静電気学会誌，**33**, 1 (2009) 8−13

J. Inst. Electrostat. Jpn.

Paper

Study of NOx Removal Processes by Microplasma Generation

Marius BLAJAN*,[1], Masaki KANAMORI*, Hidenori MIMURA**
and Kazuo SHIMIZU*

(Received August 20, 2008 ; Accepted November 26, 2008)

Microplasma discharge at relatively low voltages and very small discharge gaps is analyzed. The electrical characteristics of the microplasma electrodes and the small size of the supply circuit show that this technology can be applied for NOx removal processes especially for mobile exhaust gas sources. The effect of the discharge gas temperature and O_2 amount in the gas composition are investigated. The electrode arrangement using a parallel connection allows the treatment of different gas composition at different flow rates.

The experimental results show that with the increase of the discharge gas temperature the NOx removal efficiency increases for the gas composition without O_2. At higher gas temperatures the energy efficiency of the NOx removal process is lower. By increasing the amount of O_2 in the discharge gas the NOx removal efficiency will decrease. Due to the decomposition of O_3 at higher temperatures with the increase of gas temperature the NO removal efficiency in the presence of O_2 is decreasing and also fewer quantities of NO were oxidized to NO_2. Higher NOx removal efficiencies were obtained at lower concentrations of NO and lower gas flow rates.

1. Introduction

In the last years the problems concerning the atmospheric pollution due to the NOx emissions by stationary sources (factories) and mobile sources (automobiles, ships, airplanes) imposed a search for solutions to treat this exhaust gases. Non thermal plasma has been researched as a technology for NOx removal in decades.[1-5] Due to the very effective ways for generating ozone also the discharges at very small gaps were investigated.[6] The "*pd*" values (pressure x electrode separation) of atmospheric pressure microplasmas are similar to those for large volume, low pressure plasmas but with much higher energy densities.[7] Microplasma generation is a technology that due to its relatively low voltage discharge can be easily applied for NOx removal on small mobile sources such as automobiles and motorcycles.[8]

In previous works we have already studied NOx removal using multiple microplasma electrodes linked in series connection.[9,10] Different gas temperatures and different concentration of O_2 and NO were used in this study to analyze the NOx removal processes by atmosphericpressure microplasma. Electrical characteristics of microplasma discharge were analyzed. The experimental works that have implied more than one pair of electrodes were performed using a parallel connection between electrodes pairs.

Keywords: microplasma, NOx removal, dielectric barrier discharge

* Innovation and Joint Research Center, Shizuoka University, 3-5-1 Jyouhoku Hamamatsu, 432-8561, Japan.

** Research Institute of Electronics, Shizuoka University, 3-5-1 Jyouhoku Hamamatsu, 432-8561, Japan.

[1] blajanmarius@yahoo.com

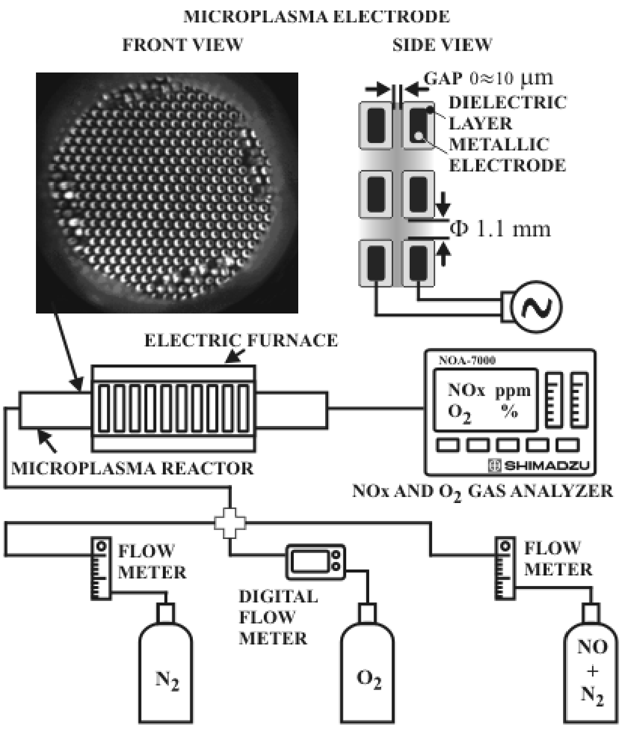

Fig. 1 Experimental setup. Gases with different specified amounts of NO, N_2 and O_2 in composition were treated by the microplasma electrodes covered with a dielectric layer and placed inside a gas tube heated by an electric furnace. The treated gas is analyzed by a NOx and O_2 gas analyzer.

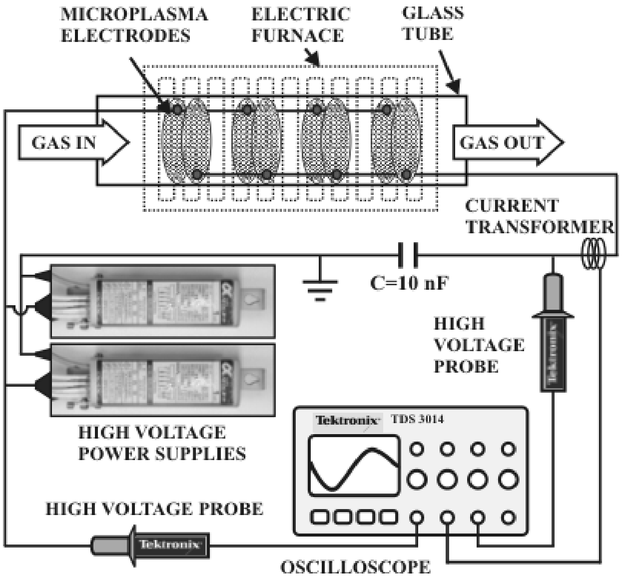

Fig. 2 A microplasma reactor. The electrodes connected in parallel are supplied with an AC voltage up to 1.2 kV peak. The high voltage supplied to the electrodes and corresponding currents and discharge power are measured by a high voltage probe, a current transformer and a digital oscilloscope.

2. Experimental setup

Microplasma generation with dielectric barrier discharge is realized with perforated metal plates electrodes covered with a dielectric layer. The electrodes have an aperture ratio of 34% and the discharge gap is set at about 0 to 10 µm. An electric furnace was used to change the gas temperature inside the reactor (Fig. 1). The experiments were performed with a gas containing NO, O_2 and N_2 in different amounts. The results were analyzed with a NOx O_2 gas analyzer (Shimadzu, NOA 7000).

The microplasma reactor (Fig. 2) is inside a glass tube with a diameter Ø 44 mm and the electrodes have a diameter Ø 42 mm. The temperature inside the reactor was set to 25°C, 100°C, 200°C, 250°C and 300°C and it was measure with a probe at the exterior of the glass tube. The value of the gas temperature is considered as being equal to that measured at the exterior of the glass tube.

Due to the relatively low discharge voltages (around 1 kV) two small high voltage power supplies (LECIP, M-1H) connected in parallel were used to supply the microplasma reactor with alternative voltages with frequencies of about 25 kHz. The peak values of the discharge voltages are measured by a high voltage probe (Tektronix, P6051), and the discharge currents by an AC current transformer (Tektronix, P6021). The discharge power is measured using a digital oscilloscope (Tektronix, TDS 3014) and is calculated by a computer from Lissajous figures. The figures are obtained by measuring the capacitance charge of capacitor C=10 nF connected between electrode and ground.

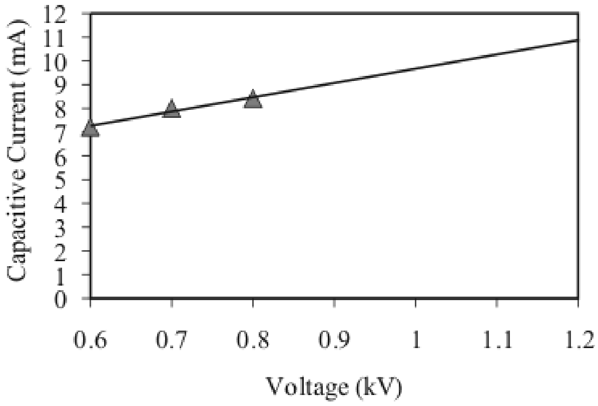

Fig. 3 Volt-Ampere tendency curve for estimation of the capacitive current of electrode with a discharge gap of 0 µm.

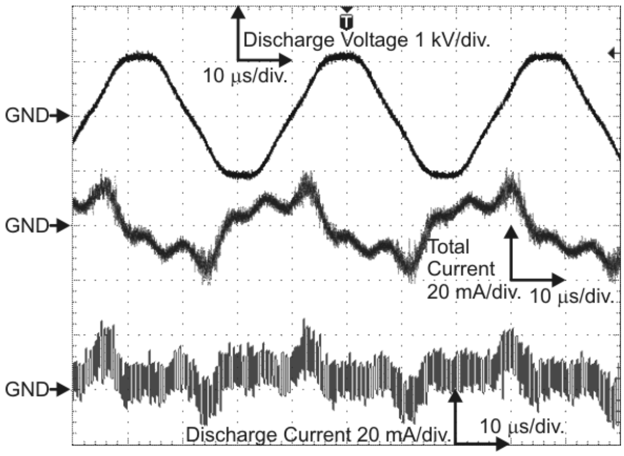

Fig. 4 Discharge voltage, total measured current and discharge current for one pair of electrodes with a discharge gap of 0 µm.

3. Electrical characteristic of microplasma discharge

The microplasma current both contains the capacitive current and the discharge component. The capacitive current was estimated using the Volt-Ampere tendency curve for the higher values of the discharge voltage (Fig. 3).

The estimated capacitive current was subtracted from the total current in order to obtain the discharge current.[11)] Capacitive current was measured to 7.2 mA at 0.6 kV. We have estimated to 11 mA for 1.2 kV according to Fig. 3. Thus it results a multiplication factor of 1.5 for estimated capacitive current at 1.2 kV. The discharge voltage, the total measured current and the discharge current are presented in Fig. 4.

A high electric field (E=10^7–10^8 V/m) could be obtained with applied voltage of 1 kV. Due to the dielectric constant of dielectric layer ε_r=10^4 and the narrow discharge gap (10 µm) assures the formation of non-thermal plasma and discharge current.[10)] Their high electron temperature ensures the production of very high concentrations of energetic and chemically active species.[12)]

The discharge power versus discharge voltage curves for 5

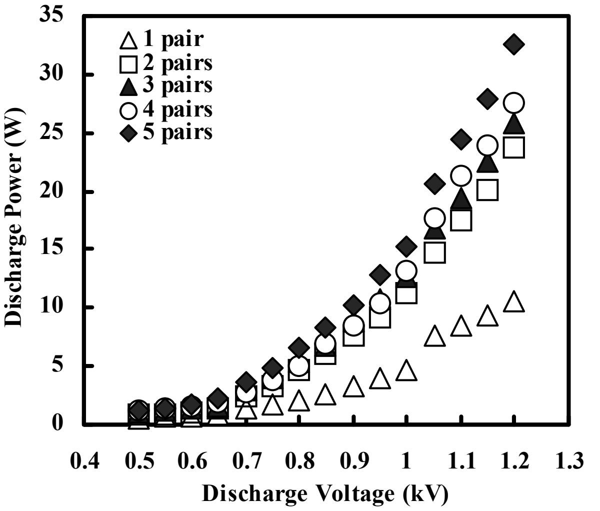

Fig. 5 Discharge power of microplasma electrodes. Up to 5 electrode pairs were used to measure the discharge power at different discharge voltages in the gas with the composition NO 6,000 ppm and N_2 balance.

pairs of electrodes are presented in Fig. 5. The measurements were performed with 5, 4, 3, 2 and 1 pair of electrodes. As the discharge gas was used NO 6,000 ppm, N_2 balance and the gas flow rate was set at 0.2 L/min. The discharge gap was set at 0 μm. The discharge power was calculated from the obtained Lissajous figures.

The discharge power increases with the increase of the discharge voltage thus for 5 pairs of electrodes at the discharge voltage of 1.2 kV it was measured a discharge power of 32.6 W. For 1 pair and 2 pairs of electrodes the discharge power at 1.2 kV was 10.6 W and 23.7 W respectively. Due to the individual difference of each electrode pair, the difference between the discharge power of 1 pair and 2 pairs of electrodes is not similar.

4. NOx removal by microplasma

The effects of the O_2 content and gas temperature on NOx removal process have been studied.

4.1 NOx removal process in absence of O_2

In order to determine the characteristics of the NOx removal process in absence of O_2, the experimental setups presented in Figs. 1 and 2 were used. In this paper NOx represents the sum of NO and NO_2.

The gas with the composition NO 505 ppm, C_3H_8 500 ppm and N_2 balance was used as a discharge gas and gas flow rate was set at 1 L/min. Four pairs of electrodes with a discharge gap of 0 μm were attached in the reactor. The temperature was set to 25°C, 100°C, 200°C and 300°C.

Increase of discharge power was confirmed with increase of the gas temperature for discharge voltage of 1.1 kV (Fig. 6).

Figure 7 presents the obtained Lissajous figures for the

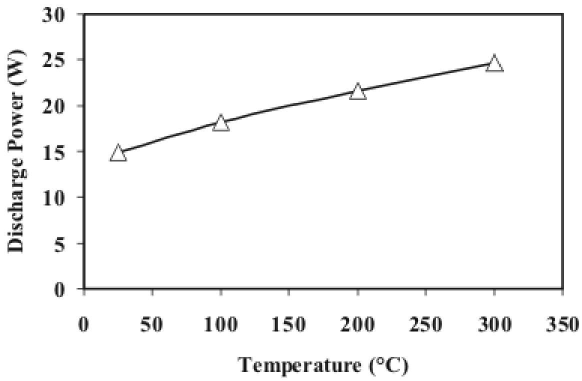

Fig. 6 Discharge power versus gas temperature for the experimental setup using 4 pairs of electrodes with a discharge gap of 0 μm at 1.1 kV discharge voltage.

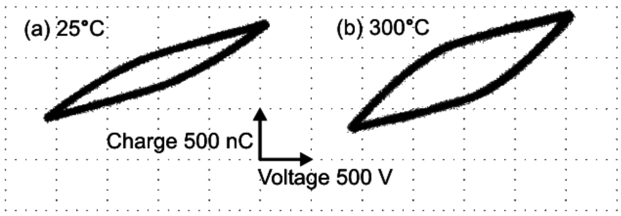

Fig. 7 Lissajous figures representing the discharge power of 4 pairs of electrodes at 1.1 kV discharge voltage with a discharge gap of 0 μm at (a) 25°C and (b) 300°C.

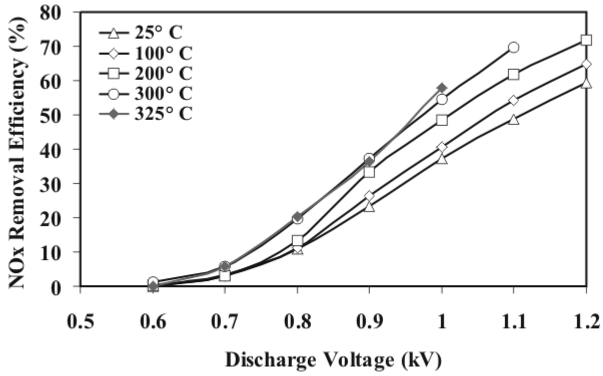

Fig. 8. NOx removal efficiency versus discharge voltage at different discharge gas temperatures.

discharge power of 4 pairs of electrodes at 25°C and 300°C at the same discharge voltage of 1.1 kV.

The characteristics of NOx removal efficiencies versus discharge voltage for the gas composition NO 505 ppm, C_3H_8 500 ppm and N_2 balance and gas flow rate of 1 L/min are presented in Fig. 8.

NOx removal efficiency of 70% was measured at 300°C with 1.1 kV. In comparison at the same discharge voltage for the gas temperature of 25°C the NOx removal efficiency was 49%.

The highest NOx removal efficiency of 72% was obtained for a gas temperature of 200°C at a discharge voltage of 1.2 kV. The highest values of removal efficiency for the gas temperatures of 300°C and 325°C were 70% and 58% at 1.1 kV and 1 kV respectively. No discharge occurred over these values of the discharge voltages at 300°C and 325°C due to the modification of electrical properties of the dielectric layer at high temperatures. The curve for the temperature of gas of 325°C shows similar characteristics with the curve for the gas temperature of 300°C.

In the absence of O_2, NO could be chemically reduced to N_2 by atomic nitrogen species, produced by electron impact:[13)]

$$e + N_2 \rightarrow e + N(^4S) + N(^4S) \tag{1}$$

$$N(^4S) + NO \rightarrow N_2 + O \tag{2}$$

where $N(^4S)$ is a ground state nitrogen atom.

NOx removal efficiency increases with the increase of the gas temperature. Discharge power is higher for higher gas temperature. The NOx removal efficiency per discharge power ratio is presented in Fig. 9. At a gas temperature of 25°C the values is 3.3 %/W in comparison with 2.8 %/W at 300°C. That could be explained by the changes in the waveform of the discharge currents. At 25°C the currents have higher peak values but with the increase of the temperature the charged currents are higher.[10)]

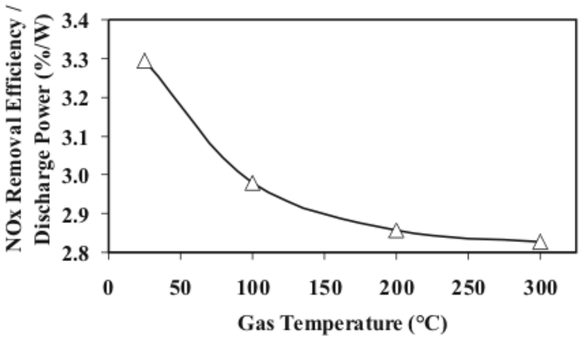

Fig. 9 NOx removal efficiency / discharge power ratio versus discharge gas temperature at a discharge voltage of 1.1 kV.

4.2 O_2 concentration effect on NOx removal

In order to simulate the condition of a exhaust gas O_2 was added in composition of the discharge gas in percentages 1%, 2% and 5%.

The characteristics of NOx removal efficiencies versus O_2 concentration for 4 pairs of electrodes are presented in Fig. 10. The composition of the gas was NO 1,010 ppm, O_2 0%, 1%, 2% and 5% and N_2 balance.

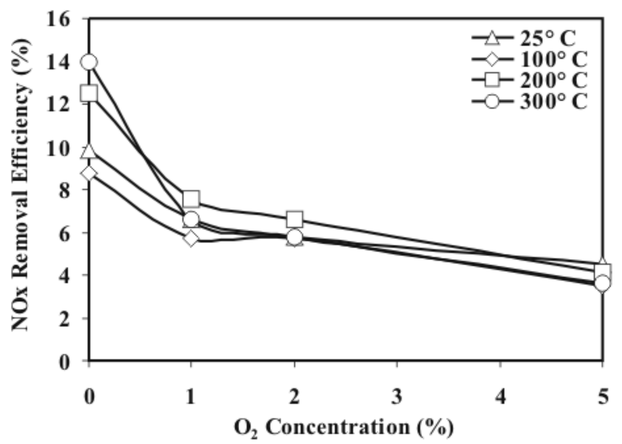

Fig. 10 NOx removal efficiency versus O_2 concentration in the discharge gas at a discharge voltage of 1 kV, 2 L/min gas flow rate and 1,010 ppm NO concentration.

The gas flow rate was set at 2 L/min. The highest NOx removal efficiency of 13.9% was measured at 300°C for the gas composition with 0% O_2 and the lowest of 3.5% was measured at 100°C for the gas composition with 5% O_2. The discharge voltage was fixed to 1 kV. At this discharge voltage the electric field is high enough to dissociate nitrogen and form NO. The dissociation energy for nitrogen is around 9 eV and the dissociation energy for oxygen is around 5−6 eV. Thus the main chemical reactions that are occurring in the microplasma are:[6)]

$$N^* + O_3 \rightarrow NO + O_2 \tag{3}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{4}$$

The results presented in Fig. 11 shows similar tendencies of the NOx removal efficiency characteristics versus O_2 concentration in the discharge gas. The gas composition was NO 1010 ppm, O_2 0%, 1%, 2% and 5% and N_2 balance. The gas flow rate was set at 1 L/min. Four pairs of electrodes were used with a discharge gap of 0 μm.

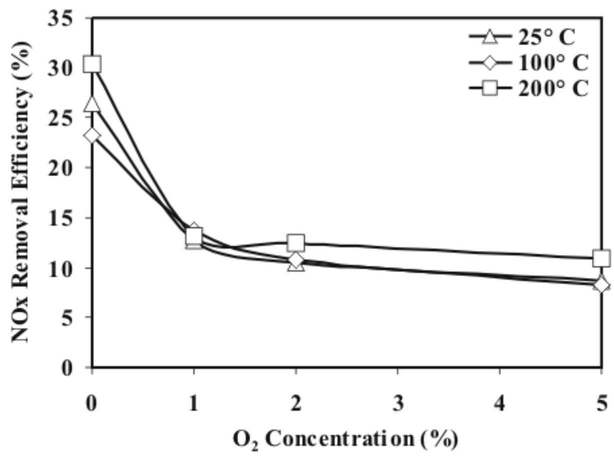

Fig. 11 NOx removal efficiency versus O_2 concentration in the discharge gas at a discharge voltage of 1 kV, 1 L/min gas flow rate and 1,010 ppm NO concentration.

NOx removal efficiencies are higher at 1 L/min gas flow rate comparatively with the values obtained at 2 L/min gas flow rate. The highest efficiency of 30.3% was measured at 200°C for the gas with 0% O_2 and the lowest of 8.3% at 100°C for the gas with 5% O_2.

Table 1 Removed NOx quantities at various gas temperatures and flow rates without O_2.

Gas Temperature (°C)	Removal quantity at 1 L/min (µg/min)	Removal quantity at 2 L/min (µg/min)
25	357	267
100	314	237
200	411	339

Table 2 Treated efficiencies of NO at various gas temperatures without O_2.

Gas Temperature (°C)	25	100	200	250
Treated Efficiency (g[NO]/kWh)	0.92	1.10	1.22	1.41

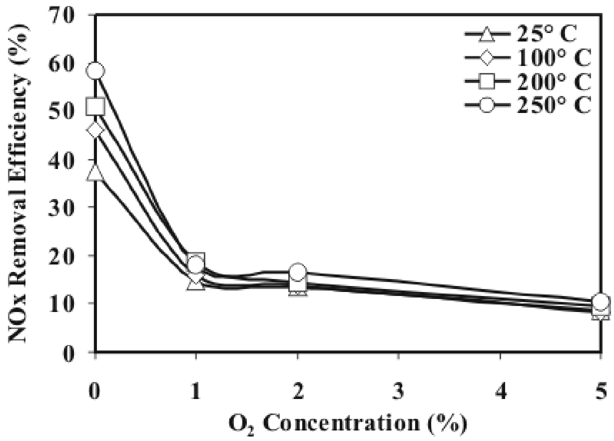

Fig. 12 NOx removal efficiency versus O_2 concentration in the discharge gas at a discharge voltage of 1 kV, 1 L/min gas flow rate and 350 ppm NO concentration.

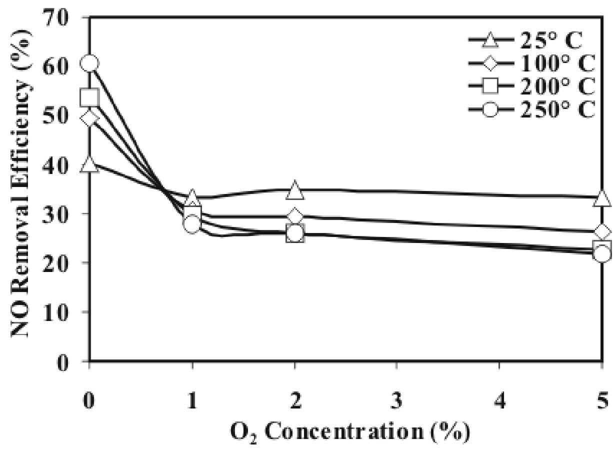

Fig. 13 NO removal efficiency versus O_2 concentration in the discharge gas at a discharge voltage of 1 kV, 1 L/min gas flow rate and 350 ppm NO concentration.

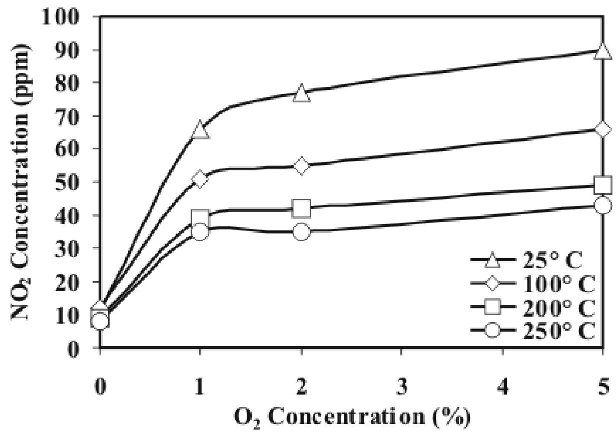

Fig. 14 NO_2 concentration versus O_2 concentration in the discharge gas at a discharge voltage of 1 kV, 1 L/min gas flow rate and 350 ppm NO concentration.

The removed NOx quantity is decreasing from 411 µg/min at a gas flow rate of 1 L/min to 339 µg/min at a gas flow rate of 2 L/min (Table 1).

The gas composition was NO 1,010 ppm initial concentration, 0% O_2 and N_2 balance at 200°C.

4.3 Heat effect on NOx removal in the presence of O_2

The NOx removal efficiency versus O_2 concentration for the gas composition NO 350 ppm, O_2 0%, 1%, 2% and 5% and N_2 balance are shown in Fig. 12. The gas flow rate was set at 1 L/min. Four pairs of electrodes were used with a discharge gap of 0 µm.

The highest NOx removal efficiency of 58.4% was measured at 250°C for the gas composition with 0% O_2 and the lowest of 8.4% at 100°C for the gas composition with 5% O_2.

According to Fig. 5, the measured discharge power for 4 pairs of electrodes is 13.1 W. Thus it result the treated NO efficiencies of the microplasma reactor for the gas composition without O_2 presented in Table 2. The highest value of 1.41 g (NO)/kWh was measured at 250°C.

The NO removal efficiency is increasing with the increase of temperature in absence of O_2 (Fig. 13). The NO removal efficiency is decreasing with the increase of temperature in presence of O_2.

That could be explained by the destruction of the O_3 at high temperatures and according with (3) fewer quantities of NO were produced. Also fewer quantities of NO were oxidized to NO_2 according to (4) in comparison with lower temperatures (Fig. 14).

5. Conclusion

Microplasma generation is a technology that could be applied for NOx removal processes. The following conclusions were obtained:

(1) The discharge power increases with the increase of the discharge voltage. For 5 pairs of electrodes, linked in parallel connection, the highest value of 32.6 W was measured at 1.2 kV discharge voltage.

(2) NOx removal efficiency increases with the increase of the

gas temperature at the same discharge voltage in absence of O_2. The highest efficiency of 72% was obtained at 200°C and at 1.2 kV.

(3) With decrease of the initial concentration of NO from 1,010 ppm to 350 ppm, NOx removal efficiency increases from 30.3% to 51.1% at 200°C without O_2 at 1 kV.

(4) At higher gas flow rates, NOx removal quantity is decreasing from 411 µg/min (1 L/min) to 339 µg/min (2 L/min) for 200°C without O_2.

(5) The highest value of NO treated efficiency of 1.41 g (NO)/kWh was measured at 250°C without O_2.

(6) NO removal efficiency increases at high gas temperature without O_2. From 40.4% at 25°C it was increased to 60.5% at 250°C for the same gas condition.

(7) Due to the destruction of O_3 at high temperatures, NO removal efficiency is higher at lower temperatures with O_2.

At higher temperatures, the oxidation process could be decreased and produced fewer quantities of NO_2. By increasing the amount of O_2 at 250°C, the NOx removal efficiency decreased from 58.4% (without O_2) to 10.5% (5% O_2).

References

1) J.S. Clements, A. Mizuno, W.C. Finney and R.H. Davis: IEEE Trans. Ind. Appl., **25** (1989) 62
2) S. Masuda and H. Nakao: IEEE Trans. Ind. Appl., **26** (1990) 374
3) M. Higashi, S. Uchida, N. Suzuki and K. Fujii: IEEE Trans. Plasma Sci., **20** (1992) 1
4) Y. Yoshioka: Int. J. Plasma Environ. Sci. Technol., **1**(2) (2007) 110
5) K. Shimizu, T. Sugiyama and Manisha Nishamani Liyanage Samaratunge: IEEE Trans. Ind. Appl., **44**(2) (2008) 68
6) J. Kitayama and M. Kuzumoto: J. Phys. D: Appl. Phys., 32 (1999) 3032
7) R. Foest, M. Schmidt and K. Becker: Int. J. Mass Spectrometry, **248** (2006) 87
8) U. Kogelschatz: Contrib. Plasma Phys., **47**(1-2) (2007) 80
9) K. Shimizu, T. Sugiyama, Manisha Nishamani Liyanage Samaratunge and M. Kanamori: “Application of micro plasma for NOx removal,” *Proc. of IEEE-IAS Meeting 2007*, New Orleans (2007)
10) K. Shimizu, T. Sugiyama, M. Kanamori and M. Blajan: “Effect of gas temperature and electrode configuration on NOx removal by microplasma,” *Proc. 6th Conference of the French Electrostatic Society*, pp. 341-346, Paris (2008)
11) K. Takashima, N. Zouzou, E Moreau, A. Mizuno and G. Touchard: Int. J. Plasma Environ. Sci. Technol., **1**(1) (2007) 14
12) A. Fridman: *Plasma Chemistry*. New York, Cambridge University Press (2008)
13) C.R. McLarnon and B.M. Penetrante: “Effect of gas composition on the NOx conversion chemistry in a plasma,” *Society of Automotive Engineers,* paper 982433, pp. 37-48 (1998).