Modelling plasmas for sustainable gas conversion

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Abstract: This contribution presents the development and findings of models of plasmas for CO_2 conversion and for NO production, focusing on one-dimensional fluid modelling of the plasma core, in either continuous or pulsed discharge modes. The simulation results are validated against dedicated experiments and give important insights into the origins of plasma contraction and about vibrational non-equilibrium.

1. Introduction

In the last years, a lot of attention has been devoted to the study of gas conversion by means of microwave (MW) discharge reactors [1], due to the possibility of achieving thermal and chemical non-equilibrium in the plasma, leading to high product yields and energy efficiencies. This process involves a complex interplay of many effects, namely transport of reactive flows, complex chemistry and electromagnetic fields. The interplay of these effects is not well known, and the possibility of predicting it through modelling is important for optimization of reactor performances [2].

In CO_2 conversion reactors, a correlation was highlighted experimentally between discharge contraction and reactor performance [3]. In plasmas for NO production, strong vibrational non-equilibrium was found experimentally either outside the plasma core for continuous wave discharges or as an effect of power pulsing for pulsed discharges [4]. Here, we develop and use a one-dimensional fluid model to understand and predict these fundamental phenomena.

2. Methods

The 1D radial time-resolved self-consistent model solves a system of coupled mass balance equations for neutral and charged species [4-6]. These equations include source terms for chemistry, together with drift-diffusion fluxes in the radial direction. Temporal and spatial profiles of gas and vibrational temperatures, spontaneous optical emission, electron density and electron temperature are compared to validate the model and the choice of input power density against experimental measurements in CO_2 and N_2 continuous and pulsed discharges at different operating pressures (mbar range) and powers (kW range), with excellent agreement.

3. Results and Discussion

Besides validation, the model is also used to complement experiments, by providing calculations of species molar fractions and reaction rates that are not directly measured.

In continuous CO_2 MW discharge, it is shown that as temperature increases with pressure in the plasma core, the neutral species composition becomes increasingly dissociated due to thermal chemistry and sharper radial gradients are formed. The temperature gradients determine a prevalence of atomic ions in the plasma core and molecular ions on the radial edges. That ion composition determines a lower relative loss of charged species in the plasma core, contributing crucially to radial contraction. The contraction is exacerbated by the associative ionization of C and O becoming the dominant ionization mechanism at high pressures and temperatures. This feature is essential to predict electron number density and mean energy in agreement with experiments for pressure conditions ranging from 100 mbar to 400 mbar.

In pulsed N_2 MW discharges, despite the relatively low gas temperatures ($\approx$2000 K), atomic nitrogen, a proxy for NO in N_2-O_2 discharges, is predicted to be forming in the plasma region within 100 μs after the start of the power pulse. The radicals survive for up to 500 μs after the pulse has ended. The model reveals that N formation is dominated by collisions involving vibrationally excited species, either with electrons or with electronically excited species in the whole plasma region. The timescale of N production can thus be controlled by the applied reduced electric field, while its quenching can be controlled by the flow rate or pulse width.

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