Chemistry in glow discharges of H_2 / O_2 mixtures. Diagnostics and modelling.

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A combined diagnostics and modelling of low pressure H_2/O_2 plasmas at different pressures and mixture ratios, generated in a hollow cathode (DC) reactor, is presented. Neutral and ion distributions are measured by mass spectrometry. Langmuir probes provide charge densities and electron temperatures. As expected, apart from the precursors, H_2O is detected in considerable amounts. Concerning the charged species, pure hydrogen and oxygen ions are detected together with mixed ones. With increasing pressure, the ion distributions are dominated by H_3O^+ for mixtures with H_2 concentrations higher than ~30%. In contrast, the protonated species O_2H^+ is hardly formed. A zero order kinetic model is used to explain the experimental results. H_2O is produced via plasma-surface interactions in a multistep process. The ion distributions are determined in each case by a balance between the relative weights of electron impact processes and proton transfer chemistry.

1. Introduction

Low pressure plasmas in electrical discharges with H_2 and O_2 are of interest in a variety of fields. In astrochemistry, the formation of H_2O and H_3O^+ is of great relevance as they can be detected in interstellar environments [1-3]. In fusion research, discharge cleaning is used to eliminate the residual molecules in a vacuum vessel, of which oxygen and water are major components [4].

In this work, we present a study of the chemistry of neutral and ionic species in H_2/O_2 plasmas based on the experimental diagnostics and kinetic modelling of hollow cathode discharges at different pressures and mixture proportions. The main surface and gas processes are identified by comparison of experimental data and model predictions, and their relative relevance under the different discharge conditions is analysed. Special attention is paid to the formation of H_2O through heterogeneous reactions and to the ions obtained from the protonation of neutral species.

2. Experimental

The DC plasma reactor used for the experiments is described elsewhere [5,6]. It consists of a stainless steel grounded hollow cathode DC reactor (34 cm length, 10 cm diameter) with a central anode. The vessel is pumped by means of a turbomolecular pump backed by a dry pump. Neutral species from the plasma are sampled with a quadrupole mass spectrometer (Balzers, Prisma QMS 200) and a plasma process monitor (Balzers, PPM421), which is also used to measure the mass and energy distributions of the ions hitting the cathode. Both of these instruments are installed in a differentially pumped vacuum chamber and sample neutrals or ions from the plasma through a diaphragm of ~ 100 µm diameter. Electron temperatures and charge densities are measured with double Langmuir probes made in our laboratory.

Mixtures of H_2/O_2 of different proportions (from pure H_2 to pure O_2), with total pressures from 0.8 to 8 Pa, are used for plasma generation. Plasma currents of ~ 150 mA and voltages of 400–550 V (depending on total pressure) are maintained during the experiments. An electron gun is employed for plasma ignition.

3. Model

A zero order kinetic model is employed for the interpretation of the experimental results. It is based on a set of coupled differential equations describing the time evolution of the concentrations of both neutral and ionic species from the ignition of the discharge until the attainment of the steady state. Similar models applied to H_2+D_2 and H_2+N_2 discharges can be found in [5,6], as well as a detailed description of the modelling method. The model accounts for the main physico-chemical processes (electron impact dissociation and ionization, ion-molecule reactions, neutralization at the wall and heterogeneous chemistry). The electron temperatures used to calculate some of the rate coefficients and the electron density are obtained from the Langmuir probe measurements. Most of the rate coefficients have been taken from literature sources (when available), or have been estimated using reasonable values that lead to a good

agreement between experiment and model. H_2O is assumed to be formed through a series of heterogeneous reactions for which both Langmuir-Hinshelwood and Eley-Rideal mechanisms have been taken into account. Bimolecular reactions between neutrals are in general unimportant for our low pressure cold plasmas and have not been included, with the exception of processes involving the excited metastable $O(^1D)$ atoms.

4. Results and discussion

Relative concentrations of the neutral and ionic species of relevance, along with the model predictions, for two of the proportions studied at a pressure of 8 Pa, are presented in Figure 1.

Experimental data is only available for the stable neutral species, i.e. H_2, O_2 and H_2O. Model and experiment show a good general agreement, with some discrepancy in the concentration of H_2O, which becomes more evident as the O_2 proportion grows. Relative concentrations for radicals, which have not been measured, are obtained from the model simulations.

Figure 2 shows the relative concentrations of the ionic species for the same two proportions considered in Figure 1. For these relatively low O_2 concentrations, the dominant ion in our plasmas is clearly H_3O^+, and we have a noticeable concentration of H_3^+, as could be expected given their proton affinities: 691.0 kJ/mol (H_2O) and 422.3 kJ/mol (H_2). As the amount of O_2 precursor grows, other species become more relevant, such as H_2O^+ and O_2^+, while pure hydrogen ions tend to sink. This behaviour is qualitatively reproduced by model simulations, although the values differ from those obtained experimentally. A study of the possible contribution of O^- is under way.

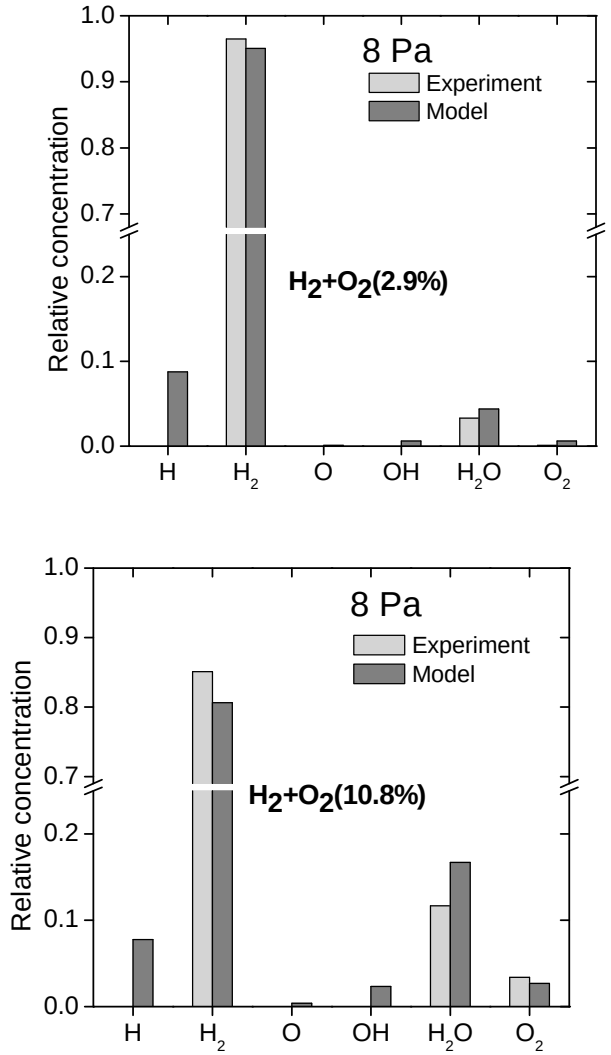

Figure 1. Distributions of neutrals for two different O_2 proportions at a total H_2+O_2 pressure of 8 Pa.

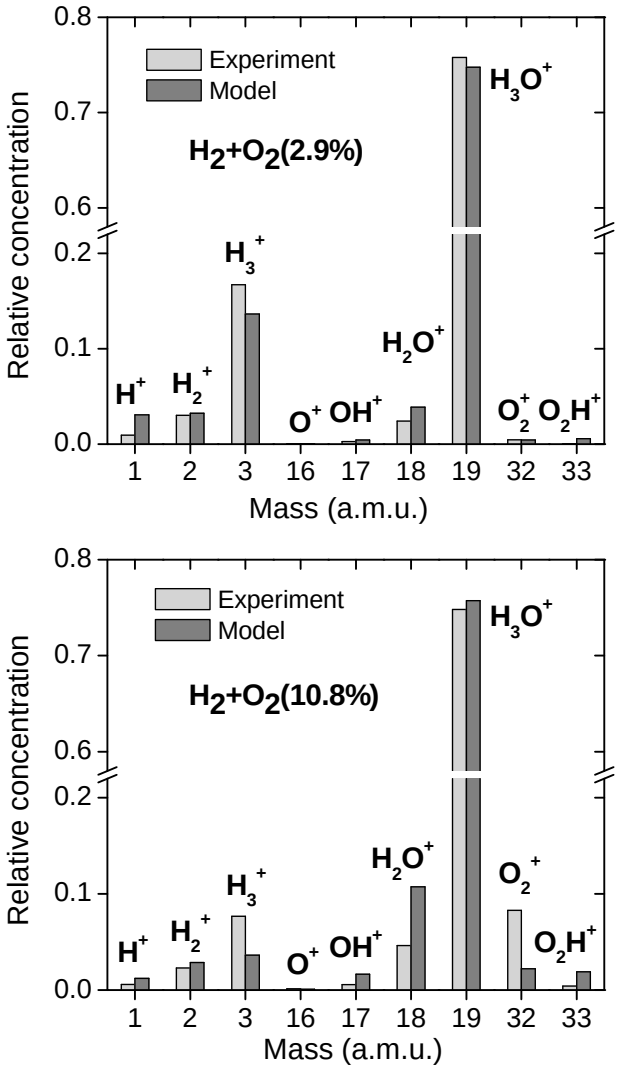

Figure 2. Relative concentrations of ions for two of the mixture ratios studied at 8 Pa.

The ionic composition of our plasmas as a function of the O_2 proportion is represented in Figure 3. Special attention was paid to low O_2 concentrations, as the chemistry is richer under these conditions.

The evolution of the three pure hydrogen ions is essentially the same. They decrease quickly with growing O_2 content, and only H_3^+ is present in relatively large amounts for the lowest O_2 concentrations. Over most of the mixture proportions studied (up to ~ 70% O_2) H_3O^+ dominates the ion distributions, decreasing markedly for the highest O_2 concentrations, where the chemistry is dominated by the two pure oxygen ions, O_2^+ and O^+. The mixed ions OH^+, H_2O^+ and O_2H^+ appear in low concentrations with stable values through the different mixtures, except for the extreme ones, where they obviously sink.

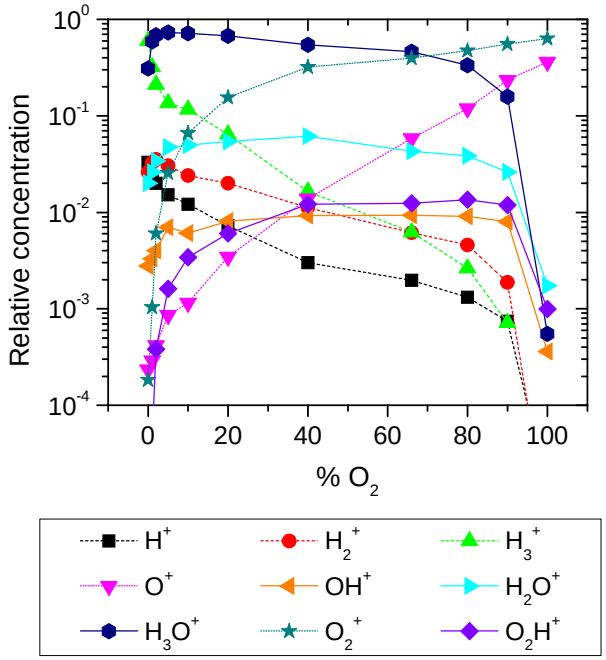

Figure 3. Experimental concentrations of ions for all the proportions studied at 8 Pa.

5. Summary and conclussions

The chemistry of low pressure hollow cathode discharges of H_2/O_2 mixtures has been studied through plasma diagnostics and kinetic modelling.

The neutral chemistry is dominated by the two precursors and H_2O, which is formed through surface processes. The ion composition changes with the mixture ratio, being dominated by H_3O^+ and pure hydrogen ions at low O_2 proportions and by pure oxygen ions at high ones. Other mixed ions appear in low concentrations for intermediate mixtures. The results are explained by a kinetic model, which contains the main physico-chemical processes.

6. Aknowledgements

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