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Fateev, Alexander; Chiper, Alina Silvia; Chen, Weifeng; Stamate, Eugen

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NOVEL METHODS OF OZONE GENERATION BY MICRO-PLASMA CONCEPT

Authors

A. Fateev, A. Chiper, W. Chen and E. Stamate

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1. Introduction

The project was planed as a supplement to already running PSO-2006-1-6365 project devoted to plasma-assisted DeNOx. Ozone is as a key agent in plasma NOx reduction because in a many step process it oxidizes NO to N_2O_5. The latter could be efficiently removed by a scrubber system. The main objective of the project is optimization of ozone production based on micro-plasma concept in order to reduce energy costs for ozone generation and total costs for plasma DeNOx.

Dielectric barrier discharges (DBD) are widely used for ozone production in pure oxygen or in dry air in various commercially available ozone generators. In the past years, many investigations have been carried out in order to improve ozone generation efficiency in terms of ozone concentration (g/Nm^3) and ozone yield (g/kWh). Unfortunately for a conventional DBD geometry used in most of all ozone generators, it is difficult to get both high ozone concentration and high ozone yield values. The ultra-short gap barrier discharge and the surface discharge were developed to generate high ozone concentration in pure oxygen [1]. Ozone generation efficiency in air decreases to about half of that in pure oxygen because the oxygen content in air is 21%, and a lot of applied energy to the system is consumed to vibrational 'pumping' of N_2 (X, v''>0) states. A short-gap electrode system increases the electric field in the gap (at the same applied voltage) and the mean electron energy. Since the density of low-energy electrons (2-3 eV), which mainly decompose ozone, decreases, it is possible to obtain a high concentration of ozone. Furthermore, the shift in electron energy distribution function towards higher mean electron energy reduces vibrational pumping of nitrogen molecules and therefore leads to a better utilization of applied energy for ozone production. In recent years, new types of plasma devices based on a micro-plasma concept have been developed. The micro-plasma is a plasma generated in very small spaces with characteristic dimension of a few hundreds micrometers. There are two types of micro-plasma devices: micro-hollow cathode discharge (MHCD) and capillary plasma electrode discharge (CPED). High values of reduced electric field can also be obtained in micro-plasma discharges [2]. As it is well-known, ozone generation efficiency increases in the transition from streamer-type DBD to atmospheric pressure glow DBD [3]. In general, stabilization of

atmospheric pressure plasma can easily be achieved if the plasma is confined in small (≈ 50 Debye length) dimensions.

In the MHCD concept the generation of oxygen atoms (from which ozone is formed) is separated spatially from the ozone production, because the ozone formation appears outside the micro-plasma. Therefore, the formed ozone will not be destroyed by the plasma, which in conventional ozonizers limits the upper achievable ozone concentration (ozone saturation effect). The MHCD concept is useful in the sense that the ozone concentration enhancement is at about the same value of ozone yield as when pure oxygen is used as a feed gas.

The concept of CPED includes both micro-plasma jets produced when capillaries cover one or both electrodes of a conventional DBD and a stable uniform glow-like discharge uniformly distributed over the discharge gap. Our calculations show that capillaries re-distribute energy input into plasma when dry air is used as a feed gas. Consequently, the ozone yield is enhanced to about the same or to even higher ozone concentration. This is important because ozone production from pure oxygen is more expensive than production from dry air.

The project aims were to
- perform a feasibility study of ozone generation by modeling of micro-plasmas based on either MCHD or CPE-discharges;
- develop and optimize an MCHD array for operation with pure oxygen in order to enhance ozone concentration to about the same ozone yield achievable for commercial available ozone generators;
- develop, investigate and optimize a CPE-discharge for operation with dry air in order to enhance ozone yield to about the same or even higher ozone concentration than achievable with commercial available ozone generators.

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2. Feasibility study of ozone generation by micro-plasma devices

2.1 Effect of plasma volume reduction on mean electron energy

Reduction of linear dimensions of plasma leads to many remarkable effects. One is a shift in the electron energy distribution function. Thus, a decrease of the electrode gap from 1 mm to 0.3 mm increases the mean electron energy from 4.8 eV to 6.2 eV in a $N_2(80\%)+O_2(20\%)$ gas mixture as shown in Figure 1 (green and red circles, respectively on curves 2 and 3).
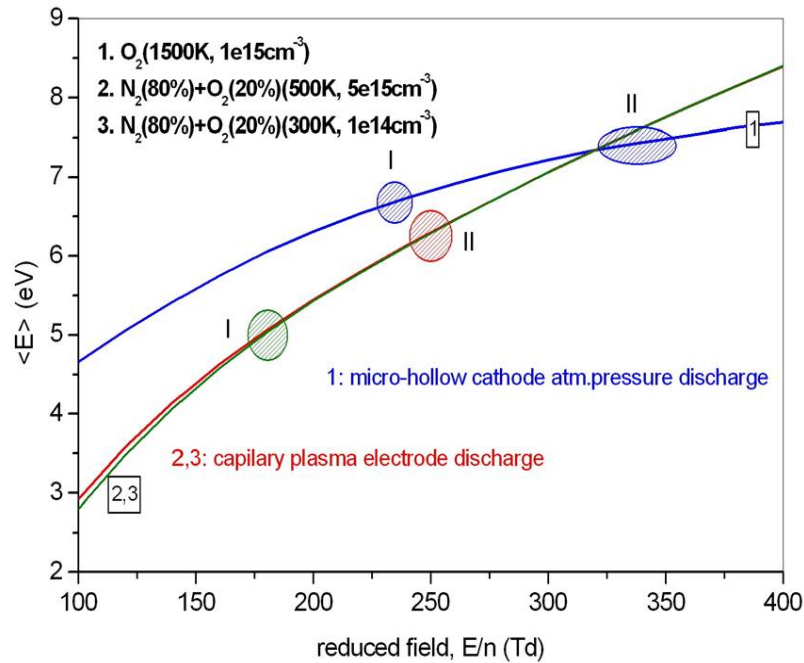

Figure 1: Mean electron energy calculated for various reduced electric filed values in pure O_2 (blue) and $N_2(80\%)+O_2(20\%)$ mixture (red and green curves).

In pure oxygen the same reduction of discharge gap from 1 mm to 0.3 mm causes less gain in the mean electron energy: from 6.5 eV to 7.2 eV, Figure 1 (blue circles I and II, respectively in curve 1). Calculations have been done for various gas temperatures (T_{gas}) and electron densities (N_e) typically realized in MHD and CPED in O_2 and $N_2(80\%)+O_2(20\%)$ mixture:

MHD: $T_{gas}=1500$ K, $N_e=1\times10^{15}$ cm^{-3};   (1)

and

$$CPED: T_{gas}=500 \text{ K}, N_e=5 \times 10^{15} \text{ cm}^{-3}; \hspace{2cm} (2)$$

$$CPED: T_{gas}=300 \text{ K}, N_e=1 \times 10^{14} \text{ cm}^{-3}; \hspace{2cm} (3)$$

A change in electron energy distribution function with reduction of the discharge gap leads in general to a shift towards electronic excitation/ionization and therefore reduces energy attenuation to vibrational excitation. The latter effect is important in the case of $N_2(80\%)+O_2(20\%)$ mixture as it will be shown below.

2.2 Ozone generation in atmospheric pressure micro-hollow discharge in oxygen

Ozone formed in various discharges by well-known three-body reaction of oxygen atoms and oxygen molecules. Oxygen atoms itself are produced due to (pre-) dissociation of oxygen molecules excited in collisions with electrons. Fast side reactions of oxygen atoms with oxygen molecules and already formed ozone reduce both the steady-state oxygen and the ozone concentrations or by other words the efficiency of ozone production [4].
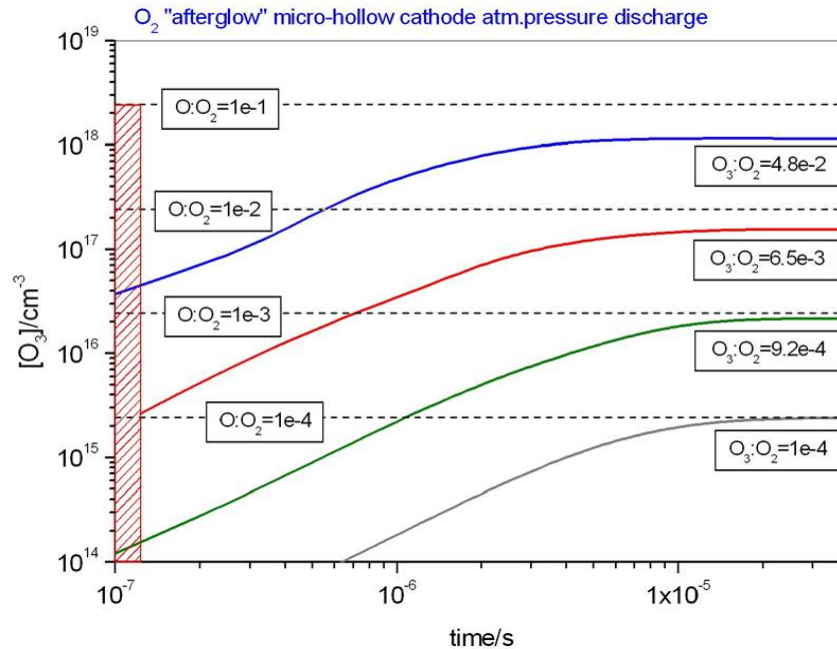

Figure 2: Ozone formation in oxygen plasma afterglow. Plasma exists during time marked by red filled rectangle. Numbers on dashed horizontal lines (left) correspond to different initial O concentrations and corresponding ratios of $O_3:O_2$ are shown under the curves (right).

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Calculations show that the complete conversion of O to O_3 can only be obtained if the relative concentration of oxygen atoms $O:O_2$ stays below 10^{-4}. As it can be seen from Figure 2 the characteristic time of ozone formation is a few microseconds. This is the key feature of MHD approach for ozone generation which has been successfully used by S. Ishii's group [1, 5]. Due to high current, extremely small plasma volume (residence time in plasma 1-2 μs) and fast gas expansion an efficient dissociation of oxygen takes place and ozone is produced outside of the plasma region in absence of electrons.
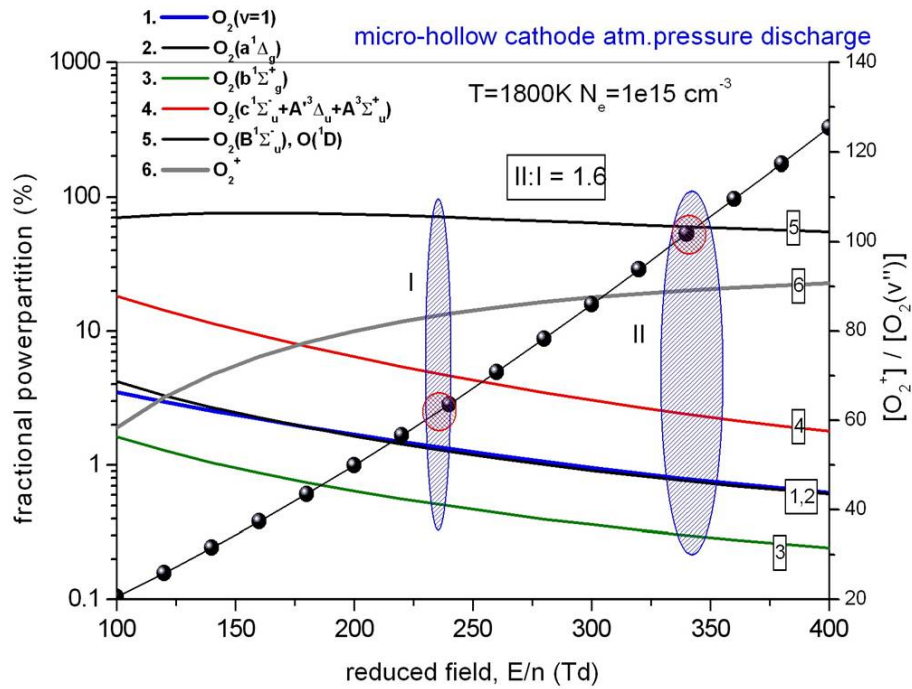

Figure 3: Fractional power partition into different excitation processes in O_2 plasma at different values of E/n and $T_{gas}=1800K$, $N_e=1x10^{15}$ cm^{-3}. Blue ovals correspond to E/n values at 1 mm (I) and 0.3 mm (II).

Reduction of the discharge gap from 1 mm to 0.3 mm (at constant value of applied voltage) increases significantly the reduced electric field but lives unchanged the mean electron energy (see Figure 1). More detailed calculations show that the energy for oxygen ionization at 0.3 mm increases compare to 1 mm, Figure 3 (curve 6, blue ovals I and II).
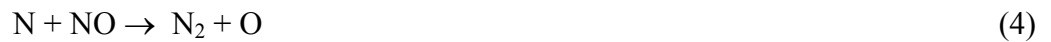
In opposite, energy input into O_2 vibrational excitation decreases, Figure 3 (curve 1). The ratio O_2^+:$O_2(v'')$ increases with rise of E/n, Figure 3 (right axes). Thus at 0.3 mm gap the ratio O_2^+:$O_2(v'')$ becomes 1.6 times higher than at 1 mm gap. Electron-ion recombination O_2^++e finally leads to the production of O atoms. However, as it can also be seen from Figure 3 (curves 4, 5) the fraction of O_2 electronically excited states, which are also responsible for O atom generation, decreased. Therefore the O net production is expected to be the same. Thus a micro-plasma device like MCD can be efficiently used to enhance the ozone concentration but not the ozone yield.

Although pervious consideration has been devoted to ozone generation in MHD, the main results will remain the same in case of CPED in pure oxygen.

2.4 Ozone generation in atmospheric pressure capillary plasma electrode discharge in air

A unique feature of the CPED compared to other parallel plate DBD configurations is the ability (at certain condition) to generate plasma jets in small (0.1-0.3 mm) capillaries [2]. Reduced electric field in these jets can reach higher values compare to that in the rest part of the plasma volume. Therefore CPED is a promising device for ozone generation in air as it will be shown below.

In air discharges the presence of the nitrogen ions, nitrogen excited (in particular, metastable) molecules and atoms increases the complexity of the reaction system [6]. Thus dissociation and excitation of nitrogen molecules lead to a number of additional reactions involving nitrogen atoms and excited molecules that can provide additional channels for oxygen atoms and finely ozone generation:

$$N + NO \rightarrow N_2 + O \tag{4}$$

$$N + NO_2 \rightarrow N_2O + O \tag{5}$$

$$N_2(A,B) + O_2 \rightarrow N_2 + O + O \tag{6}$$

$$N_2(A) + O_2 \rightarrow N_2O + O \tag{7}$$

About half of the ozone formed in air discharges results from the oxygen atoms produced in these indirect processes. As a result ozone formation in air takes about 100 µs [6]. A substantial fraction of electron energy lost in collisions with nitrogen molecules acts as "pumping" for the ground vibrational states, $N_2(X, v''>>1)$. Moderate gas temperature in the plasma jets of CPED, 400-500K compared to that in MHD, 1500K, reduces significantly the NO/NO_2 formation which causes intensive ozone consumption (discharge poisoning). The gas temperature outside jets is significantly lower.

Calculations of fractional power partition show that reduction of discharge gap causes enhancement of nitrogen and oxygen ionization (Figure 4, curves 3,5) and significantly reduces energy attenuation by vibrational "pumping" of $N_2(X, v'')$ (curve 1). Energy input into N_2 and O_2 electronic excitation does not significantly change in the range of interest for E/n (green and red ovals). The ratio $[N_2^++O_2^+]:[N_2(v'')+O_2(v'')]$ increases with E/n (right axis in Figure 4). At 0.3 mm gap ratio $[N_2^++O_2^+]:[N_2(v'')+O_2(v'')]$ becomes 5 times higher compare to that at 1 mm gap. Since NO is always produced in discharges in air in the following reactions:

$$N + O + M \rightarrow NO + M, \tag{8}$$

$$O(^1D) + N_2O \rightarrow NO + NO, \tag{9}$$

$$N_2(A) + N_2O \rightarrow N_2 + N + NO, \tag{10}$$

A shift in electron energy distribution function towards ionization will enhance 1) N and O atom generation; and consequently ozone formation and 2) NO concentration. Therefore the net ozone concentration in CPED will not be different in comparison with conventional DBD, but ozone yield is expected to be higher.
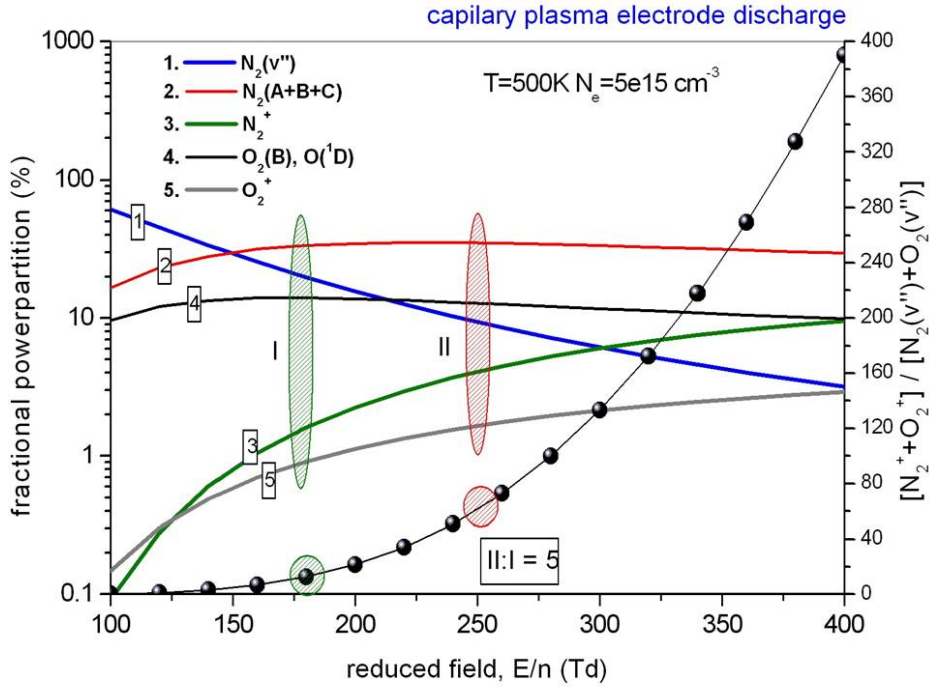
Figure 4: Fractional power partition into different excitation processes in $N_2(80\%)+O_2(20\%)$ plasma at different values of E/n and $T_{gas}=500K$, $N_e=5x10^{15}$ cm^{-3}. Green and red ovals correspond to E/n values at 1 mm (I) and 0.3 mm (II), respectively.

3. Experimental studies of ozone generation by various micro-plasma devices

3.1 Experimental observation of shift towards ionization/excitation in curved dielectric barrier discharge operating with synthetic air

For this experiment a curved dielectric barrier discharge system (see Figure 5) was built. Half-sphere aluminium electrodes were covered by replaceable STENAN® dielectric covers. One pair of covers has single micro-holes Ø=300 μm, whereas the other one does not. Micro-holes are placed in front of each other when they are mounted on the electrodes. Distance between electrodes is variable from 0 mm to 10 mm. An ac-power supply with variable frequency has been used in order to produce plasma. Electrodes are enclosed into a quartz

tube allowing optical excess to the tiny plasma column. All experiments were carried out at atmospheric pressure.
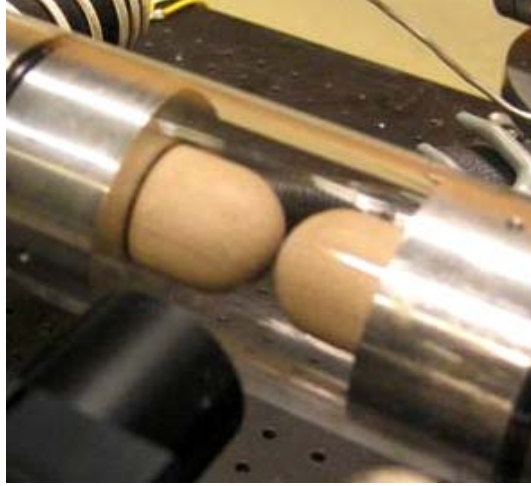

Figure 5. Dielectric-barrier-discharge with curved geometry

Optical emission measurements were made with a spectrometer equipped with a CCD-camera. The spectral resolution was 0.043 nm. A part of second positive system of N_2 together with first negative system of N_2^+ have been measured in the range of 387-407 nm. Ratios of integrated intensities of $N_2(C_1-B_4)$ and $N_2(C_0-B_3)$ bands at various frequencies of applied voltage and dielectric covers are shown in Figure 6. The same ratios for parallel-plate DBD (with the same discharge gap) are also shown (dark blue and yellow balls).

As it can been seen from Figure 6, the ratio of the integrated intensities $N_2(C_1-B_4):N_2(C_0-B_3)$ equals about 0.85 and does not depend on the applied voltage frequency, whereas $N_2^+(B_0-X_0):N_2(C_2-B_5)$ does depend on the frequency. A ratio of about 0.85 indicates that the excitation of the $N_2(C-B)$ system is mainly due to $e+N_2(X)$ collisions [7]. At frequencies more than 15 kHz ratio $N_2^+(B_0-X_0):N_2(C_2-B_5)$ becomes higher for dielectric covers with capillaries (Figure 6, red balls) compared to that without capillaries (violet squares). It indicates that capillaries enhance ionization and probably form plasma jets.

The ratio $N_2(C_1-B_4):N_2(C_0-B_3)$ for parallel-plate DBD is the same as for curved DBD, Figure 6 (yellow ball). However the ratio $N_2^+(B_0-X_0):N_2(C_2-B_5)$ (dark blue ball) is significantly less compared to that for curved DBD. This is an indication of enhanced

ionization in curved geometry (with higher E/n values) compared to the flat one (with smaller E/n values).
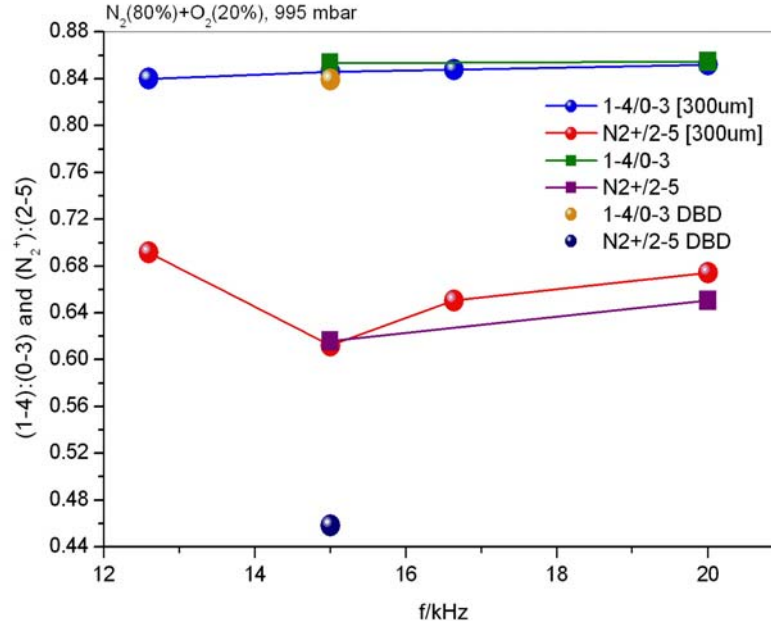

Figure 6. Ratios of integrated intensities $N_2(C_1$-$B_4)$:$N_2(C_0$-$B_3)$ and $N_2^+(B_0$-$X_0)$:$N_2(C_2$-$B_5)$ bands at various frequencies and dielectric covers arrangements. Dark blue and yellow balls at 15 kHz correspond to parallel-plate DBD.

A constant ratio $N_2(C_1$-$B_4)$:$N_2(C_0$-$B_3)$ of about 0.85 for all geometries and frequencies is in agreement with calculations shown in Figure 4: energy input into electronic excitation of N_2 has weak influence in E/n values. In opposite curved geometry and micro-holes support increase of E/n and therefore enhance ionization [7].

3.2 Ozone production by micro-hollow cathode discharge operating in pure oxygen atmosphere

For this experiment, a micro-hollow cathode discharge system (see Figure 7) for ozone production was built. The parallel-plate electrodes geometry is shown schematically. The electrodes of 50 mm in diameter are made of molybdenum plates with 200 μm thickness. There are 19 holes in each electrode with 300 μm as diameter. Each electrode is assembled in a heavy metal holder. The dielectric barriers are made of alumina with 300 μm thickness. The

dielectric spacer is sandwiched by the two heavy holders. The system was tested by applying an AC bias to electrodes with pure oxygen as input gas. It was observed that the discharge was localised at one hole and the dielectric spacer suffered some damage. This is because the dielectric spacer is too thin and its surface is bigger than the electrode's holders surface. This problem may be solved by using a dielectric spacer with smaller surface than the surface of the electrode's holder.
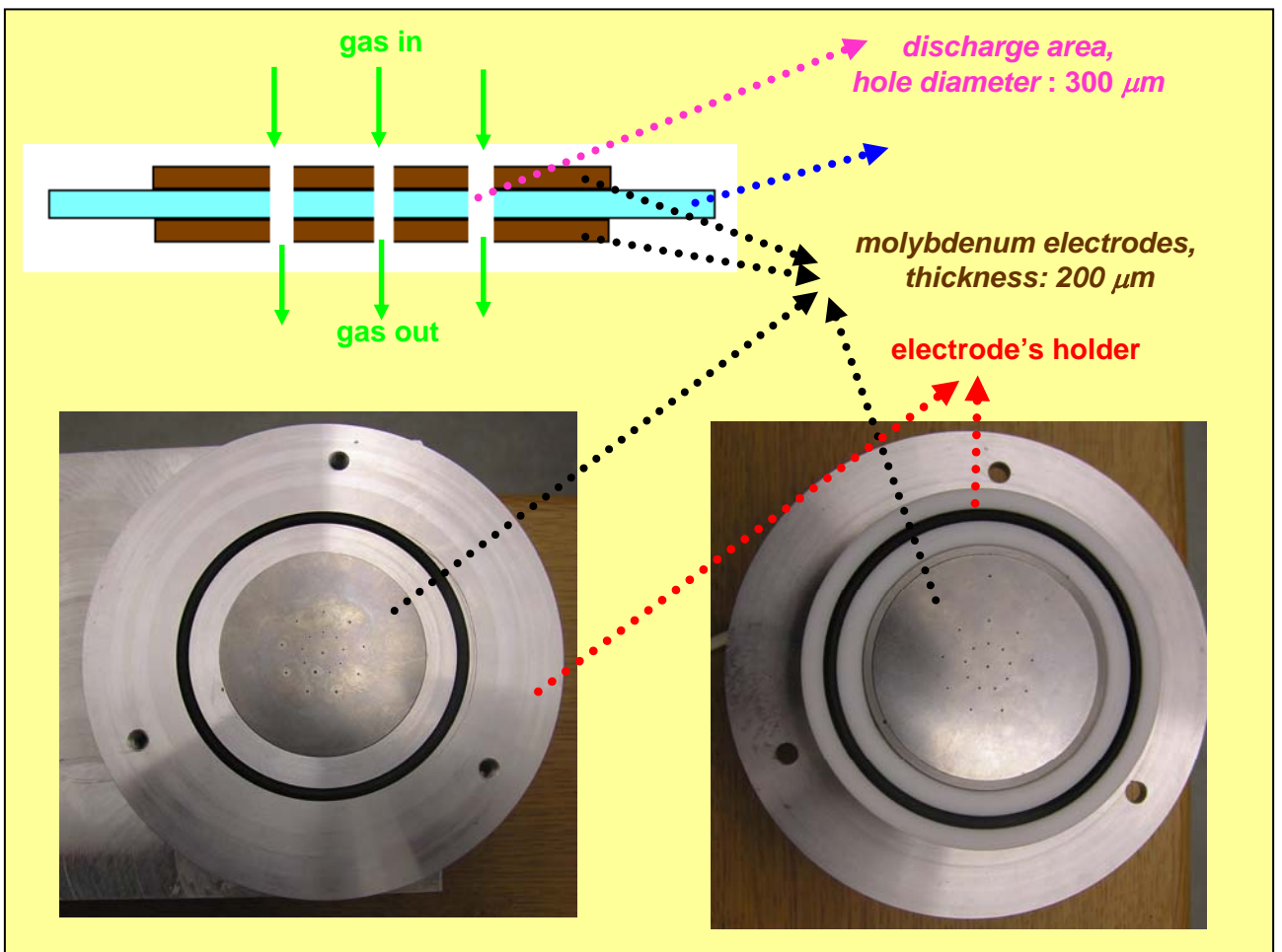

Figure 7. Schematic drawing and pictures of the micro-hollow cathode discharge system.

3.3 Ozone production by capillary plasma electrode discharge operating in pure oxygen atmosphere

Within the experiment a new discharge system (see Figure 8) for cold plasma production was built. The system can be run in either CPED mode or in DBD mode. The symmetrical parallel-plate electrodes geometry for both modes and the corresponding discharge pictures

are shown in right side of Figure 8. The dielectric barriers are made of alumina of 1 to 4 mm thick. The upper electrode is connected to the HV power supply by using an interlock, while the lower electrode is grounded. The discharge was excited by using a 14 kHz sinusoidal wave voltage, with variable amplitude between 34 to 42 kV. The electrodes are cooled with flowing air. The inter-electrode gap is adjustable between 3 mm up to 6 cm.
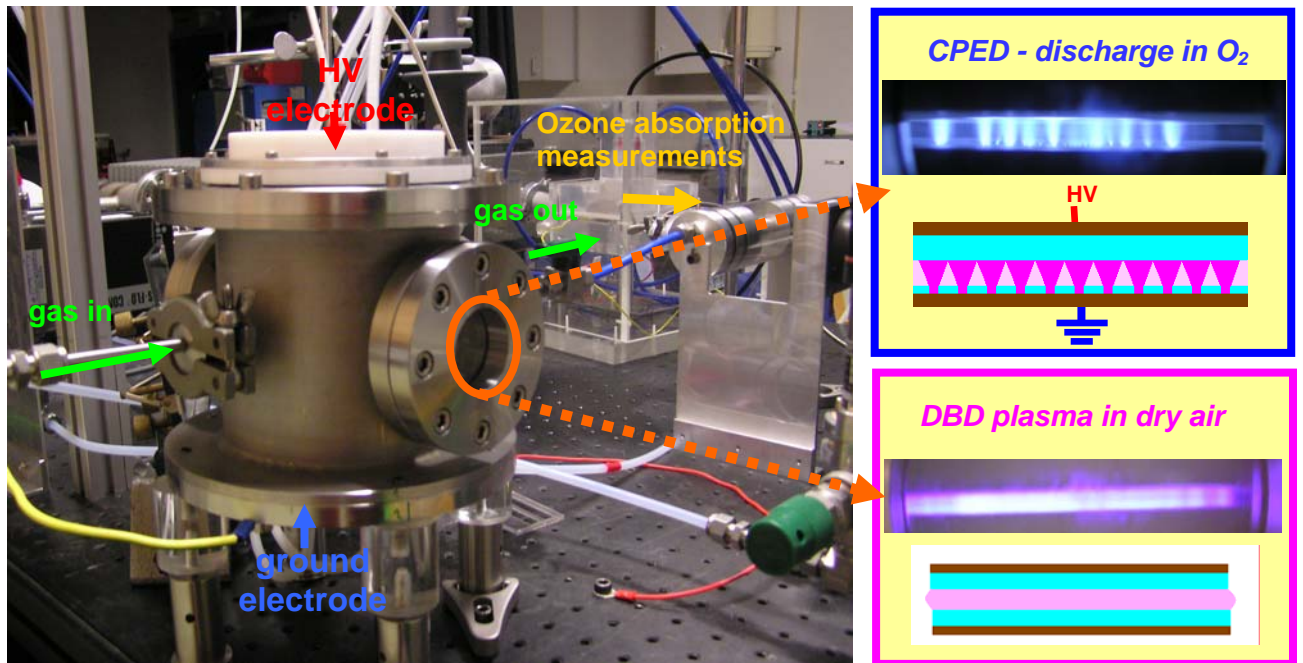

Figure 8. Pictures of the discharge system for either capillary plasma discharge or dielectric barrier discharge and their schematic drawings.

Figure 9 shows the relationship between ozone concentration and applied voltage (discharge power density) by DBD running in dry air (1 l/min). The ozone concentration decreases with increasing applied voltage. The phenomenon that ozone concentration decreases with increasing applied discharge voltage (specific discharge energy) is peculiar to ozone generation from air; it never appears in ozone generation from oxygen [9]. The reason for this is as follows: (1) the concentration of the by-product NO_x increases with increasing specific energy; (2) gas temperature increases with increasing discharge power density. These effects result in the promotion of ozone decomposition by the reaction with nitrogen oxides because most of the rate coefficients related to the ozone decomposition increase exponentially with increasing gas temperature. Therefore, keeping both the gas

temperature low and optimizing the electric field strength are quite important for efficient ozone generation.

The evolution of the ozone concentration as function of oxygen concentration by DBD plasma running in nitrogen-oxygen gas mixture, under constant applied voltage (36 kV) and constant gas flow rate (1 l/min) is emphasized in Figure 10. The ozone concentration increases linearly with O_2 concentration, since ozone is produced via the following three-body reaction [10]:
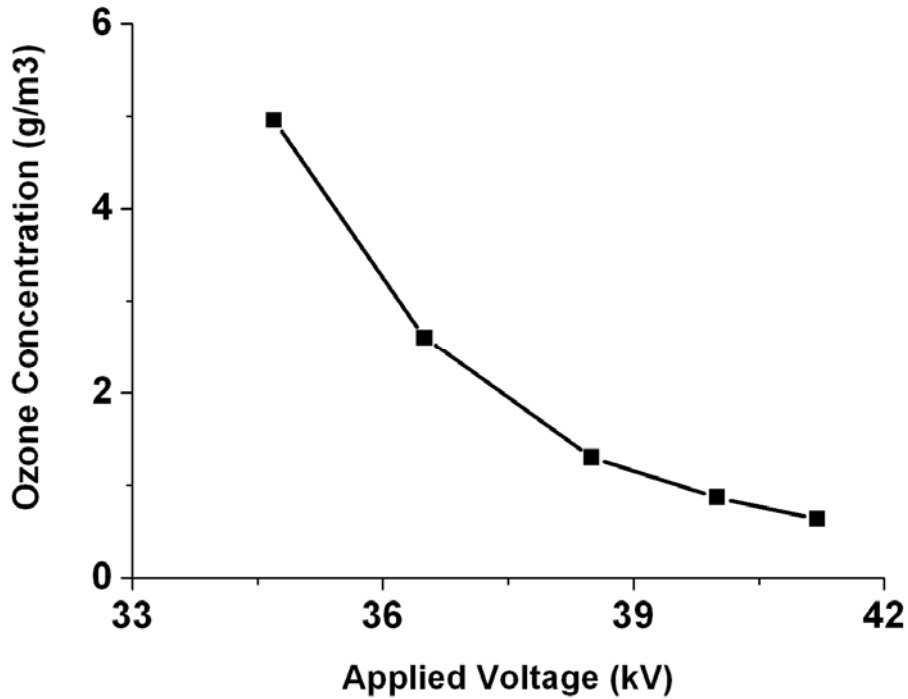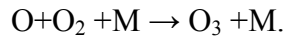
$$O + O_2 + M \rightarrow O_3 + M.$$

Figure 9. The effect of discharge applied voltage on ozone generation characteristics by DBD in air.

The effect of the of gas flow rate on ozone generation characteristics by DBD in oxygen and nitrogen gas mixture and by CPED in oxygen is presented in Figure 11 and Figure 12, respectively. It was observed for different percentage of oxygen in gas mixture that the ozone concentration weakly depends on gas flow rate.
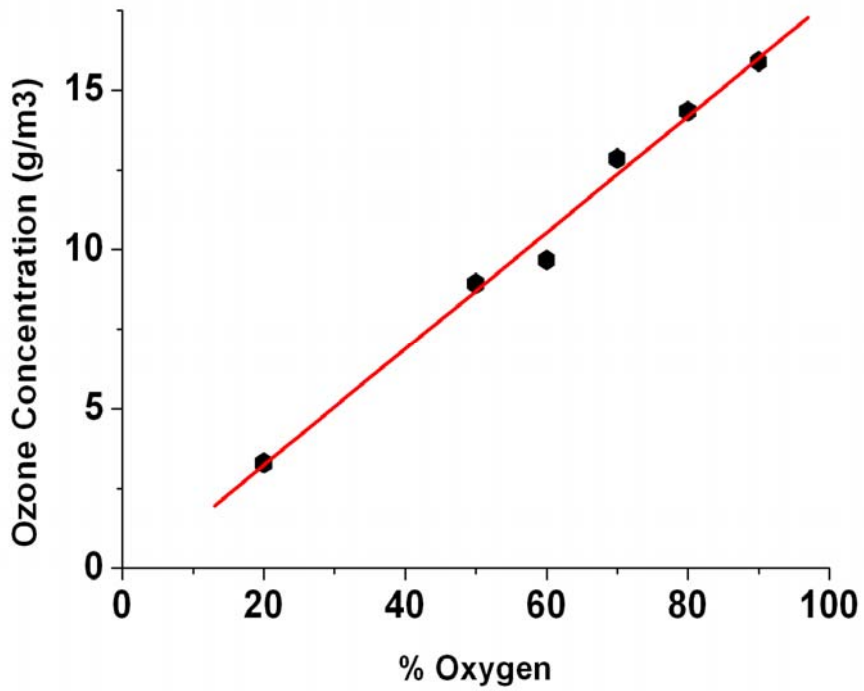
Figure 10. The effect of oxygen concentration on ozone generation characteristics by DBD in oxygen and nitrogen gas mixture.
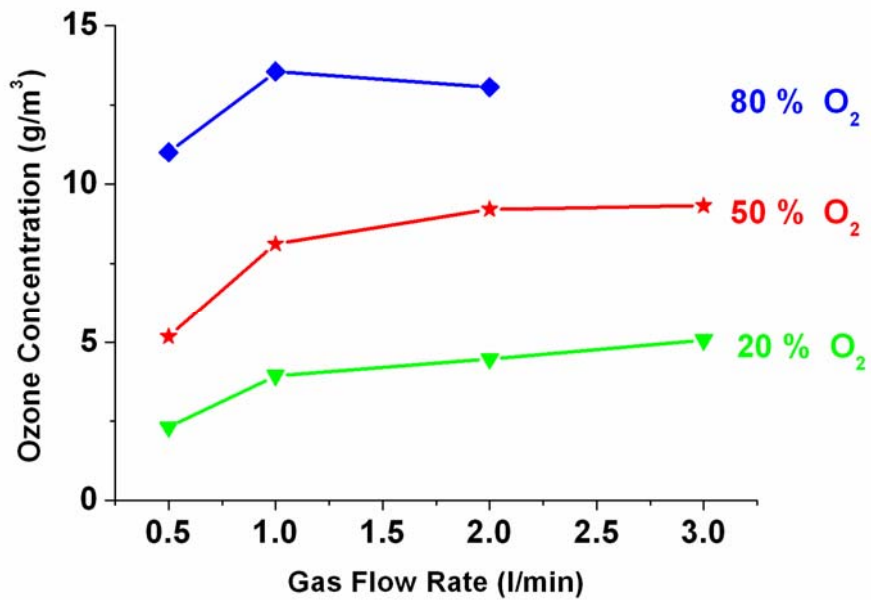

Figure 11. The effect of gas flow rate on ozone generation characteristics by DBD in oxygen and nitrogen gas mixture.

Figure 12 shows the effect of gap distance on ozone generation characteristics by CPED discharge in pure oxygen. Decreasing gap distance increases mean electron energy and decreases the number density of low-energy electrons (2-3 eV) that mainly decompose ozone [1]. Therefore, a higher concentration of ozone (about 17%) was obtained in CPED discharge decreasing the gap distance from 6 mm to 3.5 mm, keeping constant the applied voltage and gas flow rate.
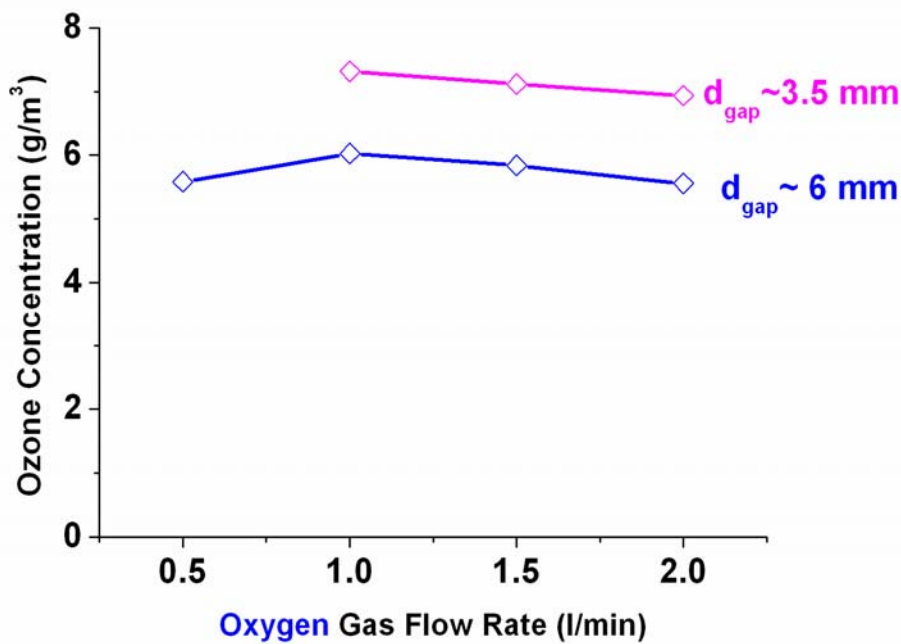

Figure 12. The effect of gas flow rate on ozone generation characteristics by CPED in pure oxygen for different gap distances.

Conclusions

1) The feasibility study proved the potential use of micro hollow cathode and capillary plasma electrode discharges for efficient ozone production in pure oxygen atmosphere.

2) Three new devices have been built and used for ozone production in oxygen and air.

  i) The curved dielectric barrier discharge shows a clear indication of enhanced ionization (higher E/n values) compared to the flat dielectric barrier discharge;

  ii) The micro-hollow cathode discharge was tested with AC bias to electrodes with pure oxygen and air as input gas. The discharge was localised to a few or just one hole causing local damage by heat. In order to avoid this situation a new design based on thin film coating directly on the ceramic plate was proposed and will be built in a near future.

iii) A capillary plasma electrode discharge that can also operate in dielectric barrier discharge mode was tested for different applied voltages, gas flow rates and inter-electrode gaps. Keeping the gas temperature low and optimizing the electric field strength lead to efficient ozone generation. Decreasing the gap distance reduced the low energetic electrons that mainly decompose ozone thus leading to higher ozone concentrations.

Since the issue of efficient ozone generation is yet very important for the ongoing project PSO-2006-1-6365 the present experiments will be continued including further characterization and optimization of the micro-hollow cathode setup and capillary plasma electrode discharge as to achieve higher concentrations and yields of ozone. The results following these modifications will be reported in the final report of PSO-2006-1-6365.

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