Dependence of Ozone Generation in a Micro Dielectric Barrier Discharge on Dielectric Material and Micro Gap Length

Tatsuya Sakoda* and Youl-Moon Sung†

Abstract - In order to investigate the optimum conditions for the effective ozone formation in a dielectric barrier discharge, measurements of ozone concentration were carried out for various conditions such as the gap length, the dielectric material and the operating gas. It was found that the optimum discharge conditions differed exceedingly in the types of operating gases and dielectric materials. In dry air, dielectric material with low dielectric constant and thermal conductivity, which might contribute to the restriction of the gas temperature rise in the discharge region, proved effective in obtaining both high ozone yield and concentration. The optimum gap length was considered to be in the range of 600-800 mm. In oxygen, using a quartz glass disk as a dielectric material, the required condition to obtain the high ozone yield and concentration was expanded.

Keywords: dielectric material, micro dielectric barrier discharge, ozone, ozone yield

1. Introduction

Ozone is a type of powerful oxidizing agent and is widely used as an environmental purification agent for disinfections, deodorization and so on. One of the most widely accepted ozone generators is the micro dielectric barrier discharge that can produce non-equilibrium plasma even at atmospheric pressure. A primary characteristic of the micro dielectric barrier discharge is the presence of a dielectric layer between the discharge gap and at least one of the electrodes[1]. The presence of the dielectric materials leads to the formation of a large number of micro-discharges in the discharge gap. It is well known that each micro-discharge consists of a thin cylindrical channel with a radius of about 100 μm. During the initial stage of the discharge, an accumulation of charge begins at the point where the micro-discharge reaches the dielectric material. This leads to the reduction of the electric field in the discharge gap, and thereafter the discharge is choked. Because the micro-discharge formation is terminated within a short time, the thermal equilibrium can't be achieved. Because of this fact, the micro-discharge channel behaves like a transient glow discharge[1]. The electron temperature in the channel is generally around 5 eV while the molecular temperature in the channel is much lower, which is a similar characteristic obtained in the radio frequency discharge plasmas operated at low pressure. Until now, there have been considerable research efforts [2-9] in the improvement of the ozone concentration and the ozone yield, in which the optimum gap length and the electrode shape were mainly evaluated. However, the experimentally obtained ozone concentrations and yields were lower than those by theoretical predictions[1], and therefore it is considered that the problems in the optimum discharge formation still remain to be solved. The most important factor to consider in obtaining high concentration and yield is how to restrict the ozone dissociation in the discharge region. Incidentally, on an air-fed ozone generator, it is well known that the nitrogen oxides (NO_x) are produced as by-products [6-9]. The NO_x formation plays a significant role in the process of ozone formation. Therefore, the air-fed ozone generator that can realize high ozone yield while restricting the production of impurities is strongly demanded.

This paper focuses on the improvement of the relatively small ozone generator. The micro dielectric barrier discharge was generated using a parallel electrode system arranged in dry air and oxygen, and measurements of ozone concentration were carried out for various conditions such as the gap length, the dielectric material and the operating gas. Based on the experimentally obtained characteristics of the ozone formation, the factors having influence over the ozone dissociation were discussed. Additionally, the ozone yield was evaluated and then the optimum discharge conditions were discussed.

2. Experiments and Methods

Fig. 1 depicts a schematic diagram of an ozone generator where a parallel electrode system was used for generating

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the micro dielectric barrier discharge. Each electrode having a Rogowski shape with a diameter of 60 mm was made of stainless steel and was cooled by passing cooling water through its interior. The temperature of the cooling water in the electrodes was kept at around -5℃. For dielectric materials, we used a 1 mm thick quartz glass disk (Q) with relative dielectric constant of around 3.8 and a 1 mm thick alumina disk (ALO) with relative dielectric constant of about 8.5. Each dielectric disk with a diameter of 100 mm was placed on an earth electrode. The gap length (d) was adjusted by changing the position of the earth electrode, and then d was adjusted from 200 to 800 μm at intervals of 200 μm. The micro dielectric barrier discharge was operated by the pseudo sinusoidal wave of which maximum value was 7 kV and output frequency was 8 kHz. The voltage rise time to a maximum value was 5 μs, and a full width at half maximum of a voltage pulse was about 10 μs. Dry air and oxygen controlled by mass flow controllers entered into the chamber from the upper side of a high-voltage electrode, in which the gas flow rate (Q_r) was kept at 3 l/min. All experiments reported here were made at atmospheric pressure. Gas passing through the discharge region was exhausted from a small hole with a diameter of 10 mm in the center of the high-voltage electrode, and thereafter the ozone concentration was measured using an ozone monitor. The discharge voltage (V_D) and the discharge current (I_D) were measured using a high-voltage probe and a Rogowski coil, respectively. In order to form the uniform dielectric barrier discharge over the discharge electrode, the discharge voltage was adjusted so that it was 1.2 times larger than the breakdown voltage for each gap length. The discharge power (W_D) was obtained by integration of the product of V_D and I_D for a period of pseudo sinusoidal wave.

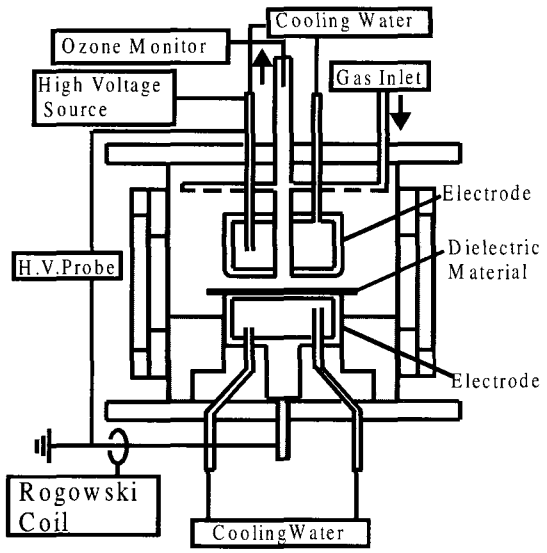
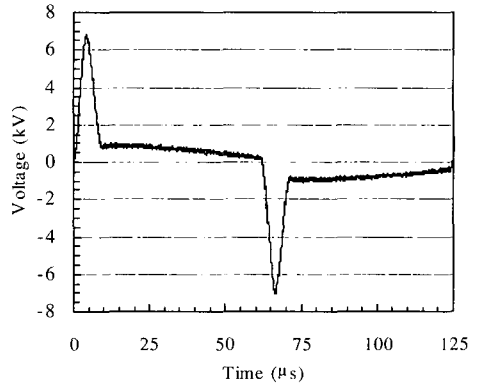


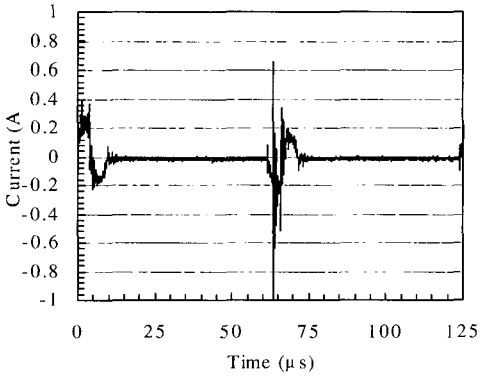
Fig. 1 Schematic arrangement of experimental apparatus

3. Experimental Results

Typical waveforms of the discharge voltage and the discharge current in an atmosphere of dry air with Q_r = 3 l/min are shown in Fig. 2. In this case, the gap length and the discharge voltage were maintained at 400 μm and 7 kV, respectively. The dielectric material was a quartz glass disk The discharge current consists of the displacement current due to capacitance and current pulses due to micro-discharges with pulse duration of several ns. In this case, the discharge power calculated by integration of the discharge voltage and the discharge current for a period of pseudo sinusoidal wave was about 19 W. The discharge powers obtained by measuring 20 times accorded within an accuracy of ± 8%. Under the same discharge condition, the discharge power was 48 W in the case where an alumina disk was used as a dielectric material. Thus, even under the same discharge state, the discharge power became high in situations where the alumina disk of which the dielectric constant was larger than that of the quartz disk was used as a dielectric material. The discharge power increased with the increases of the discharge voltage and the gap length, and was almost independent on the gas flow rate in the range of Q_r = 1-3 l/min [10].



(a) Discharge voltage

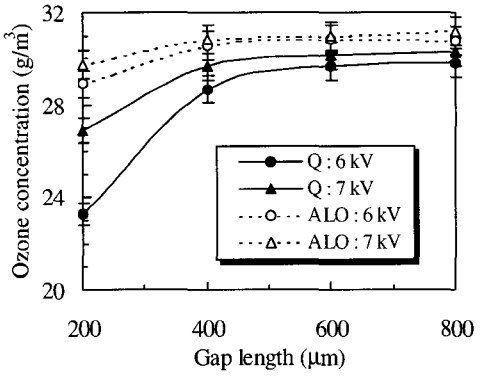


(b) Discharge current

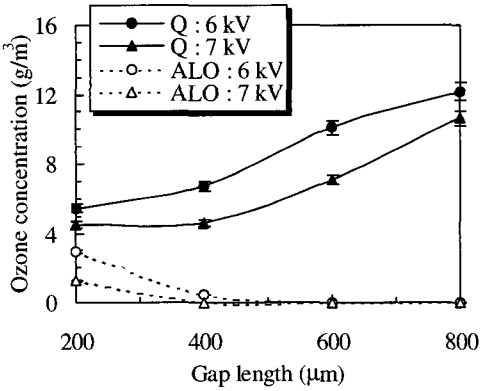
Fig. 2 Waveforms of (a) discharge voltage and (b) discharge current.

Fig. 3 illustrates the variation of ozone concentration with the gap length. The operating gases were dry air and oxygen with Q_r = 3 l/min. In oxygen, the ozone concentration at each discharge voltage becomes greater as the gap length elongates, and reaches a saturated value of around 30 g/m^3 at d = 400 μm. At each gap length, the higher the discharge voltage is, the higher the ozone concentration becomes. Additionally, the ozone concentrations obtained with the alumina disk are higher than those with the quartz glass disk. The variation characteristics of the ozone concentration in an atmosphere of dry air differ greatly from those in oxygen. The ozone concentration at each gap length decreases with the increase of the discharge voltage. In the case where the alumina disk is used, the ozone concentration diminishes as the gap length elongates. Thus, the gap length dependence on the ozone concentration is significantly dissimilar in relation to the types of operating gases and the dielectric materials. In dry air, the collision between NO and O_3, which strongly depends on the gas temperature, plays an essential role in the re-dissociations of ozone. In the case where an alumina disk with high dielectric constant and thermal conductivity was used, the gas temperature in the discharge region became high and the ozone concentration decreased through collisions between NO and O_3.

Fig. 4 illustrates the variation of ozone concentration with the discharge power. The ozone concentration in an atmosphere of oxygen increases with the augmentation of the discharge power and reaches a saturated value of around 30 g/m^3 at around W_D = 15 W regardless of the gap length. In dry air, at the range of W_D > 15 W, the ozone concentration declines with the increase of the discharge power. That is, the ozone concentration is not expected to become high when W_D >15 W. For the case of the quartz glass disk, the ozone concentrations obtained under the same discharge power become high as the gap length elongates. For the alumina disk, the ozone concentrations obtained when d > 200 μm are almost identical. The range of the discharge power for the case of the alumina disk is 17 to 61 W while that for the case of the quartz glass disk is 4.5 to 19 W. For the instance of the quartz glass disk, the discharge area is anticipated to be improved by arranging the longer gap length and the larger discharge volume. This probably leads to the increase of ozone concentration. In contrast, the discharge power for the case of the alumina is

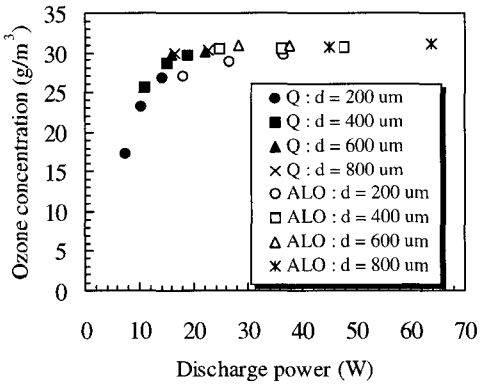


(a) In oxygen

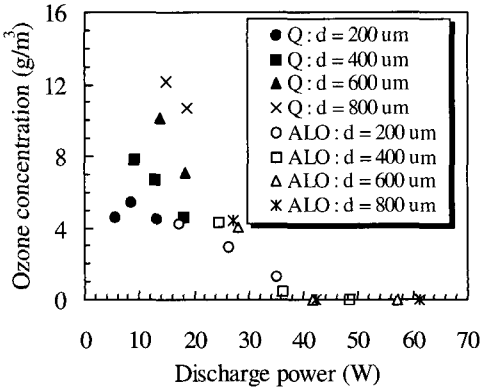


(b) In dry air

Fig. 3 Variations of the ozone concentration with the gap length in (a) oxygen and (b) dry air. The dielectric materials were the alumina disk (ALO) and the quartz glass disk (Q).



(a) In oxygen



(b) In dry air

Fig. 4 Variations of the ozone concentration with the discharge power in (a) oxygen and (b) dry air.

relatively high. Therefore, the rise of the gas temperature in and near the discharge area is expected to become remarkable, which most likely promotes the ozone dissociation.

Fig. 5 shows the variation of the decrease ratio of ozone with the elapsed time from the generation of the micro dielectric barrier discharge with d = 800 μm and V_D = 5 kV. In this case, the alumina disk was used as a dielectric material and the discharge electrodes were not cooled. The discharge powers obtained in oxygen and dry air were almost the same and were approximately 28 W. The consumed power in the dielectric material is transformed into heat energy whereby the temperature in the dielectric material and the temperature in the discharge region increase. Dry air and oxygen are almost equivalent in thermal conductivity. However, the thermal conductivity of alumina is about 15 times greater than that of quartz glass. In the case where the alumina disk is used, the gas temperature in the discharge region is estimated to significantly increase in relation to the elapsed time because the discharge electrodes are not cooled. The ozone concentrations at t = 15 s, which were standard values for the cases of oxygen and dry air were 30 and 4.4 g/m^3, respectively. The vertical axis is expressed in values of decrease ratio to each standard ozone concentration. The obtained results enable us to evaluate the gas temperature dependence on the ozone dissociation. As shown in this Fig., it is established that the decrease ratio in dry air is much larger than that in oxygen. It is considered that the gas temperature rise in an atmosphere of dry air plays an essential role in ozone dissociation.

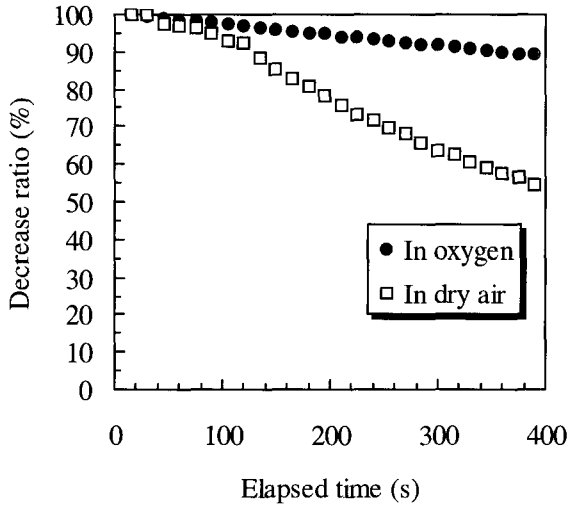


Fig. 5 Variations of decrease ratio of ozone concentration with the elapsed time following the generation of the dielectric barrier discharge with d = 800 μm and V_D = 5 kV.

4. Discussions

Ozone is formed by way of a three-body reaction between an oxygen atom, an oxygen molecule and a third collision partner.. Simultaneously, the ozone dissociation by the electron impact and the collisions between oxygen atoms and nitrogen oxides proceeds in the discharge region The following reactions are strongly related to ozone dissociation in an atmosphere of air, which are simplified, i.e., reactions involving ions and excited species are neglected [1, 7]. The dissociation processes in an atmosphere of oxygen are (R1) and (R2).

$$O_3 + e \rightarrow O_2 + O + e \quad \text{(R1)}$$

$$O + O_3 \rightarrow 2O_2 \quad \text{(R2)}$$

$$N + O_3 \rightarrow NO + O_2 \quad \text{(R3)}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(R4)}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R5)}$$

The reactions of (R2), (R4) and (R5) strongly depend on the gas temperature in the discharge region, and their reaction coefficients are given as follows,

$$k_2 = 1.9\times10^{-11} \exp(-2300/T)\ \text{cm}^3\text{s}^{-1} \quad \text{(R2k)}$$

$$k_4 = 1.5\times10^{-12} \exp(-1300/T)\ \text{cm}^3\text{s}^{-1} \quad \text{(R4k)}$$

$$k_5 = 1.2\times10^{-13} \exp(-2450/T)\ \text{cm}^3\text{s}^{-1} \quad \text{(R5k)}$$

where T is the gas temperature in the discharge region. The increase of the gas temperature is brought about by the dissipated power in the discharge gap and the consumed power in the dielectric material. We plot each reaction coefficient against T in Fig. 6.

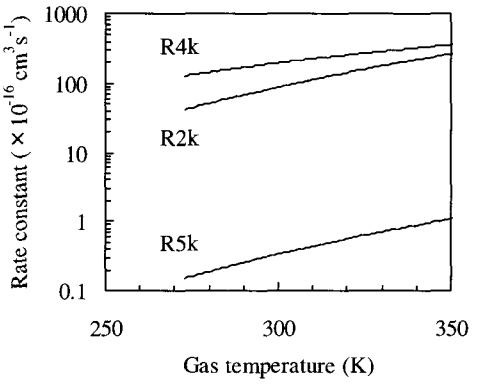
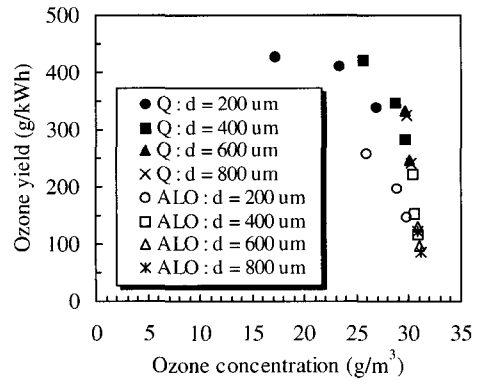
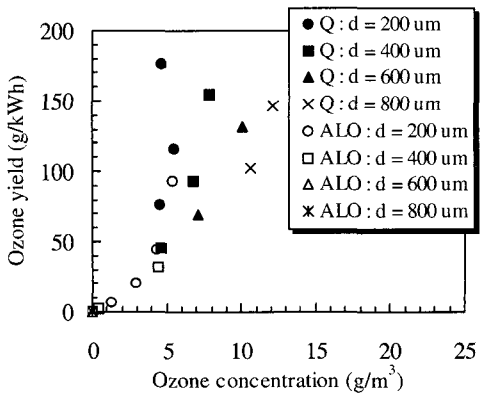


Fig. 6 Calculated dissociation rate coefficient as a function of the gas temperature in the range of 273 - 350 K.

Because it is considered that the gas temperature in the micro dielectric barrier discharge is much less than 350 K [1, 7], the calculations of the reaction rate coefficients were carried out in the range of T = 273 - 350 K. At roughly T = 300 K, the reaction rate coefficient of (R4k) is about 2 times bigger than that of (R2k). The reaction rate coefficient of (R5k) is significantly small in comparison with those of (R2k) and (R4k). Incidentally, the range of the discharge powers obtained in our experimental conditions was from 6 to 62 W. Then, the range of the injection energy per unit gas volume, which can be defined as W_D/Q_r, was from 2 to 31 Wmin/l. Yagi and Tabata [7] investigated the particle densities related to the formation and dissociation of ozone, in which the experimental results agreed with the theoretically calculated values when T = 320 K. According to their results obtained when $2 < W_D/Q_r < 30$, the density of NO is about 2.5 times higher than that of O. The density of NO_2 is extremely low in comparison with those of NO and O. Thus, among the dissociation reactions depending on the gas temperature, the collision between NO and O_3 is considered to be essential in the re-dissociation of ozone. Incidentally, the dissociation reactions of oxygen molecular and ozone, by the electron impact, depend on the reduced electric field



(a) In oxygen



(b) In dry air

Fig. 7 Variations of ozone yield with ozone concentrations in (a) oxygen and (b) dry air.

(E/n; E: electric field, n: particle density). That is, the dissociation reactions should vary with the gap length. However, as shown in Fig. 4(a), the ozone concentration in an atmosphere of oxygen is saturated in a wide range of W_D regardless of the gap length. This indicates that the electron impact is not dominant in the ozone dissociation expressed by the reaction (R1). The saturation of the ozone concentration would be brought on by the collision between oxygen atom and ozone although the influence of the collision is much less in comparison with that in an atmosphere of dry air.

Finally, we demonstrated the correlation between the ozone yield and the ozone concentration in Fig. 7, obtained in dry air and oxygen. As shown in this Fig., the ozone yield obtained in both dry air and oxygen decreases with the increase of the discharge voltage. However, as concerns the ozone concentration in an atmosphere of oxygen, the high concentrations are obtained under most discharge conditions. That is, even for the low gap lengths such as d = 200 and 400 μm, the ozone concentration becomes high as the discharge voltage increases. With regard to the ozone yield, the high yield can be obtained in most discharge conditions where the quartz glass disk is used as the dielectric material. For the case of the alumina disk, a relatively high yield is obtained only when the gap length is short. In an atmosphere of dry air, the ozone yield and the ozone concentration diminish with the amplification in discharge voltage. Especially, in situations where the alumina disk with the high dielectric constant and thermal conductivity is used, the high yield and concentration can't be obtained. As mentioned above, the collision between NO and O_3, which strongly depends on the gas temperature plays an essential role in the re-dissociation processes of ozone. The dissipated power in the discharge gap and the consumed power in the dielectric material lead to the increase of gas temperature in the discharge region. Therefore, in an atmosphere of dry air, the dielectric material with the low dielectric constant and thermal conductivity such as quartz glass is effective to obtain high ozone yield and concentration. It seems that the optimum gap length is in the range of 600-800 μm where the discharge voltage is desired to be relatively low.

5. Conclusion

Characteristics of ozone formation in dry air and oxygen were experimentally studied, in which the optimum gap length and dielectric material were discussed. The results indicated that the optimum discharge conditions differed extensively in relation to the types of operating gases and dielectric materials. In an atmosphere of dry air, the collision between NO and O_3, which strongly depends on

the gas temperature, played an essential role in the re-dissociation processes of ozone. Therefore, the dielectric material with low dielectric constant and thermal conductivity such as quartz glass, which might contribute to the restriction of the gas temperature rise, was effective to obtain both high ozone yield and concentration. The optimum gap length was in the range of 600-800 μm. In an atmosphere of oxygen, the ozone yield was superior to the ozone re-dissociation caused by the gas temperature rise whereby the ozone concentration became high. It was also confirmed that the required condition to obtain the high ozone yield and concentration was expanded in situations where quartz glass was used as the dielectric material.

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References

[1] B. Eliasson, M. Hirth and U. Kogelschatz, "Ozone synthesis from oxygen in dielectric barrier discharges," J. Phys. D: Appl. Phys., 20 (1987) 1421.

[2] Byung-Joon Chun, Sang-Keun Lee and Kwang-Sik Lee, "Ozone Generation Characteristics of a Pield Plate-Type Ozonizer", KIEE International Transactions on Electrophysical and Applications, Vol. 12C, No. 1, (2002) 33.

[3] K. Hakiai, D. Takazaki, S. Ihara, S. Satoh and C. Yamabe, "Spatial distribution and characteristics of ozone generation with glow discharge using a double discharge method," Jpn. J. Appl. Phys., 38 (1999) 221.

[4] T. Cieplak, C. Yamabe, S. Ihara, S. Satoh, J. Cieplak and I. Pollo, "Investigations on the rotating electrode effect on the ozone generation process in a plate ozonizer," Jpn. J. Appl. Phys., 38 (1999) 4930.

[5] Jae-Duk Moon, Sang-Taek Geum, "Discharge and ozone generation of a ferroelectric-ball/mica-sheet barrier," IEEE Trans. Ind. Appl. 34-6 (1998) 1206.

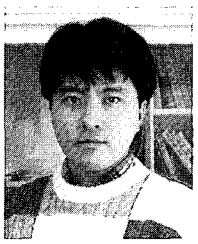
[6] J. Drimal, V. I. Gibalov and V. G. Samoylovich, "The dependence of ozone generation efficiency in silent discharge on a width of a discharge gap," Czech. J. Phys., B38 (1988) 643.

[7] S. Yagi and M. Tabata, "Mechanism of ozone generation in air-fed ozonizers," J. Phys. D: Appl. Phys., 12 (1979) 1509.

[8] Md. Fayzur Rahman and Kwang Sik Lee, "Performance Characteristics of a Pin-to-Cylinder Superposed Discharge Type Ozonizer (SDO)", KIEE International Transactions on Electrophysical and Applications, Vol. 11C, No. 4, (2001) 113.

[9] Md. Fayzur Rahman, Byung-Joon Chun, Kwang-Sik Lee and Dong-In Lee, "Effect of Temperature on the Performance Charecteristics of a Pin-Cylinder Discharge Type Ozonizer", KIEE International Transactions on Electrophysical and Applications, Vol. 2-C, No. 4, (2002) 201.

[10] M. Sakoda, T. Sakoda, S. Maeda and H. Nieda, "Studies on ozone generator of silent discharge type without spacer," Proceedings of 2001 Japan-Korea Joint Symposium on Electrical Discharge and High Voltage Engineering, (2001) 209.



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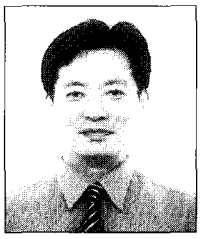

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