Appl. Phys. 44 015202
[24] Marinov D, Guerra V, Guaitella O, Booth J-P and Rousseau A 2013 Plasma Sources Sci. Technol. 22 055018
[25] Barni R and Riccardi C 2010 High Temp. Mat. Proc. 14 205
[26] Biganzoli I, Barni R and Riccardi C 2013 J. Phys. D: Appl. Phys. 46 025201