Investigation of coupling between chemistry and discharge dynamics in RF hydrogen plasmas in the Torr regime.

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Abstract

We present some results from a one-dimensional (1D) numerical fluid model of a capacitively coupled RF hydrogen discharge. A detailed description of the chemistry has been implemented taking a special care of the H production through the dissociative-attachment of the v=4-9 vibrational levels of H2. The population of these levels was described assuming a Boltzmann Vibrational Distribution Function (VDF) with a vibrational temperature Tv. The effect of the vibrational excitation, through the dissociative attachment kinetics, on the discharge dynamics is discussed. Two values of the vibrational temperature, namely 1000K and 4000K, are taken as the heading parameter of simulations performed for pressures of 33 Pa and 133Pa.

Results show that by increasing the vibrational temperature, the mole fraction of H is increased by seven orders of magnitude. Simultaneously, the ratio of the H density to the electron density varies from 10^{-7} to 10. Consequently, the electron temperature increases by 1eV, meanwhile the plasma potential is lowered by 10V. The H-atom mole fraction increases by a factor 3 for the same variation of T_v. These results clearly evidence a strong coupling between chemistry and electrical dynamics through the production of heavy negative ions.

1. Introduction

During the last decade, an extensive experimental and theoretical works have been devoted to improve and highlight the understanding of the dynamics of hydrogen plasmas. This increasing interest was not only motivated by fundamental aspects but also by a technological problems as hydrogen and hydrogen mixtures are used in a wide range of plasmas processes covering applications as diversified as microelectronics, and surface treatment. In this framework, numerical modelling has been proven to be a powerful tool of investigation [1,2]. However, although a good understanding of the discharge dynamics has been inferred from a variety of numerical codes [2], only few is known about the chemistry, and more precisely about the coupling between the chemistry and transport of neutral species and the electrical dynamics. This coupling is the basis of any realistic description of the glow discharge. In this work, we have implemented a one-dimensional (1D) numerical fluid model of a capacitively coupled RF hydrogen discharge focusing the attention on the H production channel through the attachment from the dissociation of the upper vibrationnal states of H2. The coupling between the chemistry and electrical dynamics is discussed in term of the influence of the H negative ions on the electrical properties of the discharge. To our knowledge, the only study similar to the one presented here was carried out by Cappitelli & al [3], who used PIC-MCC model for the discharge coupled to a vibrational kinetics model of H2. This study was however devoted to lower pressure regime, i. e. p<100 mtorr.

This paper is organised as follows: In section II, a brief overview of the numerical model will be given. The results of a parametric study as function of the vibrational temperature will presented and discussed in section III.
2. Description of the model.

The model deals with a conventional Radio Frequency (13.56 Mhz) capacitively coupled glow discharge. The processing discharge parameters refer to our common experimental conditions [4] corresponding to pressures ranging from 33 Pa to 133 Pa, and RF voltage of 150V. The chemistry is treated through a set of 27 reactions involving the H₂, H, H(n=2), H(n=3), H₂, H₂⁺, H⁺ species. The reaction set includes ionisation of H₂ and H, electronic excitation of H, electron-impact dissociation and dissociative attachment of H₂ and mutual recombination of ions. The model diagram can be split into two parts that respectively concern the electrical module which deals with the charged species dynamics, and the transport-chemistry module which treats the chemistry and transport of neutral species.

A. Electrical module.

The coupled set of Poisson’s equation, electron energy equation and charged species continuity equations are solved using an explicit scheme. Inertia effects in the momentum transfer equation of heavy ions are taken into account, assuming an effective electric field given by:

\[ \frac{\partial E_{\text{eff}}}{\partial t} = -\nu (E_{\text{eff}} - E) \]  

Where \( \nu \) is the collision frequency between ions and neutrals.

(1)

The charged species density conservation equation is written in the following form:

\[ \frac{\partial n_e}{\partial t} = -\nabla (-D_e \nabla n_e + z_i \mu_i E n_e) + S_e \]  

(2)

The electron-impact rate constants required for the estimation of the source terms \( S_e \) and the electron transport coefficients are calculated using an off-line Boltzmann solver. The ion transport coefficients are estimated from reference [5].

The electron energy conservation equation includes two energy transport fluxes, i.e., conduction flux and electron diffusion flux, and two source terms that correspond to the energy gain through ohmic heating of electron and to the energy loss through elastic and inelastic collisions of electron with heavy species:

\[ \frac{\partial n_e E_e}{\partial t} = -\nabla (-2/3 \kappa_e \nabla E_e + 5/3 J_e E_e) - \varepsilon_e \cdot \hat{J}_e - \sum_{\cdots \cdots} k_{\text{coll}} n_e n < E_{\text{th,coll}} > \]  

(3)

Where \( \varepsilon_e \), \( \kappa_e \) and \( J_e \) are the average energy, the thermal conductivity and the flux of electrons. \( k_{\text{coll}} \) and \( < E_{\text{th,coll}} > \) represent the reaction rate constant and the energy threshold for the collision 'coll'.

B. Neutral species transport-chemistry module

This module treats the stationary continuity equations of neutral species which may be written in the following form:

\[ -\nabla (-D_s \nabla n_s + u n_s) + < S_s > = 0 \]  

(4)

where \( u \) is the gas flow velocity which is set to zero in this work, and \( < S_s > \) is the time-averaged source terms for species \( s \).

The steady state density profile of the neutral species is calculated at the end of each RF period using the time-averages of electron density and electron-impact rate constants over one RF period. The boundary conditions used for both charged and neutral species continuity equation express the balance of the rate of transport flux and the production rate of surface processes [6]. Similar boundary conditions for the electron energy are also used.

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3. Results and discussion

We have performed two sets of simulations that respectively correspond to two values of the vibrational temperature, namely 1000K and 4000K. Fig 1 shows the axial profiles of the major charged species obtained at pressure of 133 Pa and vibrational temperature of 1000K. The discharge in this condition is electropositive, \( \text{H}^+ \) being the major positive ion. The ionisation channel in this case involves two steps: an electron impact ionisation on \( \text{H}_2 \) that produce \( \text{H}_2^+ \) followed by a fast \( \text{H}_2^+ - \text{H}_2^- \) ion conversion process. Electron density of \( 4 \times 10^9 \text{ cm}^{-3} \) corresponds to pretty low ionisation degree of about \( 5 \times 10^9 \). By increasing the vibrational temperature to 4000K (Fig 2), the density of \( \text{H} \) strongly increases by more than seven orders of magnitude in the bulk of the discharge. In fact, three regions may be distinguished in the discharge obtained at \( T_v = 4000 \text{ K} \): i) a strongly electronegative core with an electron density to negative ion density ratio greater than 10 and a flat electron density profile, ii) a small electropositive region, and iii) the sheath.

![Fig 1: Time-averages of the major charged species density at P=133 Pa and T_v=1000K](image1)

![Fig 2: Time-averaged major charged species density at P=133 Pa and T_v=4000K](image2)

The increase of \( \text{H} \) is due to an enhancement of electron dissociative attachment process from \( \nu = 4-9 \) vibrational levels, the population of which are increased when \( T_v \) is changed from 1000 to 4000 K. The same set of simulation has been performed at lower pressure, namely 33 Pa. The results are shown in Fig. 3 and Fig. 4. The same trends are observed, though the central electronegative core is much more narrow than previously.

![Fig 3: Time-averaged major charged species density at P=33Pa and T_v=1000K](image3)

![Fig 4: Time-averaged major charged species density at P=33Pa and T_v=4000K](image4)
It is also interesting to analyse the electron temperature profiles which are shown in Fig 5. At high pressure and low vibrational temperature ($P=133$ Pa, $T_v=1000K$), the electron temperature reaches 4 eV at the sheath at 0.25 cm from the boundary, while it shows a minimum around 1.5 eV at the centre. The increase of $T_e$ does practically not affect $T_e$ in the sheath. A different behaviour is obtained in the centre of the discharge where $T_e$ substantially increases and shows flat profile at a value of approximately 2 eV when $T_e$ is changed from 1000 to 400 K. It is worth noticing that the shape of $T_e$ profile at 133 Pa and 1000K explains the axial variation of $H_2^-$ in the same conditions. Indeed, the $H_2^-$ ion is produced by electron impact on $H_2$ and rapidly consumed by the $H_2^−-H_2^*$ ion conversion process. Therefore the $H_2^*$ density reflects the electron impact ionisation source term which strongly depends on $T_e$.

![Fig 5: Time-averaged electronic temperature profile.](image)

![Fig 6: Time-averaged H density profile.](image)

At lower pressure, the effect of $T_e$ is not so drastic over all the electron temperature profile. This is more affected by the changes in pressure since the bulk value increase from 1.8 to 3.8 eV and the sheath value is increased from 4 eV to 10 eV when the pressure is changed from 133 to 33 Pa. Also, the sheath thickness broadens by more than a factor 2 for the same pressure change. This is due to the decrease of the electron density.

In Fig 6, the $H_2^*$ atomic density profile obtained for the pressure and vibrational temperature values investigated in this work. The atom density increases with the vibrational temperature for the two pressure values considered. However, the change obtained at higher pressure is much more pronounced.

4. Conclusion

All the results discussed above show that vibrational excitation may drastically affect the discharge dynamics in $H_2$ plasmas. However, the vibrational temperature actually depends on the other plasma parameters and the value adopted in our simulation are realistic [7]. In particular, the relatively low $H_2$ atoms density along with the low pressure should limit the $H_2-H_2^*$ vibrational-transitional relaxation processes that usually causes the de-excitation of the upper vibrational levels. In addition the VDF (Vibrational distribution function) in actual discharge would strongly deviates from Boltzmann distribution, and would be characterised by an enhanced population of the high vibrational levels. Moreover the high $T_e$ obtained in the sheath should favor the production of the electronically excited singlet state $B(Σ^+)$ and $C(Π, σ)$ that de-excite preferentially on the $v>4$ vibrational levels which enhance the rate of the dissociative attachment process. Therefore the effects of vibrational excitation on the discharge dynamics that are stressed by the results obtained here should be at least
qualitatively meaningful. Of course quantitative predictions of such effects requires more detailed investigation of the coupling between chemistry and discharges dynamics that may be carried out by improving the transport-chemistry model of neutral species using the collisional-radiative model [2]. This model should bring self consistent estimation of the whole VDF and therefore the dissociative attachment kinetics.

References


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