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Plasma-Chemical Effects of Atmospheric Microdischarges in Porous Ceramics

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Abstract: Plasma-chemical activity of microdischarges generated inside porous ceramics by AC high voltage was investigated. Generation of ozone and removal of nitrogen oxides were tested to estimate the chemical efficiency of the discharges. The effects of discharge power, gas mixture composition and gas flow rate on ozone generation and effects of temperature and addition of hydrocarbons on nitrogen oxidation removal are described.

Keywords: microdischarges, porous ceramics, ozone generation, NOx removal.

1. Introduction

Non-thermal plasmas generated by various types of electrical discharges are widely used for various environmental and biological applications. Pulsed microdischarges inside small pores, cavities and narrow capillaries of various materials represent a promising method for flue gas treatment. An investigation of the physical properties of the pulsed microdischarges and a test of the plasma-chemical potential for the removal of various gaseous pollutants has been examined [1-3]. We studied physical properties of DC and AC microdischarges to determine the conditions of the stable generation and distribution inside the ceramics by means of various electrical and optical measurements [4, 5]. The presented work evaluates the plasma-chemical potential of AC microdischarges by monitoring the production and removal of selected species by using emission and absorption spectroscopic methods. Summary of the results of the ozone generation and removal of NOx as the function of discharge power, gas mixture composition, gas flow rate and temperature are presented.

2. Experimental

The microdischarges were generated inside ceramic disc by using AC high voltage power supply. The pore size and the thickness of the disc used for ozone generation experiments were 80 μm and 7 mm, respectively. The pore size and the thickness of the discs for NO removal experiments were 90 μm and 3 mm, respectively. The discharge voltage and current were measured by probes linked to the oscilloscope. Emission spectroscopy system consisted of a dual fiber-optic compact spectrometer with CCD detector. Gas analysis was performed by FTIR absorption spectrometer. All experiments were carried out at atmospheric pressure and the gas flow rates ranging from 0.4 to 2.0 l/min. The pressure drop across the ceramics was negligible (0.1 - 0.8 kPa). The used experimental setup is roughly depicted in Fig.1

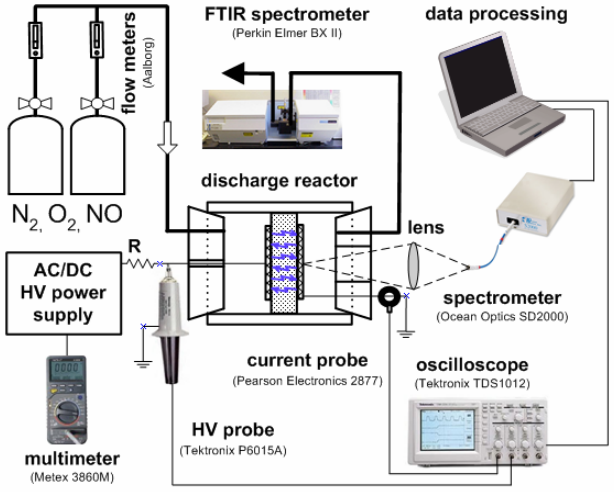

Fig.1. Schematic view of experimental apparatus.

3. Results and Discussion

Discharge properties

In the previous works [4, 5] we showed the generation of the microdischarges inside the ceramics is possible only with the ceramics of the specific pore size and above the specific applied voltage. At small voltages a surface discharge over the surface of the ceramics may be observed only. With the increase of the applied voltage, however, microdischarges inside the ceramics are gradually formed. The onset voltage of the microdischarges increases with the decreasing pore size. Figure 2 shows the visual characters of the microdischarges in nitrogen for 80 μm ceramics. For a very small pore size (2 μm and less) only a surface discharge can be observed. Upon the transition from the surface discharge to the microdischarges, the slope of the I-U characteristics increases. The slope differs for the different pore size. For the given voltage, bigger current was observed with the bigger pore

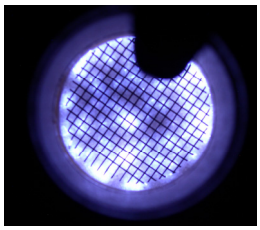

Fig.2. Photograph of microdischarges generated inside the porous ceramics (pore size 80 μm, nitrogen, exposure time 1 s, P ~ 7 W).

size. The amplitude of the current pulses increased with the discharge current, the maximal (20-35 A) observed with 50 and 80 μm pore size ceramics. Due to the best electrical properties and also discharge channel distribution inside the ceramics, the tests of the plasma-chemical activity were performed with the ceramics of 80 and 90 μm pore size.

Production of active species

The emission spectroscopy gave us valuable information on excited atomic and molecular states and the insight in ongoing plasma chemistry in N_2 and O_2 mixtures. Figure 3 presents the emission spectra of microdischarges in UV-VIS-NIR region taken at the constant power in

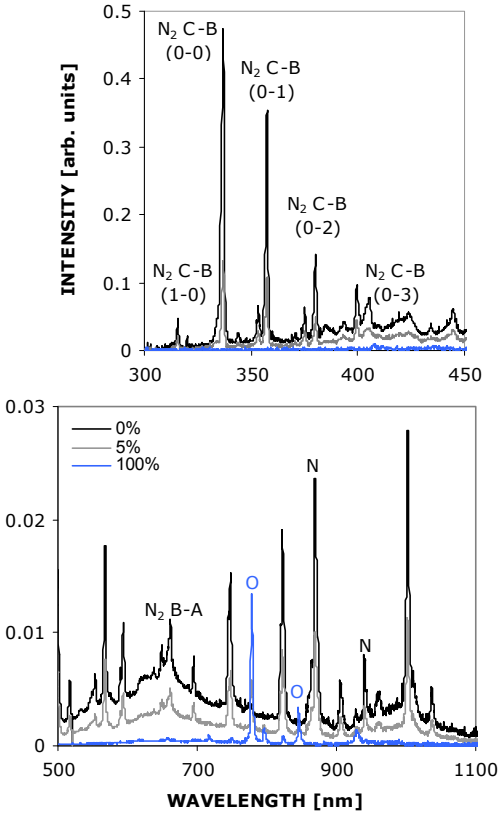

Fig.3. Emission spectra of microdischarges in UV and VIS-NIR regions in mixtures with various amount of oxygen (pore size 80 μm, U = 16.5 kV).

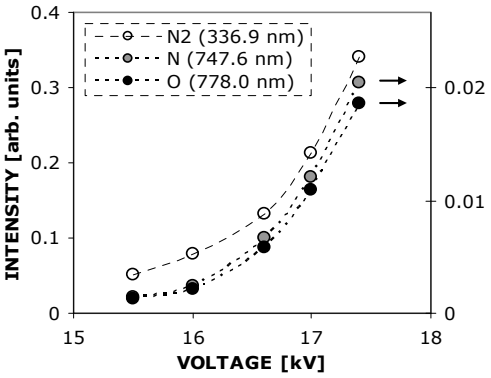

Fig.4. Emission intensity as a function of O_2 concentration (U = 17.5 kV, Q = 1 l/min).

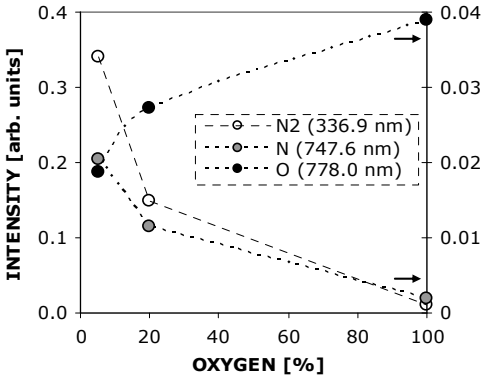

Fig.5. Emission intensity as a function of the applied voltage (5% O_2 in N_2, Q = 1 l/min).

mixtures with various amounts of oxygen. In nitrogen and air, the 2nd positive system of N_2 in the violet region corresponding to the transition $C^3\Pi u - B^3\Pi g$ of N_2 excited states, the 1st positive system of N_2 corresponding to the transition $B^3\Pi g - A^3\Sigma u^+$ and atomic N and O lines were observed. Figure 4 and 5 shows the emission intensity of N_2 spectral band, and N and O lines as functions of the applied voltage and oxygen content in the mixture, respectively. Based on the spectral bands of the N_2 2nd positive system we were able to determine rotational (T_R) and vibrational (T_V) temperatures by fitting the experimental spectra with the simulated ones using Specair software for spectral simulation [6]. The typical measured temperatures in pure nitrogen are T_R = 300±50 K, T_V = 2000±300 K, gradually increasing with the contents of oxygen in a mixture. The results indicated relatively cold plasmas with a high level of non-equilibrium. Many other unidentified bands have been observed in the spectra resulting from the material of the ceramics, which besides alumina and silica includes compounds containing Ca, Mg and Na. A further investigation and interpretation of these bands in needed.

Plasma-chemical effects of microdischarges were studied by means of the generation of ozone and removal of nitrogen oxides.

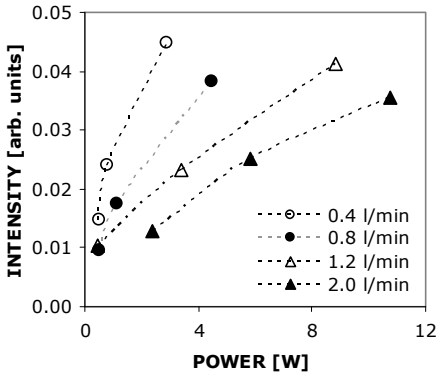

Fig.6. Ozone concentration as a function of discharge power (in oxygen).

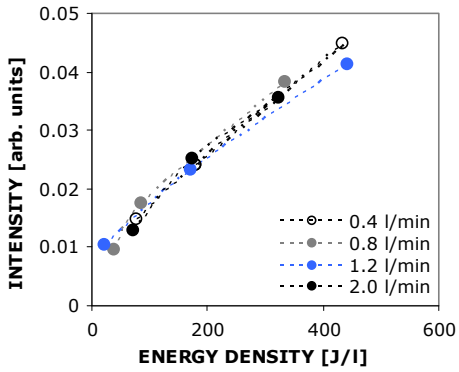

Fig.7. Ozone concentration as a function of energy density (in oxygen).

Ozone Generation

The results of the ozone generation as the function of discharge power, gas mixture composition and gas flow rate are presented in the paper. Figure 6 shows ozone generation in oxygen increased with the discharge power. For the given power, the concentration increased with the decrease of the gas flow rate. The effect of the gas flow, however, became negligible if energy density (J/l) was considered. As Fig. 7 shows, with the same energy density, the total amount of ozone generated was independent of the gas flow rate. In the air-like mixture of nitrogen and oxygen, at the certain power a maximal ozone concentration was observed. Then, with a further increase of the power, the ozone concentration decreased. The power at which the maximal concentration was observed decreased with the increasing flow rate. The analysis of the IR spectra showed that besides ozone, also N_2O_5 and HNO_3 were among the products. On the other hand, neither NO nor NO_2 were observed. The fact that no secondary pollutants are produced by the discharge is very important for gas treatment application.

Removal of NO

Simulated mixtures contained NO (1000 ppm), O_2 (10%), ethylene C_2H_4 (0-0.6%) and N_2 as the balance. The ethylene was dosed to improve the oxidation process of NO. The experiments were performed at the constant power and the gas flow rate 10 W and 0.6 l/min, respectively. The experiments were performed at the temperature of 20 and 150°C, to evaluate the effect of the temperature.

Figure 8 summarizes the results of NO removal obtained with and without the addition of C_2H_4 at the tem-

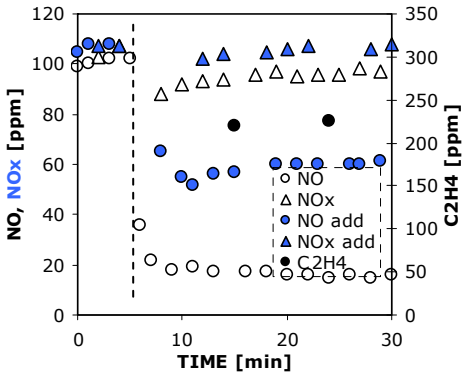

Fig. 8 Time development of NO, NOx and C_2H_4 concentrations (0.6 l/min, 20°C, 300 ppm C_2H_4).

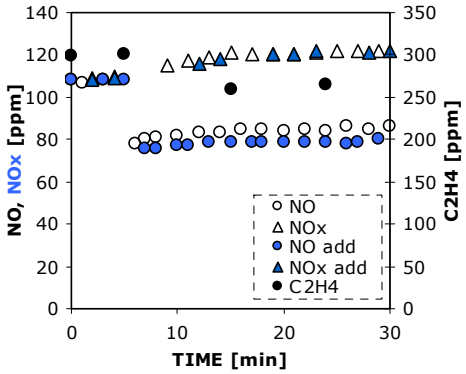

Fig. 9 Time development of NO, NOx and C_2H_4 concentrations (0.6 l/min, 150°C, 300 ppm C_2H_4).

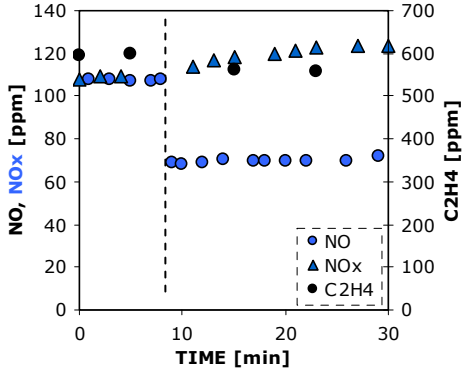

Fig. 10 Time dependence of NO, NOx and C_2H_4 concentrations (0.6 l/min, 150°C, 600 ppm C_2H_4).

perature of 20°C. Upon the discharge application (vertical dashed line in the figure) both the concentration of NO and NOx decreased. The removal efficiency of NO was nearly 80%. By the addition of C_2H_4 the removal efficiency decreased, which is an opposite tendency to what is usually observed when using dielectric barrier discharges or pulsed discharges for NO removal.

Figures 9 and 10 presents the results obtained at the temperature of 150°C for two different concentrations of C_2H_4 - 300 and 600 ppm. The higher concentration of C_2H_4 slightly improved the efficiency of NO removal. However, compared to the results obtained at room temperature NO removal efficiency was significantly smaller. Overall, the best NO removal efficiency was observed at the temperature 20°C without the addition of C_2H_4.

4. Conclusions

The plasma-chemical efficiency of microdischarges inside porous ceramics was examined by means of the generation of ozone and the removal of nitrogen oxides in various conditions. The effects of initial gas mixture composition and other parameters were evaluated. The experiments showed the microdischarges are stable sources of atmospheric pressure plasma and can be used for gas treatment. If the ceramics were loaded with catalysts, the efficiency of such hybrid plasma-catalyst system is expected to increase further.

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