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Streamer polarity dependence of NO_x removal by dielectric barrier discharge with a multipoint-to-plane geometry

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Abstract. In this paper, we experimentally investigated an effect of streamer polarity on the reduction of NO_x by using a barrier discharge plasma reactor with a multipoint-to-plane geometry. A high-frequency sine wave voltage generator and a repetitive pulse generator, which generated narrow and high-voltage pulses were used to remove nitrogen oxide (NO_x). By the optical spectrum measurement, it is clarified that electrons with high energy, more than 10 eV, are produced in the discharge region at atmospheric pressure. The intensity ratio of the first negative system of N_2^+ (391.4 nm, threshold energy 18 eV) to the second positive system of N_2 (337.1 nm, threshold energy 11 eV) neither depends on the applied voltage nor the frequency, but it depends on streamer polarity. Further, it is shown that the value is higher in a positive streamer than in a negative streamer. The use of a multipoint-to-plane electrodes caused the streamer polarity interchange every half cycle of the sine wave of the applied voltage, while in a case of the parallel plane electrodes, the positive streamer was only generated in the discharge region. The simulated gas and the exhaust gas from a diesel engine generator were used to confirm the NO_x removal performance of the reactor.

1. Introduction

The nitrogen oxides (NO_x) are the main noxious component in exhaust gases, which cause large-scale problems through deposition in acid rain (Dinelli *et al* 1990, Dhali and Sardja 1991, Li *et al* 1995). The new possibilities for NO_x removal from exhaust gas have evolved in the field of a non-thermal plasma that has a low gas temperature and a high electron temperature. This type of gas treatment has several advantages, for example, simultaneous removal of NO_x and SO_2 from the exhaust gas at high efficiencies (Gallimberti 1998, Chang *et al* 1991).

We used a dielectric barrier discharge to produce a non-thermal plasma for the gas treatment. By using a multipoint electrode a strong electric field of 164 kV cm^{-1} can produce a uniform discharge plasma with a low applied voltage of 2.5 kV. The value of the applied voltage in this study is much lower than in conventional plasma reactors (Muaffaq *et al* 1998) and the NO_x removal performance of the reactor with various gases and input energies has been investigated (Takaki *et al* 1997). It was reported that the NO_x removal by corona discharge has the polarity dependence of the gas treatment (Brandvold *et al* 1989, Masuda and Nakao 1990).

In this paper, we experimentally investigated the streamer polarity dependence of NO_x removal by the dielectric barrier discharge plasma. The experiment was performed by using a multipoint-to-plane geometry using a sinusoidal voltage generator for low-voltage operation of 2–4 kV (effective value) at high frequency (10–50 kHz) and using a repetitive pulse power generator for a high voltage of 20 kV. A monochromator was used to analyse the light emitted from the discharge region. The result shows that the light intensity is larger in the positive streamer than in the negative. The experiments were performed to find an appropriate condition for the exhaust gas treatment.

2. Experimental apparatus

The schematic diagram of the experimental set-up for NO_x reduction is shown in figure 1. The plasma reactor is a rectangular prism with dimensions 65 mm × 400 mm × 25 mm. The base and the top are made of plain aluminium and the surrounding wall of polymethylmethacrylate (PMMA). A multipoint electrode used in the experiment has 3 × 275 brass needles with tip radius of about 100 μm on an area of 117 cm^2. It was mounted on the base of the plasma reactor and was grounded. Another electrode connected to a high-voltage generator is plain and fixed on the underside of the top of the reactor. A 2 mm thick soda-lime glass was used as the dielectric barrier and placed in contact with the plain electrode. The gap length between the projection tips and the barrier was 0.5 mm. The light emission from the

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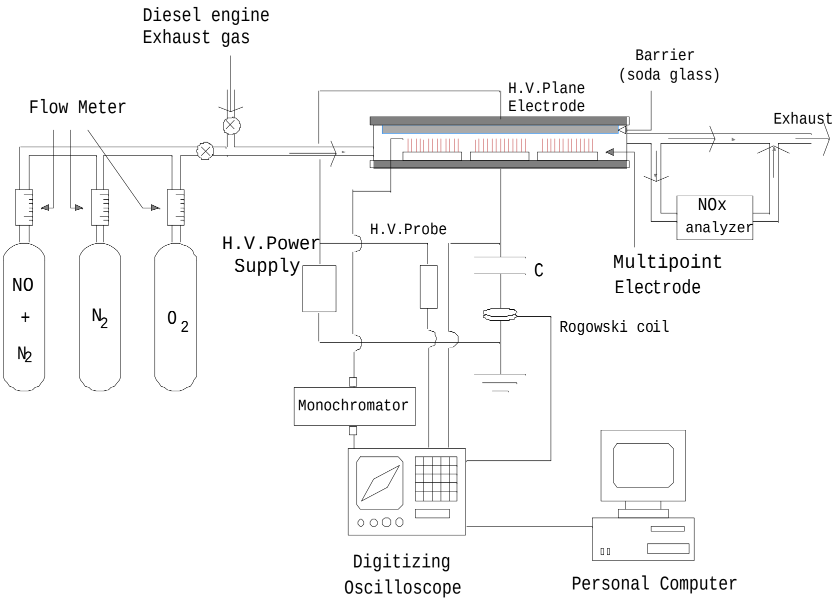

Figure 1. Experimental set-up.

discharge was focused into a monochromator (Nikon P-250) through 0.5 mm slit with length of 20 cm. The observed spectra are emission lines of the first negative system (FNS) of N_2^+ (391.4 nm) and the second positive system (SPS) of N_2 (337.1 nm). The intensity ratio of these spectral line emissions provides information on the electron energy in the discharge region (Sato and Shida 1995).

A simulated flue gas, which was composed of three kinds of premixed gases, was used to investigate the performance of the reactor. Besides the simulated gas, an actual exhaust gas was used in the experiment. The plasma reactor was installed in a slipstream of the main exhaust gas flow from a diesel engine generator (Denyo DCA-25SP1) with a rating of 20 kV A. The applied voltage was measured with a high-voltage probe (Sony Tektronix P6015) and the circuit current by a Rogowski coil (Pearson 2878F). The electric charge through the discharge can be calculated by measurement of the voltage across a capacitor, which is inserted between the reactor and the ground. A digitizing oscilloscope (TDS310) was used for monitoring the output signals of the measurement instruments. The concentration of NO_x ($NO + NO_2$) in outlet gas was measured by using a NO_x-analyser based on the chemical-luminescence method.

The experiment was performed using the sine wave and repetitive pulse voltage generators. Sinusoidal voltage of 10–50 kHz and 0–800 V_{pp} (peak-to-peak value) is generated by a power supply and stepped up by a 1:15 transformer. Figures 2(*a*), (*b*) and (*c*) show the typical waveforms of applied sinusoidal voltage, discharge current and consumed energy in the reactor, respectively. The fundamental wave of the circuit current leads the applied voltage by 90° in the phase angle due to the large capacity of the reactor. A number of small pulses superposed on the fundamental wave are caused by micro-discharges in the reactor. The consumed energy is calculated from the time integral of the product of the applied voltage and the circuit current. The discharge

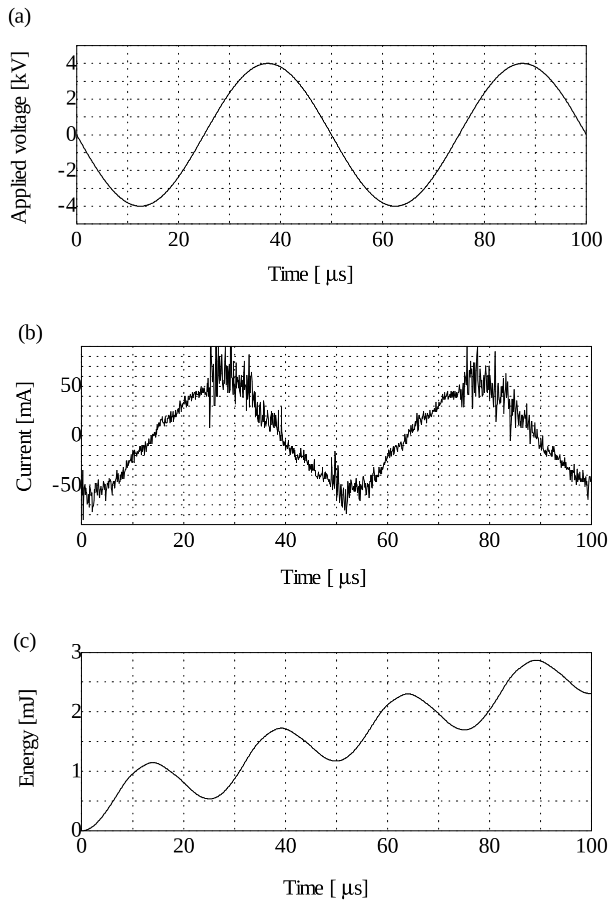

Figure 2. Typical waveforms in a dielectric barrier discharge. (*a*) applied voltage, (*b*) discharge current, (*c*) energy consumed in the reactor.

current is approximately 0.11 mA in peak-to-peak value at 20 kHz and 3 kV.

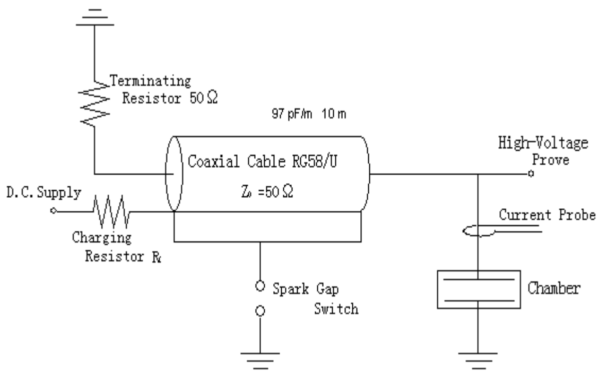

Figure 3. Equivalent circuit of the high-voltage pulse generator.

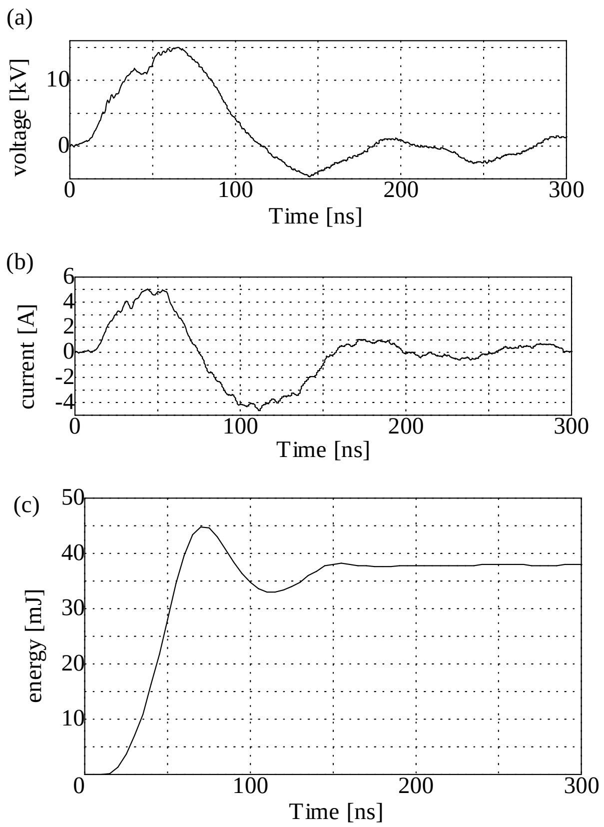

Figure 4. The typical waveforms of (*a*) a high-voltage pulse, (*b*) discharge current and (*c*) consumed energy in the reactor.

A high-voltage pulse was generated by discharging a coaxial cable RG-58 and the pulse repetition was, in principle, controlled by a gap switch (Ishii and Yamada 1985, Takaki *et al* 1997). An equivalent circuit for the pulse generator is shown in figure 3. The coaxial cable with 10 m length is used to generate a 50 ns pulse width. The core of the cable is grounded through a terminating resistor of 50O Ω at the opposite side of the reactor.

Figures 4(*a*), (*b*) and (*c*) show the typical waveforms of a high-voltage pulse, circuit current and consumed energy, respectively. The coaxial cable was charged up to 20 kV. The rise time is 50 ns when the voltage reaches 80% of the peak value. Then, the circuit current can be expressed by

$$i_c = c\,\mathrm{d}V/\mathrm{d}t. \tag{1}$$

The energy can be obtained from the applied voltage measured at time interval of ns.

3. Experimental results

3.1. NO_x removal

In the gas discharge phase, it is considered that the electron is the main source of radical generation. The following reactions are expected for the NO_x reduction process via radical formation:

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

$$N_2 + e \rightarrow N + N + e \tag{3}$$

$$NO + N \rightarrow N_2 + e \tag{4}$$

$$NO_2 + O \rightarrow NO + O_2. \tag{5}$$

Also the NO_2 will be generated through the reverse reaction as follows

$$2NO + O_2 \rightarrow 2NO_2 \tag{6}$$

$$NO + O_3 \rightarrow NO_2 + O_2. \tag{7}$$

Reactions (6) and (7) strongly depend on the gas temperature (Lowke and Morrow 1995). By controlling the energy input toward the discharge plasma, it is possible to minimize the production of NO_2 and to remove NO_x from the gas. The production of other species such as N_2O through the oxidation of NO_2 is very small and negligible in this experiment.

At first, the experiments were performed by application of the sinusoidal voltage and the repetitive pulsed voltage with a 35 ns pulse width. Figure 5 shows NO reduction as a function of energy density. The NO removal increases with energy density. The gas flow rate in the plasma reactor was 5 l min^{-1} and the gas compositions were 90% NO + N_2 and 10% O_2. The magnitude of the high-voltage pulse was set to 18 kV. The consumed energies per pulse at the positive and negative pulses were about 26.2 mJ and 24.4 mJ, respectively. It can be seen that the removal of NO is essentially possible with both polarities. The NO removal by a positive pulse is almost equal to that by a negative pulse at the same energy density. This result agrees with the previous data by other investigators (Masuda and Nakao 1990, Amirov *et al* 1993). In addition, NO removal is larger by pulse repetition than by sinusoidal wave.

As a comparison with other NO_x treatments, efficiencies based on electron beam processing, pulse corona and barrier discharge methods have been presented in detail previously (Penetrante *et al* 1997). It is interested to note that all of the data of NO removal efficiency through the reaction of N_2 + NO by pulse corona and barrier discharge show the same result. In which case, we obtained a NO_x removal efficiency by the barrier discharge with pulse voltage that is better than with the sinusoidal voltage. It was reported that the streamer inception voltage increases with a rise rate of electric field: 31.8 kV for 0.12 kV μs cm^{-1} and 37.12 kV for 0.91 kV μs cm^{-1} (Baldo *et al* 1975, Harid and Waters 1991,

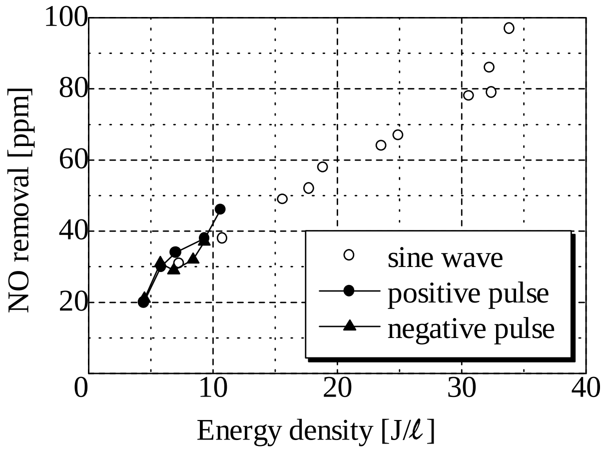

Figure 5. NO removal as a function of energy density.

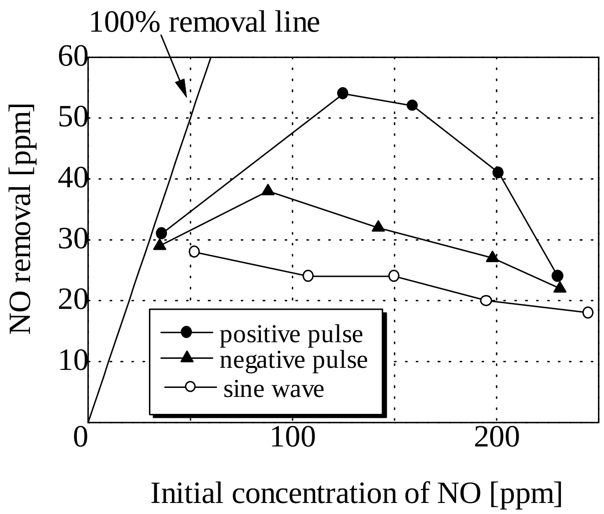

Figure 6. The relationship between NO removal and initial concentration.

Rea and Yan 1995). In this work an average value of the electric field is about 50 kV cm^{-1} at 2.5 kV and gap length of 0.5 mm. Taking into account the non-uniform field around the point tip, the electric field is calculated from the Mason formula (Mason 1955)

$$E = \frac{2V}{R \ln(1 + 4d/R)} \tag{8}$$

where V is the applied voltage, d is gap length and R is radius of the needle tip. The value of electric field is 164 kV cm^{-1} and it is raised to about three times the average value. At the frequency of 100 kHz, the inception field rate is calculated to be 1.64 × 103 kV μs cm^{-1}

It is considered that the streamer propagation is promoted by the strong electric field which makes the electron temperature and electron density increase. In such a streamer the NO removal effectively increases at the large scale of the voltage rise.

Figure 6 shows the relationship between NO reduction and the initial concentration. The gas flow rate was 5 l min^{-1} and the pulse voltage was set to 18 kV, to compare with the

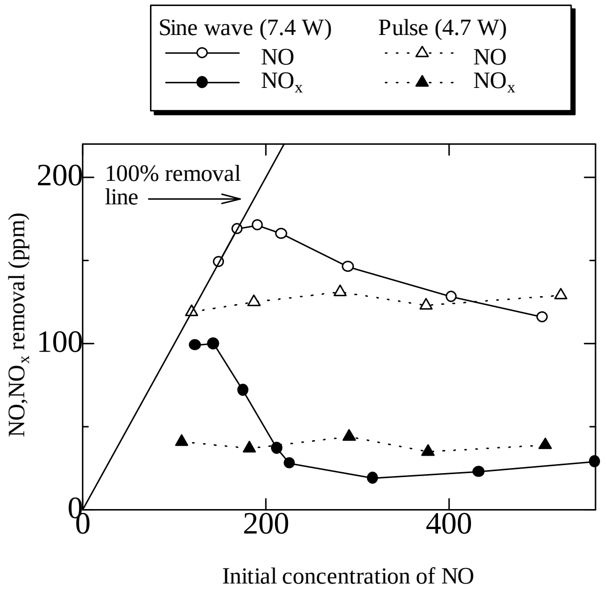

Figure 7. The dependence of NO and NO_x removal on the applied voltage waveforms at high input energy.

experimental results of sinusoidal voltage at the same energy density. We obtained an energy density of 8.2 J l^{-1} for the positive pulse voltage, whereas in the case of negative pulse voltage and sinusoidal voltage the value is 6.7 J l^{-1}. The NO removal decreases at high initial concentration. The result shows that the removal by a positive pulse is substantially greater than that by a negative pulse because the energy in the plasma is more at the positive pulse than at the negative pulse. It is considered that the application of a positive pulse leads to the formation of many positive streamers, which have a high electric field region at their heads.

Figure 7 shows the dependences of NO and NO_x removals on the applied-voltage waveforms at high input energy. The rate of gas flow into the plasma reactor is 5 l min^{-1}. The input electric power into plasma per cycle of sine wave is 0.38 mJ at 2.1 kV and 20 kHz. In the case of pulse voltage, the input power into plasma per cycle is 0.11 J at 20 kV and repetition rate 47 pulses per second (pps). The energy density is about 91 J l^{-1} and 62 J l^{-1}. The maximum value of NO removal by a sinusoidal wave is 170 parts per million (ppm) and it by a pulse voltage is 130 ppm. The NO removal by pulse wave is almost constant and independent of initial concentration, whereas at higher concentrations the NO_x removal by sinusoidal wave decreases abruptly. It was reported that the removal efficiency is greater at higher initial concentration (Amirov *et al* 1993, Yan *et al* 1993, Klein *et al* 1995). It is considered that the number of N(^{2}D) radicals increase and it would lead to NO_2 production. The NO_x removal decreases with increasing initial concentration because the oxidation of NO to NO_2 is promoted.

The experiment using an actual exhaust gas was performed. The exhaust gas from diesel engine consists of various components CO, CO_2, H_2O etc besides NO_2 and NO. The composition depends on the load condition of the diesel engine generator. Figure 8 shows the main components as a function of the load current of the diesel engine generator, with a rating of 20 kV A. It is seen that the concentration of

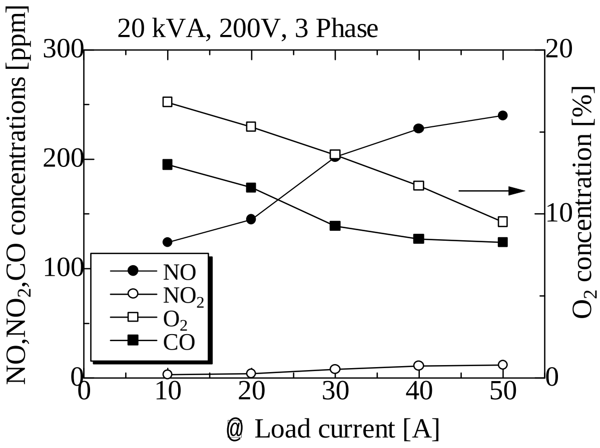

Figure 8. The concentrations of exhaust gas compositions as a function of load current of the 20 kV A diesel engine generator.

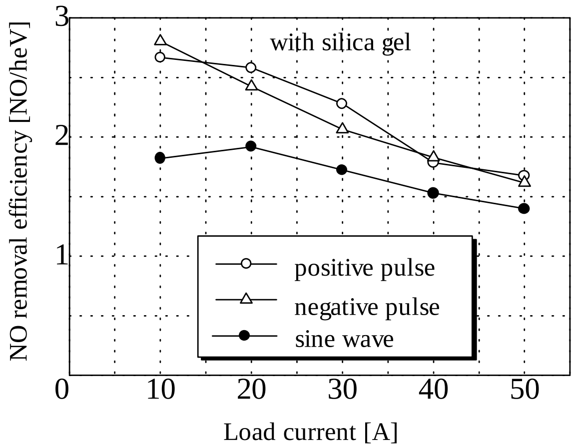

Figure 9. NO removal efficiency as a function of load current of the diesel engine generator using a silica gel as a moisture trap.

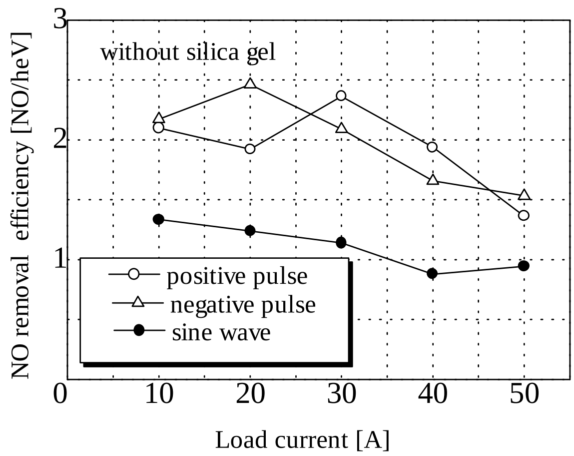

Figure 10. NO removal as a function of load current of the diesel engine without silica gel moisture trap.

O_2 decreases with a load current near to 8%, whereas NO increases to 300 ppm. The exhaust gas contains CO and O_2 at high concentration under the condition of no load, whereas the concentrations of NO and NO_2 in the gas increase with load current.

Figure 9 shows NO removal efficiency as a function of load current of the diesel engine generator using silica gel as a moisture filter for the exhaust gas. The gas flow into the plasma reactor was set to 5 l min^{-1} by dividing the total exhaust gas flow from the diesel engine (1.2 m^3 min^{-1}). Then, in the case of pulse voltage, the energy densities at both polarities are 30 J l^{-1}, whereas the energy density at a sinusoidal voltage is 26 J l^{-1}. The NO removal decreases with load current of the diesel engine because the NO initial concentration increases with the load current. This tendency coincides with the experimental results of the simulated gas as shown in figure 6. We consider that the decrease of NO_x removal is caused by the oxidation of NO. The NO removal reaches a maximum value of 56 ppm, 45 ppm and 59 ppm by positive pulse, negative pulse and sinusoidal voltage, respectively, and the G values are 2.6, 2.41 and 1.92 NO h eV. This means that the G value increases by positive pulse and is relatively low as compared with the result of the simulated gas.

Figure 10 shows the NO removal efficiency as a function of the load current of the diesel engine. The treatment was performed without silica gel at 5 l min^{-1}. The removal efficiency is greater by using the pulse voltage than by using the sinusoidal voltage. This tendency coincides with the experimental result of the simulation gas. The NO removal efficiency decreases with increasing the load current in all cases of the sinusoidal wave and the positive and negative pulses.

3.2. Spectroscopic measurements

A discharge, which has a number of electrons with high energy at atmospheric pressure, is necessary for the NO_x treatment. Therefore, it is important to investigate the electron energy during the streamer development. The observed spectra are emission lines of the FNS of N_2^+ (391.4 nm, threshold energy 18.75 eV) and the SPS of N_2 (337.1 nm, the threshold energy 11.05 eV). The use of multipoint-to-plane electrodes was compared with parallel plane electrodes to provide information of the electron energy production in the discharge region. The electron energy distribution is generally not the normal Maxwellian distribution. Spyrou and Manassis (1989) used several electron energy distribution functions. They reported that for extreme cases there is a difference of 6 eV between Maxwell and Druyvesteyn distributions. However, it is common, that the larger the ratio of light intensity (FNS of N_2^+/SPS of N_2), the higher the average energy of the electrons.

The typical wave of applied voltage and the light intensity for the SPS of N_2 and the FNS of N_2^+ are shown in figure 11. The full curve and the broken curve show the light intensity in the discharge region using the multipoint-to-plane geometry and parallel plane electrode, respectively. With regard to the discharge by multipoint-to-plane electrodes, figure 11 shows that the light intensity of the SPS of N_2 is greater in the negative streamer than in the positive, while the light intensity of the FNS of N_2^+ shows the contrary result. However, in the case of parallel plane electrodes there is no dependence of the light intensity on the streamer polarity in the discharge region.

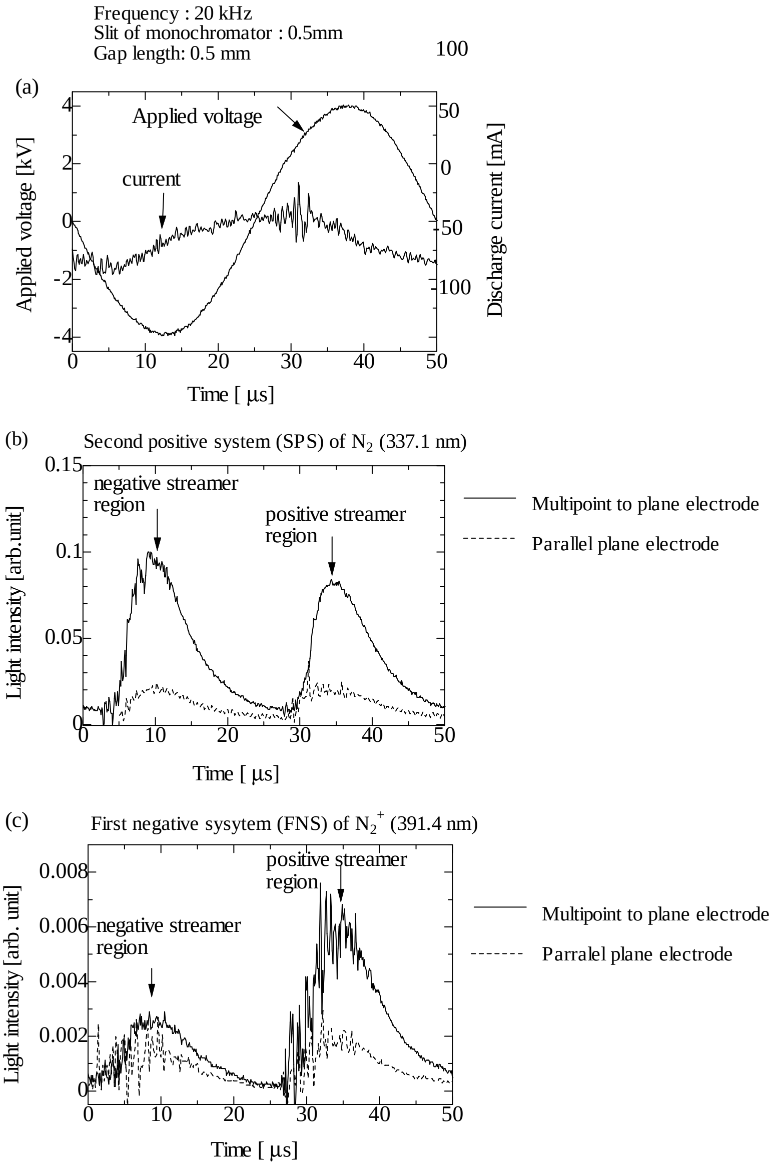

Figure 11. The typical profiles of (*a*) applied voltage, discharge current and the light intensities for (*b*) the second positive system of N_2, (*c*) the first negative system of N_2^+.

The relationship between the applied voltage and the light intensity for the SPS of N_2 and the FNS of N_2^+ are shown in figure 12. From the figure, we can recognize that the reactor produces electrons with energy that are more than the threshold value of the SPS of N_2 (11.05 eV). The SPS of N_2 emission occurs at an applied voltage greater than 1.8 kV (effective value), while the FNS of N_2^+ emission does so at voltages greater than 2.5 kV.

The spectroscopic measurement of electron energy in the plasma was reported by using the ratio of the FNS of N_2^+ and the SPS of N_2 (Spyrou and Manassis 1989, Gallimberti *et al* 1974, Yan *et al* 1993). Figure 13 shows the relationship between the intensity ratio of the FNS of N_2^+ to the SPS of N_2 and applied voltage at 20 kHz. The intensity ratio neither depends on the applied voltage nor the polarity of the streamer in the case of parallel plane electrodes. In the case of multipoint electrodes, however, it depends on polarity of the streamer. The results show that the value is more at positive polarity than at negative polarity and equal to the intensity ratio in the case of parallel plane electrodes.

The streamer polarity transforms a positive streamer into a negative streamer commonly in the barrier discharge between the parallel plane electrodes (Braun *et al* 1991). The electron temperature of positive streamer changes from 4 eV to 8 eV according to its location (Gallimberti *et al* 1974, Spyrou and Manassis 1989). This experimental result shows that the streamer in the barrier discharge between parallel planes at both polarities is similar to the positive streamer using multipoint electrodes. This means that the negative streamer between multipoint-to-plane electrodes is relatively weak as compared with the experiments by other authors (Gallimberti *et al* 1974, Spyrou and Manassis 1989, Braun *et al* 1991). Therefore, in the case of parallel plane electrodes, the positive streamer only is generated and the direction of the

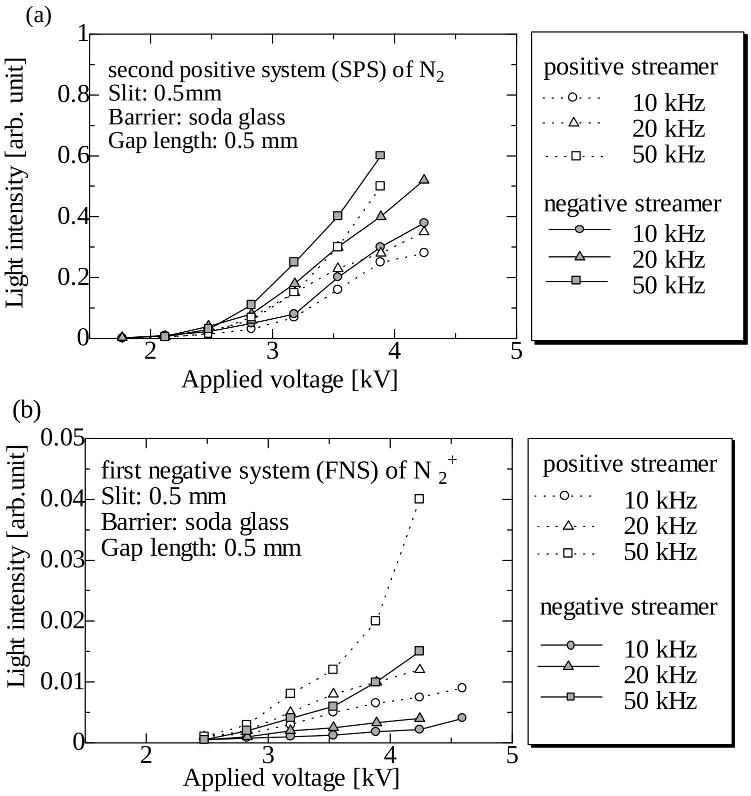

Figure 12. The relationship between the applied voltage and the light intensities of (*a*) the second positive system of N, (*b*) the first negative system of N_2^+.

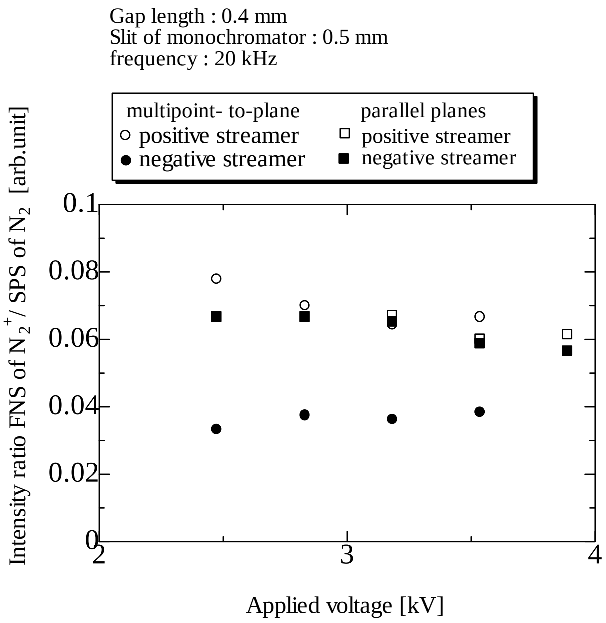

Figure 13. The relationship between the intensity ratio of the first negative system of N_2^+ to the second positive system of N_2 at different applied voltages.

development is changed by the polarity of applied voltage, while in the case of multipoint-to-plane electrodes the nature of the streamer changes according to the polarity. However, the experimental result showed that the NO_x reduction does not apparently depend on the polarity of the applied voltage, as shown in figures 9 and 10.

4. Conclusion

For an application of NO_x removal to exhaust gas treatment, a plasma reactor with multipoint-to-plane electrodes, to lower the operating voltage, is proposed. It was found from the spectrum measurements that this reactor could produce electrons in the discharge region at atmospheric pressure with energy greater than 10 eV. By adopting a frequency of several tens of kilohertz, the atmospheric discharge plasma with a large cross sectional area could be uniformly produced in a gap between multipoint electrodes and a dielectric barrier, even below 3 kV as effective value.

The spectrum observation showed that the intensity ratio of the FNS of N_2^+ to the SPS of N_2 is larger in a positive streamer than in a negative streamer. In the case of parallel plane electrodes the streamer was considered to be, substantially a positive streamer, while in the case of multipoint electrodes both positive and negative streamers were generated. Since the streamer is generated near a point of the electrode, an application of positive pulse to the multipoint electrodes leads to a formation of many positive streamers, whose heads have a region of high electric field. As a comparison, the results showed that pulse repetition is better in NO and NO_x removal and the removal efficiency is better than in a sinusoidal wave.

The spectrum measurement was consistent with the experiment of NO and NO_x removal. The positive streamer has more energetic electrons than the negative streamer, although there is no remarkable difference in the NO and NO_x removal between positive and negative streamers.

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