Diagnostics and modelling

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Abstract

A combined diagnostics and modelling of low pressure H_2/O_2 plasmas at different mixture ratios, generated in a hollow cathode (DC) reactor, is presented, significantly expanding the first results reported in [1]. 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. 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.

Experimental Setup

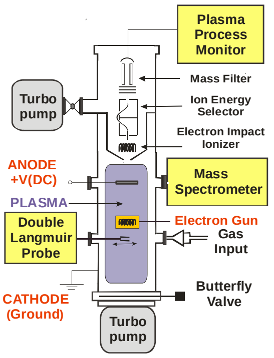


Fig. 1 Experimental Set-up

PLASMA GENERATION

The hollow cathode discharge reactor is described elsewhere [2,3].

DIAGNOSTIC TECHNIQUES

Neutral species from the plasma were sampled with a quadrupole mass spectrometer (Balzers, Prisma QMS 200) located in a differentially pumped vacuum chamber. A plasma process monitor (Balzers PPM-421) is used for the detection of ions (with ion energy resolution).

Double Langmuir probes are used to determine the electron temperature and charge density.

Kinetic 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 [2,3].

The model accounts for the main physico-chemical processes (electron impact dissociation and ionization, ion-molecule reactions, neutralization at the wall and heterogeneous chemistry). Some of the rate coefficients have been obtained from [4].

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(^{1}D) atoms.

Changes in plasma composition with gas mixture

Fig.2 Experimental relative concentrations of the stable neutral species in our plasma for the different gas mixtures at 8 Pa

H_2O, produced through heterogeneous reactions at the reactor walls, is formed in noticeable amounts, with a maximum concentration for a ~ 40% proportion of the O_2 precursor

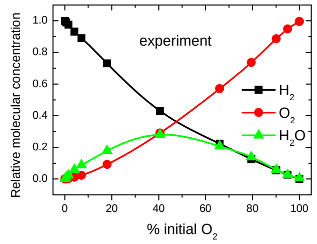
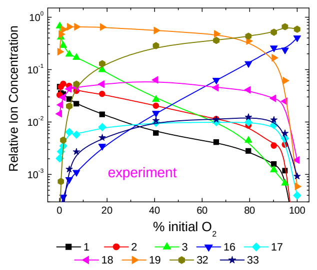


Fig.3 Experimental concentrations of ions for all the proportions studied at 8 Pa.

The three purely hydrogenous ions 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 purely oxygenic 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.



Model results

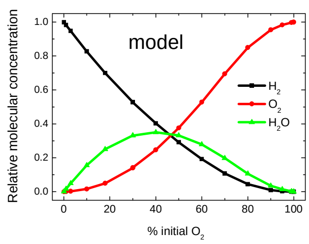


Fig.4 Predicted relative concentrations of the stable neutral species in our plasma at 8 Pa

The model simulations carried out show good agreement with the experimental data for the neutral stable species concentrations.

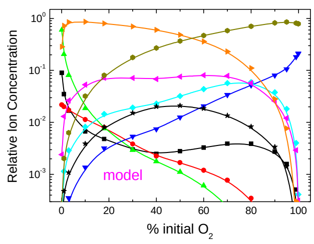


Fig.5 Predicted concentrations of ions for at 8 Pa.

The ion chemistry is very well reproduced by the model for the lower O_2 concentrations studied. H_3O^+ is the dominant species well above H_3^+, due to the higher proton affinity of H_2O (691.0 kJ/mol) as compared with H_2 (422.3 kJ/mol). As the O_2 proportion grows, discrepancies between model and experiment become more evident.

The three negative ions considered (H^-, O^- and OH^-) are predicted to be ~ 10% of the total negative charge density for most of the studied mixtures, being dominated by H^- for the higher H_2 concentrations and O^- for the lower ones. They have a limited impact in the chemistry, their main contribution being the lower electron densities available for electron impact processes.

Conclusions

- H_2 + O_2 plasmas have been studied through plasma diagnostics and kinetic modelling in hollow cathode glow discharges
- 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 hydrogenic ions at low O_2 proportions and by pure oxygenic ions at high ones
- These results are reproduced by the kinetic model, which works best for lower O_2 precursor conditions.

References

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