Memoirs of the Faculty of Engineering, Nagoya University
Vol. 37, No. 1. (1985) — Research Report —

DEVELOPMENT OF NEW TYPE OZONIZER

CHOBEI YAMABE, HIDENORI AKIYAMA*
and KENJI HORII

Department of Electrical Engineering

(Received May 31, 1985)

Abstract

Fundamental studies of new type ozonizer without dielectrics between main electrodes have been carried out. The rate constant k_1 for $O+O_2+O_2 \longrightarrow O_3+O_2$ has been measured by the absorption method using 253nm and is about $2.0\times 10^{-34}cm^6sec^{-1}$.

1. Introduction

It is well known that ozone (O_3) is a very strong oxidizing agent and it follows to a fluorine (F_2) for the force of oxidization among the oxidizing agents. For that reason, it has been used for the treatment of water and exhausted smoke, elimination of the offensive oder, bleaching, removal of organic matter and sterilization etc.. There is no trouble of the secondary contamination compared with chlorine which is used for the sterilization of drinking water because ozone resolves itself into oxygen finally, eventhough it is used overmuch. The thermochemical reactions of ozone generation are given as follows.

$$O_2 \longrightarrow O+O-118\,\text{kcal} \qquad (R-1)$$

$$O+O_2 \longrightarrow O_3+25\,\text{kcal} \qquad (R-2)$$

these equations being combined,

$$3O_2 \longrightarrow 2O_3-68\,\text{kcal} \qquad (R-3)$$

That is, the energy of 34 kcal is needed to generate 1 mole ozone and this energy corresponds to the ozone yield of about 1200 g/kwh. One of the biggest problems for the conventional ozonizer with a silent discharge is a large amount of power consumption (i. e. low ozone yield). The maximum ozone yield which has been

* Department of Electrical Engineering, Kumamoto University

obtained using silent discharge method is about 200 g/kwh with oxygen and about 90 g/kwh with air. It is an actual condition that these values are very small compared with the value of 1200g/kwh. If these ozone yields are improved further, the rapid expansion of the field with ozonizer will be expected.

As oxygen is a negative gas and very sensitive for the electron attachment, the increase of steepness of voltage rise is useful[1,2] for the establishment of uniform discharge and the improvement of ozone yield by means of the activity of the collisional ionization by electrons before the occurrance of electron attachment.

A new type ozonizer without dielectrics between main electrodes has been made to investigate the possibility of the improvement of the ozone yield and the characteristics of ozone generation.

2. Experimental apparatus and procedure

The schematic diagram of ozonizer is shown in Fig. 1. The capacity of electronics boad used as a capacitor shown in Fig. 1 is about 1600 pF. The thickness of electronics boad is about 1.6 mm. Both the anode and cathode are made by copper tubes with the same diameter of 6 mm and about 25 cm long. The gap length between them is about 5 mm. The mixtures of O_2/N_2, O_2/He, O_2/CO_2, O_2/Ar and O_2 only are used as the raw gas materials and their mixture ratio is varied properly. The repetition rate of discharge is fixed at 1 Hz considering the exchange of the gas in the ozonizer. The main discharge current and voltage between main electrodes are measured by a low inductive resistance (0.5 Ω) and C-R divider respectively. The generated ozone is measured chemically using Potassium Iodide solution.

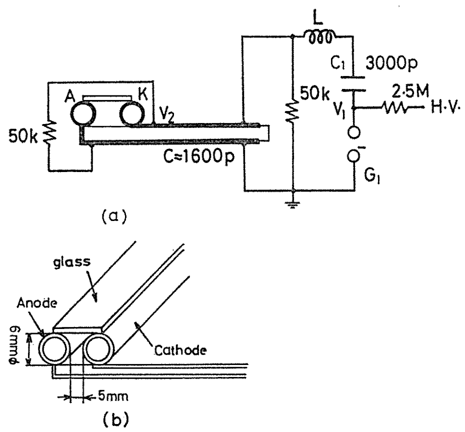


Fig. 1. Schematic diagram of ozonizer.

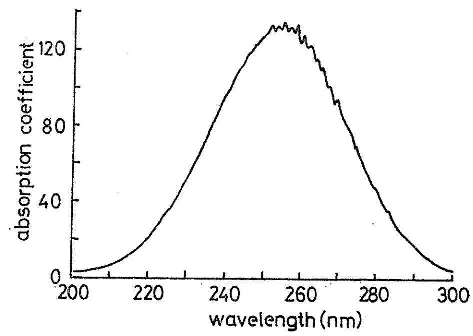


Fig. 2 Absorption spectrum of ozone.

The ozone absorbs the light very well whoes wavelength is about 253 nm as shown in Fig. 2. Therefore, the ozone generation with time is measured by the absorption measurement of ultraviolet rays of the 253 nm from a mercury lamp. The block diagram for the absorption measurement is shown in Fig. 3. The light with the wavelength of 253 nm is selected from the transmission light through the ozonizer by a interference filter (λ_{max}=253 nm, $\Delta\lambda_{1/2}$=19.5 nm) or monochrometer and its intensity with time is measured by a photomultiplier. It has been confirmed that the ozone generated by the irradiation of ultraviolet rays of mercury lamp is negligible small.

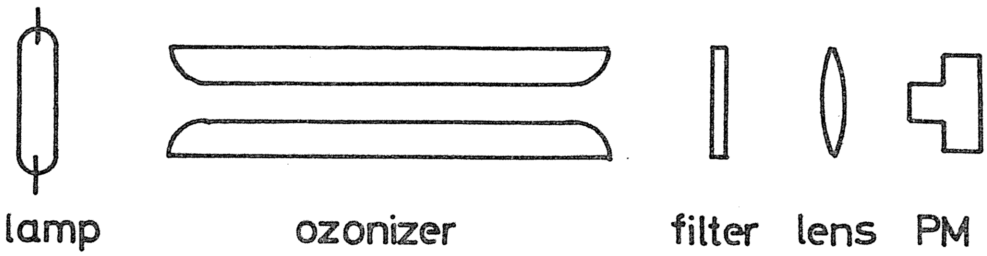


Fig. 3. The block diagram for the absorption measurement.

3. Experimental results

The following parameters which influence on the ozone generation are considered.

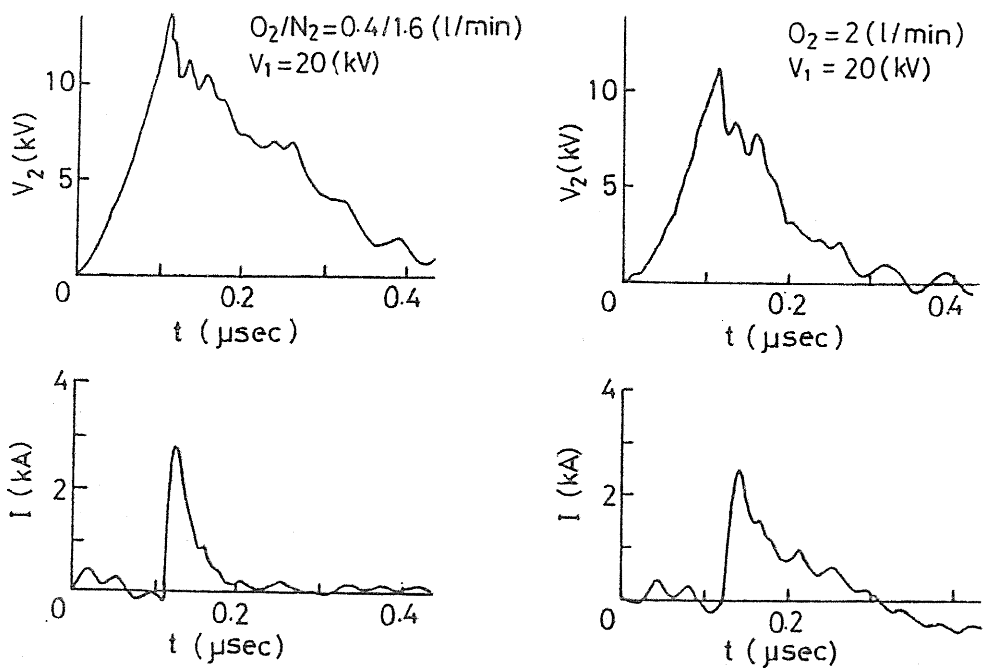


Fig. 4. Typical waveforms of the voltage V_2 and main discharge current I in O_2/N_2 mixture and O_2 only.

(1) input energy into the discharge volume
(2) gas composition in raw gas mixtures
(3) humidity in raw gas material
(4) repetition rate of discharge
(5) steepness of voltage rise

Typical waveforms of the voltage between main electrodes V_2 and main discharge current I are shown in Fig. 4. In this case, O_2 only and $O_2/N_2=1/4$ mixtures are used and the voltage V_1 on capacitor C_1 is 20kV. The steepness of voltage rise is about 10kV/0.1μs. The main discharge current builds up rapidly at near the maximum of the voltage V_2 and the full width at half maximum of the current is about 30 ns and it decreases gradually after the peak.

3. 1. Effect of input energy on ozone generation

The amount of ozone generation per one discharge and ozone yield η against input energy into the discharge volume are measured and the results are shown in Fig. 5 (a), (b). The input enegy into the discharge volume is calculated by the measured waveforms of the voltage V_2 and current I. The ozone concentration increases with input energy and saturates at higher input energy due to the change of discharge condition and NO_x generated by discharge. That is, it seems that the dissociation of oxygen does not occurs effectively by the change of discharge condition. The influence of produced NO_x will be discussed later. A maximum ozone yield of about 20g/kwh has been obtained at low input energy and the yield decreases at higher input energy. From these results, it is not always profitable for the increas of ozone yield to increase the input energy and it seems to be effective to generate a rather weak discharge.

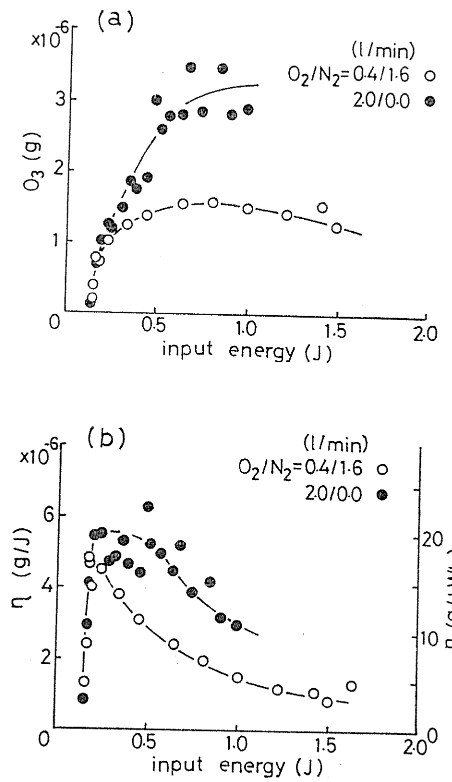


Fig. 5. Ozone concentration vs. input energy (a) and ozone yield η vs. input energy (b).

3. 2. Effect of gas composition on ozone generation

The ozone concentration, ozone yield η and spark onset voltage V_b are shown in Figs. 6~8 for various gas mixtures of He/O_2, CO_2/O_2, N_2/O_2 and Ar/O_2. The ozone generation with both He/O_2 and CO_2/O_2 becomes maximum at the same

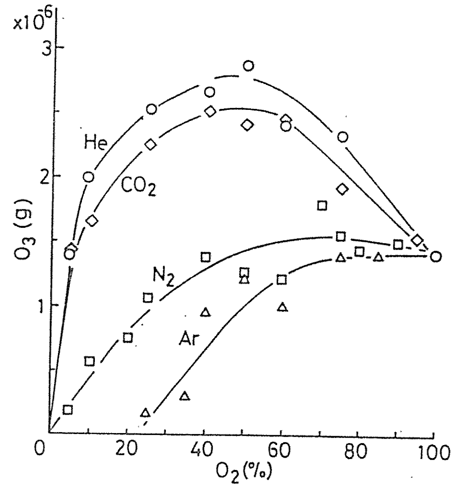


Fig. 6. Ozone concentration vs. per cent of O_2 for He, CO_2, N_2 and Ar.

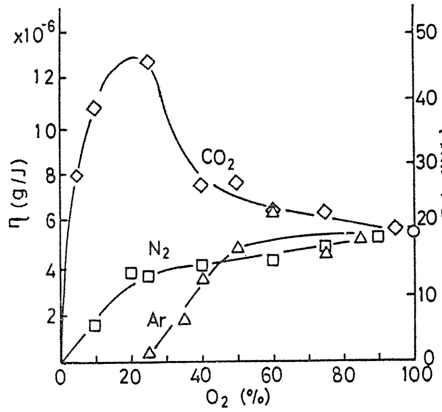


Fig. 7. Ozone yield η vs. per cent of O_2 for CO_2, N_2 and Ar.

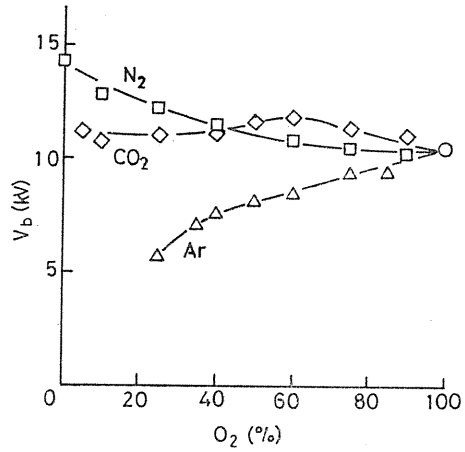
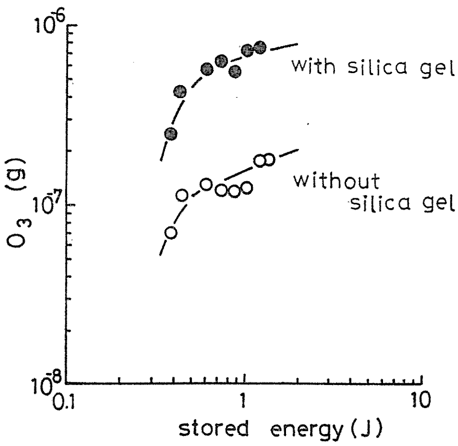


Fig. 8. Spark onset voltage V_b vs. per cent of O_2 for N_2, CO_2 and Ar.

mixture ratio of 1/1 and is two times larger compared with that with O_2 only. The nitrogen or argon being added, the ozone generation increases with oxygen concentration as shown in Fig. 6. In the case of mixtures with CO_2, the maximum point of ozone yield shifts to the low concentration of oxygen and appears at oxygen concentration of about 20% as shown in Fig. 7. The maximum value with CO_2 is about two times larger compared with the value with O_2 only. For the adding of nitrogen or argon, the ozone yield increases with oxygen concentration such as ozone concentration. The variation of spark onset voltage V_b with oxygen concentration depends on the kind of gas mixtures (Fig. 8), that is, the spark voltage decreases for nitrogen, increases for argon and is about constant for carbon dioxide with oxygen concentration respectively. According to the above results, it seems to be useful for the increase of ozone generation and ozone yield to add carbon dioxide or helium to oxygen.

3. 3. *Effect of humidity in raw gas materials*

The influence of humidity in raw gas materials (air) on the ozone generation has been measured for next both cases (i) raw gas materials is fed to ozonizer after passing through the silica gel (ii) raw gas materials is fed to ozonizer directly. The results are shown in Fig. 9. The ozone concentration with dried raw gas materials is about five times larger compared with that without treatment.



But, the raw gas materials used except air in this experiments, it is fed directly from a tank to ozonizer, so it seems that the influence of the dew point on the ozone generation is relatively, small at the dew point of about −50℃ for raw gas materials.

Fig. 9. Effect of humidity on Ozone concentration in air.

3. 4. Repetition rate of discharge vs. ozone concentration

The relationship between ozone concentration and repetition rate of discharge is measured to investigate how the amount of produced ozone is influenced when the produced ozone encounters with next discharge. In this case, the gas mixture ratio, total gas flow rate and applied voltage V_1 are fixed at $O_2=1$, $O_2/N_2=0.2/0.8$ and $0.5/0.5$, $O_2/He=0.5/0.5$ 1/min and $V_1=20$ kV. These results are shown in Fig. 10. The dashed line in the figure shows the calculated minimum repetition rate of discharge (~1. 7Hz) which is needed to exchange the gas completely in the ozonizer. According to the results, it is found that the ozone produced by discharge is considerably destroied by the following discharges. The difference between the calculated minimum repetition rate and experimental results is due to the occurrence of turbulence and the incomplete exchange of the gas in the ozonizer.

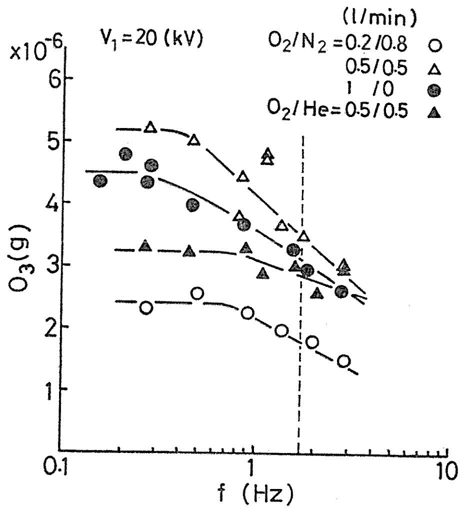


Fig. 10. Ozone concentration vs. repetition rate of discharge in O_2/N_2 and O_2/He mixtures.

3. 5. Effect of steepness of applied voltage rise on ozone generation and spark onset voltage

It has been reported[1,2] that the voltage with high steepness of voltage rise is effective for the improvement of the ozone yield due to the increase of discharge area.

The inductance L shown in Fig. 1 is used to vary the steepness of voltage rise. The O_2 only (=2. 0 1/min) and mixtures of O_2/N_2 (=0. 4/1. 6 1/min) are used

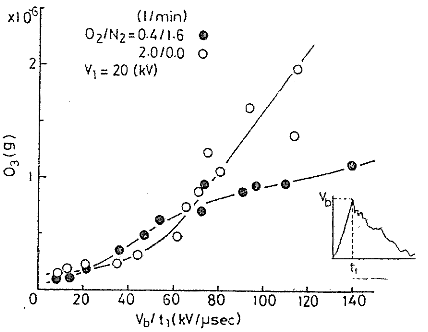


Fig. 11. Ozone concentration vs. average steepness of voltage rise V_b/t_1.

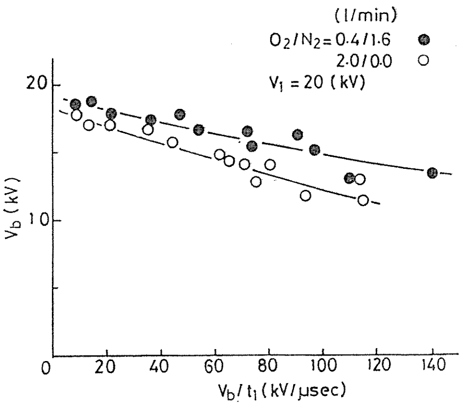


Fig. 12. Spark onset voltage V_b vs. V_b/t_1.

as raw gas materials at $V_1=20$kV. The t_1 shows the time up to the peak of the voltage as shown in Fig. 11 and the ozone concentration increases with the average steepness of voltage rise V_b/t_1 and the spark onset voltage V_b decreases with the value of V_b/t_1 as shown in Fig. 12. It is important for the increases of ozone concentration to make the steepness of voltage rise increase from the above results.

3. 6. Measurements of rate constant of ozone generation

Assuming that the total oxygen atoms are generated at the discharge instantly and after the discharge, the ozone is generated by the following reaction,

$$O+O_2+M \xrightarrow{k_1} O_3+M \qquad (R-4)$$

the variation of oxygen atoms with time is given by the following equation.

$$\ln[O]/[O]_i=-k_1^*t \qquad (1)$$

Where, $k_1^*=k_1[O_2][M]$, $[O]_i$ is the number of oxygen atoms at $t=0$ and M is the third body. Assuming that all of oxygen atoms finally turn into ozone, the equation (1) is substituted by the following equation.

$$\ln[\{[O_3]_f-[O_3]\}/[O_3]_f]=-k_1^*t \qquad (2)$$

Where, $[O_3]_f$ is the ozone concentration at $t=\infty$.

The law of Lambert-Beer being applied to the intensity of trasmittance light and ozone concentration,

$$\ln\ln[I_t/I_f]=-k_1^*t+c_1 \qquad (3)$$

$$\ln[\ln(I_t/I_f)/\ln(I_i/I_f)]=-k_1^*t+c_2 \qquad (4)$$

Where, I_i, I_f and I_t are the transmittance light intensity at $t=0$, ∞ and t respectively. Consequently, the value of k_1^* can be obtained by the measurements of I_t

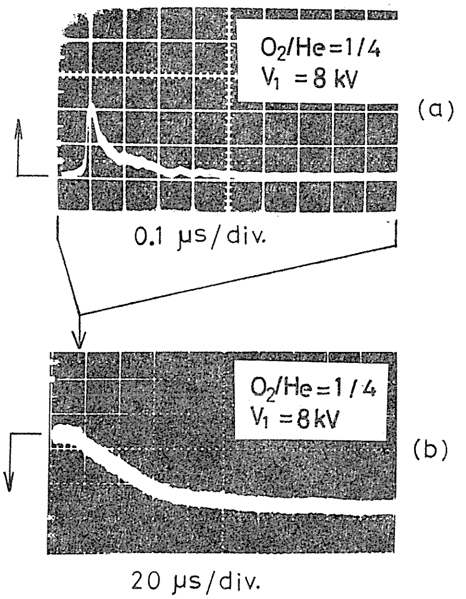


Fig. 13. Typical waveforms of discharge light (a) and transmittance light through ozonizer (b) in mixture of $O_2/He=1/4$ at $V_1=8kV$.

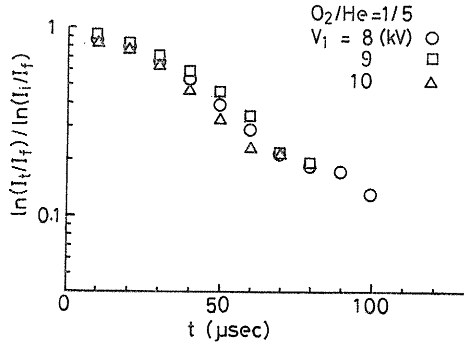


Fig. 14. The variation of the intensity of transmittance light with time for various voltage V_1 in $O_2/He=1/5$ mixture.

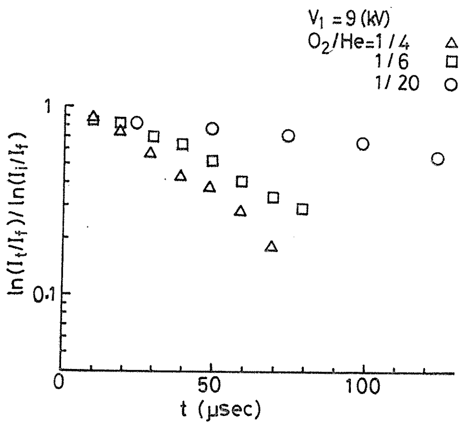


Fig. 15. The variation of the intensity of transmittance light with time for various O_2/He mixtures at $V_1=9$ kV.

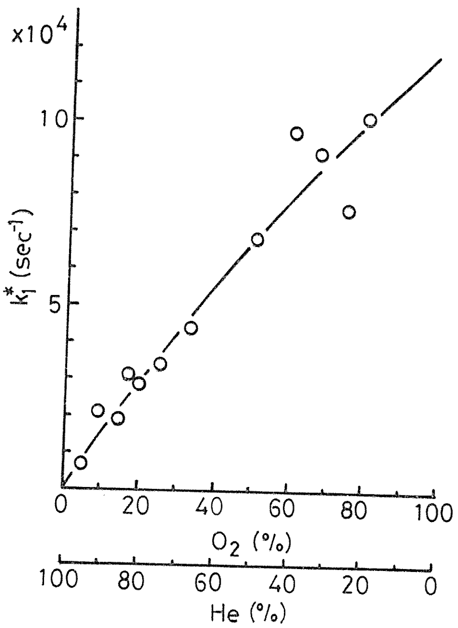


Fig. 16. The values of k_1^* against the per cent of O_2 and He.

and I_f. Typical waveforms of discharge light and transmittance light which is absorbed by ozone in mixture of $O_2/He=1/4$ at $V_1=8\,kV$ are shown in Fig. 13 (a) and (b). The experimental results for the variation of the intensity of transmittance light with time are shown in Figs. 14 and 15. The results shown in Fig. 14

have been obtained as a parameter of the applied voltage V_1 in the mixture of $O_2/He=1/5$. The variation of intensity of transmittance lihgt is almost same when the applied voltage V_1 is changed from 8 kV to 10 kV. These results show that the reactions between produced particle by discharge can be neglected. The variation of the intensity of transmittance light at $V_1=9$ kV is shown in Fig. 15 for various mixtures of O_2/He. The values of $k_1{}^*$ obtained from the slope of the line in Fig. 15 against the per cent of O_2 are shown in Fig. 16. The $k_1{}^*$ increases with the per cent of O_2 and is about 12.1×10^{-4} sec^{-1} at 100 % O_2. Assuming that the generation of ozone depends on the reactions of (R-5) and (R-4), the rate constant k_1 is given by the following equation, $k_1=k_1{}^*/[O_2][O_2]=2.0\times10^{-34}$ cm^6sec^{-1}. This value is about 0.3 times smaller compared with 6.3×10^{-34} cm^6sec^{-1} obtained previously[3].

4. Disscussin

A comparison of ozone generation characteristics in O_2 only and O_2/N_2 mixture is discussed here. The main ozone generation and extinction reactions in both O_2 and O_2/N_2 as raw gas materials are as follows[4].

$$O_2+e \xrightarrow{k_0} 2O+e \qquad (R-5)$$

$$O+O_2+O_2 \xrightarrow{k_1'} O_3+O_2 \qquad (R-6)$$

$$O+O_3 \xrightarrow{k_2} 2O_2 \qquad (R-7)$$

$$e+O_3 \xrightarrow{k_3} O_2+O+e \qquad (R-8)$$

$$O+O_2+N_2 \xrightarrow{k_1''} O_3+N_2 \qquad (R-9)$$

$$N_2+e \xrightarrow{k_4} N_2^*+e \qquad (R-10)$$

$$N_2^*+O_2 \xrightarrow{k_5} 2O+N_2 \qquad (R-11)$$

$$N_2^*+N_2 \xrightarrow{k_6} N_2+N_2 \qquad (R-12)$$

$$N_2^*+O_2 \xrightarrow{k_7} O_2+N_2 \qquad (R-13)$$

$$N_2^*+O_3 \xrightarrow{k_8} O_2+O+N_2 \qquad (R-14)$$

The rate constants k_0, k_3 and k_4 depend on the electron energy distribution, and k_1', k_2, $k_5\sim k_8$ depend on the gas temperature in the reaction volume. A $N_2{}^*$ is an excited nitrogen molecules which has enough energy to dissociate the oxygen molecules. On the other hand, the characteristics of ozone concentration in both O_2 only and $O_2/N_2=1/4$ has been shown in Figs. 5~7. These results being compared, although the amount of oxygen in $O_2/N_2=1/4$ mixtures is one fifth compared with that in O_2 only, both ozone concentration and yield in O_2/N_2 mixtures are about a half and they are not proportional to the oxygen concentration. The decrease of the ozone concentration with input energy appears at high input energy into the discharge volume in O_2/N_2 mixtures as shown in Fig. 5 (a).

When the nitrogen is included in raw gas materials, the excited nitrogen molecules N_2^* and NO_x are produced by discharge. The excited nitrogen molecules N_2^* can dissociate the oxygen molecules as shown in the reaction (R-11) and acts to increase the ozone concentration. On the other hand, the NO_x molecules seem to act to decrease the ozone concentration by the following reactions[5].

$$O + NO_2 \longrightarrow NO + O_2 \qquad (R-15)$$

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (R-16)$$

The influence of N_2^* and NO_x on the ozone generation process is discussed. The molecules of $N_2(A^3\Sigma_u^+)$ and $N_2(B^3\Pi_g)$ are thought[6] to be the excited nitrogen molecules N_2^* which produce the atomic oxygen by the reactions of (R-10) and (R-11). These N_2(A) and N_2(B) molecules have a energy larger than 5.1eV which

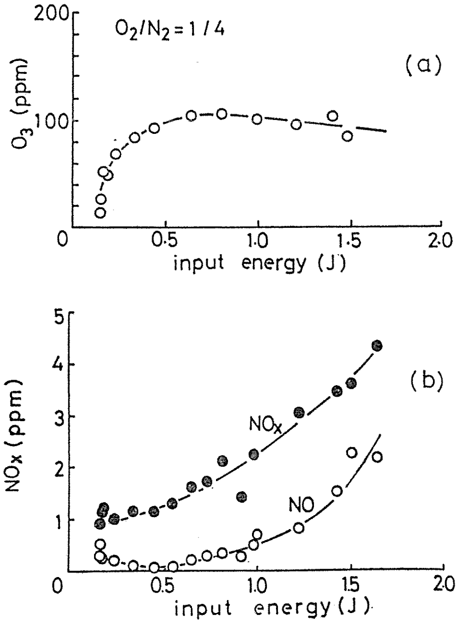


Fig. 17. Ozone concentration vs. input energy (upper) and NO_x and NO concentration vs. input energy (lower) in $O_2/N_2=1/4$ mixture.

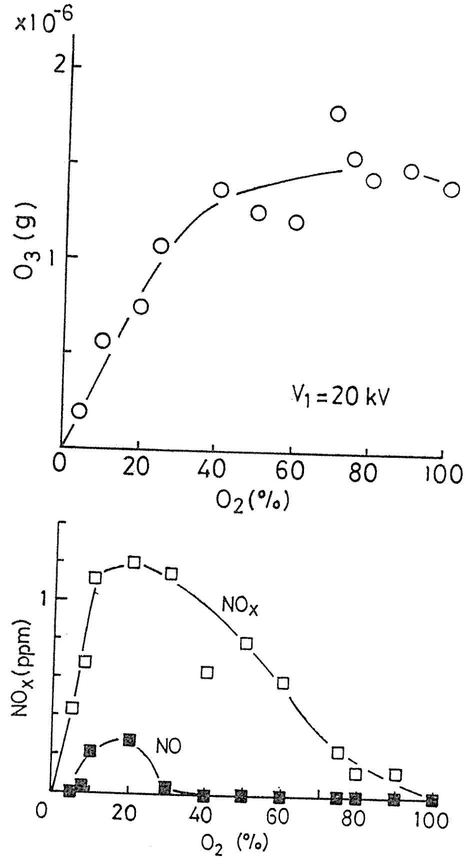


Fig. 18. Ozone concentration vs. per cent of O_2 (upper) and NO_x and NO concentration vs. per cent of O_2 (lower) at V_1=20kV.

is a dissociation energy of oxygen molecules and the excitation probability of these $N_2(A)$ and $N_2(B)$ molecules by the collisions with electrons is high. A de-excitation of $N_2(A)$ occurs mainly by the collisions with oxygen molecules and the oxygen molecules of ground state $O_2(X)$ are excited to $O_2(B^3\Sigma_g^-)$ mainly by an electronic transfer and the atomic oxygen is generated immediately by the dissociation of $O_2(B)$ as shown by the following reactions[7].

$$N_2(A)+O_2(X) \longrightarrow N_2(X)+O_2(B) \quad (R-17)$$

$$\longrightarrow N_2(X)+O(^1D)+O(^3P) \quad (R-18)$$

According to the previous results which have been obtained by the conventional ozonizer, the ozone concentration saturates and finally decreases to zero when the input power increases in air. It is thought that the destruction of ozone occurs by the generated NO_x molecules[8]. The amount of NO_x generated by discharge has been measured as functions of input energy and ratio of O_2/N_2 respectively and these results are shown in Fig. 17 and Fig. 18. The ozone concentration obtained is also shown in both figures. Both concentrations of NO and NO_x increase rapidly at the input energy of about 0.7 J. At the low input energy (less than 0.7 J), the interaction between ozone and NO_x can be neglected in order to the rich of ozone concentration compared with that of No_x. But, when the ozone concentration saturates and the concentration of NO and NO_x becomes high enough not to be neglected, the ozone concentration occurs to decrease. Although both concentration of NO and NO_x are maximum at the ratio of $O_2/N_2=1/4$ as shown in Fig. 18, they are very small amount of values (i. e. 1 ppm for NO_x and 0.3 ppm for NO). In this experiment, the destruction of ozone by NO_x seems to be neglected due to the small concentration of NO_x compared with the ozone concentration. The ozone concentration of 1μg corresponds to about 66ppm.

Conclusion

The ozonizer without dielectrics between main electrodes has been made to study the characteristics of ozone generation in O_2 and O_2/N_2 mixtures. Although the obtained ozone yield of about 20 g/kwh is lower compared with that of conventional silent discharge type, it is expected that the ozone yield will be increased if the steepness of voltage rise is increased more.

The rate constant k_1 for $O+O_2+O_2 \longrightarrow O_3+O_2$ has been measured by the absorption method using the wavelength of 253nm and is about $2.0\times10^{-34}cm^6sec^{-1}$.

Acknowledgment

The authors would like to thank N. Oyama for valuable help during these experiments. This work was supported in part by the Grant-in-Aid for Developmental Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

1) J. Salge and P. Braumann: 4th International Symposium on Plasma Chemistry, 735 (1979)
2) J. Salge, H. Karner, M. Labrenz, K. Scheibe and P. Braumann: 6th Int. Conf. on Phenomena in Ionized Gases, 94 (1980)
3) L. G. Hogan and D. S. Burch: J. Chem. Phys., **65**, 894 (1976)
4) N. Tabata, M. Tanaka and S. Yagi: Trans. IEE Japan, **97B**, 100 (1977)
5) S. Yagi, M. Tanaka and N. Tabata: Trans. IEE Japan, **97A**, 609 (1977)
6) N. Tabata, S. Yagi and M. Tanaka: Trans. IEE Japan, **98B**, 123 (1978)
7) J. A. Meyer, D. H. Klosterboev and D. W. Setser: J. Chem. Phys., **55**, 2084 (1971)
8) S. Yagi, M. Tanaka and N. Tabata: J. Phys. D: Appl. Phys., **12**, 1509 (1979)