O$_2$ dissociation in Ar-O$_2$ surface-wave microwave discharges

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Oxygen dissociation in Ar-O$_2$ microwave surface-wave discharges at $p = 1 - 25$ mbar is theoretically investigated, focusing on the dependence of the dissociation degree on pressure and on the mixture composition. It is shown that the dissociation degree is higher for high Ar content discharges, due to the modifications in the electron energy distribution function (EEDF) and to the effectiveness of the dissociation channel involving the Ar($4s$) states in this case. Furthermore, for mixtures predominantly constituted by argon the dissociation degree passes through a minimum at pressures around 4-8 mbar, reflecting the peculiarities of the energy transfer from the microwave field to the electrons for the various electron energies.

1. Introduction

Afterglow systems based on oxygen containing surface-wave microwave discharges meet several applications in the fields of biomedicine [1–4] and surface treatment [5, 6], with further potential in areas such as nanotechnology [7–9]. In numerous applications the major role is played by the O-atoms, although most of the time a synergetic effect between the O-atoms and ions or UV photons is observed. For example in the removal of biological contaminants/etching of hydrocarbons the crucial process is the chemical sputtering induced by the Ar$^+$ ions and O-atoms [10], while in the bacterial inactivation [3, 11, 12] and etching of polyolefins (hexatriacontane - HTC) [5] the synergetic effect between the O-atoms and the VUV/UV radiation, which can originate e.g. from the NO(A) and NO(B) molecules or the resonant state Ar atoms, has been found. Therefore, it is important to understand the formation of O-atoms under different discharge conditions in mixtures, which besides the O-atoms can also provide the reactive species required by the application processes. The aim of this work is the study of O$_2$ dissociation in one of the most frequently used Ar-O$_2$ mixture. For this purpose we developed a zero-dimensional kinetic model presented in the next Section. Section 3 contains the results and their discussion.

2. Model

The kinetic model is based on the solutions of the electron Boltzmann equation for the microwave field, coupled to a system of rate-balance equations for the neutral and charged heavy species. For more details the reader should refer to [9, 13–15], where the gas phase and surface reactions taken into account in the model, as well as all other parameters used, are described. A surface wave microwave discharge generated in a small diameter tube is a plasma column with a decreasing electron density profile as discussed in [16,17]. At the end of plasma column the electron density reaches a value $n_{ec}$ corresponding to the critical density for surface wave mode propagation in a homogeneous, cold, collisionless plasma, surrounded by a dielectric of permittivity $\varepsilon_g$. The surface wave mode can only propagate provided the electron density is larger than this critical value, obtained from $\omega_{pe} > \sqrt{\omega^2 + \varepsilon_g}$, with $\omega_{pe}$ denoting the electron plasma angular frequency, which for a quartz tube ($\varepsilon_g = 4$) at 2.45 GHz gives

$$n_{ec} = 3.74 \times 10^{11} \text{ cm}^{-3}.$$  

The calculations are conducted for this critical electron density, so that the species densities are obtained at the end of the plasma column, being thus the initial conditions of the afterglow. The latter is dominated by the gas phase chemical kinetics and surface pro-
cesses [4,9,14,18]. The sustaining microwave field for the discharge plasma is self-consistently calculated. For this purpose the continuity and transport equations for the electrons, different positive ions and O$^-$ ions are solved, in order to describe the charged particle motion to the wall under the presence of the radial space-charge field. The reduced electric field is determined using the requirement that under steady-state conditions the total rate of ionization must compensate exactly for the rate of electron loss [15].

The calculations have been carried out in the 1-25 mbar pressure range in mixtures from pure O$_2$ to 95%Ar-O$_2$. The dissociation degree of oxygen molecules, defined as $\frac{[O]}{2[O_2]}$, with $[O_2]$ denoting the initial density of O$_2$ in the mixture, has been determined, as well as the sustaining electric field. The surface recombination probability of O-atoms strongly influences the O-atoms density. Its value has been chosen as $\gamma_{O(2p)} = 8 \times 10^{-3}$, in accordance with the measurements of Macko et al. [19], while the gas temperature has been fixed to 500 K [9,17]. The system studied is an Ar-O$_2$ surface-wave discharge generated in $R=0.25$ cm tube with 2.45 GHz.

3. Results

The O$_2$ dissociation degrees calculated for different initial mixture compositions are shown in Figure 1 as a function of pressure. According to the calculations, the highest dissociation degree occurs in the higher Ar content mixture. Furthermore, the dissociation degree exhibits a different pressure dependence with the mixture composition. While in high Ar content mixture discharges it shows a well defined minimum at around 4 mbar, with decreasing Ar percentage in the mixture this minimum becomes less pronounced, and in pure O$_2$ just a slight increase of the dissociation degree can be observed at about 15 mbar.

The dissociation of the molecules in the discharge is influenced by the electron collisions, as well as by the chemical kinetics of the system. The electron dissociation rates calculated for the different mixture compositions, here presented for the 90%Ar (Figure 2) and 100%O$_2$ (Figure 3) mixtures exhibit a very similar behaviour with pressure as the dissociation degree, establishing dominant effect to be that of the electron colli-

Fig. 1: O$_2$ dissociation degree as a function of pressure for different mixture compositions.

Fig. 2: Rates for selected electron induced processes in case of 90%Ar-10%O$_2$ discharge.

The dissociation threshold is about 6 eV, whereas the O$_2$ and Ar ionization ones are at $\sim 11.1$ and $\sim 15.7$ eV, respectively. The cross section of some important electron impact processes are shown in Figure 4, as well as the self-consistent calculated EEDFs (Electron Energy Distribution Functions). The modifications in the EEDFs near the dissociation and ionization thresholds clearly correspond to the dissociation and excitation rates dependencies with pressure and mixture composition. For instance, in low argon content
mixtures the dissociation degree does not show a very marked minimum. On the other hand, in discharges predominantly formed by Ar, the shape of the EEDF is more dependent on the electrons collisions with Ar atoms, with excitation and ionization thresholds at 11.5 eV and 15.76 eV, respectively, the electrons being able to acquire enough energy to dissociate O$_2$ molecules. This leads to a "bump" in the EEDF at energies of about 4–10 eV.

With increasing O$_2$ percentage in the mixture the electrons lose their energy essentially in O$_2$ excitation, which has lower energy threshold than argon excitation. Dissociation is thus less efficient than in high Ar content mixtures. This effect is well represented by the EEDFs, which reveal that the energy range interesting for the O$_2$ dissociation is more populated at elevated Ar percentages in the mixture than in pure O$_2$. Furthermore, in high Ar content mixtures the collisions of O$_2$ molecules with Ar(4s) atoms also contribute to the oxygen dissociation [15].

Three-body recombination of O-atoms starts to play role at pressures higher than 10 mbar and mixtures with significant amounts of O$_2$. For instance, in the case of a 50%Ar mixture at 25 mbar, its contribution to the O($^{3}$P) destruction is 4%, while in pure O$_2$ this value increases to 12%.

Further insight can be given by looking at the power absorbed from the field by the electrons of energy $u$, defined as $\frac{eE^2}{m} \nu_c(u) + \omega \nu_c(u)$, where $E$ is the RMS field, $e$ and $m$ the electron charge and mass, respectively, $\nu_c(u)$ the electron-neutral collision frequency for momentum transfer, and $\omega$ the field frequency [23, 24], which can be the measure of discharge’s efficiency. The power transfer reaches a maximum when $\nu_c = \omega$ [23, 24]. When this condition is satisfied for the group of electrons that are able to ionize, the discharge is expected to be the most efficient. For certain group of electrons this condition can be reached with the variation of the pressure. The comparison of $\nu_c$, defined for the Ar atoms with energies of 20 eV, with $\omega$ is presented in Figure 5, giving information about predominantly Ar discharges. Here the condition is find to be satisfied at 4 mbar, in good correlation with the calculated minimum
in the oxygen dissociation degree. The choice of the energy to calculate \( \nu_c \) is merely indicative of electrons with enough energy to ionize argon. As a matter of fact, if the same figure is represented choosing a different electron energy the curve is simply slightly shifted in pressure.

The same information can be obtained from an equivalent criterion, by considering the limiting cases of energy independent collision frequencies, \( \nu_c(u) = \nu_c \) and \( \nu_c(u) = \omega \). Imposing the same energy transfer in both cases we have

\[
E^2(\nu_c) \frac{\nu_c^2 + \omega^2}{\nu_c^2} = E^2(\omega) \frac{\omega^2 + \omega^2}{2\omega^2},
\]

or

\[
\alpha^2 = \frac{E^2(\nu_c)}{E^2(\omega)} = \frac{\nu_c^2 + \omega^2}{2\nu_c\omega}.
\]

The parameter \( \alpha \) is depicted in Figure 5, where a minimum at a pressure consistent with the minimum in the dissociation degree can be observed. The exact details of the relationship between the two minima and the modifications in \( \alpha \) and in the EEDF by considering different electron energies are under investigation.

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