Emission spectrometry of microplasma for NOx removal process

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Abstract: Emission spectra of the microplasma discharge in N₂, NO and O₂ gas mixture was analyzed. The diagnosis of microplasma discharge was performed in order to understand the processes of NOx removal. An experimental Marx Generator was used as a pulsed power supply. Emission spectra for N₂ gas show N₂ second positive band system (N₂ SPS) and N₂ first negative band system (N₂ FNS). 1000 ppm NO in N₂ emission spectra show N₂ SPS, N₂ FNS and NO γ band. 950 ppm NO and 5% O₂ in N₂ gas emission spectrum shows N₂ SPS and N₂ FNS with lower intensities comparing with microplasma discharge in N₂ gas. Emission signal of the photomultiplier shows short lifetime emission signal for N₂ SPS of 337.1 nm. Lifetime of emission signal is longer (2 µs) than that of N₂ SPS due to the excitation by the collision of N₂ metastable states.

Temperature measurements are also carried out, which show the temperatures are specific for non-equilibrium plasmas.

Keywords: Microplasma, Marx generator, dielectric barrier discharge, emission spectrometry.

1. Introduction

Microplasma can be found in many applications. In the last years, the technology was used also for NOx removal. Although there is an interest for application driven research, microplasma phenomena are not fully understood. Emission spectrometry is one of the methods to analyze plasma process [1], [2].

The aim of this paper is to analyze the emission spectrum of the microplasma in a simulated exhaust gas.

2. Experimental setup

The experimental setup is shown in Fig. 1. Emission spectra were measured by an ICCD camera (Ryoushi-giken, SMCP–ICCD 1024 HAM-NDS/UV), a spectrometer (Ryoushi-giken, VIS 351) and by a photomultiplier tube (Hamamatsu Photonics, R3896). A pulse generator (Tektronix, AFG 3021B) was used to trigger the Marx Generator consisted of semiconductor switches and the ICCD camera. Obtained data were transferred to a computer.

The discharge voltage and the corresponding discharge current were measured by a high voltage probe (Tektronix, P6015), an AC current transformer (Tektronix, P6021) and a digital oscilloscope (Tektronix, TDS 2014B).

Compositions of simulated gases used in experiments were N₂, NO 1000 ppm in N₂, and NO 950 ppm, O₂ 5% in N₂. Experiments were carried out in atmospheric pressure and the gas flow rate was set at 2 L/min. Concentration of NO and NOx were measured by a NOx analyzer (Shimadzu, NOA-7000).

A Marx generator with 4 stages MOSFET switches shown in Fig. 2, was developed to use as high voltage supply to microplasma electrodes. It has an output voltage up to ~1.8 kV peak (negative pulse, rise time 80 ns, pulse width 500 ns ~ 1 µs, frequency 1 kHz ~ 24 kHz). Trigger signal for ICCD camera was set at 1 µs (Fig. 3).

Capacitors are charged in parallel connection at a given voltage V (500 V in this case). When the MOSFET switches are closed, capacitors are discharging in series connection thus results an output voltage 4V (2 kV in this case).
3. About microplasma

Microplasma electrodes are metallic electrodes covered with a dielectric layer (Fig. 4). Due to small discharge gaps (0–100 μm) and to the assumed specific dielectric constant of \( \varepsilon_r = 10^4 \), a high intensity electric field (\( 10^7 - 10^8 \) V/m) could be obtained with relatively low discharge voltages around 1 kV. Electrode size was 20 mm versus 40 mm. Electrode has holes to flow for gas treatment, which diameter is Ø 2mm and its aperture ratio of 36%. Discharge gap was set at 50 μm in our study.

Emission spectra of microplasma discharge was observed from the side part of electrodes. Thus the observed microplasma area had 40 mm versus 50 μm.

4. Emission spectrum of microplasma

Emission spectrum of the microplasma discharge in \( \text{N}_2 \) show peaks of \( \text{N}_2 \) second positive band system (\( \text{N}_2 \) SPS) and \( \text{N}_2 \) first negative band system (\( \text{N}_2 \) FNS) (Fig. 5).

This spectrum was obtained at discharge voltage 1.4 kV, rise time of 80 ns, pulse width of 500 ns, and discharge frequency of 1 kHz.

**Table 1. List of detected systems and peaks for the microplasma in \( \text{N}_2 \) gas.**

<table>
<thead>
<tr>
<th>Species (system)</th>
<th>Transition</th>
<th>Peak Position (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 ) SPS</td>
<td>( \text{C}^3\Pi \rightarrow \text{B}^3\Pi )</td>
<td>315; 337.1; 357.7; 375.5; 380.5; 400</td>
</tr>
<tr>
<td>( \text{N}_2^+ ) FNS</td>
<td>( \text{B}^2\Sigma_g^+ \rightarrow \text{X}^2\Sigma_g^- )</td>
<td>427.8</td>
</tr>
</tbody>
</table>

These elementary processes describe the radiation kinetics for the second positive band system of nitrogen, wavelength 337.1 nm, at atmospheric pressure [3]:

Excitation of nitrogen molecules in the ground state by direct electron impact:

\[
e + \text{N}_2(X^2\Sigma_g^+) \rightarrow \text{N}_2(C^3\Pi_u) + \text{e} \quad (\Delta E=11\text{eV})
\]
Spontaneous radiation of formed excited state of nitrogen:
\[ \text{N}_2(C^3\pi_u)\gamma \rightarrow \text{N}_2(B^3\pi_g) + \nu \quad (\tau_c = 40 \text{ ns}) \]  

(2)

As shown in Fig. 6 and according with reaction (2), the lifetime of photomultiplier signal of N\(_2\) SPS was about 40 ns.

Emission spectrum of the microplasma discharge for NO 1000 ppm in N\(_2\) show peaks of NO \(\gamma\) band, N\(_2\) SPS, and N\(_2\) FNS (Fig. 7).

List of detected peaks is presented in Table 2. NO \(\gamma\) band is excited by the collision of N\(_2\) metastable states [1], [4]:
\[ \text{N}_2(A) + \text{NO}(X) \rightarrow \text{N}_2(X) + \text{NO}(A) \]  

(3)

NO(A) \rightarrow NO(X) + \nu \quad (\text{NO } \gamma \text{ band}) \]  

(4)

According to reactions (3) and (4), process of light emission of NO \(\gamma\) band (260.1 nm) is longer, thus the lifetime of photomultiplier signal for NO \(\gamma\) band was about 2 \(\mu\)s (Fig. 8).

Fig. 8 shows waveforms of discharge voltage discharge, current and emission signal of NO \(\gamma\) band.

Table 2. List of detected systems and peaks for the microplasma in 1000 ppm NO in N\(_2\) as balance.

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<th>Species (system)</th>
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<td>N(_2) second positive</td>
<td>C(^4\Pi)→B(^3\Pi)</td>
<td>315; 337; 337.7; 375.5; 380.5; 400</td>
</tr>
<tr>
<td>N(_2)(^+) first negative</td>
<td>B(^2\Sigma_u^+)→X(^2\Sigma_g^+)</td>
<td>427.8</td>
</tr>
<tr>
<td>NO (\gamma) band</td>
<td>A(^2\Sigma_u^+)→X(^2\Pi)</td>
<td>226.9; 237; 247.9; 259.6; 260.1; 271.5; 285</td>
</tr>
</tbody>
</table>

Emission spectrum of the microplasma discharge in NO 950 ppm, O\(_2\) 5% and N\(_2\) balance is presented in Fig. 9, which shows peaks of N\(_2\) SPS and N\(_2\) FNS (Table 3). Intensities of peaks are lower than those measured for nitrogen, due to the quenching effect of O\(_2\) [5], [6]. Weak peaks were also measured for the NO \(\gamma\) band. That could be explained by presence of O\(_2\) molecules to oxidize to remove NO molecules [7].

Fig. 9 Emission spectrum for NO 950 ppm and O\(_2\) 5% in N\(_2\) balance.

Fig. 10 shows waveforms of discharge voltage, discharge current, and emission signal of N\(_2\) SPS (wavelength of 337.1 nm) in NO 950 ppm, O\(_2\) 5% in N\(_2\) balance.

Fig. 10 Waveforms of discharge voltage, discharge current and emission signal of microplasma (N\(_2\) SPS 337.1 nm) in NO 950 ppm, O\(_2\) 5%, N\(_2\) balance.
Emission intensity of N₂ SPS in Fig. 10 is lower than in N₂ gas (Fig. 6). These are also explained by quenching of O₂ molecules.

Spectra of N₂ SPS, was used for evaluation of plasma temperature to investigate the characteristics of microplasma. We used SPECAIR software [8], [9], for spectral simulation by fitting the experimental data with simulated ones (Fig. 11). Calculated data, electronic temperature Te of 8200 K, vibrational Tv of 3100 K and rotational temperature Tr of 360 K, are presented in Table 4. These temperatures are specific for the non-equilibrium plasmas [2].

Table 3. List of detected systems and peaks for the microplasma in N₂, NO and O₂ gas mixture.

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<th>Species (system)</th>
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<tr>
<td>N₂⁺ first negative</td>
<td>B^3Σ⁺→X^3Σ⁺</td>
<td>427.8</td>
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</table>

5. Conclusion

Diagnosis of microplasma are carried out by using a Marx generator, an ICCD camera, and a photomultiplier. Estimation of electron temperature, rotational temperature, are also carried out to investigate the characteristics of microplasma. The experiments and calculation data conclude shown bellow:

1) Analysis of emission spectrum shows N₂ SPS, N₂ FNS for the microplasma discharge in N₂ gas.
2) NO 1000 ppm in N₂ emission spectrum show presence of N₂ SPS, N₂ FNS and NO γ band.
3) Emission spectrum of NO 950 ppm and O₂ 5% in N₂ show N₂ SPS, N₂ FNS, with lower intensities comparing with emission spectrum of microplasma discharge in N₂.
4) Lifetime of emission signal measured by a photomultiplier tube corresponding to wavelength 337.1 nm of N₂ SPS was about 40 ns. Lifetime of emission signal of NO γ band was about 2 µs, which has relatively long lifetime by excitation of N₂ metastable states.
5) Temperature estimation of microplasma discharge show high electron and vibrational temperatures and low rotational and translational temperatures. These temperatures are specific for non-equilibrium plasmas.

By analyzing the spectrum of the microplasma discharge could be helpful to understand NOx removal process.

References