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The dynamics of ozone generation and mode transition in air surface micro-discharge plasma at atmospheric pressure

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Abstract. We present the transient, dynamic behavior of ozone production in surface micro-discharge (SMD) plasma in ambient air. Ultraviolet absorption spectroscopy at 254 nm was used to measure the time development of ozone density in a confined volume. We observed that ozone density increases monotonically over 1000 ppm for at least a few minutes when the input power is lower than $\sim 0.1 \,\mathrm{W/cm^2}$. Interestingly, when input power is higher than $\sim 0.1 \,\mathrm{W/cm^2}$, ozone density starts to decrease in a few tens of seconds at a constant power density, showing a peak ozone density. A model calculation suggests that the ozone depletion at higher power density is caused by quenching reactions with nitrogen oxides that are in turn created by vibrationally excited nitrogen molecules reacting with O atoms. The observed mode transition is significantly different from classical ozone reactors in that the transition takes place over time at a constant power. In addition, we observed a positive correlation between time-averaged ozone density and the inactivation rate of Escherichia coli on adjacent agar plates, suggesting that ozone plays a key role in inactivating bacteria under the conditions considered here.

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Contents

| 1. Introduction | 2 |
|-------------------------|----|
| 2. Experimental setup | 3 |
| 3. Experimental results | 4 |
| 4. Discussion | 7 |
| 5. Summary | 9 |
| Acknowledgment | 10 |
| References | 10 |

1. Introduction

Biomedical applications of atmospheric pressure plasmas have been extensively investigated [1–6]. For instance, atmospheric pressure plasmas are capable of inactivating bacteria, fungi and viruses in tens of seconds to minutes. Plasmas appear to have healing effects on cancers and wounds [7, 8]. The combination of plasma-induced healing and bactericidal effects appears to have opened up promising new applications in biomedicine. We have developed a surface micro-discharge (SMD) plasma system, previously described in greater detail [9]. SMD has strong effects on various types of bacteria, including antibiotic-resistant bacteria (e.g. MRSA), as well as on spores, biofilms and viruses [10, 12]. In addition, SMD has no negative effects on porcine skin under the conditions investigated, suggesting that SMD is capable of treating cells and tissues with minimal or no undesired damage (e.g. mutagenicity) [13].

SMD operates in ambient, static air at or near room temperature and consists of a planar powered electrode separated from a grounded mesh by a thin dielectric material. The electrode is powered with an alternating current voltage source, with a frequency of the order of 10Hz–10kHz and a voltage ~ 10 kV_{pp}. Power dissipation in the plasma ranges from 0.1 mW/cm^2 – 10 W/cm^2 electrode area. Multiple filamentary discharges are generated on the dielectric between the grounded mesh. The discharge is easily scalable to wider treatment areas and is not influenced by the electrical properties of treated objects since there is no direct current flow to treated surfaces. Treated objects are usually placed about 1–10 mm away from the SMD electrode, so that an 'afterglow' plasma gas reacts with the objects. The most common configuration involves using a confined volume next to the plasma, enclosing the surface to be treated. Treatment times for typical biomedical applications range from tens of seconds to several minutes. As we note below, this enclosed volume coupled with the relatively long treatment times results in discharge neutral chemistry that has, apparently, not been extensively studied in air DBD so far.

In the SMD configuration, since charged species from the filamentary discharge do not reach the treated objects, reactive oxygen and nitrogen species (RONS) are thought to play a dominant role. Our numerical simulations with extensive reaction paths indicated that major reactive species in SMD include O₃, NO₂, N₂O, N₂O₅, HNO₂, HNO₃, and H₂O₂ in the afterglow region [14]. It is well known that different RONS have different effects on cells and tissues. For instance, ozone is known to be a strong bactericidal and oxidizing agent [15, 16], whereas nitric oxide (NO), often stored in the form of nitrites and nitrates *in vivo*, is one of the most important signaling molecules in aerobic biology [17, 18]. Therefore, the time- and space-distributions

of these reactive species are crucial to control the response of treated cells and tissues and to develop clinically practical SMD-based biomedical device technology.

In this paper, we discuss the afterglow plasma chemistry in SMD through measurement of the time evolution of ozone density in the enclosed region next to the plasma zone. As we see below, SMD shows surprisingly dynamic behavior of the distributions of RONS. Of course, air plasma chemistry has been studied extensively for decades [19, 21]. For instance, it is well established that ozone is preferentially generated at relatively low power (sometimes called a 'silent discharge') in air dielectric barrier discharges (DBD). Other forms of lowpower air discharges that produce ozone include the 'corona' discharges that form around highvoltage surfaces with sharp points or small radii of curvature. When the input power exceeds a certain level, ozone is quenched by nitric oxide and nitrogen dioxide (sometimes referred to as 'discharge poisoning'). This general picture also seems to be applicable to SMD plasmas. However, as we discuss below, the transition in SMD from the 'ozone mode' to the 'nitrogen oxides mode' is observed to occur in a significantly different manner to that of classical ozone reactors.

In the next section we describe the experimental setup. Then we show our experimental results and discuss the mechanisms of mode transition using a parameterized analytical model. Finally, we summarize our results.

2. Experimental setup

Our SMD electrode consisted of a planar copper electrode and a stainless steel mesh electrode, separated by a dielectric plate. The grid size of the mesh electrode was 4 mesh/inch. An alumina (Al₂O₃) plate of 0.76 mm in thickness was used as dielectric between the electrodes. Figure 1 shows the schematic design of our experimental setup. A sinusoidal alternating current signal was amplified by a high voltage amplifier (Trek Inc., model 10-10B HS). A high voltage of $5-15 \text{ kV}_{\text{pp}}$ was applied between the planar electrode and the grounded mesh electrode. The power consumption in the discharge was measured by the Lissajous method, inserting a $0.1 \,\mu\text{F}$ capacitor in series [22]. We note that the frequency of the applied voltage was adjusted to change the input power, instead of the magnitude of the voltage. The frequency range used in this study was from 5 Hz to 10 kHz, corresponding to input power from 1.5×10^{-4} and 2.2 W/cm^2 . A quartz tube 10 mm high and 30 mm in diameter was placed on the grounded mesh electrode. The diameter of the planar electrode was the same as that of the quartz tube. No visible emission was observed outside the quartz tube. An alumina plate or an agar plate was placed on top of the quartz tube to form the confined volume.

Ozone generated by the SMD device was measured in the confined volume by ultraviolet (UV) absorption spectroscopy. An argon/mercury lamp was used as a UV source. Two iris diaphragms with 1 mm diameter apertures were set at 5 mm above the grounded mesh electrode adjacent to the quartz tube outside the confined volume. UV light passing through the two diaphragms was collected by an optical fiber. The fiber was connected to a UV spectrometer (Avantes, AvaSpec-2048 fibre optic spectrometer). The intensity of UV light at 254 nm was used to calculate ozone density based on Beer's law. The photoabsorption cross section used was 1.15×10^{-21} m². The optical path length was 26 mm. The time resolution and detection limit of our measurements were ~1 s and ~5 ppm, respectively. No significant difference in ozone density was observed between experiments using the alumina plate or the agar plates,

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Figure 1. Schematic diagram of the experimental setup. The insert shows a plasma discharge on the SMD electrode. The photograph was taken without a plate on top of the quartz tube.

under the conditions considered here. Therefore, we report on ozone density obtained with the alumina plate in the following discussion.

The bactericidal properties of SMD were evaluated via *Escherichia coli* (*E. coli*; DSM 1116). A bacteria suspension with a density of about 10^8 cells/ml was prepared in phosphate buffered saline as a master suspension. To change the bacteria density, 10^2 and 10^4 diluted suspensions were also prepared. Subsequently, $100 \mu l$ of each suspension was smeared out on Mueller–Hinton agar plates with a diameter of 86 mm. The agar plates inoculated with bacteria were kept in ambient conditions (~20 °C, ~40 % relative humidity) for two hours in order to dry the surfaces of the plates. The agar plates were placed on the quartz tube with the surface down. Then *E. coli* cells on the agar plates were exposed to SMD plasma for 30 seconds. Three plates were treated for each condition in order to evaluate experimental error. After the treatment, the agar plates were incubated at 36 °C for 14 hours, so that the surviving bacteria formed visible colonies and colony-forming units (CFUs) were counted. For a comparison and a calculation of bacterial reduction by the plasma treatment, a 10^5 diluted suspension was smeared out on an agar plate in order to evaluate the density of the master suspension, dried for 2 hours and incubated for 14 hours.

3. Experimental results

Figure 2 shows time evolution profiles of ozone density under different input power conditions. The amplitude of the applied voltage was 15 kV_{pp} . The error bars in figure 2 represent the standard deviation from three independent measurements. Figure 3 is the generation rate of ozone calculated by the slope of ozone density when SMD is ignited (i.e. at t = 0 in figure 2). When the input power was lower than 0.1 W/cm^2 , the ozone density increased for the first



Figure 2. (a) Time evolution of ozone density (n_{O3}) under different power inputs. (b) Time evolution with power input of 0.56 W/cm^2 and higher. The applied voltage was 15 kV_{pp} .



Figure 3. The production rate of ozone at 15 kV_{pp} calculated by the slope of the ozone density at t = 0 in figure 2.

tens of seconds and reached a steady state at $\sim 1 \text{ min.}$ At 0.1 W/cm^2 , the steady state density was around 4000 ppm. The slope of ozone density at t = 0 increased with power, as shown in figure 3, indicating that the net generation rate of ozone increases. When the power increased



Figure 4. Bactericidal effect of the SMD plasma and averaged ozone density for the first 30 s at different input powers. The applied voltage was 5, 10 and 15 kV_{pp}, but the results scaled only with power density under these conditions.

further, we observed a peak in ozone density: ozone density increased for the first few to tens of seconds, followed by a rapid decrease below our detection limit (~ 5 ppm). The production rate of ozone at t = 0 gradually decreased, as shown in figure 3. In addition, the period of time during which ozone was detected became shorter and the maximum ozone density decreased as the power increased. At powers higher than 2.6 W/cm², almost no ozone was detected.

Figure 4 plots averaged ozone density for the first 30 s as a function of input power. The applied voltages were 5, 10 and 15 kV_{pp} . We see a clear transition point at around 0.1 W/cm^2 . The averaged ozone density increases monotonically at powers lower than 0.1 W/cm^2 , whereas the averaged density drops at higher power than 0.1 W/cm^2 . These results are quite consistent with time-resolved density in figure 2. Interestingly, figure 4 shows that averaged ozone density depends only on the input power. Almost no difference is observed among different input voltages as long as the input power is the same.

Figure 4 also shows the relation between the bactericidal property (expressed as a log reduction from the initial bacterial density on the agar plate) and averaged ozone density for 30 s at various applied voltages. The treatment time was 30 s. Thermal effects were not responsible for the observed bactericidal property, since the measured gas temperature was less than about 25 °C during SMD exposure. The intensity of UV emission mainly from the N₂ second positive system was less than 110 nW/cm² and was not high enough to explain the observed bactericidal effect [9]. The bactericidal property appears to follow the profile of the measured time-averaged ozone density, indicating a positive correlation between them. The inactivation rate was the highest at 0.1 W/cm^2 , corresponding to the highest ozone density. Figure 4 shows that input power is a key scaling parameter and not the amplitude of the applied voltage.

4. Discussion

As mentioned earlier, ozone generation kinetics and the associated reaction mechanisms have been widely investigated and reported in the literature. However, the observed transient behavior of ozone in the confined SMD configuration appears not to have been fully explained by the results with classical ozone generators. For instance, Kogelschatz et al [22] observed a mode transition from ozone to nitrogen oxides. These authors noted that ozone was quenched when the power deposited was around 0.5 eV/molecule in their reactor. We note that they reported a *normalized* power deposition by gas flow rate, since gas flowed through their plasma zone. In other words, by using the rate of power deposition (i.e. eV/s) in the plasma and then dividing by the number of molecules flowing through the plasma per second, they obtained their normalized power deposition in terms of eV/molecule. This is a steady state value, in contrast to our intrinsically transient situation. Furthermore, the reaction-diffusion configuration in the confined SMD system is different from the flow reactor used by those authors. Typically, gas residence times in ozone plasma reactors are of the order of one second or less, whereas as we note above, the SMD configuration operates with residence times of tens of seconds to several minutes. As a result, the characterization following Kogelschatz et al [22] is not applicable to our measurements. We observed the mode transition over time at a constant input power. In fact, if we attempt to estimate a similarly normalized power deposition value, ozone in our SMD system was quenched at an average value of $\sim 5 \text{ eV/molecule}$. This is ~ 10 times higher than the threshold reported by those authors. This clearly indicates that the energy input per molecule is not the proper global parameter to comprehensively describe the complex, transient and non-linear behavior of air plasma chemistry.

NO is thought to be the major quencher of O_3 : NO reacts with O_3 to generate NO_2 and O_2 . NO₂ further quenches O_3 and is converted into NO_3 [23]. A widely accepted explanation of NO generation is a reaction between N atoms and O_2/O_3 [21, 22]. However, our preliminary numerical simulation with extensive chemical reaction mechanisms [14] indicated that the reaction rate between N atom and O_2/O_3 is not fast enough to generate NO and quench O_3 at rates that match the measurements. Also, neither thermal decomposition of N_2O_5 into NO_2 and NO_3 nor decomposition of O_3 explains the observed dynamic behavior of O_3 density, because the temperature increase in the vicinity of the electrode is only ~10 degrees from room temperature when the ozone density starts to drop. A plausible alternative channel is reaction between vibrationally excited nitrogen molecules ($N_2(v)$) and O atoms. The idea is that as discharge power increases, the fraction of vibrationally excited nitrogen increases, thereby greatly increasing the rate of creation of NO. A more detailed discussion can be found, for instance, in [19, 21]. Our recent numerical model of SMD with detailed chemical reaction paths [14] does not yet include vibrationally excited nitrogen. Hence, we developed a simpler, parameterized model to support this hypothesis that $N_2(v)$ is a key species to quench O_3 .

The parameterized model describes the time development of O_3 and NO density in a wellmixed control volume without spatial gradient. The model includes four reaction paths, as shown in table 1, and three fitting parameters: the O atom density (n_0), vibrational temperature at steady state (T_v^0) and time constant of vibrational temperature increase (τ_v). These fitting parameters are determined to reproduce the measured time-dependent ozone density. The model equations are as follows:

$$\frac{\mathrm{d}n_{\mathrm{O}_3}}{\mathrm{d}t} = k_1 n_{\mathrm{M}} n_{\mathrm{O}} n_{\mathrm{O}_2} - k_3 n_{\mathrm{NO}} n_{\mathrm{O}_3} - \frac{n_{\mathrm{O}_3}}{\tau_{\mathrm{dif}}},\tag{1}$$

Table 1. A list of reactions and the rate constants. The unit of the rate constant is m^3/s for R2 and R3 and m^6/s for R1 and R4.

| Reaction | Rate constant | Reference |
|-----------------------------------|--|---|
| $O + O_2 + M \rightarrow O_3 + M$ | 3.4×10^{-46} | [26] |
| $N_2(v) + O \rightarrow NO + N$ | $1.0 	imes 10^{-17}$ | [19] |
| $O_3 + NO \rightarrow NO_2 + O_2$ | 1.9×10^{-20} | [26] |
| $O + NO + M \rightarrow NO_2 + M$ | 1.0×10^{-43} | [26] |
| | Reaction $O + O_2 + M \rightarrow O_3 + M$ $N_2(v) + O \rightarrow NO + N$ $O_3 + NO \rightarrow NO_2 + O_2$ $O + NO + M \rightarrow NO_2 + M$ | ReactionRate constant $O + O_2 + M \rightarrow O_3 + M$ 3.4×10^{-46} $N_2(v) + O \rightarrow NO + N$ 1.0×10^{-17} $O_3 + NO \rightarrow NO_2 + O_2$ 1.9×10^{-20} $O + NO + M \rightarrow NO_2 + M$ 1.0×10^{-43} |

$$\frac{dn_{\rm NO}}{dt} = k_2 n_{\rm N_2(v)} n_{\rm O} - k_3 n_{\rm NO} n_{\rm O_3} - k_4 n_{\rm O} n_{\rm NO} n_{\rm M} - \frac{n_{\rm NO}}{\tau_{\rm dif}},\tag{2}$$

$$n_{N_2(v)} = n_{N_2} F_{v>12} = n_{N_2} \exp\left(-\frac{12\Delta\varepsilon_v}{k_b T_v}\right),$$
 (3)

$$T_{\rm v} = T_g + T_{\rm v}^0 \{1 - \exp\left(-t/\tau_{\rm v}\right)\},\tag{4}$$

where n_i (i = O₃, O, O₂, NO, N₂(v), N₂) is the density of each chemical species. M denotes the third body. k_i (i = 1 - 4) is the rate constant of the *i*th reaction listed in table 1. τ_{dif} (= 40 s) is the time constant of diffusion loss to the ambient air outside the reactor and obtained by measuring the decay rate of ozone density after SMD was turned off. $\Delta \varepsilon_v$ (= 0.29 eV) is the vibrational energy for harmonic oscillators. $k_{\rm b}$ is the Boltzmann constant and $T_{\rm g}(=300\,{\rm K})$ is the gas temperature. In equation (3), vibrationally excited nitrogen at levels above v = 12 contribute to NO generation. The vibrational energy distribution function (VEDF) is approximated by Maxwell distribution for simplicity. The equations were solved using an ordinary differential equation solver in MATLAB [24]. Figure 5 shows a comparison between the observed ozone density and the model. The fitted parameters are $n_0 = 1.4 \times 10^{17} \,\mathrm{m}^{-3}$, $T_v^0 = 4700 \,\mathrm{K}$ and $\tau_{\rm v} = 2$ s. These parameters were uniquely determined to reproduce the measured ozone density: $n_{\rm O}$ and $T_{\rm v}^0$ decide the slope of the rising rate and decay rate of ozone density, respectively. The time of peak ozone density was determined by τ_v . Our model shows that ozone is quenched by NO generated by $N_2(v)$ and O atom in the first 20 s. NO is dominant against O₃ after that. We note that generation and loss of NO₂ and NO₃ are not included in the parameterized model. It is most likely that NO is further oxidized to NO₂ and NO₃ in actual SMD plasmas. Figure 5 indicates that the vibrational temperature of nitrogen reaches steady state in a few seconds after SMD is ignited. The steady state vibrational temperature in our model was \sim 4700 K. Our preliminary optical emission spectroscopy showed that vibrational temperature reaches steady state in less than 5 s. The measured vibrational temperature was \sim 3000 K. Although the measured vibrational temperature was lower than the model prediction, we think the prediction is not inconsistent with our measurement because it was made using the first three excited states of nitrogen. Some state-to-state modeling results showed a long tail in the high energy part of VEDF, indicating that the distribution is generally not Maxwellian [19, 25]. It is quite possible that the actual vibrational temperature was higher than our measurement when we measured higher vibrational states and calculated the effective vibrational temperature while assuming a Maxwell distribution. In addition, our preliminary numerical simulations with detailed chemical reaction paths showed that volume averaged O atom density is of the order of $\sim 10^{18}$ m⁻³, in reasonable agreement with the value determined by fitting the experimental results to the model.

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Figure 5. Ozone concentrations n_{O3} from the experimental results at 0.3 W/cm^2 and the model calculation. NO concentration n_{NO} from the model as a function of plasma-on time t. The vibrational temperature T_v is on the right axis.

Those results suggest that the proposed mechanisms in the parameterized model are at least part of the real mechanism.

The observed mode transition from predominately ozone to nitrogen oxides could be quite important in practical applications of SMD. For instance, ozone emission from the plasma discharge is a key problem in atmospheric plasma applications in ambient air, especially for *in vivo* application. The maximum ozone level allowed is 0.1 ppm in the working environment when exposed to ozone for 48 hours per week ($8h/day \times 6 days/week$) by the US National Institute for Occupational Safety and Health (NIOSH) [27].

From our experimental results for the mode transition, a possible treatment strategy could be as follows. SMD is ignited at $\sim 0.1 \text{W/cm}^2$ in a confined volume adjacent to the treated surface. Ozone will sterilize the treated surface for the first 10–20 seconds. By keeping the SMD plasma without adjusting the input power, voltage, and frequency, ozone will be quenched and converted into nitrogen oxides. Nitrogen oxides will be further converted into nitric acid or nitrous acid in ambient air when trace amounts of water vapor are present. Then those species could be a source of NO molecules to stimulate wound healing [18] or perhaps to initiate a long-term sterilization effect [28]. A recent numerical simulation of wound healing showed that both short-term and long-term bactericidal activities are equally important [29].

5. Summary

We report on the dynamic behavior of ozone created in SMD in a confined volume by UV absorption spectroscopy. When the input power was lower than $\sim 0.1 \text{ W/cm}^2$, the ozone concentration increased monotonically with time. On the other hand, when the input power was higher than $\sim 0.1 \text{ W/cm}^{-2}$, we observed that ozone density started to decrease $\sim 10 \text{ s}$ after SMD exposure. A significant difference in the mode transition between SMD and classical ozone generators is that the mode transition is observed over time at a constant input power in SMD plasmas. Our parameterized model suggested that vibrationally excited nitrogen

molecules reacting with O atoms generated nitric oxide, thereby initiating the transition to an ozone-poisoning mode. We observed a positive correlation between the ozone density and the inactivation rate of *E. coli* cells on an adjacent agar plate, suggesting that ozone is the key antibacterial species under the conditions considered here. The observed dynamic behavior of plasma chemistry is important for practical applications because emission of ozone during SMD treatment can be minimized. In addition, the size and cost of the device could be reduced because we do not need to modulate the amplitude and frequency of applied voltage to control the distributions of chemical species. Furthermore, it is quite possible to exploit the biochemical and therapeutic strengths of both ozone and nitrogen oxides at a constant power. These results will contribute to the practical realization of an SMD-based biomedical device.

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11