Nitrogen Oxidation by Atmospheric Plasmas

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Abstract: Plasma conversion of nitrogen is an efficient reaction. This can be enhanced by catalysts combined with non-thermal plasmas (NTP) to achieve efficient chemical reactions. However, the large number of active species and complicated elementary processes make qumakeative analysis difficult. In order to analyze the elementary process during plasma conversion and catalysis, a parallel-plate atmospheric pressure RF plasma jet with MnO_2 catalyst is used to generate a homogenous discharge. N_2/O_2 admixed to helium is fed into the plasma. The product nitrogen oxide is measured by in situ Fourier-transform infrared spectroscopy (FTIR) combined with a multi-pass cell. Preliminary results show that the densities follow the sequence $NO_2 > N_2O > NO$. The maximum conversion of NO is found at 70% $N_2/(N_2+O_2)$ admixture.

Keywords: plasma catalysis, rf plasmas, nitrogen oxidation.

1. Introduction

The study of plasma dischargdischargeing nitrogen and oxygen has been studied for many motivated by their broad range of applications in different fields. The formation of NO is especially interesting since it can be used for the determination of gas temperature [1], analysis of plasma surface interaction [2], or biological processes such as tissue/wound treatment [3]. Non-thermal plasma (NTP), such as microwave, pulsed-power gliding-arc, and glow discharge is used to observe the densities of NO concentrations and other intermediates. The elementary process is that the O and N radicals react with N_2 and O_2, respectively and produce NO, which is called the Zeldovich mechanism. By combining radio frequency [4], microwave [5], or dielectric barrier discharge plasma [6] with heterogeneous catalysts, a considerable yield of NO that exceeds that of individual components, is found. The gas temperature of NTP is much lower than that of thermal N_2 oxidation. In order to increase the production of NO, the mechanisms in a reactor optimized for plasma catalysis must be investigated. However, there exist difficulties because of the abundant chemical reactions involving ground and excited neutrals, radicals, ions, and electrons.

In our study, the plasma catalysis surface process during nitrogen oxidation is analyzed. The 13.56 MHz RF plasma is used to generate a homogenous discharge and MnO_2 is the catalyst. A plug flow scheme is used to feed N_2/O_2 admixed to helium. The absolute density of nitrogen oxidation production is measured by *in situ* Fourier-transform infrared spectroscopy (FTIR) combined with a multi-pass cell. The absorption spectrum of products is fitted by the algorithm.

2. Experiment

The sketch of the experimental setup is shown in figure 1. Two copper electrodes, with a dielectric barrier of 1 mm thin glass with MnO_2 catalyst, are inserted into a steel plasma chamber. The plasma volume is 26 mm × 13 mm × 1 mm inside a gas channel with 54 mm × 14 mm × 1 mm. An oil cooling system is used to fix the temperature to 20℃. The gas with varying admixture is fed by mass flow controller (MFC). The exhaust from the plasma is analyzed with FTIR (Vertex 70v, Bruker Corporation). A multi-pass cell is used to enhance the transmittance signal by increasing the path length up to 7.2 m and the temperature is 300 K. Based on the Beer–Lambert law and the data in HiTRAN database [7], the density of products is calculated from fitting the transmittance spectrum using a python script [8].

A 13.56 MHz rf generator is applied to one electrode via a matching network, the other electrode is grounded. The output voltage and current of the plasma are measured by a V-I probe. The absorbed power P in the plasma can be calculated by measuring the phase shift ϕ between voltage U and current I.

$$P = UI\cos\phi \quad (1)$$

By comparing the V-I values with and without plasma, the actual absorbed plasma power can be calculated.

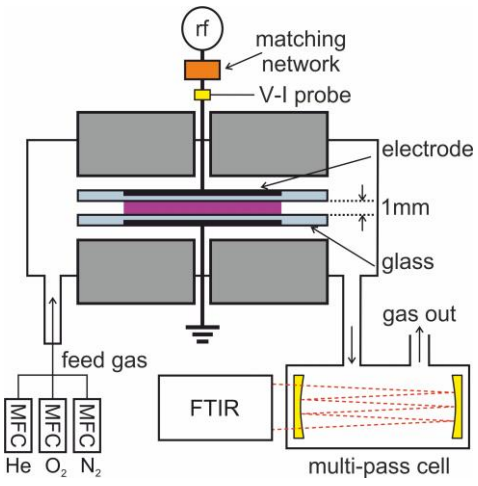

Figure 1. Experimental setup.

3. Results

Figure 2 shows the NO absorption spectrum for an admixture of 0.8% gas mixture to helium with the ratio of N_2/O_2 = 1:1 and 50 W generator power. The species are

assumed to be in equilibrium at 300 K inside the multipass cell. Figure 3 shows the densities of NO, N_2O and NO_2 for an admixture of 0.8% gas mixture to helium at different ratios of N_2/O_2 and 50W generator power. Under the high fraction of N_2, more NO is produced with less NO_2 and N_2O. The absorbed power in the plasma (black dots in figure 3) decreases with the increase of $N_2 : O_2$ ratio. Table 1 shows the relevant chemical reactions involving N_xO_y production. The NO production is apparently limited by the high N_2 dissociation barrier, which leads to a low conversion rate.

Table 1. Reactions involving N_xO_y during discharge

Reaction	
$He^+ + N_2 \rightarrow N_2^+ + He$	(R1)
$He^+ + O_2 \rightarrow O_2^+ + He$	(R2)
$He^+ + NO \rightarrow NO^+ + He$	(R3)
$N_2^+ + e^- \rightarrow 2N$	(R4)
$O_2^+ + e^- \rightarrow 2O$	(R5)
$NO^+ + e^- \rightarrow N + O$	(R6)
$N + NO \rightarrow O + N_2$	(R7)
$N + O_2 \rightarrow O + NO$	(R8)
$N + NO_2 \rightarrow 2O + N_2$	(R9)
$N + NO_2 \rightarrow O + N_2O$	(R10)
$N + NO_2 \rightarrow N_2 + O_2$	(R11)
$N + NO_2 \rightarrow 2NO$	(R12)
$O + N_2O \rightarrow N_2 + O_2$	(R13)
$O + N_2O \rightarrow 2NO$	(R14)
$O + NO_2 \rightarrow NO + O_2$	(R15)
$NO + O_2 \rightarrow O + NO_2$	(R16)
$NO + N_2O \rightarrow N_2 + NO_2$	(R17)

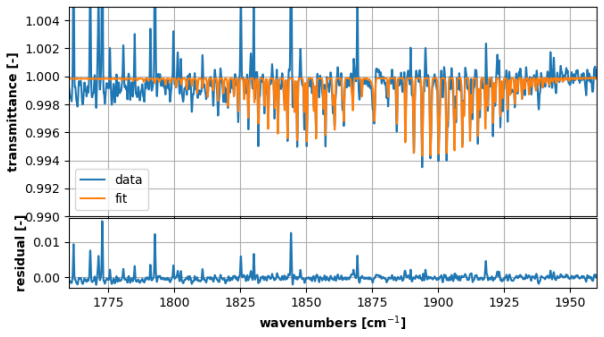

Figure 2. Fitting of the NO infrared transmission spectrum

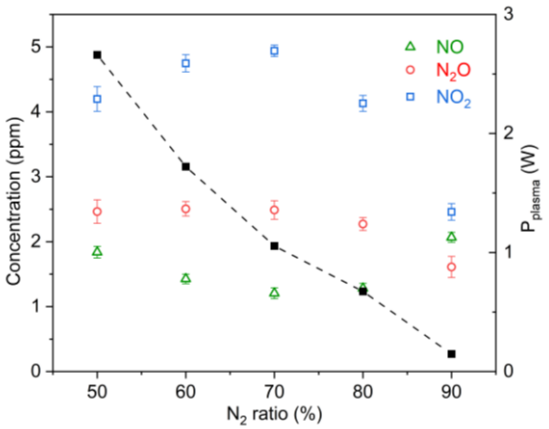

Figure 3. Densities of NO, N_2O and NO_2 under different gas mixtures

4. Outlook

By adjusting the flow rate, generator power, the ratio of N_2/O_2 and the type of catalyst, the dependence of different species production on individual parameters can be analyzed. The production of NO is highly related to the excited species, such as $N_2\left(C^3\Pi_u\right)$, $N_2^+\left(B^2\Sigma_u^+\right)$, and $O\left(3p^5P\right)$. By using optical emission spectra (OES), it is feasible to measure those excited species under those parameters and analyze the chemical mechanisms.

5. References

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