Diagnostics and modelling

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Abstract

Low pressure plasmas with H_2 and O_2 are of interest in a variety of fields, such as astrochemistry [1], discharge cleaning of vacuum vessels in fusion research [2], or surface treatment [3]. In this work, H_2/O_2 plasmas generated in a hollow cathode discharge at 8 Pa, spanning the whole range of mixture ratios, are studied. Neutral and positive ion distributions are measured by mass spectrometry. Langmuir probes provide charge densities and electron temperatures. As expected, apart from the neutral precursors, H_2O is detected in considerable amounts. The ion distributions are dominated by H_3O^+ for most O_2 initial proportions ($5\%<O_2<70\%$). H_3^+ and O_2^+ are the major ions for $O_2<5\%$ and $O_2>70\%$, respectively.

A zero order kinetic model has been developed to explain the experimental results. H_2O is produced via plasma-surface interactions in a multistep process. The positive ion distributions are determined in each case by a balance between the relative weights of electron impact processes and proton transfer chemistry. Estimations of negative ion concentrations predict that they represent globally less than 10-20% of the total negative charge in all the cases.

Experimental Setup

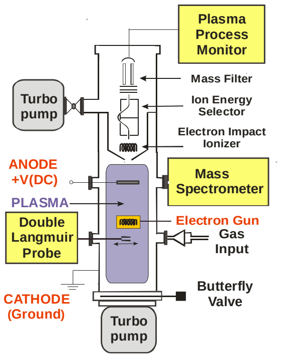


***Fig. 1** Experimental Set-up*

PLASMA GENERATION

The hollow cathode discharge reactor is described elsewhere [4-6].

DIAGNOSTIC TECHNIQUES

Neutral species were sampled with a mass spectrometer located in a differentially pumped vacuum chamber. A plasma process monitor was used for the detection of ions.

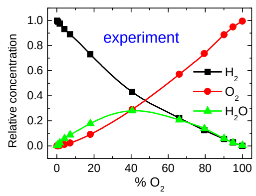
Double Langmuir probes were used to determine the electron temperature and charge density.

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 neutral and ionic species from the ignition of the discharge to the attainment of the steady state. Similar models applied to H_2+D_2 and H_2+N_2 discharges can be found in [4,5]. In this work negative ions have also been included.
- The model accounts for the main physico-chemical processes (electron impact dissociation and ionization, ion-molecule reactions, neutralization at the wall and heterogeneous chemistry). Several of the rate coefficients were obtained from refs. [7,8].
- Bimolecular reactions between neutrals are in general unimportant for low temperature plasmas and have not been included, except for processes involving the metastable $O(^1D)$ and $O_2(^1\Delta)$ species.

Experimental Results

***Fig.2** Relative concentrations of stable neutrals with discharge on, as a function of the initial O_2 fraction.*

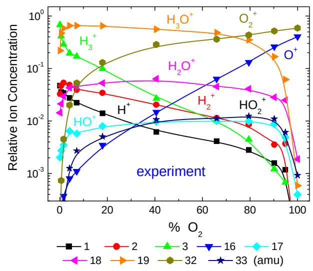


H_2O, is formed in noticeable amounts through heterogeneous reactions at the reactor walls, with maximum concentration for initial O_2 ~ 40%.

***Fig.3** Relative concentrations of positive ions.*

The three purely hydrogenous ions decrease quickly with growing O_2 initial content. H_3^+ is present in relatively large amounts only for the lowest O_2 concentrations.

Over most of the mixture proportions ($O_2 \lesssim 70\%$), H_3O^+ is the major ion, 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.



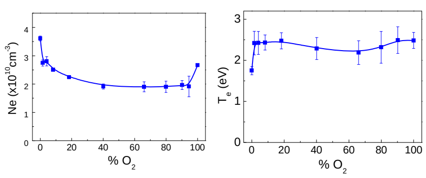


***Fig.4** Charge density and T_e (Maxwellian) measured with a double Langmuir probe*

Model Simulations

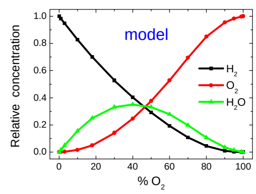


***Fig.5** Predicted concentrations of stable neutrals. They show good agreement with the experiment.*

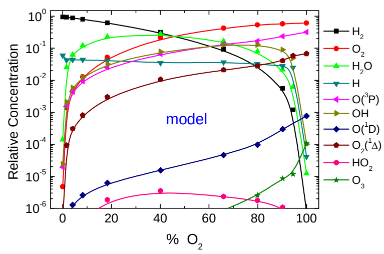


***Fig.6** Predicted concentrations of all the neutral species.*

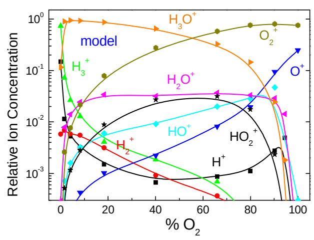


***Fig.7** Predicted concentrations of positive ions.* The tendencies in the ion proportions are reasonably well reproduced by the model. As the O_2 fraction grows, discrepancies between model and experiment become more evident. Major species are sufficiently well reproduced with the exception of H_3^+, which decreases with O_2 concentration far more quickly than observed experimentally.

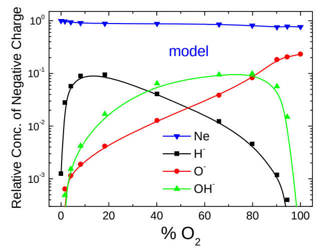


***Fig.8** Predicted concentrations of negative ions.* The three negative ions (H^-, O^- and OH^-) are at most ~ 10-20% of the total negative charge. They have a limited impact in the chemistry. Their main contribution is to decrease the electron densities available for electron impact processes.

Summary and Conclusions

- H_2 + O_2 plasmas at 8 Pa for all H_2/O_2 ratios have been experimentally studied and modelled.
- 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^+ at low O_2 fractions and by pure oxygenic ions at higher ones.
- The tendencies in the observed behaviors of the stable and ion species are reasonably reproduced by the kinetic model.

References

[1] E. Herbst, *Chem. Soc. Rev.* **30** (2001) 168.
[2] M. Mushiaki, *Fusion Eng. Des.* **47** (1999) 85-.
[3] F. Fumagalli, O. Kylian, et al., *J.Phys.D-Appl. Phys.* **45** (2012) 135203.
[4] E. Carrasco et al., *Plasma Phys. Control. Fusion* **54** (2012) 124019.
[5] M. Jimenez-Redondo, et al. *Phys. Chem. Chem. Phys.* **13** (2011) 9655.
[6] E. Carrasco, et al., *Phys. Chem. Chem. Phys.* **13** (2011) 19561.
[7] V. G. Anicich, *J. Phys. Chem. Ref. Data*, **22** (1993) 1469.
[8] D.X. Liu et al., *Plasma Sources Sci. Technol.* **19** (2010) 22.