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Study of transient spark discharge focused at NOx generation for biomedical applications

M Janda, V Martišovitš, K Hensel and Z Machala

Division of Environmental Physics, Faculty of Mathematics, Physics and Informatics Comenius University, Mlynská dolina F2, Bratislava 84248, Slovakia

E-mail: janda@fmph.uniba.sk

Abstract. The paper is focused at nitrogen oxides generation by transient spark (TS) in atmospheric pressure air. The TS is a DC-driven self-pulsing discharge with short duration (~10-100 ns) high current pulses (>1A), with the repetition frequency 1-10 kHz. Thanks to the short spark duration, highly reactive non-equilibrium plasma is generated, producing ~300 ppm of NO_x per input energy density 100 $J.l^{-1}$. Further optimization of NO/NO_2 production to improve the biomedical/antimicrobial effects is possible by modifying the electric circuit generating the TS.

1. Introduction

Non-thermal plasmas generated by electrical discharges can be maintained at low gas temperatures, but have high electron energies responsible for their chemical activity. For this reason, several plasma based technologies were successfully implemented in the recent years, in processes such as surface modification, plasma assisted combustion, or hazardous waste processing [1-3]. In the past few years, a fast development of biological and medical cold plasmas applications has been observed [4], since cold plasmas provide multiple agents that can efficiently kill bacteria, yeasts, and other hazardous microbes. It is very important to assess the role of the plasma agents involved. At present, the major role in atmospheric pressure plasmas generated in air is typically attributed to reactive oxygen and nitrogen species (RONS) [5, 6], as well as to charged particles [7, 8].

The aqueous RONS are formed from dissolved NO, NO_2 and OH radicals generated by plasma in the gas phase [9]. The first step in the water bio-decontamination optimization process is thus better understanding of the NO and NO_2 generation in the gas phase. Partially, this problem has already been addressed by many authors in exhaust gas cleaning applications by electrical discharges [10-13]. However, they mostly studied NO reduction, or oxidation to NO_2, and finally to HNO_3. A recent paper [14] investigated the NO and NO_2 formation and their bactericidal effects in hybrid glow-spark discharges in air. Here we present a study focused on the synthesis of NO, NO_2 and their precursors (O and N species) by the transient spark (TS) discharge in air.

The TS is a dc-driven self-pulsing discharge with the typical repetition frequency 1-10 kHz. The TS is initiated by a streamer transforming to a short spark current pulse. Streamers are considered to be crucial for the efficiency of plasma induced chemistry at atmospheric pressure, since the electric field in the streamer's head can reach more than 200 kV/cm [15, 16], so that the chemical and ionization processes are very efficient there. On the other hand, transition of streamers to classical spark or arc discharge [17, 18], generating thermal plasma, is usually not desired. The thermal plasma

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is certainly not suitable for treatment of tissues or sterilization of surface sensitive to heat. Moreover, much more power is required to sustain these discharges. High energy costs allow their utilization only for applications where one can either expect valuable products (e.g. H_2) or needs to completely destroy dangerous pollutants [19-21].

However, the TS spark current pulses are sufficiently short (~10-100 ns) to avoid the plasma thermalization. Plasma generated during the spark phase of the TS is therefore highly reactive, since the electron density as high as 10^{17} cm^{-3} can be achieved [22]. The transient spark chemical activity is therefore comparable with the nanosecond repetitive pulsed (NRP) discharge [23]. The TS advantage is no need of special and expensive high voltage pulsers with high repetitive frequency and nanosecond rise-times used to generate NRP discharges [24-26]. The TS has already been successfully tested for several biological and environmental applications [6, 9, 27]. Basic research of TS using several electrical and optical diagnostic methods was also performed [22, 28-32]. However, further research is needed for better understanding of chemical processes initiated by the TS. In this work we present additional research of TS using optical emission spectroscopy (OES) combined with the post-discharge gas composition analysis.

2. Experimental set-up

A dc HV power supply connected to the anode via a series resistor (R = 9.84 MΩ) was used to generate a positive TS discharge. The distance d between the stainless steel electrodes (point-to-point configuration with anode at the top) was 6 mm. The electrodes were made of a 2-mm diameter rod. The anode tip was sharpened whereas the cathode was blunt. The curvature radius of the anode tip was of the order of 100 μm. The curvature radius of the cathode was of the order of a millimeter.

The electrodes were placed in a closed 100 mm long glass tube with the inner radius 4 cm and two valves for the gas inlet and outlet. The one side of the glass tube was enclosed by Teflon window with openings for the electrodes. The other side was enclosed by the CaF_2 window enabling optical diagnostic. The experiments were carried out in synthetic air from the pressure tanks (N_2:O_2 = 4:1, N_2: 99.99% purity, O_2: 99.5% purity), with flow rate 1.3 - 2.6 $l.min^{-1}$. We used a gas analyzer Kane KM9106 Quintox to measure the gas composition after passing through the discharge reactor. It can detect NO and NO_2 in the range of 0-1000 ppm with an accuracy of 3 %.

The discharge voltage was measured by a HV probe Tektronix P6015A and the discharge current was measured on a 50 Ω or 1 Ω resistor shunt. The 1 Ω resistor shunt was used when we measured the spark current pulse, whereas the 50 Ω resistor shunt was used to measure the streamer current. Electric signals were recorded by a 200 MHz digitizing oscilloscope Tektronix TDS2024.

For fast recording of time-integrated broadband spectra (200 - 1100 nm), we used a two-channel compact emission spectrometer Ocean Optics SD2000 (spectral resolution 0.6 - 1.7 nm). The light collection was provided by a pair of parabolic mirrors focused on a small area near the anode tip. These mirrors, together with the optical fiber core diameter, determined the spatial resolution to be 300 μm. The experimental set-up is depicted in figure 1.

3. Results and discussion

Transient spark is initiated by a streamer, when the potential on the stressed electrode V reaches voltage V_{TS}, characteristic for the TS. The streamer forms a relatively conductive plasma bridge between the electrodes. This leads to partial discharging of the electric circuit internal capacity C. The current from the partial discharging of C heats up the gas inside the plasma channel generated by the streamer. The transition to spark occurs when gas temperature inside the plasma channel increases to ~1000 K [30].

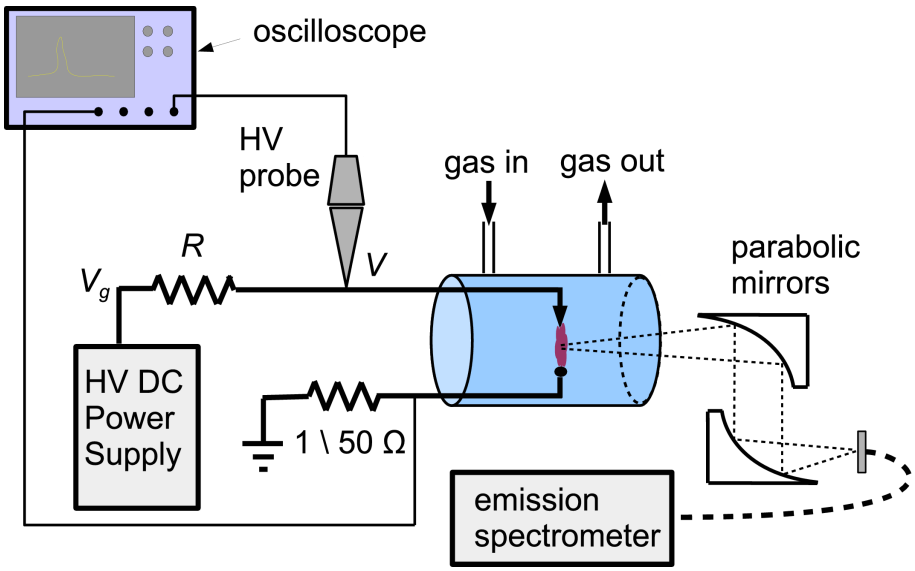


Figure 1. Simplified schematic of the experimental set-up.

During the spark phase, the electric circuit internal capacity discharges completely and the voltage on the HV electrode drops to almost zero (figure 2). The discharge current reaches a high value (~1-15 A). Transition to an arc after the spark phase is restricted by the ballast resistor *R*. It limits the current delivered to the plasma after *C* is discharged. As a result, the plasma starts to decay after the spark pulse. Eventually, the plasma resistance exceeds the *R* and the potential on the stressed electrode gradually increases, as the capacitor *C* recharges. A new TS pulse, initiated by a new streamer, occurs when the potential on the anode reaches the breakdown voltage V_{TS} again. The TS is thus based on repetitive charging and discharging of *C*. The repetition frequency *f* of this process can be controlled by the generator voltage V_g and is typically in the range 1-10 kHz [29].

The TS repetition frequency increase is accompanied by the increase of the mean discharge current I_{mean} and discharge power *P* (figure 3). However, several other TS discharge characteristics change as well. The breakdown voltage decreases, and the spark pulses are getting broader and smaller [29, 30].

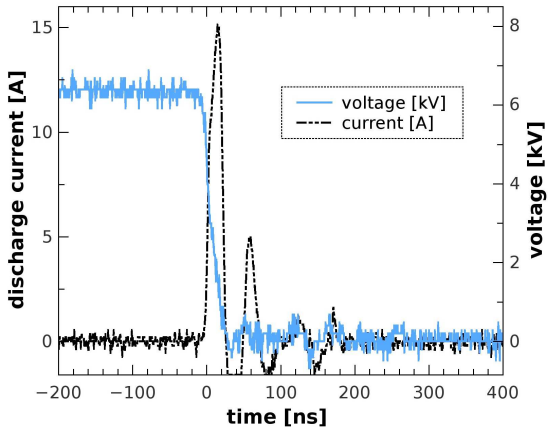


Figure 2. Typical transient spark voltage and current waveforms, $f \approx 2$ kHz.

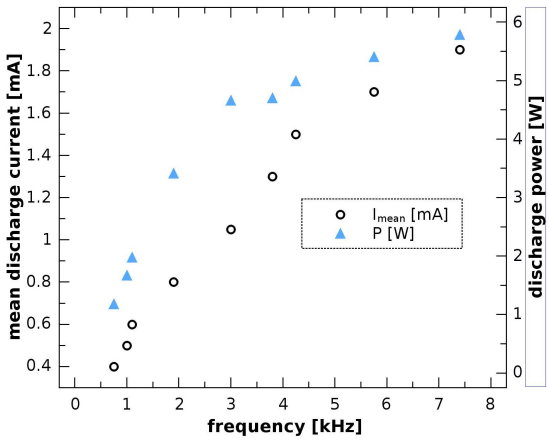


Figure 3. The discharge mean current I_{mean} and discharge power *P* as functions of TS repetition frequency.

The analysis of the electric circuit representing the TS described in [29], and the measurement of the discharge channel diameter by the time-resolved imaging [33] enabled us to estimate the electron density n_e in TS from the current and voltage waveforms [22, 29]. After the streamer, $n_e \approx 10^{14}$ cm^{-3} was obtained, which is in an agreement with values found in the literature [15, 34-36]. During the spark phase, the electron density as high as 10^{17} cm^{-3} can be achieved at $f < 4$ kHz. Generated plasma is thus strongly ionized for a short time. However, the TS spark current pulses are sufficiently short to avoid thermalization of generated plasma. With increasing frequency, smaller and broader spark current pulses occur and the peak electron density decreases to ~10^{16} cm^{-3} [22].

The time-integrated emission spectroscopy study confirmed that TS pulses generate highly reactive non-equilibrium plasma with excited atomic radicals (O^*, N^*), excited molecules N_2^* and ions N_2^{+*} (figure 4). The rotational temperature T_r derived from the N_2 2nd positive system time-integrated spectra, ranging from 500 to 1500 K, was much lower than the vibrational temperature T_v (3800-5000 K) [29]. The TS emission characteristics change with increasing frequency as well. Below ~3 kHz, the atomic lines emission (O^*, N^*) and N_2 2nd positive system dominates in the spectra, but at higher frequencies, these atomic lines almost disappear. This might be interpreted as a decrease of the TS ability to produce radicals and to induce chemical changes at higher frequencies, but it was not confirmed by the measurement of the nitrogen oxides densities.

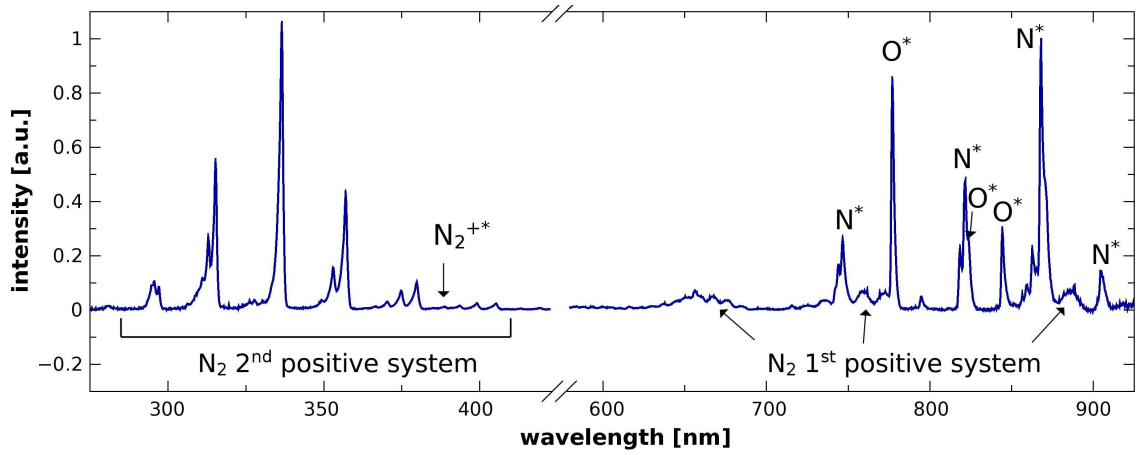


Figure 4. Typical time-integrated spectrum of the TS discharge in air, $f \sim 2$ kHz.

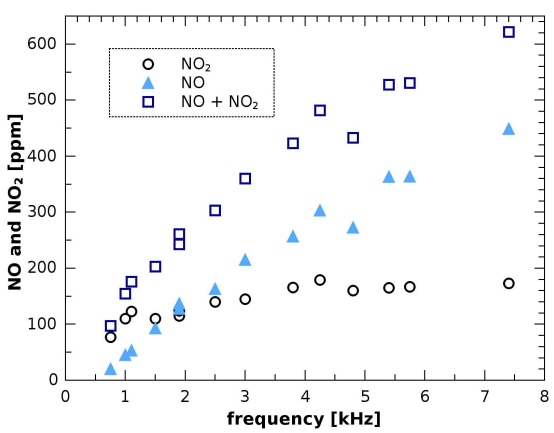


Figure 5. The NO and NO_2 densities produced by TS as functions of f, gas flow rate 1.7 l.min^{-1}.

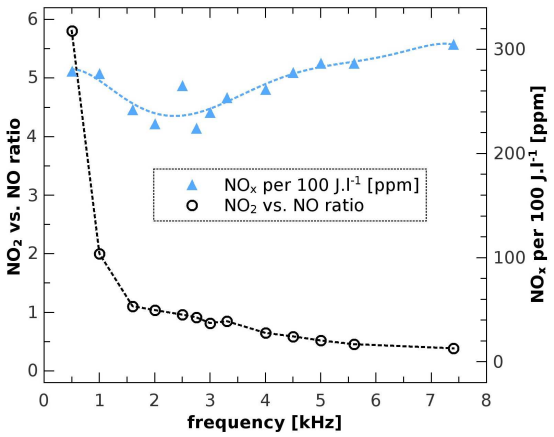


Figure 6. The NO and NO_2 produced by TS per energy input 100 J.l^{-1}, averaged for flow rates 1.3-2.6 l.min^{-1}.

Due to increasing input power, the densities of both NO and NO_2 increase with *f* (figure 5). In order to asses the NO_x generation efficiency, it is necessary to take into account the discharge power changes with increasing TS repetition frequency. Based, on the recalculated densities of NO and NO_2 generated per input energy density 100 $J.l^{-1}$ (figure 6), the NO generation efficiency tends to improve with increasing *f*, while the NO_2 generation efficiency decreases. However, the sum of NO and NO_2 densities do not change significantly. These results show that the ability of TS to induce chemical changes cannot be evaluated using the total NO_x density (NO + NO_2).

More likely, it is the NO_x synthesis mechanism that changes with the increasing TS repetition frequency. The decrease of NO_2/NO ratio (figure 6) with increasing TS frequency could mean that there is less O to oxidize NO further to NO_2. Thus, it could be related with the disappearance of atomic emission lines at higher TS frequencies. However, further research including kinetic modeling is required to explain the mechanism of the NO_x generation by the TS discharge and dependence of NO_2/NO ratio on TS repetition frequency.

4. Conclusions

The aim of our study was to investigate the NO and NO_2 generation, which are significant biomedical and biocidal agents, by the Transient Spark (TS) discharge in atmospheric pressure air. The TS is a streamer-to-spark transition type discharge initiated by a streamer, with the spark pulse duration and amplitude limited by a small amount of energy stored in the circuit internal capacity *C*. The TS repetition frequency (1-10 kHz) can be controlled by the applied voltage. Similar type of plasma, even at higher pulse repetition frequencies, can be generated using nanosecond repetitive pulsed high voltage power supplies. The advantage of our approach is simpler and cheaper electric setup using DC high voltage power supply.

The TS discharge can be maintained at low energy conditions (~1 mJ/pulse) by an appropriate choice of the resistances and capacities in the electrical circuit, so that the generated plasma stays out of thermal equilibrium. The non-equilibrium state of plasma generated by TS was confirmed by the optical emission spectroscopic study. Our research confirmed high reactivity of plasma generated by the TS. In dry synthetic air, the sum of NO and NO_2 densities more than 600 ppm was achieved with power input below 6 W (~300 ppm per 100 J of energy deposited per 1 liter of gas). In future, we plan to optimize the NO_x production by varying various electric circuit parameters (external resistor, internal capacitor, distance of electrodes).

The TS characteristics change with the increasing TS repetition frequency. At higher frequencies, the decrease of the breakdown voltage, smaller and broader spark pulses, and lower electron density during the TS spark phase were observed. These changes also influence the generation of excited atomic species and nitrogen oxides. The atomic lines emission intensity decreases and the NO/NO_2 ratio increases with increasing TS repetition frequency. This indicates changes in the TS chemical reactivity or the mechanism of NO_x generation changes with increasing TS repetition frequency. Further research including kinetic modeling is required to resolve this problem.

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