In-situ tracking of key species in nitrogen fixation process by a wam air glow discharge through multiple laser spectroscopies

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Abstract: The fixation of atmospheric nitrogen into valuable compounds through reactive plasma processes attract intense interests due to its easy operation and compatibility with distributed renewable energy sources. In this work, several laser spectroscopies were applied to study the nitrogen fixation process in a DC-driven warm air glow-discharge. The spatial distributions of gas temperature, densities of NO, N, and O were obtained and compared. The behind mechanisms of observed spatial patterns of these species were discussed and analized.

Keywords: Nitrogen fixation, laser spectroscopy, air glow-discharge, spatial distributions.

1. Introduction

Considering the large demand for fertilizers and serious environmental issues like global warming, the need of developing efficient and sustainable nitrogen fixation (NF) methods is imperative. The NF process assisted by non-thermal plasmas (NTPs) has shown distinct advantages in easy operation under moderate conditions, compatible with renewable sources like wind or solar energy without emission of greenhouse gases. In recent years, it has been considered as one of the most prospective NF options in the industry and attracted wide attention from the fields of physics, chemistry and energy. However, the practical energy efficiency of NF by NTPs is still way less than the theoretical one, which was estimated as 2.5 times higher than that of the H-B process [1], dominantly hindered by the unknown behind mechanisms. Therefore, it is significantly important to pour efforts to the fundamentals in the plasma fixation of nitrogen to raise its energy efficiency and selectivity, through approaches of advanced in-situ diagnostics and simulation modelling.

In this work [2], we focus on one of the typical NF plasma sources called pin-to-pin DC-driven air glow discharge at atmospheric pressure. Various advanced laser diagnostics are applied to in-situ probe key physicochemical properties including gas temperature, atomic N and O, and NO molecule in the discharge column. Quantitative spatial distributions of interested key species are obtained under different discharge conditions.

2. Experimental setup and spectroscopic methods

The schematic of the experimental setup is presented in Fig. 1. The glow-like discharge was ignited between two tungsten pin electrodes with the gap distance of 5 mm. The anode (d = 1.5 mm) was powered by a DC high - voltage power supply (HAPS06-6000, DPAI Ltd., China) through a resistor (1 kW, 50 kΩ) and the cathode (d = 5 mm) was grounded. The electrodes were fixed coaxially inside a cross-like borosilicate glass tube by two aluminum holders. The transversal and longitudinal parts of the cross-like tube have inner diameters of 40 mm and 12 mm, and lengths of 120 mm and 56 mm, respectively. Two Brewster windows and one view window, all made of fused quartz, were set at two sides and front-view of the borosilicate glass tube, for laser beam transmission and fluorescence collection, respectively. Compressed air under the pressure of 1 atm, was used as the working gas flowing from the anode towards the cathode along the axial z-axis.

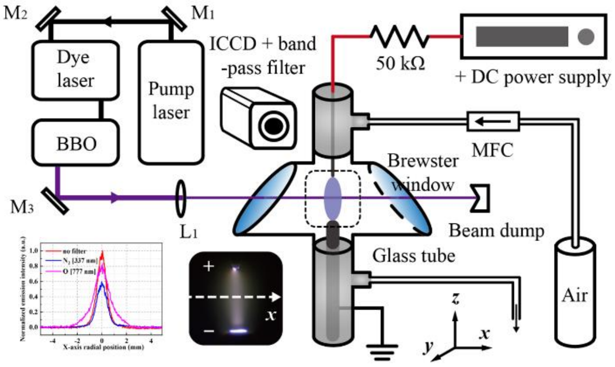

Fig. 1. Schematic diagram of the laser diagnostic system and the studied warm pin-to-pin air glow discharge for nitrogen fixation.

Different laser spectroscopic methods with detailed specifications, as listed in Table 1, were applied to study the NF process in the gap-middle of the air glow-discharge.

Table 1. The spectroscopic methods used in this work.

Method	Parameters / species	Detailed specifications
Rayleigh scattering	T_g	532 nm laser with 78µm beam waist.
QCL-AS & LIF	NO	Absorption spectroscopy by Mid-infrared QCL operating at 5.2 µm, through the rotational-vibrational transition R(6.5) between the vibrational levels ($X_{0.5}, v = 0$) → ($X_{0.5}, v = 1$) of $NO(X^2\Pi)$.
TALIF	N	Laser beam at 206.65 nm for two-photon excitation and 744 nm for fluorescence.
TALIF	O	Laser beam at 226 nm for two-photon excitation and 844 nm for fluorescence.
TALIF	Kr	Laser beam at 204.13 nm for two-photon excitation and 826.3 nm for fluorescence, and for calibration of TALIF of N.
FPF-TALIF	O_3	Applied a 266 nm laser for full photolysis of O_3, and a 226 nm laser for TALIF of O fragment, for self-calibration [3].

3. Results and discussions

The radial profiles of determined gas temperature T_g, and species including O, N, and NO are presented in Fig. 2-4, under different discharge currents and air flow rates. As can be seen, the results give a higher T_g peak (from 2000 K to 3000 K) when the discharge current increases from 25 mA to 45 mA. In addition, as the air flow rate rises to 10 slm, the T_g distribution over 1000 K level shrinks distinctly. Similar variation trends of spatial patterns were observed for these atomic and molecular species of interest. Similar to that of T_g, with the peak in the discharge center were observed for the atomic O and N species. It needs to point out that the maximum level of atomic N density (~ 1.5×10^{20} m^{-3}) is around two orders of magnitude lower than that of the O atom or NO molecule (10^{22} m^{-3}).

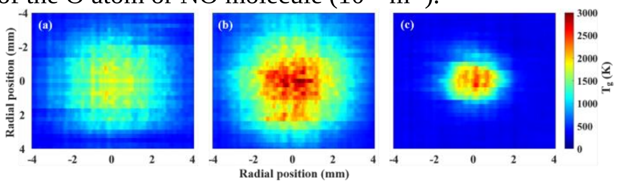

Fig. 2. Spatial distributions of T_g under (a) 25 mA, 1 slm (b) 45 mA, 1 slm (c) 45 mA, 10 slm.

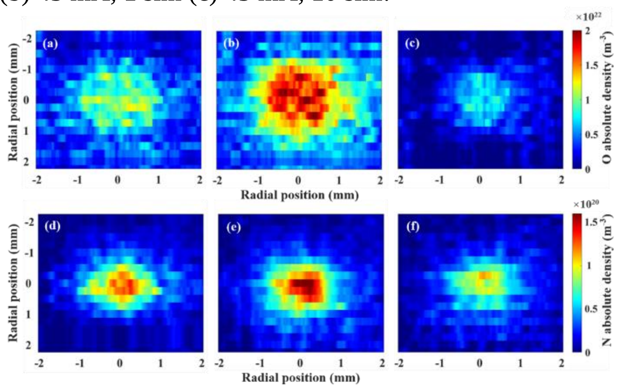

Fig. 3. 2D radial maps of atomic O and N densities under (a,d) 25 mA, 1 slm (b,e) 45 mA, 1 slm (c,f) 45 mA, 10 slm.

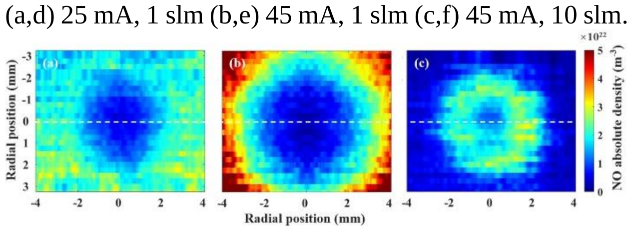

Fig. 4. 2D radial maps of NO density under (a) 25 mA, 1 slm (b) 45 mA, 1 slm (c) 45 mA, 10 slm.

It is to observe a hollow distribution of NO production with low density in the center but high density in the edge of the studied air glow plasma. It is of a similar density level to that of O atom, which indicates that in the hot discharge core the dominant NO formation is depending strongly on the atomic O through the first Zel'dovich reaction.

To figure out the behind mechanisms of the hollow-like NO distribution in the air glow discharge, a steady-state 1D kinetic rate-equation modelling was built based on the convection–diffusion equation. It demonstrates that the central hollow pattern of NO is mainly induced by the effects of species transport because of radial diffusion due to the steep spatial gradient of gas temperature in the discharge column. Furthermore, a similar hollow patterns of NO_2 was predicted in the discharge radial plane in the gap-middle. And, it implies that the reverse reaction by atomic N plays an important role in the loss of NO in the central hot discharge core.

4. Conclusions

The fixation of atmospheric nitrogen into oxynitride by non-thermal plasma has drawn intense interest both in research and practical domain. This work quantized and visualized the gas temperature, absolute densities of atomic O, N and molecular NO in a DC air glow discharge by means of various advanced laser diagnostics. The results indicates the essential role of atomic O in the formation process of NO through the first Zel'dovich reaction. On the contrary, the atomic N is proved to lead to a negative effect because of its dominant fast reverse conversion of NO. And, it demonstrates that the nitrogen fixation in the air warm glow discharge can be improved, for example by selectively enhancing the energy transfer to the process of atomic O production and suppressing the reverse reaction by atomic N, and improving the flow condition inside the reactor to take away NO (and NO_2) immediately after formation from the hot discharge core.

5. References

[1] B. Patil, Plasma Chem. Plasma Process. 36, 1 (2015).
[2] Z. Shu, Plasma Sources Sci. Technol. 32, 2 (2023).
[3] Z. Shu, Plasma Sources Sci. Technol. 30, 5 (2021).