Surface recombination in Pyrex in CO_2 DC glow discharges

Pedro Viegas(*)[1], André Filipe[1], Jorge Silveira[1], Tiago Cunha Dias[1], Ana Sofía Morillo Candás[2], Olivier Guaitella[2], Vasco Guerra[1]

[1] *Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Portugal*

[2] *Laboratoire de Physique des Plasmas (UMR 7648), CNRS, Univ. Paris-Saclay, Sorbonne Université, École Polytechnique, France*

(*) *pedro.a.viegas@tecnico.ulisboa.pt*

CO_2 plasmas are an efficient way to convert green house gas CO_2 on Earth or to produce valuable products in space, for instance using the Martian CO_2 atmosphere. Indeed, through plasma, CO_2 can be converted into CO, which can be transformed into added value fuels, and breathable O_2. In CO_2 conversion plasmas, atomic oxygen is extremely important as reactant either for dissociation ($CO_2 + O \rightarrow CO + O_2$) or for recombination ($CO + O + M \rightarrow CO_2 + M$). O is essentially produced by electron-impact dissociation ($CO_2 + e \rightarrow CO + O + e$) and, particularly at low pressures (below 50 mbar), it can be lost by recombination on the wall through heterogeneous surface kinetics processes. As such, wall recombination plays a very important role in these plasmas. Yet, the recombination probability in CO_2 plasmas and the responsible processes still lack dedicated studies.

In the work by Morillo-Candás et al. (2019) [1], the wall loss frequencies of O atoms were measured in the positive column of a CO_2 DC glow discharge in a Pyrex tube (borosilicate glass) of 10 mm inner radius, at 50 ºC outer wall temperature, for several pressure values between 0.27 mbar (0.2 Torr) and 6.7 mbar (5 Torr) and several discharge currents between 10 mA and 50 mA. It was noticed that the O recombination probability is significantly lower than the one in an oxygen glow discharge in similar conditions (see fig. 1), measured by Booth et al. (2019) [2]. This implies that CO and CO_2 from the plasma interacting with the Pyrex surface not only avoid additional recombination of O but they may also be passivating sites for O recombination. Indeed, the same study [1] measured CO densities and fractions to be much higher than the ones of O. Since both species are expected to be produced mostly via electron-impact dissociation, it was concluded that most atomic oxygen is lost by recombining with O or O_2 (thus forming O_2 or O_3) and not with CO (in that case forming CO_2). However, the processes responsible for these features are still unknown.

In this work we employ numerical simulations to assess the dominant surface mechanisms in CO_2 glow discharges. The simulations are obtained from a mesoscopic model employing deterministic and Kinetic Monte Carlo methods [3-5]. The simulations assess the experimental conditions by Morillo-Candás et al. (2019) [1], but also a new set of experiments with currents of 20 mA and 40 mA, pressures between 1.3 mbar (1 Torr) and 10 mbar (7.5 Torr), wall temperatures of -20 ºC, 5 ºC, 25 ºC and 50 ºC and different CO_2-O_2 mixtures (25% CO_2, 50% CO_2, 75% CO_2 and 100% CO_2). Addressing the different sets of experimental data, with a large number of conditions, is important to verify the robustness of the model and thus of our knowledge of surface interactions. The surface reaction scheme employed in the mesoscopic model in previous works [3-5] is further developed to include the possible interactions of O_2 and CO with the surface and the possibility of O_3 and CO_2 formation as a result. It includes Eley-Rideal (E-R) recombination mechanisms involving gas-phase species O, O_2 and CO interacting with chemisorbed O_S and CO_S species, as well as physisorbed O_F, $O_{2,F}$ and CO_F species, and Langmuir-Hinshelwood (L-H) recombination between physisorbed species and other adsorbed species. The model involves a large number of parameters whose values have a high degree of uncertainty. This work assesses the influence of those parameters on numerical results and on their coherence with the knowledge obtained from experiments.

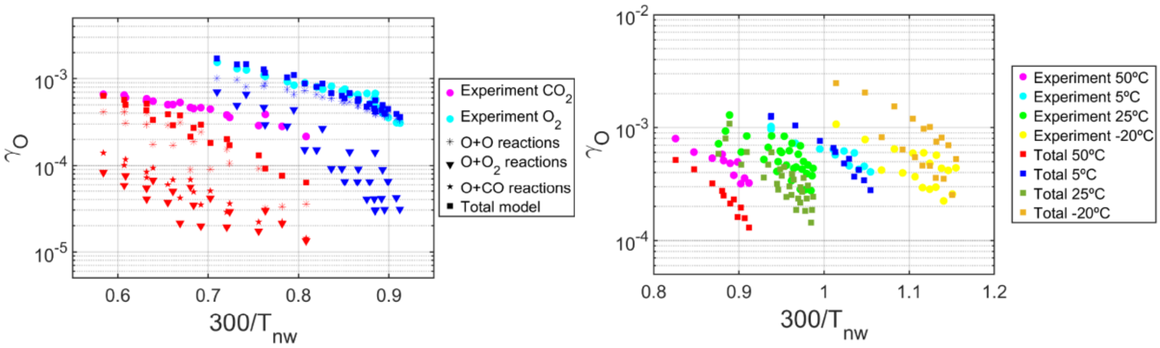

Fig. 1: Measured and simulated atomic oxygen recombination probability as function of the inverse of the near-wall temperature. On the left, for wall temperature of 50 ºC, in O_2 and CO_2 plasmas, with the contributions of the different processes. On the right, for different wall temperatures and O_2-CO_2 mixtures (25% CO_2, 50% CO_2, 75% CO_2 and 100% CO_2).

Fig. 1 shows examples of simulation results, compared to different measurements, for a given set of parameters. The example shows that the model can describe recombination in both O_2 and CO_2 plasmas (and mixtures of those), while holding consistency for different wall temperatures, current and pressure values. For the case of a CO_2 plasma, the simulation results show that recombination reactions between oxygen species are dominant over those between O and CO, in coherence with the analysis of experiments by Morillo-Candás et al. (2019) [1]. At 50 ºC wall temperature, the recombination is due to a mixture of different mechanisms: L-H recombination $O_F + O_F$, E-R recombination $O_2 + O_F$, E-R $O + O_S$ and L-H $O_F + O_S$. These results show that this kind of mesoscopic model can have predictive capabilities when changing conditions, which makes it an excellent tool to contribute to predict different reactor performances.

Acknowledgements

This work was supported by the Portuguese FCT - Fundação para a Ciêencia e Tecnologia, I.P., by project references: UIDB/50010/2020 (https://doi.org/10.54499/UIDB/50010/2020), UIDP/50010/2020 (https://doi.org/10.54499/UIDP/50010/2020), LA/P/0061/2020 (https://doi.org/10.54499/LA/P/0061/2020), PD/BD/150414/2019 (PD-F APPLAuSE) and PTDC/FIS-PLA/1616/2021 (PARADiSE, https://doi.org/10.54499/PTDC/FISPLA/1616/2021). ASMC acknowledges LabEx Plas@par, receiving financial aid from the French National Research Agency (ANR) under project number ANR-11-IDEX-0004-0 and project SYCAMORE (ANR-16-CE06-0005-01).

References

[1] A. S. Morillo-Candás *et al., Plasma Sources Sci. Technol.* **28** (2019) 075010
[2] J. P. Booth *et al., Plasma Sources Sci. Technol.* **28** (2019) 055005
[3] V. Guerra, *IEEE Transactions on Plasma Science* **35** (2007) 1397
[4] V. Guerra and D. Marinov, *Plasma Sources Sci. Technol.* **25** (2016) 045001
[5] D. Marinov *et al., Plasma Process. Polym.* **14** (2017) 1600175