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Characteristics of Dielectric Barrier Discharge Ozone Synthesis for Different Pulse Modes

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Abstract This paper features the pulse polarity effect on ozone generation efficiency by adjusting the applied voltage and the flow rate in a coaxial dielectric barrier discharge reactor. Results show that utilization of unipolar pulse has better performance when compared with the bipolar mode, but on the other hand, utilization of the positive pulse has slightly higher efficiency than that of negative mode. Meanwhile, changing the gas flow rate shows a minor effect on ozone generation. Utilization of bipolar pulse would decrease the breakdown voltage and ozone generation efficiency when compared with unipolar pulse while it would lead to higher ozone concentrations at fixed applied voltage. The maximum ozone yield reaches 186.9 g/kWh at 6 kV positive pulse with ozone concentration of 11.9 g/Nm^3.

Keywords Ozone generation · Dielectric barrier discharge · Pulse polarity · Ozone production efficiency

Introduction

With increasing the demand for various applications including water treatment, flue gas treatment, color removal, disinfection and medical therapy, ozone has attracted much attention due to its preeminent oxidability. Nowadays ozone is generally generated by discharge process in so-called ozonizers, but the ozone yield is relatively low. Therefore it is important to understand the barrier during ozone production and improve the ozone generation efficiency.

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Dielectric barrier discharge (DBD) is a well-known method, which is widely used for ozone generation by inserting dielectric layer into gas discharge space between two electrodes. The existence of dielectric layer can prevent the formation of arc discharge, induce large electric field intensity and produce high-energy electron which would contribute to ozone generation process [1]. With narrow rising edge, pulse power supply has shown outstanding performance in dielectric barrier discharge ozone generation [2–10]. The fast increasing voltage would lead to a higher electric field and produce higher energy electron to excite and ionize oxygen molecules without wasting energy to inspire molecular to vibrational state or to provide kinetic energy to ions. With the development of power source technology, the researchers have made some progress in DBD ozone generation performance by employing different pulse modes. Sung et al. [2] studied the effect of power characteristics and gas flow rate on ozone concentration in a cylindrical DBD ozonizer and found that ozone production efficiency more depended on power than gas flow rate. Takamura et al. [11] studied ozone generation using positive and negative nanoseconds pulsed discharges and found that the ozone production efficiency in negative mode is higher than that in positive mode. Malik et al. [12] mentioned that the highest ozone generation efficiency was obtained in negative streamer discharges in shielded sliding discharge. In addition, Malik et al. [13] also investigated the effect of positive versus negative streamer mode in surface dielectric discharge and concluded that negative pulse would lead to higher ozone generation efficiency with N_2–O_2 feeding gas. But due to the limits of their experiment setups, Sung and the other researchers only investigate part of the contents. There is no thorough and systematic study on the effects of different pulse modes in DBD process.

In this paper, the influence of applied voltage, gas flow rate on ozone concentration and ozone generation efficiency has been investigated. Also, a research is made into the ozone production performance under different pulse modes in atmosphere dielectric barrier discharge. The reasons which lead to different behaviors with relevant studies are also discussed.
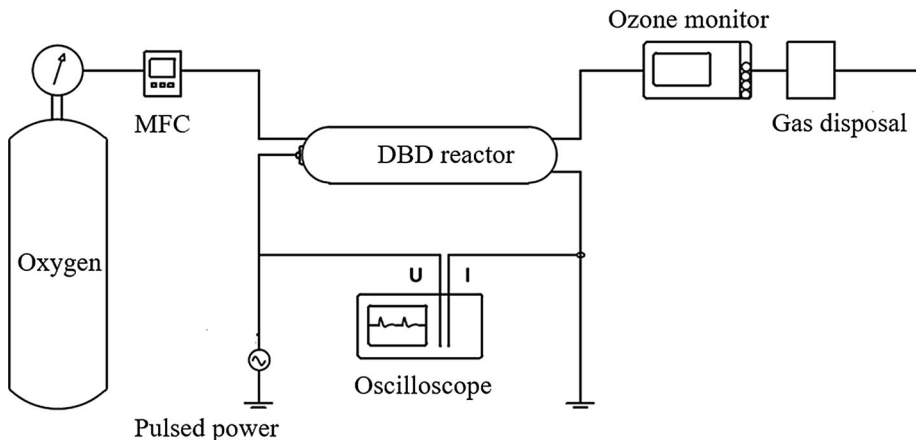

Fig. 1 Schematics of the experimental system

Experimental Setup

Figure 1 shows a schematic diagram of the experimental setup. High purity dry oxygen was controlled by a mass flow controller (ALICAT km7100) in the range of 0.4–3 SLPM (standard liter per minute) in this experiment. The internal structure of ozone generator is shown in Fig. 2. The coaxial discharge ozonizer mainly consists of a stainless steel inner electrode connected to high voltage supply and a stainless steel outer electrode connected to the ground. An enamel dielectric of 0.4 mm in thickness covers the inner electrode surface. The gap width is 0.6 mm. The discharge channel length is 200 mm. Generated ozone is measured by a UV ozone monitor (BMT 964, measuring range 0–200 g/Nm^3). Pulse power supply provides energy for ozone generation, of which the repetition rate was 5–300 Hz. It has a rise time of $\sim$400 ns. Typical voltage–current waveforms in different polarity conditions are shown in Fig. 3. The peak voltage of pulsed power supply ranges from 0 to 60 kV in unipolar pulse mode and 0–30 kV in bipolar pulse mode. In the bipolar mode, there is an asymmetry in the discharge voltage for positive and negative pules and this asymmetry is almost the same for both situations in Fig. 3c, d.

The pulse voltage and the discharge current are measured by an oscilloscope (Tektronix MDO3054) connected with high voltage probes (Tektronix P6015A) and a current monitor (Pearson model 2877). The power P (W) into the DBD reactor was calculated by simultaneously integrating the measured applied voltage (V) and current (I) as follows:

$$P = f \cdot E_p = f \times \int_0^\tau V(t) \cdot I(t) dt, \tag{1}$$

where f stands for the power frequency (Hz), E_p stands for energy per pulse (J). Specific input energy (SIE, J/L) was defined as the ratio of power P (W) to gas flow rate Q (SLPM) as follow:

$$SIE = 60P/Q, \tag{2}$$

Considering that 1 kWh is equivalent to 3.6×10^6 J, ozone generation efficiency (OE, g/kWh) was calculated as follows:
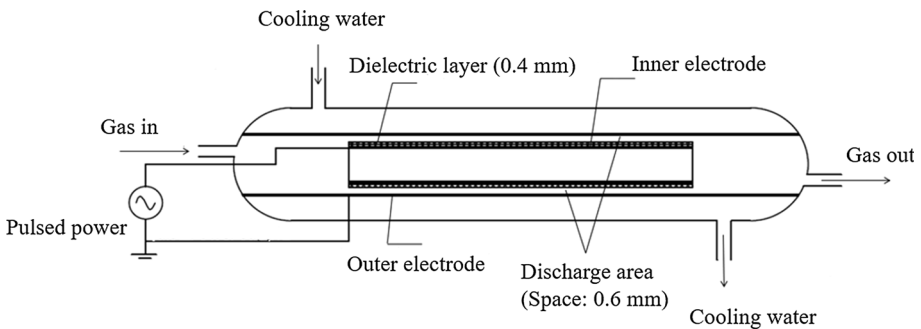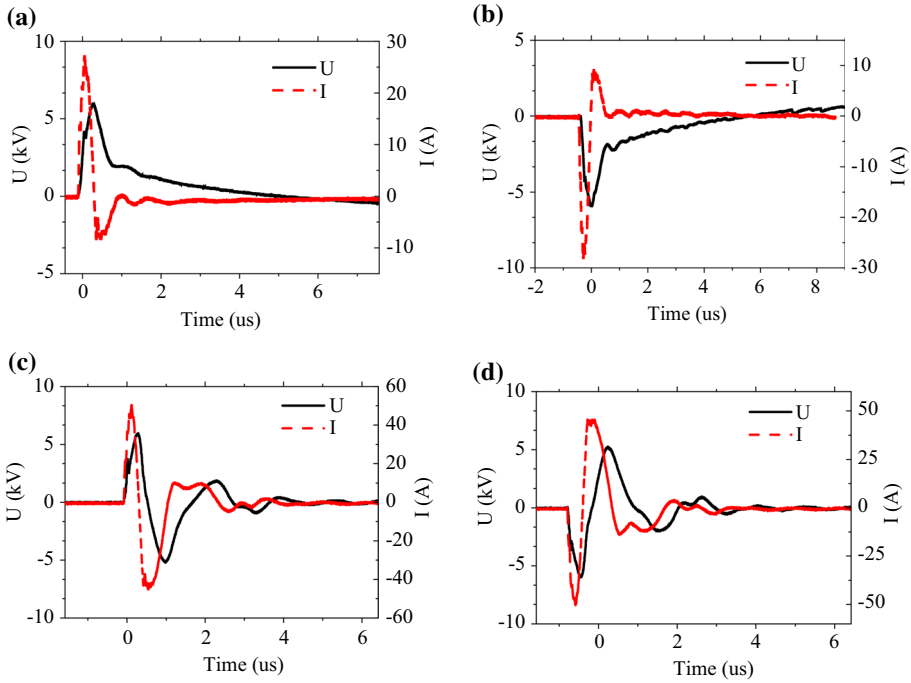

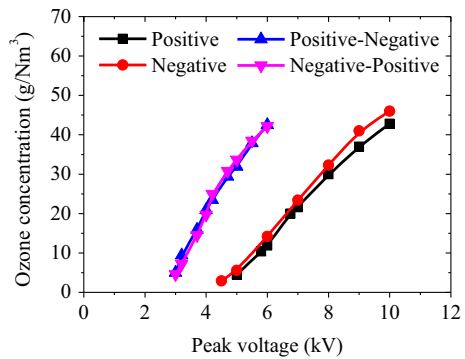Fig. 2 Internal structure of ozonizer

Fig. 3 Typical waveforms in different polarity conditions: **a** positive pulse; **b** negative pulse; **c** positive–negative pulse and **d** negative–positive pulse

Fig. 4 Ozone concentration as a function of the peak voltage

$$OE = \frac{\frac{C\left(\text{g/Nm}^3\right)}{1000} \times \frac{Q\left(\text{SLPM}\right)}{60}}{P} \times 3.6 \times 10^6 = 60\frac{CQ}{P} \qquad (3)$$

where C stands for the ozone concentration in g/Nm^3.

Results and Discussion

Influence of Peak Voltage

Figure 4 depicts ozone concentration variation with peak voltage at 1 SLPM flow rate. It shows that ozone concentration increases with the increase of peak voltage. As for positive pulse input, when peak voltage rises from 5 to 10 kV, the corresponding ozone concentration increases from 4.5 to 42.8 g/Nm^3.

It is observed from the figure that utilizing bipolar power supply would reduce the breakdown voltage of gas in the gap when compared with the unipolar mode. This observation can be attributed to the different process of charge accumulation in discharge gap when using bipolar or unipolar pulse power. When discharge occurs, charged particles drift from gas to dielectric layer, causing charge accumulation. This accumulation would induce contrary electric field which would, therefore, decrease the electric field intensity during the discharge period. As for bipolar power source, the charge accumulates on dielectric layer during the first half cycle of pulse, and when voltage polarity shifts, the direction of electric field caused by this part charge is the same to the electric field direction generated by the second half cycle of the pulse, resulting in an enhanced electric field and an earlier breakdown in gas. Also, it shows that for every single voltage, the ozone concentration is much higher in bipolar pulse condition than that in unipolar pulse condition and the ozone concentration in the negative pulse condition is slightly greater than that in the positive mode as observed in [14].

Figure 5 gives the power variation with peak voltage at 1 SLPM oxygen flow rate. The power also increases with peak voltage. As for positive pulse input, when the peak voltage rises from 5 to 10 kV, the corresponding power increases from 1.58 to 15.4 W. Ozone yield versus peak voltage is shown in Fig. 6a. Moreover, ozone yield versus power is plotted in Fig. 6b to show the ozone production performance with the same input energy density.

Figure 6a, b shows that with increasing peak voltage or specific input energy, the ozone yield would increase at first and then decrease overall. For example, when the peak voltage rises from 5 to 10 kV with negative pulse power supply, the corresponding ozone yield first increases from 135.9 to 167.1 g/kWh and then decreases up to 117.9 g/kWh. Similar conclusion is obtained in [15] when using an AC power supply. With the reactor under low voltage condition, the energy of the excited electron is low. Only when the electron energy

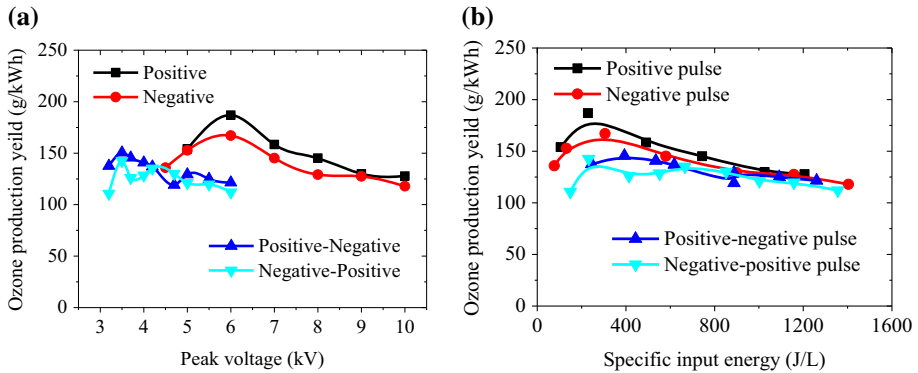Fig. 5 Power as a function of peak voltage
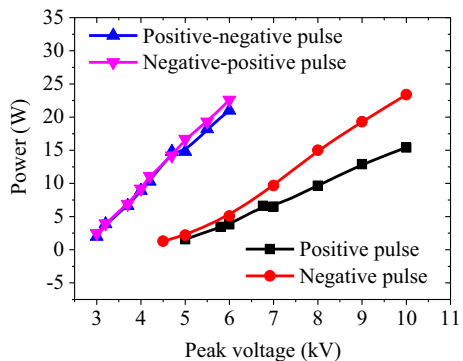
Fig. 6 Ozone yields as a function of peak voltage (**a**) and specific input energy (**b**)

is higher than 6 eV, the oxygen molecule will be effectively ionized to promote ozone generation [16]. This explains why ozone generation starts with low production yield.

The two-step ozone generation process can be described as follows:

$$O_2 + e \rightarrow 2O + e \tag{R1}$$

$$O + O_2 + O_2 \rightarrow O_3 + O_2 \tag{R2}$$

From the reaction (R1), it can be inferred that, with more high-energy excited electrons, more oxygen atom can be obtained to promote the following three-body impact ozone production as shown in reaction (R2).

Meanwhile, the degradation of ozone is mainly induced by reaction (R3) and (R4).

$$O + O_3 \rightarrow O_2 + O_2 \tag{R3}$$

$$O_2 + O_3 \rightarrow O + O_2 + O_2 \tag{R4}$$

The temperature will rise with increasing input energy. The ozone degradation is more intensive under high temperature. As a consequence, the ozone yield decreases. Complete conversion of oxygen atoms to ozone can only achieve at very low atom concentrations. The relative atom concentration is of the order of 10^{-3} in typical ozonizers [16]. Also, it shows that utilizing unipolar power supply would lead to higher maximum ozone yield compared with bipolar power supply. Moreover, it is worth mentioning that the two different modes of bipolar pulse power supply, positive–negative pulse or negative–positive pulse, have little difference in influencing ozone concentration.

From Fig. 6a, ozone generation efficiency in unipolar mode is observed to be higher than that in a bipolar mode, which is on the contrary to results obtained in [2]. For example, in unipolar power condition the ozone yield reaches to the maximum of 186.9 g/kWh at 6 kV. While in bipolar condition, the maximum ozone yield is about 150.5 g/kWh at 3.5 kV. The possible reason may come from two aspects: At first, due to the maximum ozone monitor limits in [2], the plasma is still in low energy density at the maximum ozone concentration of 20 g/Nm^3. This is also verified by the linear ozone concentration dependence of ozone generation efficiency in the explored working conditions in [2] and the relative low ozone generation efficiency compare with earlier results [2, 6, 8].
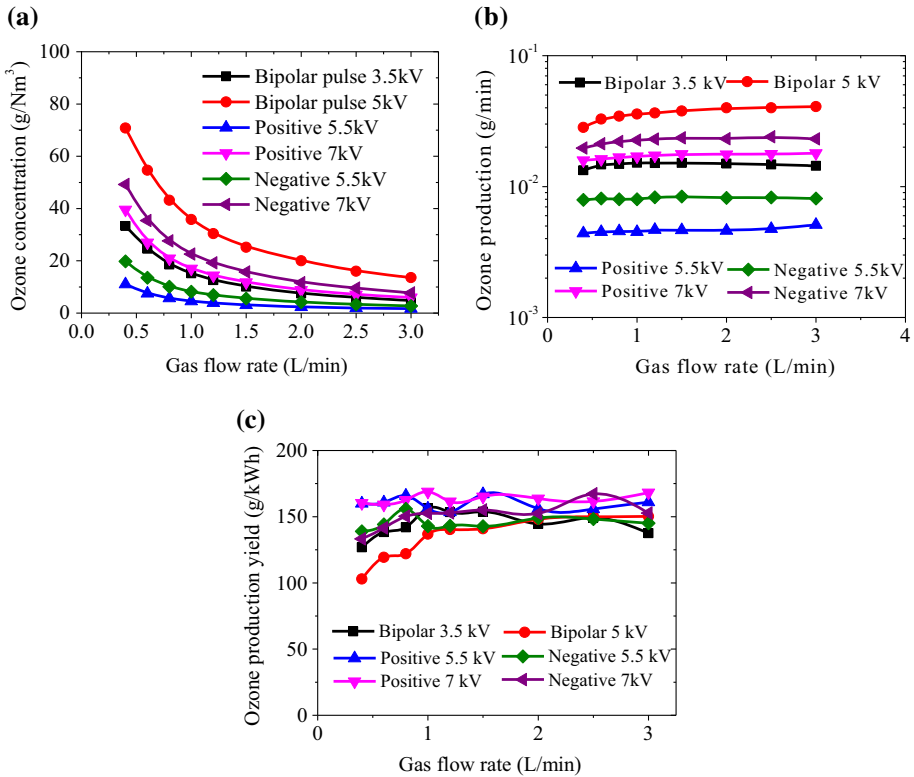
Fig. 7 Variations of ozone concentration (**a**), ozone production (**b**) and ozone yield (**c**) as a function of oxygen flow rate at different pulse modes

Moreover, the contradictory conclusions may come from the different comparison bases. They are related to ozone concentration [2] and the input specific input energy respectively. It can be observed that positive pulse power supply would lead to slightly higher ozone yield than negative pulse power in low specific input energy region, which is consistent with the results reported in [17] in O_2 DBD. When the voltage is at 10 kV, the ozone yields are 169 and 119 g/kWh with positive and negative pulse power supply, respectively.

Influence of Gas Flow Rate

Figure 7a–c illustrate the influence of oxygen flow rate on ozone concentration and ozone production and ozone yield respectively. It is shown that ozone concentration gradually decreases with the increase of gas flow rate regardless peak voltage differs. With peak voltage of bipolar pulse at 5 kV, the ozone concentration varies from 70.8 to 13.6 g/Nm³ when the flow rate increases from 0.4 to 3 SLPM. With increasing gas flow rate, ozone production keeps a stable value. When the peak voltage of bipolar pulse power rises to 5 kV, the ozone production would increase from 0.028 to 0.040 g/min firstly and then keeps a constant value with increasing gas flow rate. Moreover, It is depicted in Fig. 7c that when using bipolar pulse at 5 kV, the yield increases from 103.0 to 150.2 g/kWh when the flow rate increases from 0.4

to 3 SLPM and the growth speed with gas flow rate gradually slows down. In other cases, the yield keeps constant and fluctuates slightly in a reasonable range.

Conclusion

In this paper, different factors are investigated to explore their performances on dielectric barrier discharge ozone generation in different pulse modes. The main conclusions are as follows:

1. Using bipolar pulse would lead to a lower breakdown voltage and lower ozone generation efficiency when compared with unipolar pulse. Additionally, utilization of positive pulse would lead to slight higher ozone generation efficiency than negative pulse. The highest ozone yield achieved in this study is 186.9 g/kWh using positive pulse.
2. Ozone concentration decreases with the increase of oxygen flow rate while ozone production remains stable with increasing gas flow rate in different pulse modes.

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