

## Insights into nanosecond repetitively pulsed CO<sub>2</sub> discharges by time-resolved optical emission spectroscopy

T.P.W. Salden<sup>1,2,\*</sup>, M.Ceppelli<sup>1</sup>, L.M.M. Martini<sup>1</sup>, G. Dilecce<sup>3,1</sup>, P.Tosi<sup>1,3</sup>

<sup>1</sup>Department of Physics, University of Trento

<sup>2</sup>Department of Applied Physics, Eindhoven University of Technology

<sup>3</sup>CNR Institute for Plasma Science and Technology

\*Contact e-mail: t.p.w.salden@tue.nl

Nanosecond repetitively pulsed discharges are seen as a promising way to achieve plasma (catalytic) conversion of CO<sub>2</sub> into value added compounds in a commercially interesting, industrially viable manner; the non-equilibrium conditions unlock thermodynamically unfavourable reaction pathways. It has been demonstrated that a further enhancement of conversion is possible by utilizing a burst pulse pattern rather than a continuous one, under the hypothesis that this further augments the non-equilibrium features of the plasma and provides suitable conditions for vibrational ladder climbing to occur [1]. The short duration nature of these discharges—as well as the fast equilibration times at atmospheric pressure—necessitate fast diagnostics that are capable of probing the time evolution of discharge conditions in a non-invasive manner.

While running in low frequency continuous- or burst-mode, each pulse in the discharge is uncorrelated to the preceding one, i.e. it does not encounter a memory effect and will form its own streamer. Decreasing the pulse separation however means that a pulse will encounter a progressively stronger memory effect from the preceding pulse, altering discharge conditions and even traversing the electrode gap along the same discharge channel [1, 2]. As such, the electrical characteristics of the discharge as well as the emission produced by it change considerably. Time-resolved spectroscopic analysis of specific spectral lines has allowed both the study of transient conditions in the discharge as well as identifying underlying mechanisms or reaction pathways for the emission.

The Stark broadening of the long lasting oxygen  $3s\ ^5S_0 \leftarrow 3p\ ^5P^{J=1,2,3}$  triplet allows for an estimate of the electron density  $n_e$  along the evolution of the burst discharge pattern, with a maximum corresponding with 5% ionization, when assuming an electron temperature of 2.0 eV. The ratio of highly excited C<sup>+</sup> and C<sup>++</sup> lines that are present confirm this assumption, yielding a rough  $T_e$  estimate of 2.0 eV to 2.5 eV.

The addition of a small fraction of N<sub>2</sub> allows the gas temperature  $T_g$  to be determined as well when

there is electron impact excitation occurring in the discharge, employing the (0, 0) band of the N<sub>2</sub> second positive system. Other common spectroscopic markers such as the CN Violet system or the C<sub>2</sub> Swan bands have to be discarded as there are chemical pathways that form a rotationally hot population and will thus not represent  $T_g$  due to insufficient rotational energy transfer to thermalize the state. A peak temperature of around 2500 K was found, which compares well with earlier results based on LIF thermometry and modelling [3, 4].

The overall picture that arises from these observations is of a highly ionised spark discharge in quasi-LTE, as opposed to the thermal spark encountered in NPG discharges in air-like mixtures [5]. Based on time-resolved spectra, it appears that CO<sub>2</sub> dissociation and O<sub>2</sub> formation are both processes that occur over longer ( $\geq 1\ \mu\text{s}$ ) timescales and only occur after a delay, implying that other processes than electron impact play an important role.

### Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 813393. M.C. acknowledges support by the Progetto Strategico di Ateneo ERICSOL of the University of Trento.

### References

- [1] C. Montesano et al. In: *Journal of CO2 Utilization* 39 (2020), p. 101157.
- [2] C. Montesano et al. In: *Journal of CO2 Utilization* 49 (July 1, 2021), p. 101556.
- [3] L. M. Martini et al. In: *Plasma Chemistry and Plasma Processing* 38.4 (July 2018), pp. 707–718.
- [4] S. Heijkers et al. In: *The Journal of Physical Chemistry C* 123.19 (2019), pp. 12104–12116.
- [5] N. Minesi et al. In: *Plasma Sources Science and Technology* (2020).