Kinetic mechanisms in CO_2-O_2 plasmas: Development of a reaction mechanism

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This contribution reports the development of a reaction mechanism for CO_2-O_2 plasmas. To this purpose, simulations from a 0D self-consistent kinetic model are compared with recent experimental data obtained in low-pressure DC discharges. The comparison allows a refinement of the available kinetic schemes and the development of a new reaction mechanism (i.e., a set of reactions and rate coefficients validated against benchmark experiments) for CO_2-O_2 plasmas.

Investigating the impact of O_2 on CO_2 conversion is relevant because O_2 is a product of CO_2 dissociation and can be present as an impurity in industrial CO_2 emissions. Besides, by enlarging the range of operating conditions, kinetic schemes validated for pure O_2 and pure CO_2 can be further refined. The research teams at Instituto Superior Técnico (IST) from Universidade de Lisboa, Laboratoire de Physique des Plasmas (LPP) from École Polytechnique carry out a joint investigation of CO_2-O_2 and CO_2 plasmas. A set of measurements of gas temperature, vibrational temperatures of CO_2, E/N, O(3P), $CO(X^1\Sigma^+)$ and $CO_2(X^1\Sigma^+_g)$ densities and O(3P) loss frequencies was recently obtained. The plasma source chosen is a DC glow discharge, operating at pressures in the range p=0.1-10 Torr and discharge currents I=10-50 mA, in a Pyrex tube of radius R=1 cm, which is stable, axially homogenous, and easily accessible to a variety of diagnostics. The simulation results were obtained with the LoKI (LisbOn Kinetics) [1] simulation tool solving a Boltzmann-chemistry global model. The admixture of O_2 has a detrimental impact on CO_2 decomposition [2] and several reasons can be assigned for it, one of them being the quenching of vibrationally excited CO_2, which may lead to molecular dissociation through the so-called ladder climbing mechanism [3]. Another possible explanation is the enhancement of the reverse reaction producing back CO_2 from electronically excited CO in collisions with O_2 [4]. Therefore, molecular oxygen plays an important role in CO_2 plasma kinetics. Understanding the impact of the different elementary processes on the overall kinetics, along with the validation against experimental data, will contribute to further develop the existing models and thus to better control and enhance CO_2 conversion. For this purpose, a proper description of the CO_2 chemistry and vibrational population is fundamental along with a detailed kinetic scheme for O_2, as partially done in [5-7].

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[1] V. Guerra et al, Plasma Sources Sci. Technol. 28 (2019) 073001
[2] M. Grofulović et al, Plasma Sources Sci. Technol. 28 (2019) 045014
[3] A. Fridman Plasma Chemistry (2008) (Cambridge: Cambridge University Press)
[4] A.S. Morillo-Candas et al, J. Phys. Chem. C 124 (2020) 17459−17475
[5] A.F. Silva et al, "A reaction mechanism for vibrationally cold CO_2 plasmas", accepted for publication, (2020)
[6] A. Annušová et al, Plasma Sources Sci. Technol. 27 (2018) 045006
[7] T. Silva et al, J. Phys. D: Appl. Phys. 51 (2018) 464001