Pathways in Plasma-Catalytic NH_3 Synthesis: Bulk and Surface Contributions in Low-Pressure N_2/H_2 Glow Discharges

M Budde(*)[1], F Santos[2], A R P Gonçalves[3], S S Baghel[3], P Pereira[3], J-P Booth[1], L Marques[4], N Pinhão[3], C D Pintassilgo[3,5], L L Alves[3], and O Guaitella[1]

[1] *LPP, CNRS, École Polytechnique, Sorbonne Université, Université Paris-Saclay, IP-Paris, 91128 Palaiseau, France*

[2] *EPABE, Faculty of Engineering, University of Porto, 4200-465 Porto, Portugal*

[3] *Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Portugal*

[4] *Centro de Física das Universidades do Minho e do Porto, Universidade do Minho, Braga, Portugal*

[5] *Faculdade de Engenharia, Universidade do Porto, Portugal*

(*) maik.budde@lpp.polytechnique.fr

The synthesis of ammonia (NH_3) in low-temperature plasma is gaining traction due to its potential for localised energy-efficient gas conversion, where the established large-scale Haber-Bosch process is not feasible. While some research efforts focus on maximising conversion yields, fundamental studies remain essential due to the intricate interplay between plasma and surfaces, which are widely recognized as the primary sites for NH_3 formation.

This study presents results in nitrogen (N_2) – hydrogen (H_2) plasmas in simple low-pressure DC glow discharges, a system previously validated for chemical kinetic model development [1]. Through optical emission spectroscopy and ex situ infrared absorption spectroscopy, the effect of H_2 admixture and other discharge conditions is explored.

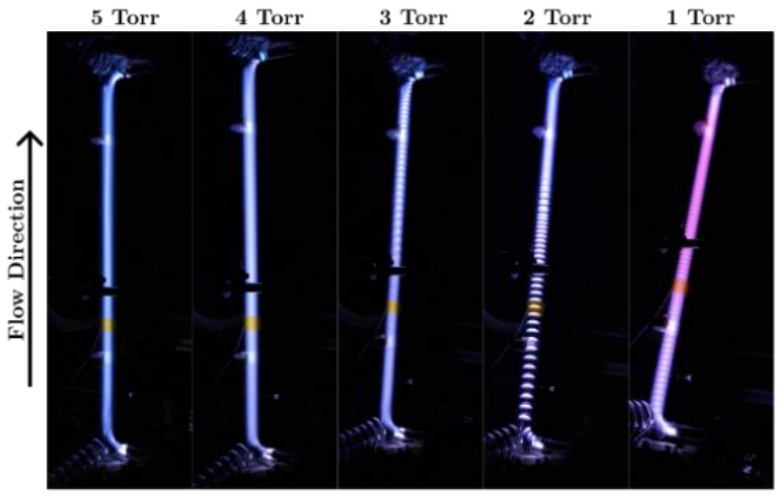

Fig. 1: Pure H_2 glow discharge at different pressures.

Discharges in pure H_2 show greater spatial inhomogeneities and gradients (Fig. 1), compared to heavier gases. NH_3 production depends strongly on the electrode state, particularly the cathode. Notably, the data suggest two mechanisms for NH_3 formation: a bulk plasma pathway, which is less sensitive to reactor conditions, and a surface-mediated pathway, whose influence is more pronounced (Fig. 2) [2].

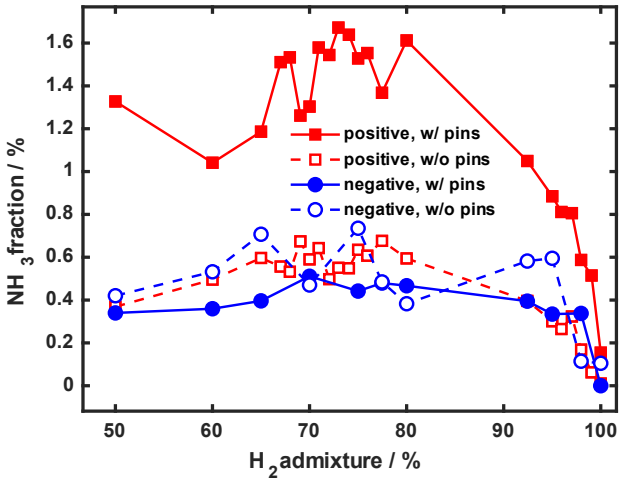

Fig. 2: NH_3 production depending on the input fraction of H_2 for different reactor configurations: with and without tungsten pins to measure the voltage drop along the plasma.

Acknowledgements:

This work has been supported by Agence Nationale de la Recherche, France through the financial support of the PLASINTER project under the project ANR-23-CE50-0012 and by FCT - Fundação para a Ciência e Tecnologia, I.P., under projects
UID/50010/2025 (https://doi.org/10.54499/UID/50010/2025),
UID/PRR/50010/2025 (https://doi.org/10.54499/UID/PRR/50010/2025),
UID/PRR2/50010/2025 (https://doi.org/10.54499/UID/PRR2/50010/2025),
LA/P/0061/2020 (https://doi.org/10.54499/LA/P/0061/2020) and
2022.04128.PTDC (doi.org/10.54499/2022.04128.PTDC).

References:

[1] Liu et al., *J. CO_2 Util.* **97** (2025) 103128

[2] Yin and Venugopalan, *Plasma Chem. Plasma Process.* **3(3)** (1983) 343-350