Plasma-surface coupled modelling of ammonia production in DC discharges

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The search for a cleaner and more energy-efficient process for the synthesis of ammonia (NH_3) is a global concern, to which low-temperature plasma technology has emerged as a potential solution [1]. In this context, understanding the main kinetic paths leading to the plasma-assisted synthesis of NH_3 has topical interest, not only for the large-scale production of fertilizers at low cost, but also for the mitigation of ammonia generation in fusion machines. It is currently believed that plasma-surface interactions could be the dominant mechanisms for this process [2]. In this work we will propose, improve and validate kinetic models for N_2-H_2 plasmas, including the interplay between the volume and surface reactions.

We present the first steps of our research program on nitrogen-hydrogen plasmas under different surface conditions, leveraging complementary modelling and diagnostics analyses. We model cylindrical DC glow discharges (23 cm long and 2 cm inner diameter) with borosilicate glass walls [3], produced in N_2-H_2 gas mixtures with low H_2 concentrations (< 5%), at 5 sccm continuous flow, p = 50-500 Pa pressures and I_{dc} = 10-40 mA discharge currents.

The experimental measurements include: the reduced electric field E/N (where E is the electric field and N is the gas density), using the potential difference between two tungsten Langmuir probes immersed in the plasma; the electron density n_e, using microwave reflectometry with a hairpin resonator; the partial pressure of ammonia (FTIR absorption) and the relative concentrations of the main ion species, using mass spectrometry.

Simulations use the coupled solution of the electron Boltzmann equation (written under the two-term approximation [4]), and the chemical rate-balance equations of a kinetic scheme for nitrogen-hydrogen plasmas [5], which considers the main heavy species N_2(X, v=0-44), H_2(X, v=0-14), NH_3, N(^{4}S), H(^{1}S), in addition to: 13 electronic excited states (6 for N_2, 2 for N and 5 for H); positive ions N^+, N_2^+, N_3^+, N_4^+, H^+, H_2^+, H_3^+, N_2H^+, NH^+, NH_2^+, NH_3^+ and NH_4^+; negative ions H^- and NH_2^-; surface species H(S,F), N(S,F), NH(S), NH_2(S), (physically (F) or chemically (S) adsorbed on the wall); and other molecules and radicals. The surface kinetics is inspired by the mesoscopic model of Gordiets *et al.* [6], considering physical adsorption/desorption, chemical adsorption, surface transport, and Eley-Rideal and Langmuir–Hinshelwood recombination processes.

The model is solved numerically using the LisbOn KInetics (LoKI) simulation tool [4], comprising an electron Boltzmann equation solver (LoKI-B) and a Chemical solver (LoKI-C), which are coupled via a series of convergence cycles, ensuring a self-consistent solution for the electron energy distribution function, the species densities, and the reduced electric field, for given pressure, mixture composition and discharge current.

Figure 1 shows initial results for E/N vs I_{dc}, at p = 100 Pa and 5% H_2, and for the NH_3 partial pressure as a function of the H_2 concentration, at p = 130 Pa and I_{dc} = 20 mA. When comparing simulations with

measurements, one observes a fair agreement for the reduced electric field and a good qualitative agreement for the evolution of the NH_3 pressure with the $\%H_2$. However, the model still predicts absolute NH_3 densities that are 1 order of magnitude below the experimental measurements.

The model results confirm that the main production mechanisms of NH_3 occur at the surfaces (Langmuir-Hinshelwood, Eley-Rideal and NH_4^+ recombination), while the main destruction mechanisms are due to collisions with the atomic metastable $N(^2D)$ and with N_2H^+, the most abundant ion.

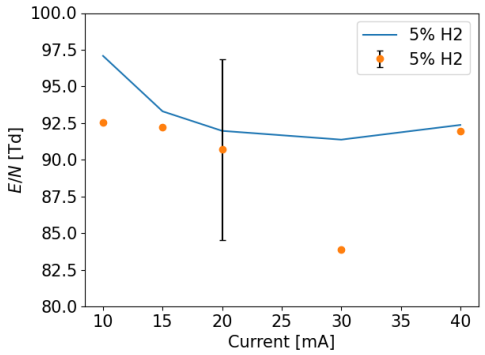

Fig. 1(a): Reduced electric field as a function of the discharge current, from numerical simulations (line) and experimental measurements (points) for 130 Pa pressure and 5% hydrogen concentration.

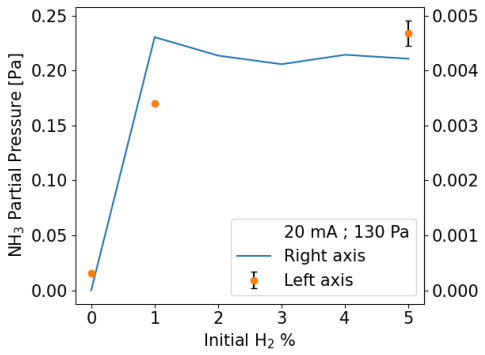

Fig. 1(b): Partial pressure of NH_3 as a function of hydrogen concentration, numerical simulations (line, right scale) and experimental measurements (points, left scale) for 130 Pa pressure and 20 mA discharge current.

We will also show simulations and measurements of the ammonia concentration and the relative densities of the most important ions, as a function of pressure and discharge current. In the future we aim to improve the model predictions of the NH_3 density, and to clarify the mechanisms of its creation and destruction. This will involve a critical review of the rate coefficients adopted in the kinetic scheme, with a special focus on the wall reactions, the reactions leading to the production/destruction of mixed H/N species, and the electron-impact reactions that will mostly affect the trends as a function of current.

Finally, the coupling of the volume and surface models has proved challenging. The evolution of the two kinetic schemes is mostly independent, with only a small number of species (such as $H(^1S)$ and $N(^4S)$) bridging the gap. In this regard, the convergence of simulations has proven to be highly dependent on the initial conditions adopted, and further work must be done to clarify this and optimize the calculation workflow.

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