Characterization of an atmospheric N_2-O_2 Gliding Arc Discharge by FTIR and LIF
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Abstract: Non thermal plasmas are currently being studied as a cleaner alternative for nitrogen fixation in fertilizer industries. A gliding arc plasmatron (GAP) operated at atmospheric pressure with N_2 and O_2 (1:1) and 120-300 mA current has been studied . FTIR of NO and NO_2 (mention the IR bands) is used to understand the yield control with various plasma parameters where LIF of NO (226.3 nm excitation 247 nm fluorescence) has been used to study the NO density in the arc and near arc regions.

Keywords: Atmospheric Plasma, Gliding Arc, Nitrogen Fixation, Plasma Spectroscopy, Laser Induced Fluorescence, FTIR

1. Introduction

Nitrogen is an abundant element which is fundamental for any living organism but in its most abundant form, molecular N_2, requires a high dissociation energy to break its triple bond. The conversion of N_2 into nitrogen compounds like nitrogen oxides (NO, NO_2) and ammonia (NH_3) is known as nitrogen fixation. Such process has become crucial as the fertilizers produced with industrial nitrogen fixation are estimated to currently feed around 50% of the world population [1]. In such framework the Haber-Bosch (HB) is the dominant process for industrial nitrogen fixation and, despite its energy efficiency it is responsible for approximately 1% of the CO_2 emissions in the 2019 [2] and due to the high temperatures (650 K – 750 K) and the high pressures (100 bars) needed [3] large and centralized facilities are required to for the production costs to be competitive [4]. Plasma based nitrogen fixation has been gaining interest due to a lower theoretical energy cost (0.35 MJ/mol N vs 0.48 MJ/mol N for the HB), the lack of CO_2 emissions and the overall better compatibility with renewable and more intermittent energy sources [3]. Specifically, atmospheric non thermal plasmas are particularly promising as they would allow a relatively easy upscaling and industrial implementation. Among them, interesting results have been achieved with the GAP, with the current best performance, known to the author, of 2.5 MJ/mol N and a NO_x yield of 5.5% without catalysts [5]. This work focuses on the characterization of a GAP operating at atmospheric pressure with a N_2-O_2 gas mixture by means of spectroscopy. In particular, LIF has been used to study the spatial profile of the NO and atomic O concentrations and FTIR for the characterization of the NO and NO_2 yields of the exhaust gas mixture.

2. Setup and Methods

In the GAP described in this work, the arc is generated between two electrodes which are represented in figure 1. The cathode is a hollow cylinder open towards the other electrode with an inner section of 17.5 mm of diameter, while the anode is a L-shaped toroid with an inner cavity of 14.2 mm of diameter. A gas mixture of 5 slm of N_2 and 5 slm of O_2 is tangentially injected between the electrodes.

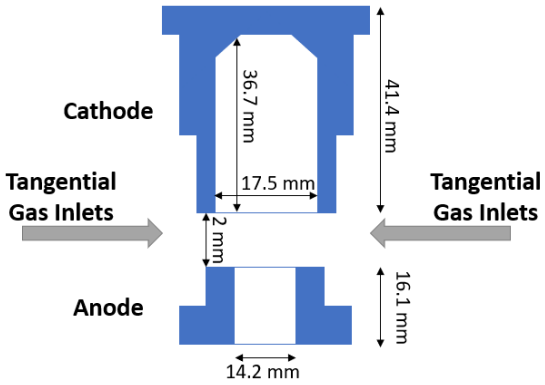

Fig. 1. Schematics of the GAP electrodes described in this work.

Such geometry allows the gas to operate in the reverse vortex flow (RVF) regime. This ensures a better heat insulation and a higher fraction of the gas flowing through the arc [6,7]. The cathode is connected through a series of resistances (fixed at 4 kΩ) to a DC power supply (Technix SR12KV-15KW). The power supply can provide voltages and currents up to 12 kV and 1.25 A with a negative polarity. The arc elongates in a quartz tube where the plasma generated is visible, allowing optical spectrometry to be performed in the discharge and post-discharge region. A pump-probe SIRAH dye laser (pumped by the third harmonics of a ND-YAG laser at 355 nm) with a coumarin 450 dye was used to generate a wavelength of 452.8 nm and frequency doubled by a BBO crystal (226.4 nm X, v=0→A NO,v'=0). The incidence position of the beam has been adjusted to obtain a spatially resolved evolution of the NO density in the post discharge region. The fluorescence emission was collected with an Andor iStar iccd camera equipped with a 248 nm filter with a 10 nm FWHM (A,v=0→X,v"=2). Both the electrodes and the quartz tube are cooled using an external fan. The GAP exhaust is then connected to a gas cell with an optical path of 12.5 cm

equipped with silicon windows where the output gas composition is sampled with a Vertex 80v FTIR (Bruker) spectrometer. The internal RT-DLaTGS (Deuterated Lanthanum α-alanine-doped Triglycine Sulphate) detector in the mid-IR region is used to measure the sample gas absorbance. A 2 mm aperture and a resolution of 1 cm^{-1} are used. A brief representation of the setup is shown in figure 2.

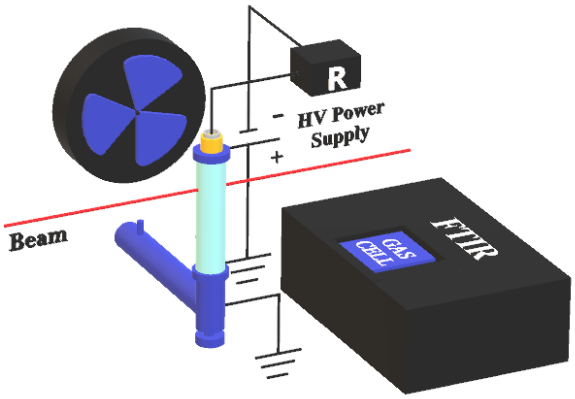

Fig. 2. Schematics of the experimental setup, the path of the laser beam and the position of the FTIR are highlighted.

Figures 3 and 4 show two examples of the beam at 1 cm and 3cm from the anode respectively. The fluorescence signal has been integrated and the NO density obtained has been adjusted according to the expected temperature of the gas in the probed area. The choice temperatures is based on the simulation of a similar setup under analogous conditions [8].

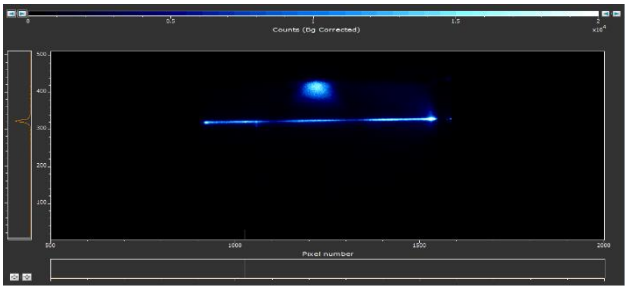

Fig. 3. ICCD camera imaging with a 248 nm filter of the plasma. The laser beam distance from the anode is set at 1.0 cm.

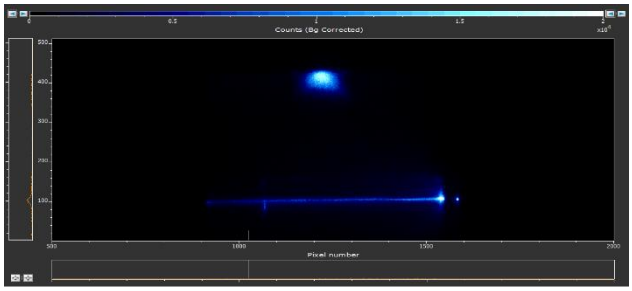

Fig. 4. ICCD camera imaging with a 248 nm filter of the plasma. The laser beam distance from the anode is set at 3 cm.

3. Results and Discussion

As the plasma vibrationally excites N_2 and O_2 molecules the production of reactive N and O atoms through electron impact excitation is favoured. The production of NO is then possible through the following reactions known as the Zeldovich process: $N_2+O \rightarrow NO+O$ and $N+O_2 \rightarrow NO+N$. In a GAP the initially produced NO is then known to either dissociate through the back reaction or to convert into NO_2 according to the following reactions: $NO+O(+M) \rightarrow NO_2(+M)$ [9].

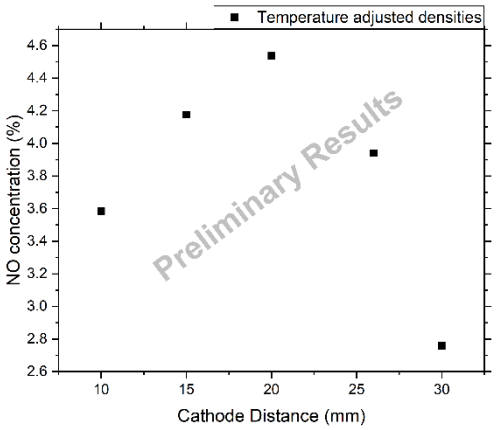

Fig. 5. NO concentration in the gas mixture at different distances from the anode.

Figure 5 shows how the NO concentration evolves as a function of the distance from the anodes. The NO, mostly generated in the close proximity of the plasma, quickly decays due to either conversion into NO_2 or through inverse Zeldovich reactions. Combining this information with a NO_x yield of 2.08% at the exhaust measured with the FTIR, it is safe to assume that more than half of the NO observed is globally lost as it reconverts into N_2 and O_2.

4. Conclusions

This novel experimental approach allows to estimate the inefficiencies of nitrogen fixation in an atmospheric GAP and to improve the understanding of the process by providing crucial information on the evolution of the gas composition. Further research should tackle the inhibition of the Zeldovich back reactions as it could drastically lower the energy cost for for the process and, thus, make plasma nitrogen fixation a more competitive industrial alternative.

5. Acknowledgements

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6. References

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