Influence of ultrasonic irradiation on ozone generation in a dielectric barrier discharge

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Abstract. An atmospheric pressure dielectric barrier discharge (DBD) was generated in an N₂/O₂ gas mixture at room temperature with and without ultrasonic irradiation to investigate ozone production. Powerful ultrasonic irradiation with the sound pressure level of approximately 150 dB into the DBD can enhance ozone production especially when the DBD was driven at a frequency of 15 kHz.

1. Introduction

Ozone is a strong oxidizing agent, decays without harmful by-products, and is useful for a variety of applications, including oxidation, ashing, sterilization, decontamination and cleaning [1]. Ozone is mainly produced by using an electrical gas discharge such as a dielectric barrier discharge (DBD) and corona discharge at around atmospheric pressure or above. These electrical gas discharge methods are practically useful for the production of high concentration ozone at high gas flow rates.

There are competing processes of formation and decomposition of ozone with the gas discharge methods. It is therefore important to adjust the plasma parameters so that the ozone formation is maximized while its decomposition is minimized. Here, the first important reaction for ozone generation is the generation of atomic oxygen by electron impact dissociation.

\[
O_2 + e \rightarrow 2O + e. \quad (1)
\]

In a second step, atomic oxygen reacts with molecular oxygen to form ozone.

\[
O_2 + O + M \rightarrow O_3 + M \quad (2)
\]

where M is a third collision partner. Detailed description of ozone production in discharges may be found in refs. [2,3]. It is noted that the ozone formation is very sensitive to temperature and a moisture content of the gas to be introduced into the discharge [3].

Improving ozone production efficiency is a key issue for developing new types of ozone generators. It is reported that the ozone production efficiency can be improved by introducing ultrasound into a gas discharge. Introduction of ultrasonic energy using a piezoelectric transducer enhances the ozone production when a negative direct current (DC) corona discharge is generated in a pure O₂ gas [4,5]. However the highest ozone concentration reported in [4,5] is less than 200 ppm only. In addition the use of the piezoelectric transducer is not energy-effective for introducing ultrasound into a certain gas-discharge volume due to the significant acoustic impedance mismatch between the transducer and the surrounding gas. On the other hand, high-power gas-jet ultrasonic transmitters generate acoustic waves directly in a gas without such a big mismatch. Furthermore they can potentially be integrated into large-scale setups easily. Introduction of ultrasonic waves using the high-power gas jet ultrasonic transmitters into atmospheric pressure plasmas has been studied for adhesion improvement of polymer
surfaces [6-11] and ozone production [12]. Pure O$_2$ gas was fed to a DBD in order to generate ozone [12]. It is reported that ozone production can be efficiently enhanced by ultrasonic irradiation into the DBD particularly when the DBD is generated at a frequency of 15 kHz. It is economically interesting to investigate if similar effect can be obtained in N$_2$/O$_2$ gas mixtures. In the present work, an atmospheric pressure DBD is generated and a gas mixture of N$_2$/O$_2$ is fed to the DBD. The influence of ultrasonic irradiation into the DBD on ozone production is studied.

2. Experimental methods
Ozone was produced in the DBD both with and without ultrasonic irradiation. The DBD setup used in the present work is shown in figure 1. It is a modification of the DBDs introduced previously [13-20]. The DBD is generated between two parallel-plate water-cooled electrodes driven by either of alternating current (AC) power supplies; Power Amplifier 1140L (ENI) driven by a Sweep Generator (Model 164 Wavetek) or a high voltage generator (Model 6030 SOFTAL Electronic GmbH) driven by a Pulse/Delay Generator (BNC 555 Berkeley Nucleonics Corp.). The ENI power supply is used for applying 15 kHz sinusoidal AC voltage between the electrodes, while the SOFTAL power supply is used for ~ 40 kHz sinusoidal AC voltage. Voltage and current are measured with a high voltage probe (PPE20kV, LeCroy) and a 47 Ω resistor, respectively. The average electrical power applied to the DBD is calculated by time integrating the product of voltage and current over several periods and then dividing the result by the time corresponding to that number of periods. A change of the frequency from 40 to 36.8 kHz using the SOFTAL power supply corresponds to a discharge power from 30 W to 150 W. Figure 1 (b) shows a schematic diagram of the setup.

![Figure 1. The experimental setup. The design (without the high power gas-jet transmitter) (a), and a schematic diagram (b).](image-url)
The bottom aluminium electrode (50 mm × 50 mm) is covered with an alumina (Al₂O₃) plate (100 mm × 100 mm × 3 mm), while the upper aluminium electrode has a 42 mm diameter perforated hole covered with a stainless steel mesh (Wire diameter: 0.2 mm. Open area: ~ 70 %). The gap between the alumina plate and the mesh is adjusted to be ~ 0.5 mm. A 40-mm inner-diameter cylindrical acoustic waveguide (poly(methyl) methacrylate. PMMA) is attached above the upper electrode for the transmission of ultrasound. A high-power gas-jet ultrasonic generator (SonoSteam®, FORCE Technology) is placed near the top of the waveguide. The radiated acoustic field is probed using the B&K free-field ¼” microphone Type 4939 with the preamplifier Type 2670, and the signal is processed by means of the Portable Pulse Analyzer (Brüel & Kjær Sound and Vibrations, Denmark). The fundamental frequency of the ultrasound is ~ 30 kHz, and the sound pressure level (SPL) within the frequency range from 20 to 40 kHz is 165 dB. The DBD and the ambient air are separated using a thin polyethylene membrane clamped between the outer-wall of the waveguide and the upper part of the powered electrode. The ultrasound SPL measured at the discharge is 154 dB, i.e. the abatement of the SPL after passing the waveguide, the membrane and the mesh is 11 dB. A typical sound pressure spectrum is presented elsewhere [7]. A gas mixture of N₂ and O₂ (both purity of 99.999 %) is introduced from a side of the DBD. The gas flow rates are controlled by mass flow controllers. The gas passing the DBD is collected from the other side of the gas inlet, and the ozone concentration is measured by means of an ultraviolet (UV) absorption method [21,22]. In this method the sample gas is fed into a 5-mm long absorption cell through which UV light at approximately 254 nm is guided. The UV intensity after passing the absorption cell is detected by a UV sensitive photodiode. The ozone concentration is calculated by the ratio of the UV intensities measured with the sample gas and with a gas that does not contain ozone. After measuring ozone concentration, the sample gas is further fed into a Fourier Transform Infrared spectroscopy (FTIR. MB-100 BOMEM) for detection of N₂O₅ gas.

3. Results and discussion
Ozone concentrations were measured at various O₂ contents in the feeding gas, while fixing the O₂ flow rate at 10 SLM. The DBD was generated at a frequency of 15 kHz and the plasma power was fixed at ~ 120 W. The ozone concentration increases almost linearly as the O₂ content increases as shown in figure 2.

![Figure 2](image-url)

Figure 2. Ozone concentration at various O₂ gas contents in the feeding N₂/O₂ gas mixture. The O₂ gas flow rate: 10 SLM. The plasma power: ~ 120 W. Open and solid squares represent the ozone concentration with and without ultrasonic irradiation, respectively.

Ultrasound irradiation consistently improves ozone production. It is indicated that ultrasonic irradiation can be useful for improving ozone production even in N₂/O₂ gas mixtures. However, it is noted that the ozone concentration measured in the present study was approximately one order lower than that
using the O\textsubscript{2} DBD at the same O\textsubscript{2} flow rate and the plasma power [12]. It is partly because the energy introduced to the DBD was used not only for the ozone production but also production of N\textsubscript{2}O\textsubscript{y} which was detected by means of the FTIR.

Figure 3 shows measured ozone concentrations when the DBD was generated at 15 kHz (a) and ~ 40 kHz (b). The O\textsubscript{2} and N\textsubscript{2} flow rates were fixed at 10 SLM. In each case the ozone concentration increased as the input power to the plasma increased. Ultrasonic irradiation tends to improve ozone production when the DBD was driven at 15 kHz (Figure 3 (a)). On the other hand, when the DBD was generated at ~ 40 kHz, ultrasonic irradiation to the DBD resulted in no significant change of the ozone concentration (figure 3 (b)). A similar result is reported when a DBD is generated in a pure O\textsubscript{2} gas [12], but the measured ozone concentrations in the present work are again approximately one order lower than those in Ref. [12].

![Figure 3. Ozone concentration at different power to the plasma. The DBD was generated at 15 kHz (a) and ~ 40 kHz (b). The O\textsubscript{2} and N\textsubscript{2} flow rates are both 10 SLM.](image-url)

Figures 4 and 5 show the voltage and current waveforms of the DBD driven at the frequencies of 15 kHz and ~ 40 kHz, respectively. Here, the voltage is the potential difference of the upper mesh electrode relative to the bottom electrode. The left panels (a) show the voltage and current waveforms without ultrasonic irradiation, while the right panels (b) show those with the ultrasonic irradiation. In both cases of the DBDs the ultrasonic irradiation does not influence the current waveforms significantly, i.e. when ultrasound is irradiated into the DBD, no significant change in the electrical properties of the discharge is observed.

The current waveforms of the DBD at 15 kHz are nearly symmetric between the positive and negative half-cycles as shown in figure 4. On the other hand, the intensity of the micro-discharge current pulses of the DBD driven at ~ 40 kHz was higher during the positive half-cycle of the current than during the negative one, although the voltage waveform is sinusoidal and symmetric (figure 5). The approximate numbers of the spiky peaks at positive and negative half-cycles are between 50 and 60 and between 60 and 70, when the driving frequencies are 15 and ~ 40 kHz, respectively. There are no clear differences at different polarizations of the voltages with/without ultrasonic irradiation. It is therefore indicated that the asymmetric current waveforms at ~ 40 kHz are attributed to the different intensities of the current peaks. This asymmetry is partly due to the asymmetric structure of the DBD setup in the present work. The same kind of asymmetric current waveforms is reported for a surface discharge where one of the electrodes is directly exposed in the discharge [23]. In order to apply same power to a DBD, application of higher voltage is generally necessary at a lower frequency, because the electrical impedance of the DBD is higher at the lower frequency. In fact, the peak-to-peak voltage at 15 kHz (figure 4) is approximately 20 % higher than that at ~ 40 kHz (figure 5). One possible explanation of
the less asymmetric current waveforms for the DBD driven at 15 kHz is that when the upper electrode is negatively biased, the discharge ignition at 15 kHz might be easier than that driven at ~40 kHz because of the higher voltage applied at 15 kHz.

It is reported that in a corona discharge the electron density is higher near the positively biased electrode where the atomic oxygen is favourably produced [24-26]. In the present work, the upper mesh electrode is directly exposed in the DBD while the bottom electrode is covered with the alumina plate. This configuration is similar to a corona discharge in a sense of the asymmetric electrode system. When the positive and negative currents flow through the upper mesh electrode, the discharge is like positive and negative coronas, respectively.

![Figure 4. Voltage (smooth) and current (spiky) waveforms of the DBD generated at 65 W at 15 kHz. (a) Without ultrasound, (b) with ultrasound. The O$_2$ and N$_2$ flow rates are both 10 SLM.](image)

A laminar boundary gas layer usually sticks at a material surface at atmospheric pressure. When powerful ultrasound is irradiated to the DBD, the thickness of the boundary gas layer at the alumina surface can be reduced [6-12,27]. This improves gas mixing and diffusion processes near the alumina surface. It is therefore suggested that at the frequency of 15 kHz the density of atomic oxygen can be higher near the alumina surface and thus the ozone production can be efficiently enhanced by ultrasonic irradiation. It is noted here that atomic oxygen, which is neutral and thus does not influence
the electrical properties of DBD, can survive for more than $10^{-5}$ s after a micro-discharge [2,3]. This could be the reason why no significant change of the electrical properties was observed by the ultrasonic irradiation, while ozone production could be increased. It is reported that the ultrasound enhances ozone production only for the negative corona [4,5], showing a good agreement with the present result. Furthermore, the results in the present work show in good agreement with those obtained using the pure O$_2$ DBD [12].

4. Conclusions
Ozone production in a DBD in an N$_2$/O$_2$ gas mixture was investigated with and without ultrasonic irradiation. The ultrasonic irradiation did not significantly influence the ozone production for the DBD driven at ~ 40 kHz, while the ozone production was increased for the DBD driven at 15 kHz with ultrasonic irradiation. The difference can be attributed to the distribution of atomic oxygen, suggested by the difference in the current waveforms. It is indicated that at the lower frequency the concentration of the atomic oxygen would be higher near the alumina surface and that ultrasonic irradiation can efficiently enhance mixing and diffusion of the gas, resulting in the enhancement of ozone production. However, the typical measured ozone concentration was approximately one order lower than that produced in a pure O$_2$ DBD with similar conditions.

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