

The plasma road to sustainable chemical conversion workshop

Book of abstracts



Funchal, Madeira, 3-5 September 2023



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The [Institute for Plasmas and Nuclear Fusion](#), Universidade de Lisboa and Universidade da Madeira, organize the workshop "[The plasma road to sustainable chemical conversion](#)," to bring together renowned experts in plasma-assisted sustainable chemistry and energy applications of cold plasmas. It aims at fostering opportunities for collaboration in these topics, which include CO₂ and CH₄ reforming, and NO_x and NH₃ synthesis.

The workshop is held at [Colégio dos Jesuítas](#), the historical building of the [University of Madeira](#). Funchal is easily accessible by airplane and offers a large and diversified offer for housing.

The workshop features invited lectures by renowned experts, a small number of oral presentations chosen from the contributed abstracts, and one poster session.

Organising committee

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- Vasco Guerra, IST, Universidade de Lisboa

The plasma road to sustainable chemical conversion workshop

Schedule of the workshop:

Sunday 3 rd September		Monday 4 th September		Tuesday 5 th September	
18:00 – 20:00	Reception	8:30 – 9:00	<i>Opening address</i>	9:00	Richard van de Sanden
		9:00	Mikhail Benilov	9:25	Ahmed Gohniem
		9:25	Ante Hecimovic	9:50	Juan Pablo Trelles
		9:50	Timo Gans	10:15	Paolo Tosi
		10:15 – 12:15	<i>Poster Session</i>	10:40 – 11:00	<i>Coffee break</i>
				11:00	Annemie Bogaerts
		12:15 – 14:00	<i>Lunch break</i>	11:25	Gerard van Rooij
		14:00	Ana Morillo-Candas	11:50	Milan Simek
		14:25	Nikolay Britun	12:15	Tiago Dias
		14:50	Maik Budde	12:40 – 14:30	<i>Lunch break</i>
		15:15	Daniela Pietanza	14:30	Svetlana Starikovskaia
		15:40 – 16:00	<i>Coffee break</i>	14:55	Dmitry Lopaev
		16:00	Dmitry Voloshyn	15:20	Pedro Viegas
		16:25	Tomoyuki Murakami	15:45	Eric Moreau
		16:50	Nuno Pinhão	16:10 - 16:30	<i>Coffee break</i>
		17:15	Vasco Guerra	16:30	Peter Bruggeman
				16:55	Rony Snyders
		17:20	Tiago Silva		
		17:45 – 18:00	<i>Closing session</i>		

Program

- Sunday, September 3rd

18:00 – 20:00 Reception

- Monday, September 4th

08:30 – 09:00 *Opening Address*

09:00 – 09:25 **Mikhail Benilov** Modelling low-current quasi-stationary gas discharges: mathematical aspects and a practical guide.

09:25 – 09:50 **Ante Hecimovic** Advances in CO₂ plasma conversion at atmospheric pressure and oxygen separation.

09:50 – 10:15 **Timo Gans** Self-limiting trade-off between CO yield and CO₂ conversion energy efficiency in atmospheric pressure Ar-CO₂ plasmas: picosecond laser spectroscopy.

10:15 – 12:15 *Poster session*

12:15 – 14:00 *Lunch break*

14:00 – 14:25 **Ana Morillo-Candas** Strategies to enhance the CO₂ conversion in low temperature plasmas studied by isotope tracing.

14:25 – 14:50 **Nikolay Britun** A comprehensive characterization of a He-based atmospheric nanosecond jet discharge for gas conversion.

14:50 – 15:15 **Maik Budde** Importantly rather than Impurity – Additional gases in CO₂ plasma conversion.

15:15 – 15:40 **Daniela Pietanza** On the coupling of vibrational and electronic kinetics with the electron energy distribution function for plasma assisted CO₂.

15:40 – 16:00 *Coffee break*

16:00 – 16:25 **Dmitry Voloshyn** Ozone kinetics in the afterglow of a pulse-modulated DC discharge in O₂ an experimental and modelling study of surface mechanisms and ozone vibrational kinetics.

16:25 – 16:50 **Tomoyuki Murakami** Numerical simulation and complex network analysis of reacting chemistry in plasma treated water.

16:50 – 17:15 **Nuno Pinhão** Vibrational cross sections of methane: from individual cross sections to polyad groups.

17:15 – 17:40 **Vasco Guerra** Development of reaction mechanisms for plasma chemistry.

- Tuesday, September 5th

09:00 – 09:25 **Richard van de Sanden** Plasma conversion of CO₂, N₂/O₂ & CH₄.

09:25 – 09:50 **Ahmed Gohniem** Combustion and Energy Processes and the Role of Plasma.

09:50 – 10:15 **Juan Pablo Trelles** Microwave Plasma CO₂ Conversion Enhanced by Concentrated Solar Radiation.

10:15 – 10:40 **Paolo Tosi** Investigation of plasma activation mechanisms of highly stable molecules in atmospheric pressure plasmas.

10:40 – 11:00 *Coffee break*

11:00 – 11:25 **Annemie Bogaerts** Electrification of chemical reactions.

11:25 – 11:50 **Gerard van Rooij** Methane Plasma Chemistry to aid the Energy and Materials Transition in the Process Industry

11:50 – 12:15 **Milan Simek** Streamer-based discharge on water surface for nitrogen fixation - a diagnostic study.

12:15 – 12:40 **Tiago Dias** A close look at time-locality assumptions on the modelling of nanosecond-pulsed discharges.

12:40 – 14:30 *Lunch break*

14:30 – 14:55 **Svetlana Starikovskaia** O₂ dissociation at moderate pressures: are there advantages of high electric fields and high specific energy input?

14:55 – 15:20 **Dmitry Lopaev** Dynamics of negative ions in dc O₂ discharge.

15:20 – 15:45 **Pedro Viegas** Plasma-induced reversible surface modification and its impact on oxygen heterogeneous recombination.

15:45 – 16:10 **Eric Moreau** How the ionic wind can be used for airflow control and EHD propulsion, and how it could improve the efficiency of plasma reactors.

16:10 – 16:30 *Coffee break*

16:30 – 16:55 **Peter Bruggeman** Pathways for Nitrogen Fixation by Plasma Catalysis.

16:55 – 17:20 **Rony Snyders** Experimental study of microwave and gliding arc plasma discharges utilized for the fixation of nitrogen into NO.

17:20 – 17:45 **Tiago Silva** Understanding nitrogen fixation while studying volume and surface kinetics in N₂-O₂ plasmas.

17:45 – 18:00 *Closing session*

Poster session

1. **Rui Almeida** Breakdown in axisymmetric device with dielectric spacer at 1 atm.
2. **Pedro Almeida** An extended Townsend criterion for multidimensional geometries.
3. **Nuno Ferreira** Modelling low-current periodic pulses in corona discharges.
4. **Ataollah Eivazpour** Stability of negative corona discharges at inception.
5. **Yuri Gorbanev** Nitrogen fixation by an arc plasma at elevated pressures.
6. **Vladislav Kotov** On reaching the strong $T \ll T_{\text{vibr}}$ vibrational non-equilibrium in CO.
7. **Igor Fedirchuk** Green H₂ synthesis from NH₃ cracking using plasma: Comparison between the performance of different plasma reactors.
8. **Pedro Viegas** Atomic wall recombination in oxygen plasmas.
9. **C. A. Aggelopoulos** Investigation of cold atmospheric plasma for environmental remediation/sanitation and materials activation/regeneration.
10. **Sergey Soldatov** CO₂ splitting in atmospheric microwave plasma sustained with ultra-fast energy pulsations.
11. **Aleksandr Pikalev** Plasma diagnostics for oxygen separation experiments.
12. **Abhyuday Chatterjee** Nitric oxide and O atomic density kinetics in a low pressure N₂-O₂ surfaguide microwave using Laser Induced Fluorescence.
13. **Lex Kuijpers** Determination of atomic oxygen density and reduced electric field in oxygen-containing plasmas through OES methods.
14. **Anja Herrmann** Mapping the density of Nitrogen radicals in RF inductively coupled flow Reactors.
15. **Lanie McKinney** Numerical Modeling of Plasma Reactors for CO₂ Conversion with Applications to Mars In-Situ Resource Utilization.
16. **Nuno Pinhão** Reforming of methane in a DBD reactor: A reaction kinetics model
17. **T. P. W. Salden** The PIONEER database: introducing a platform for meta-analysis of CO₂ conversion experiments
18. **Tom Butterworth** Probing the dynamics of a gliding arc discharges in air.
19. **Gromov Mikhail** Insights into methane reforming to olefins via nanosecond pulse plasma.
20. **Dihya Sadi** Plasma/surface interaction for efficient CO₂ recycling: plasma-membrane coupling.
21. **Edmond Baratte** Experimental and numerical study of the conversion mechanisms in the low-pressure CO₂-CH₄ glow discharge
22. **Tiago Silva** An assessment on vibrational rate coefficients with interest to chemistry of CO₂ plasmas.
23. **Kaja Primc** Rising EU climate targets to 55% GHG emissions reduction: Exploitation of emerging plasma-assisted sustainable resources for energy production
24. **Tiago C Dias** Effect of the magnetic field on the electron kinetics under AC/DC electric fields.

Abstracts

Invited lectures and oral communications

Modelling low-current quasi-stationary gas discharges: mathematical aspects and a practical guide

Mikhail Benilov

*Departamento de Física, Universidade da Madeira, 9000 Funchal, Portugal
Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Lisbon, Portugal*

benilov@staff.uma.pt

The work aims at developing an integrated approach suitable for the computation of the whole range of existence of a low-current quasi-stationary discharge from its inception to a non-stationary transition to another discharge form, such as a transition from the Townsend discharge to a normal glow discharge, or the corona-to-streamer transition, or the appearance of Trichel pulses in negative corona discharges. This task includes three steps: (i) modelling of the ignition of a self-sustaining discharge, (ii) modelling of the quasi-stationary evolution of the discharge with increasing current, and (iii) the determination of the current range where the quasi-stationary discharge becomes unstable and the non-stationary transition to another discharge form begins. Each of these three steps is considered in some detail with a number of examples, referring mostly to discharges in high-pressure air.

From the mathematical perspective, the problem of ignition of self-sustaining discharges is an eigenvalue problem. Several methods for its numerical solution are discussed and compared. The method of choice, the so-called resonance method, is physics-based and requires solving a boundary-value problem for steady-state linear partial differential equations, which may be routinely done by means of ready-to-use solvers, including commercial ones. A simple and robust method of exact (in theoretical terms) evaluation of self-sustainment conditions, developed in this way, is of theoretical interest and provides a useful reference point in the investigation of breakdown in high-voltage electrical equipment in low-frequency, e.g., 50 Hz, electric fields, where the time of variation of the applied voltage is much longer than the ion drift time. Moreover, in certain conditions the breakdown voltage coincides with the voltage of ignition of a self-sustaining discharge.

The solution describing the ignition of a self-sustaining quasi-stationary discharge, obtained at the first step, may be conveniently extended to higher currents by means of stationary solvers. The most time-consuming step when using stationary solvers is usually finding a suitable initial approximation, which requires intelligent guesswork. Fortunately, in simulations of low-current self-sustaining discharges this step can be performed in a routine way using the resonance method. This integrated approach is discussed in some detail and examples of its application to corona discharges of different configurations and both polarities are shown.

As the current of a quasi-stationary discharge increases, the discharge will lose stability and a non-stationary transition into another discharge form occurs. The loss of stability against small perturbations may be studied by means of solving the eigenvalue problem resulting from linear stability theory. An alternative approach to investigation of stability is to apply a perturbation to a steady-state solution and to follow the development of the perturbation by means of a time-dependent solver. This approach, which allows studying stability against arbitrary perturbations, is illustrated by examples of the stability of positive and negative point-to-plane coronas against perturbations of various amplitudes.

Advances in CO₂ plasma conversion at atmospheric pressure and oxygen separation

Ante Hecimovic^{1(*)}, Rodrigo Antunes¹, Christian K. Kiefer¹, Arne Meindl¹, Katharina Wieggers², Andreas Schulz², Ursel Fantz¹.

¹ Max Planck Institute for Plasma Physics, 85748 Garching b. München, Germany

² University of Stuttgart, IGVP, 70569 Stuttgart, Germany

(*) ante.hecimovic@ipp.mpg.de

Upscaling and industrial application of plasmas for CO₂ conversion are limited largely by: 1) best performance obtained at sub-atmospheric pressure (100-200 mbar) and 2) the most effective way to remove the oxygen molecules from the plasma effluent. In this contribution ways to solve these two problems are discussed. The CO₂ conversion at atmospheric pressure is limited by strong CO recombination due to limited gas quenching. Two approaches are tested to increase the gas quenching, either by employing a nozzle in the effluent [1], aimed at mixing the hot and cold gases, or using cooled effluent channels [2], aimed at enhancing gas quenching by gas-surface interaction. Results presented in Figure 1 demonstrate that rapid gas cooling leads to a significantly improved performance close to atmospheric pressure. High conversions at atmospheric pressure encouraged the use of oxygen permeation membranes for O₂ separation. LCCF membranes have been demonstrated to be reliable and compatible with high temperatures and chemical composition in the plasma torch effluent [3]. With an experimental setup containing 21 membranes placed in the effluent up to 41 sccm (4.7% of the available O₂) is extracted. These results along with a measurement of the total power used (by the power supply and peripheral devices) allows to benchmark the CO₂ plasma conversion technology with electrolysis. The benchmarking demonstrates; that the plasma conversion technology is a promising addition to the portfolio of the gas conversion techniques with comparable performance and particular suitability for dynamic, intermittent operation.

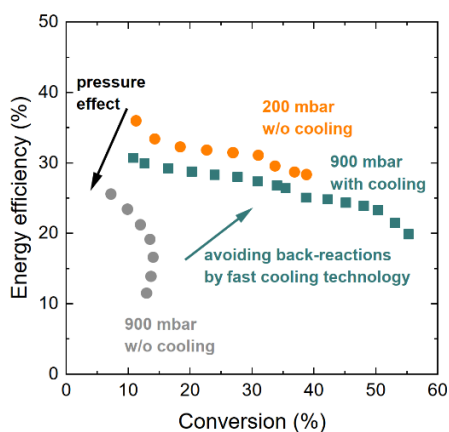


Fig. 1: The conversion and the energy efficiency obtained in microwave plasma torch with and without cooling of the gas in the plasma effluent, from [2].

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- [2] A. Hecimovic, C.K. Kiefer, A. Meindl, R. Antunes, U. Fantz, *Journal of CO₂ Utilization* 71 (2023) 102473
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Self-limiting trade-off between CO yield and CO₂ conversion energy efficiency in atmospheric pressure Ar-CO₂ plasmas: picosecond laser spectroscopy

James Dedrick¹, Alex Foote¹, Andrew Gibson², Kari Niemi¹, Steven Thomas¹, Jüri Raud¹, Joshua Boothroyd³, Zaenab Abd-Allah⁴, Jérôme Bredin¹, Michael North¹, Deborah O'Connell⁵, Timo Gans⁵(*)

¹ University of York, York, UK

² Ruhr-University Bochum, Bochum, Germany

³ University of Antwerp, Antwerp, Belgium

⁴ Manchester Metropolitan University, Manchester, UK

⁵ Dublin City University, Dublin, Ireland

(*) timo.gans@dcu.ie

Electrically-driven plasmas are a promising candidate for enabling rapid-response, catalyst-free or catalyst-supported conversion of CO₂ into CO. In this study, we investigate CO₂ to CO conversion with a radio-frequency non-thermal plasma operating at atmospheric pressure in argon with CO₂ admixtures of up to 3% using radio-frequency power input at 40.68 MHz. The plasma design is a modified version of the COST Reference Microplasma Jet [1].

Absolute measurements of ground-state O and CO densities are undertaken via picosecond two-photon absorption laser induced fluorescence (ps-TALIF) spectroscopy [2]. CO densities in the far-effluent region, as determined by ps-TALIF and independent Fourier-transform infrared spectroscopy (FTIR), show close quantitative agreement. A global plasma chemical kinetics model has been developed based on the same framework and assumptions as described in Schröter et al. [3]. Generally, excellent agreement has been observed between experimental results and computational predictions.

The CO yield and production energy efficiency are investigated with respect to CO₂ admixture and gas flow rate, producing a maximum yield of 97.5%. A significant increase in the CO density between the outlet and far-effluent region is observed. This is explained in terms of electron power deposition into CO vibrational states, which subsequently decay to increase the density of ground-state CO downstream. Energy deposition into vibrationally excited CO leads to an inherent self-limiting trade-off between CO-yield and CO₂ conversion energy efficiency in high-conversion regimes – see figure 1.

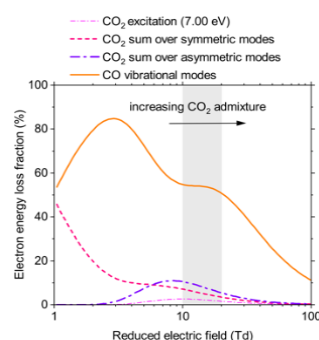


Figure 1: Electron energy loss fraction with respect to reduced electric field at the outlet for Ar-CO₂ (1.5%) and 30 W plasma power. The shaded region shows the typical range of reduced electric field that is applicable to the investigated plasma source. An indicative conversion of 70% is assumed for the high-conversion regime.

[1] J. Golda *et al.*, 2016, *J. Phys. D: Appl. Phys.* **49** 084003

[2] S. Schröter *et al.*, 2020, *Plasma Sources Sci. Technol.* **29** 105001

[3] S. Schröter *et al.*, 2018, *Phys. Chem. Chem. Phys.*, **20**, 24263-24286

Strategies to enhance the CO₂ conversion in low temperature plasmas studied by isotope tracing

A.S. Morillo-Candas^{(*)1,2}, E. Baratte¹, H. L. Rodrigues³, B.L.M. Klarenaar⁴
V. Guerra³, O. Guaitella¹

² Laboratoire de Physique des Plasmas, Ecole Polytechnique-CNRS 91128 Palaiseau, France

¹ Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

³ Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade Lisboa, Portugal

⁴ Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

(*) ana-sofia.morillo-candas@polytechnique.edu

Isotope tracing has a large potential for the study of chemical reactivity in non-equilibrium plasmas providing, for instance, information on the different processes involved in the oxygen exchange between gas phase species in C¹⁶O₂/C¹⁶O-¹⁸O₂ plasmas or on O(¹D), a distinctive species of the dissociation path in CO₂ plasmas, critical to assessing its efficiency [1]. We use this technique to study and evaluate two strategies oriented to enhance the final CO₂ conversion in CO₂-containing plasmas by reusing the produced atomic oxygen in secondary reactions in (1) a ¹²C (graphite) surface or (2) in the gas phase, using ¹³CO₂-¹²CH₄ mixtures.

The time evolution of the gas phase species in a pulsed radio frequency discharge, with and without a graphite-coated surface, is followed by FTIR absorption spectroscopy. The data is treated with a MATLAB script [1,2], updated to include ¹²CH₄, ¹³CH₄, ¹²C₂H₂, ¹³C₂H₂, ¹²C₂H₄, ¹²C₂H₆ and H₂O.

The experimental data, interpreted with the help of recent gas-phase chemistry models [1, 3], allows us to follow on time the distribution of all C and O isotopes within the gas mixture, to distinguish between surface and gas phase kinetics, and therefore to thoroughly compare both strategies. Both ¹³CO₂-¹²C (graphite) and ¹³CO₂-¹²CH₄ mixtures lead to an enhanced final conversion compared to ¹³CO₂ plasmas, but with significant differences. In the first case, the back reaction is strongly suppressed since the available O atoms are shown to oxidize non-thermally graphite. The final CO₂ conversion does not saturate and reaches values >95% after 5 s of plasma ON. ¹³CO₂-¹²CH₄ mixtures on the other hand, reach a saturation (see comparison in Fig.1). The appearance of ¹²CO₂ and, at longer time scale, of ¹³CH₄, reaching similar densities as the remaining ¹²CH₄, suggests back reactions that still limit the final conversion.

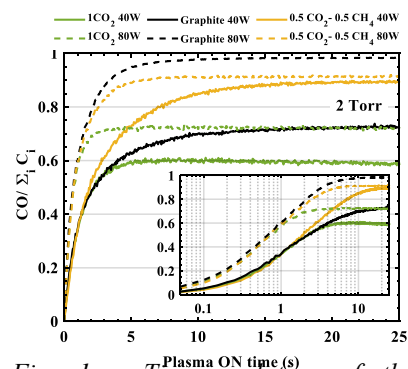


Fig. 1: Time evolution of the conversion fraction as a function of the accumulated plasma ON time

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A comprehensive characterization of a He-based atmospheric nanosecond jet discharge for gas conversion

Nikolay Britun^{(*)1}, Michael K. T. Mo¹, Shih-Nan Hsiao¹, Masaru Hori¹

¹ Center for Low-temperature Plasma Sciences, Nagoya University, 464-8603, Nagoya, Japan

^(*)britun@plasma.engg.nagoya-u.ac.jp

Winning the Green Race is getting more and more critical for humanity and for our planet itself. In this regard, efficient conversion of potentially harmful gases as well as synthesis of selective compounds required by industry and agriculture are of great importance. The conversion of carbon dioxide (CO₂) and the synthesis of N-containing compounds (e.g. NO, NO₂, etc.), i.e. nitrogen fixation, are two common examples for which a possibility of plasma-based conversion has been studied [1-4] and both thermal and non-equilibrium plasma cases have shown their advantages. However, the theoretically predicted efficiency limits in the latter case are higher [1], making the non-equilibrium plasma domain more attractive from a fundamental point of view.

In this work the efficiency of CO₂ conversion and the energy cost of NO synthesis are studied in a nanosecond atmospheric He-based discharge working in jet geometry [5-7]. The ns-discharge has been characterized by optical emission spectroscopy and laser-induced fluorescence allowing us to obtain the main discharge parameters, such as the plasma density, the strength of electric field, the behaviour of plasma emitters, the dynamics of rotational and vibrational temperatures, and last but not least, the density of the CO and NO ground state molecules. The number density of these molecules has been deduced based on a direct calibration in the same discharge.

Our results show that the electron density between the electrodes exceeds $5 \times 10^{15} \text{ cm}^{-3}$, whereas the electric field reaches about 25 kV/cm [6]. The vibrational temperature of N₂ molecules as high as 0.3 eV has been detected, whereas the gas temperature remains at nearly 300 K [5]. The population of the He ³S₁ (metastable) state, at the same time, exceeds 10^{14} cm^{-3} [8]. A very high voltage growth in the electrode gap ($\approx 3 \times 10^{11} \text{ V/s}$) provokes generation of the ionization wavefronts propagating with a speed of about $5 \times 10^5 \text{ m/s}$, containing electrons and He metastables and playing a critical role in radical generation downstream. The obtained energy efficiency of NO formation in our case varies depending on the discharge conditions (e.g. the gas admixture used), approaching typical values found previously in spark [9] and microwave [10] discharges ($< 5 \text{ eV/molecule}$). The found range for energy cost implies an efficient non-thermal mechanism of NO formation.

We acknowledge the JSPS KAKENHI Tokusui Project (Grant 19H05462).

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Importantly rather than Impurity – Additional gases in CO₂ plasma conversion

Maik Budde^{1,2*}, Arianna Brecia^{1,3}, Steijn Vervloedt^{1,4}, Richard Engeln^{1,5}
(Times 12, centred)

¹ Department of Applied Physics and Science Educations, Eindhoven University of Technology
5600MB Eindhoven, The Netherlands

² Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

³ Università degli Studi di Milano-Bicocca, Piazza dell'Ateneo Nuovo, 1 - 20126, Milan, Italy

⁴ Present affiliation: Experimental Physics II, Ruhr University Bochum, Bochum, Germany

⁵ Present affiliation: ASML, Veldhoven, The Netherlands

(*) m.budde@tue.nl

Low-temperature plasma for CO₂ conversion is a complex environment with a plethora of ongoing processes. The conversion process itself, leading to CO and O₂, as well as common impurities, like N₂ or H₂O, extend the complexity beyond CO₂ [1,2,3]. A thorough understanding requires the inclusion of these addition gases. By means of in situ quantum cascade laser absorption spectroscopy in a CO₂ glow discharge at low pressure fundamental processes between CO₂ and the above mentioned gases are studied, yielding time-resolved rovibrational temperatures, see figure 1, as well as conversion fractions [4].

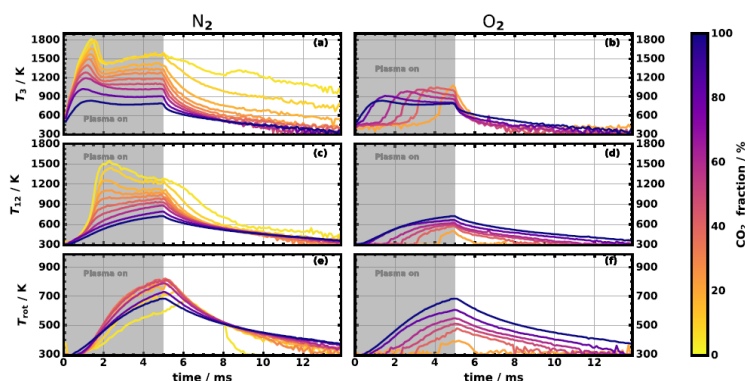


Figure 1: Rovibrational temperatures of CO₂ in the presence of N₂ (left column) and O₂ (right column).

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On the coupling of vibrational and electronic kinetics with the electron energy distribution function for plasma assisted CO₂ dissociation

Lucia Daniela Pietanza^{(*)1}, Gianpiero Colonna¹, Mario Capitelli¹

¹ *Istituto per la Scienza e Tecnologia dei Plasmi (ISTP), Consiglio Nazionale delle Ricerche (CNR), Bari, Italy*

(*) luciadaniela.pietanza@cnr.it

In this contribution, we will present the results obtained by using a 0D self-consistent kinetic model for the description of the plasma assisted CO₂ dissociation in different types of discharges, focusing on the important role of vibrational and electronic excited states in the global kinetics. The CO₂ plasma community is strongly focused on the development of advanced kinetic simulation models for the investigation of the complex chemistry of non-equilibrium CO₂ plasmas with the support of rigorous experimental validation procedures [1]. The kinetic model presented is based on the simultaneous and self-consistent time dependent solution of the equations describing the vibrational and electronic excited state population densities and the plasma composition in a state-to-state approach and the electron Boltzmann equation for the free electron kinetics [2-3]. The model has been applied also to the description of glow discharge conditions, finding a satisfactory agreement with simulation and experimental investigations present in literature [4-5]. Our simulations can describe the conditions for the activation of the vibrational-induced CO₂ dissociation process [6]. These conditions are linked to the achievement of sufficiently high CO₂ vibrational excitation, characterized by non-equilibrium vibrational distribution function (vdf) on the CO₂ asymmetric mode with a plateau on the higher vibrational levels, created by the combined effect of electron-vibration and vibration-vibration collisions. Our simulation results are in satisfactory agreement with the Kotov's criterion for the onset of vibrational dissociation with the prediction of a threshold activation value for the power density as a function of the plasma parameters [6-7]. The electronic excited states play a significant role in the overall kinetics. They can affect the eedf, especially, in the post-discharge, creating characteristic peaks due to superelastic electronic collisions and influencing the calculation of the electron impact rates. These effects are very important for the so-called thick plasmas becoming less important for thin plasmas [8]. Special attention has been devoted to the possible inclusion of other electronic excited states in the kinetics and to the refinement of their corresponding kinetic description.

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Ozone kinetics in the afterglow of a pulse-modulated DC discharge in O₂: an experimental and modelling study of surface mechanisms and ozone vibrational kinetics

J-P. Booth¹, O. Guaitella¹, E. Baratte¹, Shu Zhang¹, D. Lopaev², S. Zyryanov², T. Rakhimova², D. Voloshin^{(*)2}, A. Chukalovsky², A. Volynets², Yu. Mankelevich²

¹Laboratoire de Physique des Plasma (LPP), CNRS, Sorbonne Université, École Polytechnique, Institut Polytechnique de Paris, 91120 Palaiseau, France

²Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University, 1(2), Leninskie gory, GSP-1, 119991 Moscow, Russian Federation

(*) dvoloshin@mics.msu.su

The chemical kinetics of oxygen atoms and ozone molecules were investigated in a fully-modulated DC discharge in pure oxygen gas in a borosilicate glass tube, using cavity ringdown spectroscopy (CRDS) of the optically forbidden O(³P₂) → O(¹D₂) absorption at 630nm. Measurements were made over a range of tube temperatures (10 and 50°C) gas pressures (0.5-4 Torr) and discharge current (10-40 mA). The discharge current was square-wave modulated (on for 0.2 seconds and off for 1 second), allowing the build-up to steady-state and the decay in the afterglow to be studied. The O atom density decays non-exponentially in the afterglow, indicating a surface loss probability dependent on incident active particle fluxes. The ozone density passes through a maximum a few 100ms into the afterglow, then decays slowly. An existing time-resolved self-consistent 1D radial model of O₂ positive column discharges was upgraded to interpret the new results. The ozone behaviour in the afterglow can only be modelled by the inclusion of: 1) surface production of O₃ from the reaction of O₂ molecules with adsorbed O atoms, 2) reactions of vibrationally-excited ozone with O atoms and with O₂(a¹Δ_g) molecules, and 3) surface loss of ozone with a probability of around 10⁻⁵. The example of simulation results and the experimental data comparison is shown in figure 1. At 0.5 Torr, models with only gas-phase production of O₃ strongly underestimate the observed ozone densities (whether or not vibrational kinetics is included). At higher pressure (4 Torr) the model without vibrational kinetics seriously overestimates the ozone concentration (by factor ~2.5), whether or not ozone surface processes are included.

This study was supported by the Russian Science Foundation, Project No. 21-72-10040

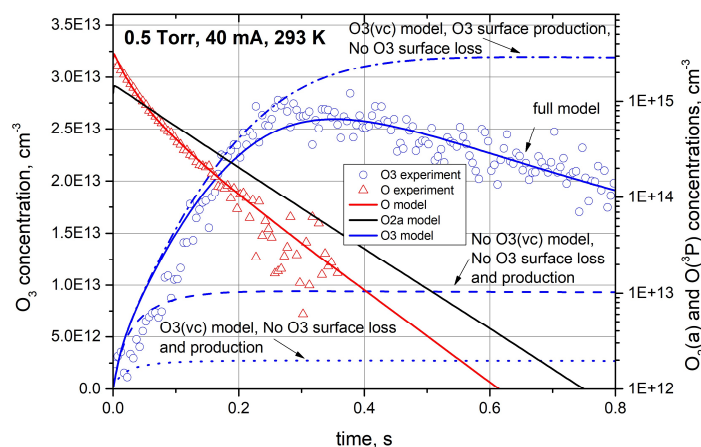


Fig. 1: Evolution of the measured (O₃(0,0,0), O(³P)) and calculated (O₃(0,0,0), O(³P), O₂(a)) axial concentrations in the afterglow of the O₂ discharge at $p=0.5$ Torr, $I_d=40$ mA, $T_w=293$ K.

Numerical simulation and complex network analysis of reacting chemistry in plasma treated water

Tomoyuki Murakami (*)¹

¹ Faculty of Science and Technology, Seikei University, 180-8633 Tokyo, Japan

(*) tomo-murakami@st.seikei.ac.jp

Low-temperature plasmas have been widely studied in the fields of biomedicine, agriculture, sustainable energy conversion. In these applications, plasma-treated water is gaining increasing attention because they can produce abundant reactive species, whereas the aqueous chemistry is complex and its mechanism is not fully understood. We still have some challenges to reach comprehensive understanding of the nature of plasma-treated liquid chemistry. This study proposes mathematical/numerical approaches to tackle the issue. The complex network analysis based on the graph-theory, one of the information mathematics, enable us to reveal the hidden feature of liquid chemistry through the visualization and centrality-based identification of the reacting network [1, 2]. A newly-developed one-dimensional reaction-diffusion model with hundreds of reaction processes of air-saturated water can simulate the influence of the irradiation of plasma-induced reactive species on the liquid chemistry by quantifying how various plasma species permeate into the liquid and what reactions are triggered.

This work was partially supported by JSPS KAKENHI JP19K03813, JP20KK0089 and JP23H01404

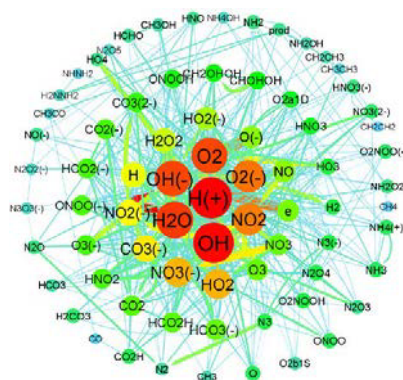


Fig. 1: Complexity visualization. Network diagram of the liquid chemical set. Species with high degree are illustrated as larger circle and located in the centre region.

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Vibrational cross sections of methane: from individual cross sections to polyad groups

N Pinhão^{(*)1}, T C Dias¹ and V Guerra¹

¹ Instituto de Plasmas e Fusão Nuclear Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

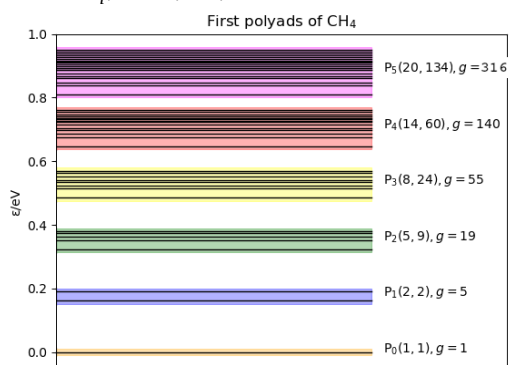
(*) npinhao@ctn.tecnico.ulisboa.pt

Methane (CH₄) is used in many types of plasma applications from dry reforming, thin film applications, plasma-assisted combustion, fusion studies in tokamaks or the study of outer atmospheres, e. g. of Titan. The modeling of these plasmas depends on reliable electron collision cross sections (cs) for the gases involved.

CH₄, like the other spherical-top molecules (STM), has four fundamental frequencies of vibration, with degeneracies of, respectively, (1, 2, 3, 3). Due to the near coincidence between the frequencies of the bending modes, ν_2 and ν_4 , and of the stretching modes, ν_1 and ν_3 , it has not been possible to experimentally separate the individual electron vibrational cs [1]. The rovibrational spectra of STM, show a complex structure of bands, the so-called polyads, which has motivated the development of high-resolution theoretical analysis of those spectra [2]. In case of CH₄, the vibrational levels are grouped in polyads, P_n, with n satisfying the relation

$$n = 2\nu_1 + \nu_2 + 2\nu_3 + \nu_4 \quad (1)$$

where $\nu_i, i = 1, \dots, 4$ are the number of vibrational quanta in each of the four modes.



The figure shows the first six polyads of CH₄, the number of levels and sublevels, and the compound degeneracy of states within each polyad.

The methane cross sections have been reviewed by Song et al [3], and recently extended by Bouwman et al [4] with cs for neutral dissociation. These sets, however, do not consider polyad groups.

In this work we study the effect of including the treatment of the vibrational polyad groups and propose an updated complete and consistent cs set. Two different methods were used to solve the Boltzmann equation: the LoKI-B solver [5] based on the two-term approximation and a density gradient expansion for electron swarms. The new cs set was adjusted using a genetic algorithm [6].

Acknowledgments

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Development of reaction mechanisms for plasma chemistry

T. Silva, T. C. Dias, C. Fromentin and V. Guerra

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

Low-temperature plasmas have been used in a manifold of applications, due to the inherent ability to produce highly reactive species. The potentiality comes together with great complexity and, although these plasmas were vastly studied, important details of its kinetics remain uncertain.

The kinetic scheme describing the interactions between the heavy species and their connection with the electrons is one of the pillars of low-temperature plasma modelling. Therefore, the definition of a *reaction mechanism*, *i.e.*, sets of reactions and corresponding rate coefficients that are validated against benchmark experiments is mandatory to make sensible modelling predictions of the system under study. This procedure must still be improved in the low-temperature plasma community, where extensive validation of electron-impact cross sections by swarm analysis is well established, but the validation of plasma-chemistry models against benchmark experiments remains to some extent elusive. Indeed, although many modellers follow the procedure of comparing their results against experiment for many years, a community consensus on recommended practices and definition of experiments as golden standards to assess the results of the models is still missing [1].

In this work we report on a vast modelling work carried out at IST-Lisbon in collaboration with Laboratoire de Physique des Plasmas (LPP) in Paris that has led to the definition of reaction mechanisms e.g. for CO₂ [2], CO₂-O₂ [3], CO₂-N₂ [4] and CO₂-CH₄ plasmas. Further work involving IST, LPP and the Lomonosov Moscow State University (MSU) additionally led to a refined reaction mechanism for O₂ plasmas [5].

It is argued that the development of kinetic schemes for plasma chemistry should adopt a paradigm based on the comparison against standard validation tests. However, more experimental data from various independent researchers is necessary to evaluate possible problems of reproducibility or systematic errors, and to extend the conditions for validation.

Acknowledgements

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Plasma conversion of CO₂, N₂/O₂ & CH₄

Richard van de Sanden^{1,2}

¹*DIFFER), Eindhoven, The Netherlands*

²*Department of Applied Physics, EIRES, Eindhoven, The Netherlands*

(*) m.c.m.vandesanden@diffier.nl; m.c.m.v.d.sanden@tue.nl

In this talk I will give an overview of the status and our understanding of plasma conversion of CO₂, N₂/O₂ and CH₄ using microwave generated plasmas. The background is renewable energy driven chemistry in which the (non-)thermal properties of plasma (difference in temperatures between the electrons, the molecules and their vibrational degrees of freedom), possibly with the assistance of catalysts, can drive chemical conversions beyond the thermal equilibrium limit. Important aspects as energy and conversion efficiency and the chemical conversion processes at play, as determined using several (in situ) diagnostics, will be highlighted. In addition, some novel approaches in which plasma are combined with electrochemical conversion using hydrogen or oxygen transporting membranes and their potential advantages, will be discussed.

Combustion and Energy Processes and the Role of Plasma

Ahmed F Ghoniem^(*)

Massachusetts Institute of Technology, Cambridge, MA, USA

^(*) ghoniem@mit.edu

The performance of some combustion and renewable fuel production processes are often determined, at least in part, by finite-rate kinetics. In combustion, these include ignition delays, burning velocities and extinction limits. Nonoptimal values of these combustion properties could render the process dangerously unstable or, especially while using some renewable fuels, incompatible with engine designs. For instance, thermoacoustic instability in configurations similar to those used in many practical systems has been shown to scale with flame extinction limits highlighting the role of fuel chemistry in operating combustion under high power conditions. Similarly, operating systems near the lean flammability limits to control emissions is often complicated by difficulties to initiate ignition, or could be associated with other types of instabilities. In the case of thermochemical processes for the production of hydrogen, CO₂ reuse for fuel production, or gasification of biomass, diffusion limits are often overcome by reducing particle size or membrane thickness, but surface chemistry limitations persist. Changing the operating temperature to overcome these limits can negatively affect the selectivity. In both cases of combustion and fuel production, introducing plasma has been shown to help enable operation beyond observed limits, improve yield and selectivity, and improve productivity. For instance, plasma has been used to enable ignition below flammability limits, and plasma actuation has been shown to reduce pressure oscillations under conditions when thermoacoustic coupling is observed. While still under investigations, mechanisms responsible for such changes are likely related to the aforementioned kinetic effects. Plasma gasification has also been demonstrated at scale. While still in early stages, enhancement of catalytic processes in membrane reactors and chemical looping for fuel production have also been proposed recently. The talk will review some of these observations, fundamentals related to their mechanisms and research and developments need to expand their applications.

Microwave Plasma CO₂ Conversion Enhanced by Concentrated Solar Radiation

Juan Pablo Trelles ^{(*)1}

¹ Department of Mechanical and Industrial Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States of America

(*) email of corresponding author

The conversion of carbon dioxide (CO₂) using renewable energy can help fulfil the demand for fuels and chemicals while reducing CO₂ emissions. Solar-plasma chemical synthesis combines the use of electricity to sustain plasma with concentrated solar radiation (Fig. 1a) to achieve processes that are more economically viable than solar thermochemical and plasmachemical methods [1]. An implementation of this concept is Solar-Enhanced Microwave Plasma (SEMP) (Fig. 1b). The evaluation of a SEMP reactor operating with up to 900 W of microwave power together with up to 525 W of incident solar power from a high-flux solar simulator at atmospheric pressure revealed that under all the studied conditions, the absorbed solar radiation leads to increased conversion efficiency (Fig. 1c) [2, 3]. The highest conversion efficiency obtained with CO₂-N₂ (1:8.75 by volume, representative of flue gas from fossil fuel power plants) is ~15.5%, whereas the highest conversion efficiency using CO₂-Ar (1:7 vol.) is ~9.5% – both observed at the specific energy input (SEI) of ~1.8 eV/molecule. The enhanced process performance appears to be the consequence of the greater power density of the microwave plasma due to the absorption of solar radiation, circumventing the limitations of skin-depth power absorption.

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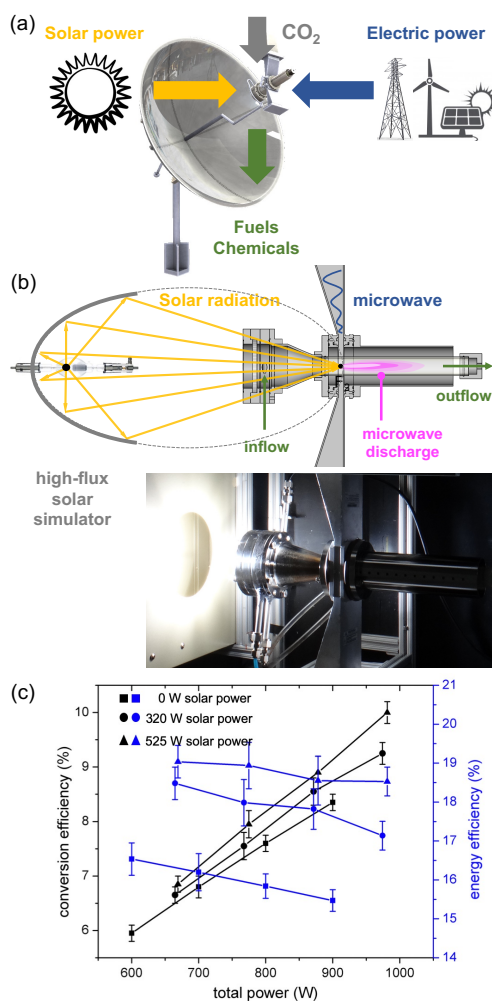


Fig. 1: (a) Solar-plasma CO₂ conversion, (b) solar-enhanced microwave plasma (SEMP) reactor schematic and during operation, (c) conversion and efficiency versus total power for operation with 8 slpm of CO₂-Ar (1:7 vol.).

Investigation of plasma activation mechanisms of highly stable molecules in atmospheric pressure plasmas

Luca Matteo Martini¹, Giorgio Dilecce², Paolo Tosi^{(*)1}

¹ *Department of Physics, University of Trento, 38123 Povo Trento, Italy*

² *CNR – Institute for Plasma Science and Technology, 70126 Bari, Italy*

(*) paolo.tosi@unitn.it

The decarbonization of society requires replacing fossil with renewable resources as a source of fuels and chemicals. One could use CO₂, N₂, and H₂O to obtain this, provided an efficient method exists to activate these highly stable molecules.

Ideally, the process should direct energy towards molecular dissociation while minimizing gas heating. To this purpose, the plasma approach utilizes the unique non-equilibrium properties of gaseous discharges. Despite increasing research, plasma activation of tightly bound molecules has yet to reach the maturity needed for industrial applications. The challenge of making the latter commercially viable lies in finding the right tradeoff between bulk conversion and overall energy efficiency. To obtain the desired product yield and efficiency, it is crucial to have control over the dissociation mechanism and to be able to monitor it. We have exploited the flexible pulsing schemes of nanosecond repetitively pulsed discharges to control both the conversion and the efficiency of the process. To monitor the dissociation, we must adopt a new approach to studying plasma chemistry beyond merely measuring the reaction products that exit the reactor. We require local, time-resolved diagnostics to gain insight into the plasma at the appropriate time scale. Our recent contributions in this area will be presented during the workshop.

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Electrification of chemical reactions: Plasma-based CO₂, CH₄ and N₂

Annemie Bogaerts

Research group PLASMANT, University of Antwerp, 2160 Antwerp, Belgium

annemie.bogaerts@uantwerpen.be

Plasma technology is promising for the electrification of chemical reactions, such as CO₂ and CH₄ conversion into value-added compounds, and N₂ fixation for fertilizer applications [1-4]. However, before enabling large-scale industrial application, the processes should be further improved in terms of conversion, energy efficiency and product formation. This can be done by experiments, while more insight in the underlying mechanisms can be obtained by computer modelling.

I will present some recent results obtained in our group PLASMANT, illustrating how modeling can help to better understand the underlying mechanisms, in order to improve the applications.

Examples will include: reactor design improvements for enhanced performance, placing a carbon bed after a plasma reactor for trapping the O/O₂ and thus limiting again the recombination reactions with CO back into CO₂, thereby drastically increasing the CO yield and removing O₂ from the gas mix, the effect of gas recirculation for higher CO₂ conversion, the effect of quenching nozzles to avoid recombination reactions, plasma chemical kinetics models, surface chemical kinetics models, and combined plasma-surface chemical kinetics models for various plasma catalysis applications, as well as N₂ fixation into NO_x in various plasma reactors, supported by chemical kinetics modeling, also followed by lean-NO_x trap conversion for very energy-efficient NH₃ production.

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Methane Plasma Chemistry to aid the Energy and Materials Transition in the Process Industry

G.J. van Rooij

¹ Department of Circular Chemical Engineering, Faculty of Science and Engineering, Maastricht University

g.vanrooij@maastrichtuniversity.nl

A carbon neutral and circular economy requires utilization of waste materials and biomass as feedstock for the production of new materials. Moreover, the energy input must be of zero carbon footprint, which currently implies that it concerns electric energy input that is intermittently available. Plasma technology carries distinct advantages and/or promises that make it suitable to make an impact in the transition to a circular economy such as compatibility with (intermittent) sustainable energy and unique opportunities for efficiency and/or selectivity in reactions with CO₂, N₂, and CH₄.

This presentation focuses on CH₄ pyrolysis as to achieve carbon coupling. It is known that fast heating and quenching of CH₄ as can be provided for with plasma allows to form C₂-molecules and to prevent further polymerization to solid carbonaceous material. The Hüls process, currently employed at industrial scale, relies on this principle to produce acetylene. The Kassel mechanism that is usually referred to as kinetic explanation for acetylene selectivity suggests that there is also a window of opportunity for ethylene (C₂H₄), an important building-block for the chemical industry. We compare different flow configurations in microwave plasma discharges that confirm the combined influence of residence time and heavy particle temperature on selectivity. We use this as a basis to extrapolate to its implementation in a present day process industry environment and sketch a scenario how this serves circularity and sustainability ambitions.

Streamer-based discharge on water surface for nitrogen fixation - a diagnostic study

Petr Hoffer¹, Václav Prukner¹, Garima Arora¹ and Milan Šimek^{(*)1}

¹ Department of Pulse Plasma Systems, Institute of Plasma Physics of the CAS, Czech Republic

(*) simek@ipp.cas.cz

We recently proposed and tested a flow-through plasma reactor, that produces transient discharges on surface of a thin layer of water [1]. The discharge geometry utilizes carefully designed compartments with high voltage and grounded electrodes, all immersed in water. When a thin (~1 mm) layer of water covers the partition separating the HV and grounded compartments, an intense electric field (several kV/mm) on the air-water interface initiates ionization waves (Fig. 1). Next, multiple plasma filaments expand above the water surface. A significant advantage of this design is that the discharge is in contact only with the liquid. This feature significantly increases the wear resistance of the reactor and minimizes the contamination of the plasma-activated water by the electrode material. With the given geometry, the reactive species produced by the discharge in the immediate vicinity of the water surface are easily dissolved (preliminary analysis of the production showed maximum NO₂- or H₂O₂ yields of 35 or 30 mmol/kWh) [1].

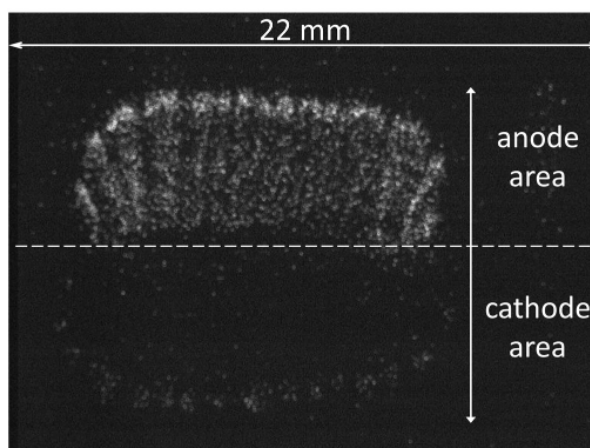


Fig. 1: Ionization waves propagating along the water surface captured by the 4-Picos ICCD camera.

In this presentation, we will discuss the results of a diagnostic study based on time-resolved ICCD emission spectroscopy and four-channel ICCD imaging revealing the basic phases of the discharge (starting with ionization waves and ending with transient spark filaments) and demonstrating that each successive discharge phase is characterized by its particular morphology and spectrometric signatures (e.g. N₂ bands occurring during ionization waves or Stark broadened H/N/O atomic lines during the final spark phase).

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A close look at time-locality assumptions on the modelling of nanosecond-pulsed discharges

T. C. Dias^(*), V. Guerra

Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Portugal

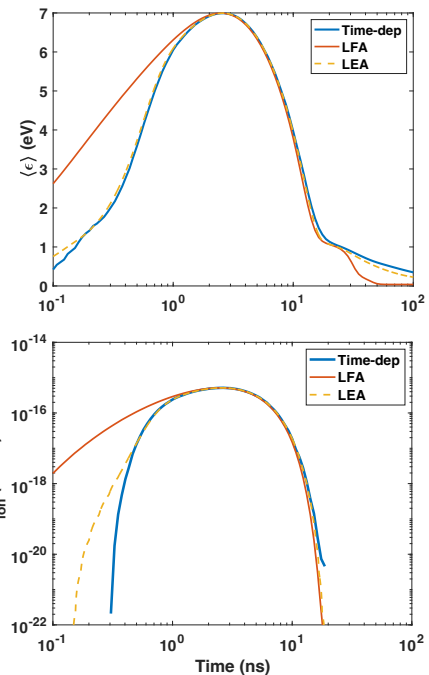
(*) Email: tiago.cunha.dias@tecnico.ulisboa.pt

The use of nanosecond-pulsed discharges (NPD) has been growing quickly due to their interest for plasma assisted conversion of different molecules. However, their potential comes together with great complexity and a detailed study of the fundamental processes in the discharge is necessary to find the most efficient configuration for a determined application. NPD are characterized by very high reduced electric fields, E/N (~ 1000 Td), with rising times on the nanosecond timescale, which turns their modelling deeply challenging, specially in what regards the electron kinetics and their coupling with the heavy species.

The electron kinetics in gas discharges is described by the electron Boltzmann equation (EBE) and is often solved following one of two assumptions: the local-field approximation (LFA), also known as the quasi-stationary approximation, which identifies the solution of the EBE with the steady-state calculation assuming locality in space and time, being satisfactory when the electron energy relaxation is sufficiently fast; and the local-energy approximation (LEA), where the rate-coefficients and the electron power distribution along the different collisional channels depend on the local value of the electron mean energy. In the latter the EBE is typically solved for a wide range of E/N in steady-state conditions and, then the results are converted into a lookup table as a function of the electron mean energy. Moreover, an additional equation for the electron mean energy is included, using the input power from the electric field and the power losses obtained from the lookup table.

In this work we focus on time-locality and evaluate the impact of the LFA and LEA assumptions on the temporal evolution of the electron kinetics in a NPD. We use the electron kinetics Monte Carlo solver LoKI-MC [1]. The initial version of the code solves only configurations with homogeneous DC electric fields. Here, we generalize the formulation to time-dependent electric fields to obtain an accurate solution in a nanosecond pulse. Then, this solution is compared against the LFA and LEA, in various pulses, pressures and background gases.

The figure on the right shows a comparison of the electron mean energy $\langle \varepsilon \rangle$ and ionization coefficient k_{ion} for an electric-field pulse in air at 10 Torr, using the time-dependent and the LFA and LEA approaches. The results underline the importance of comparing the electron energy relaxation time with the characteristic times of the pulse before using the LFA. The LEA succeeds significantly more due to the presence of the “memory” effect introduced by the additional equation for the electron energy, as it will be shown in the workshop.



Acknowledgements

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CO₂ dissociation at moderate pressures: are there advantages of high electric fields and high specific energy input?

Zhan Shu¹, Georgy Pokrovskiy¹, Nikolay Popov², Svetlana Starikovskaia^{1(*)}

¹ *Laboratory of Plasma Physics (CNRS, Ecole Polytechnique, Univ. Paris-Sud, Observatoire de Paris, Sorbonne Universit'e, l'Institut Polytechnique de Paris), Ecole Polytechnique, route de Saclay, 91128 Palaiseau, France.*

² *Skobeltsyn Institute of Nuclear Physics, Moscow State University, Moscow, 119991, Leninsky gory, Russia.*

(*) svetlana.starikovskaia@lpp.polytechnique.fr

There exists two competing mechanisms of dissociation of carbon dioxide in a discharge: vibrational pumping and dissociation by electron impact where the former is more efficient but yields less and the latter requires more energy but can provide bigger values of dissociation fraction. Vibrational pumping is realized at low values reduced electric field ($E/n = 50-100$ Td, n here is a gas density) and electronic excitation and dissociation *via* excitation of electronically excited states is realized at high values of reduced electric field ($E/n > 100-200$ Td). High E/n values provide efficient ionization, so higher values of the electron density and the electric current will be achieved. However, the value of the maximal current is limited by a power of the high voltage generator and the more is the value of E/n to be maintained, the less are the time periods at which it is possible. This limit entails the necessity to shorten the incident high voltage pulse and justifies the motivation of use of nanosecond discharges.

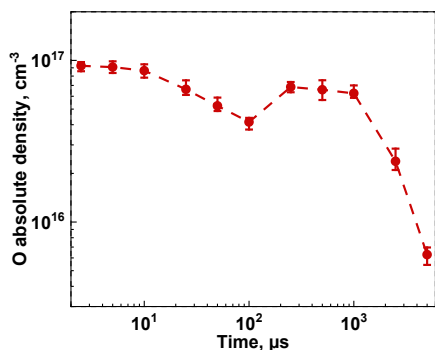


Fig. 1: TALIF data on O-atoms density in nanosecond capillary discharge in 20 mbar nanosecond capillary discharge in CO₂,

discharge was initiated in the new gas portion was used. TALIF measured O-atom density (Fig.1) is in good agreement with numerical calculations for capillary discharge [1]. Paper [1] presents experiments on the temperature measurements in CO₂ capillary discharge and the model describing fast gas heating and O-atoms density. The model contains 21 reactions including reactions with electronically excited species.

Specific energy deposited in plasma (SED) is defined by different factors including the discharge geometry and the pulse duration. The SED value is a key parameter defining plasma chemistry of excited species. It has been shown recently that in capillary nanosecond discharges, the SED can be as high as a few eV/molecule. The nanosecond discharge was initiated in the capillary tube with 2.0 mm of internal diameter and 53 mm inter-electrode distance. High-voltage pulses (9 kV amplitude, 30 ns FWHM and 10 Hz repetitive frequency) were delivered via the coaxial cable. CO₂ under 20 mbar pressure flowed at the rate of 10 sccm so that each

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Dynamics of negative ions in dc O₂ discharge

J-P. Booth¹, O. Guaitella¹, E. Baratte¹, Shu Zhang¹, D. Lopaev^{(*)2},
T. Rakhimova², D. Voloshin², A. Chukalovsky², Yu. Mankelevich²

¹Laboratoire de Physique des Plasma (LPP), CNRS, Sorbonne Universite, École Polytechnique, Institut Polytechnique de Paris, 91120 Palaiseau, France

²Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University (MSU), 1(2), Leninskie gory, GSP-1, 119991 Moscow, Russian Federation

(*) d.lopaev@gmail.com

The experiments on studying dynamics of negative ions by laser photodetachment were carried out at the same discharge parameters and experimental conditions as during the time-resolved CRDS measurements in DC pulsed discharge. The following modulation was used: 0.2s – discharge is on, 0.8s – afterglow (discharge is off). Identical discharge tubes were used in LPP and MSU. In MSU the O⁻ and O₂⁻ ions dynamics was measured by laser photodetachment using two lasers, at 532 nm and 1064 nm. The O₂(a) molecules dynamics was measured by IR OES. In LPP the O(³P) atoms density dynamics was measured by on-resonance O(³P₂) → O(¹D₂) absorption at 630 nm by the time-resolved CRDS while O⁻ density dynamics was detected by off-resonance absorption. The current and electric field dynamics and actinometric ratio I_O/I_{Ar} were also measured to compare the surface conditions of the tubes. Wall temperature of +50C was fixed by external thermostatic chiller. Gas pressure range from 0.2 to 2 Torr and discharge current range from 10 to 40 mA was studied. The O⁻ and O₂⁻ dynamics is determined by fast detachment reactions with O(³P) atoms and O₂(a) molecules. Wall loss probabilities for O(³P) atoms and O₂(a) molecules were obtained by describing experimentally measured dynamics of corresponding species. Experiments were analysed using a self-consistent one-dimensional 1D model of a pulsed dc glow discharge in a tube. Example of the calculated curves and experimental data on the dynamics of the O atoms and O₂(a) mole fractions at pressure of 1.5 Torr is shown in Fig. 1. Fig. 2 shows the O₂⁻/O⁻ density ratio dynamics. Comparison of model curves with experimental data for O₂⁻/O⁻ made it possible to evaluate the rate constant of the quasi-resonant charge exchange reaction O⁻+ O₂(a) → O₂⁻+O.

This study was supported by the Russian Science Foundation, Project No. 21-72-10040

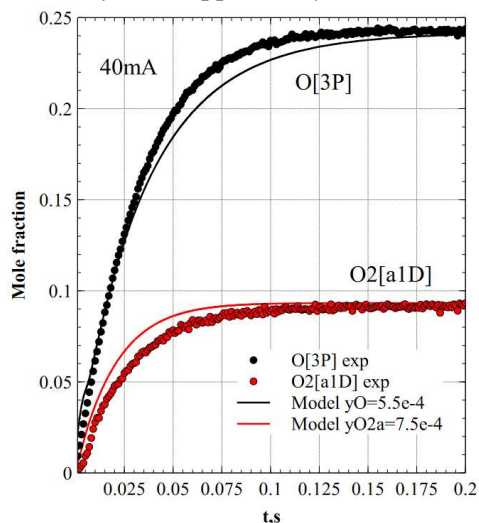


Fig. 1: Dynamics of O atoms and O₂(a) mole fractions at pressure of 1.5 Torr

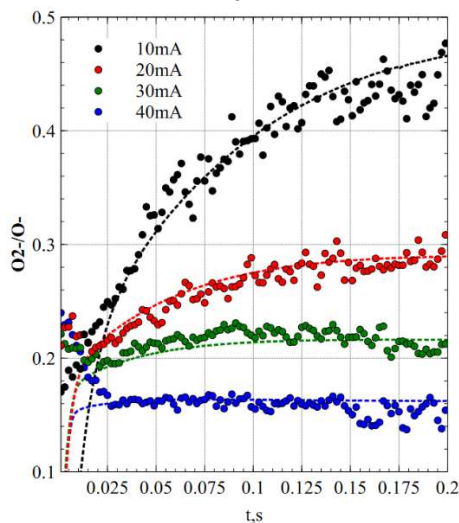


Fig. 2: Dynamics of the O₂⁻/O⁻ at a pressure of 1.5 Torr and different discharge currents

Plasma-induced reversible surface modification and its impact on oxygen heterogeneous recombination

José Afonso¹, Luca Vialetto^{2,3}, Vasco Guerra¹ and Pedro Viegas^{1(*)}

¹ *Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal*

² *DIFFER - Dutch Institute for Fundamental Energy Research, 5612 AJ Eindhoven, The Netherlands*

³ *Theoretical Electrical Engineering, Faculty of Engineering, Kiel University, Kaiserstrasse 2, D-24143 Kiel, Germany*

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

A decrease with pressure of the atomic oxygen recombination probability on Pyrex has been reported in [1] for an oxygen glow discharge plasma operating in the pressure range between 0.27 mbar (0.2 Torr) and 1 mbar (0.75 Torr). Moreover, an increase of the recombination probability with current is observed in this pressure range, which is not the case at higher pressures. In this work it is shown that this change in regime results from a modification of a Pyrex surface, which may impact intermediate pressure plasma reactors where plasma-surface interactions are present. Numerical simulations from a mesoscopic model employing deterministic and Kinetic Monte Carlo methods [2-4] describe very well the experimental data and suggest that the modification is induced by the production and destruction of metastable chemisorption sites at the surface. As such, the Langmuir-Hinshelwood (L-H) and Eley-Rideal (E-R) recombination mechanisms take place involving not only physisorption and stable chemisorption sites, but also metastable chemisorption sites, produced by the impact of fast O₂ ions and neutrals, and where recombination can take place with lower energy barrier [5]. The production of metastable chemisorption sites decreases with pressure due to the incident energy of these particles and increases with current due to the flux of incident particles. The presence of metastable sites can be reversed by increasing the plasma pressure, since the destruction of these sites takes place through the collision of incident neutrals from the plasma, which does not decrease with pressure.

Acknowledgements

This work was partially supported by the Portuguese FCT-Fundação para a Ciência e a Tecnologia, under projects UIDB/50010/2020, UIDP/50010/2020 and PTDC/FISPLA/1616/2021 (PARADiSE).

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How the ionic wind can be used for airflow control and EHD propulsion, and how it could improve the efficiency of plasma reactors ?

Eric Moreau, Nicolas Benard

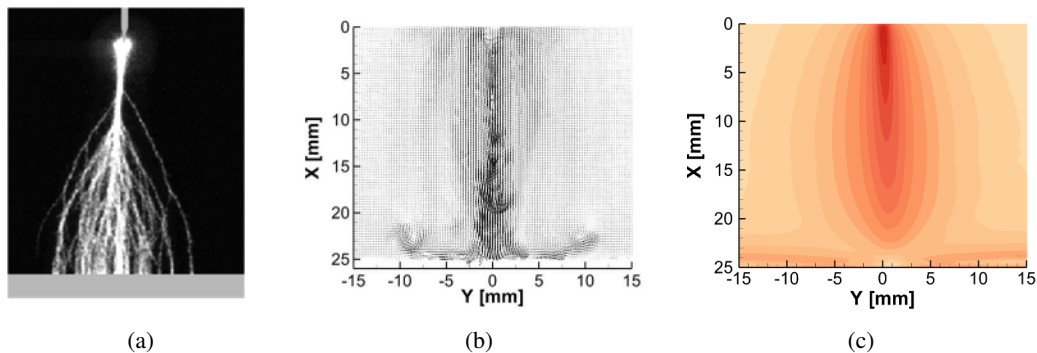
Institut PPRIME, Université de Poitiers, France

(*) eric.moreau@univ-poitiers.fr

On the one hand, in most engineering applications, corona discharges are used to modify the gas chemistry, for ozone production, reduction of gaseous pollutants, surface treatment or assisted-combustion to name a few examples. On the other hand, they can be used for their electroaerodynamic properties, either for manipulating the trajectory of particles in electrostatic precipitators, or to induce an airflow called *ionic wind*. For about twenty years, this last phenomenon has been the subject of lots of studies because of its numerous applications, mainly for airflow control by plasma actuators [1] and more recently for electric propulsion [2, 3].

Indeed, when a high potential difference is applied between two electrodes in atmospheric air, molecules are ionized and under certain conditions of electrode geometry, a corona discharge can be induced. Due to the electric field, the produced ions are submitted to Coulomb force, resulting in their motion, usually from the high voltage electrode toward the grounded collecting one. The set of all these Coulomb forces results in a volume electroaerodynamic (EAD) force occurring inside the discharge. Moreover, the numerous collisions that occur between ions in motion and neutral air molecules results in a momentum transfer at the origin of the ionic wind [1, 4].

In this oral presentation, we will present electrical, optical and mechanical properties of DC and AC point-to-plate corona discharges, point-to-plate dielectric barrier discharges and surface dielectric barrier discharges. More especially, we will focus on the ionic wind produced by these different discharges and we will discuss why this ionic wind should be taken into account in non-thermal plasma chemistry reactors and how it can be used to improve the efficiency of such reactors. Finally, we will present the two main applications of plasmas studied at University of Poitiers : airflow control by plasma actuators and atmospheric electroaerodynamic propulsion.



ICCD image of a positive streamer corona discharge (a), instantaneous (b) and time-averaged (c) velocity of the ionic wind produced by a needle-to-plate corona discharge.

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Pathways for Nitrogen Fixation by Plasma Catalysis

Brian Bayer¹, Sai Raskar², Oluwatosin Ohiro³, Bryan Goldsmith³, Igor Adamovich², Aditya Bhan¹, Peter Bruggeman^{(*)4}

¹ Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, USA

² Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH, USA

³ Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, USA

⁴ Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN, USA

(*) pbruggem@umn.edu

Coupling non-thermal plasma with heterogeneous catalysis offers a sustainable electrically driven route to produce NH₃, a molecule that is vital for sustaining global food production. We report on the gas-phase and surface-mediated pathways that are responsible for reactions of N₂ and H₂ in plasma catalysis to form NH₃ at near-ambient temperatures and pressures using a combination of molecular beam mass spectrometry (MBMS) measurements [1] and kinetic modelling of gas phase and surface reactions. We used a setup that couples plasma-derived species with a packed bed of non-porous transition metal wool catalysts. Operational conditions were systematically chosen to enable rapid transport of plasma-derived intermediates to catalytic surfaces and thereby facilitate analysis of underlying reaction pathways.

MBMS measurements show that conversion of plasma-derived species and formation of NH₃ is enhanced when Fe, Ni, or Ag catalysts are placed downstream of the plasma jet. Through correlation of quantities and rates of N consumption with NH₃ formation in the packed bed of catalyst, we show that NH₃ formation can be described by surface reactions involving N radicals. Rates of N consumption and NH₃ formation by surface reactions correspond over Fe, Ni, and Ag catalysts demonstrating that N species engender NH₃ (Figure 1) [2].

A key goal of the work was to experimentally assess the computationally predicted role of N₂(v) in plasma catalysis. State-to-state kinetic modelling, validated by threshold ionization MBMS measurements [1], shows that total N₂(v) densities produced by the plasma exceed N densities by over two orders of magnitude. MBMS measurements show that N₂(v) consumption is enhanced in the presence of the catalyst and are in quantitative agreement with state-to-state modelling that includes reactions for vibrational relaxation of N₂(v) on the metal surfaces, which does not contribute to NH₃ formation. Related surface processes are currently being investigated.

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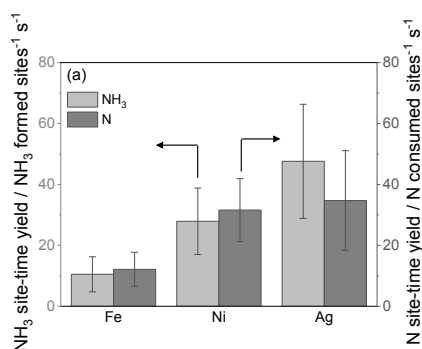


Fig. 1: Comparison between site time yields for NH₃ formation and N consumption over Fe, Ni and Ag [2].

Experimental study of microwave and gliding arc plasma discharges utilized for the fixation of nitrogen into NO_x

Rony Snyders^{1,2}

¹*Chimie des Interactions Plasma-Surface (ChIPS), CIRMAP, Université de Mons, 7000 Mons, Belgium*

²*Materia Nova Research Center, Parc Initialis, 7000 Mons, Belgium*

(*) rony.snyders@umons.ac.be

Nowadays, plasma-assisted nitrogen fixation (NF) processes have been demonstrated as a highly promising alternative to the environmentally impacting Haber-Bosch process [1]. Therefore, the community develops abundant attempts to optimize these processes in term of energy cost and conversion yield. Among numerous plasma technologies, low-pressure pulsed microwave (MW) discharges and atmospheric gliding arc plasmas (GAP) are found to particularly suit well thanks to the significant molecular vibrational excitation they allow. In this contribution, we overview our recent experimental efforts to contribute towards a better understanding of these plasma technologies for NF into NO_x.

In a first part, we specifically report on the NO formation in a low-pressure surfaguide-type MW 2.45 GHz discharge working in the 0.5-12 Torr pressure range in N₂:O₂ gas mixtures. Evaluation of the NO density is obtained by using Fourier Transform Infrared (FTIR) calibrated spectroscopy. For this purpose, the corresponding ro-vibrational absorption bands of the corresponding molecular species were monitored at different discharge conditions. In particular, the vibrational excitation of N₂ is found correlating with the obtained production yield of NO, using optical emission spectroscopy (OES). Particular attention is devoted to estimate the evolutions of the NO yield and energy cost at different discharge conditions. Minimum energy cost of about 8 MJ mol⁻¹ corresponding to the yield of about 7% are found for NO formation. Our experimental observations are supported by plasma modelling, confirming the decisive role of N₂ and O₂ vibrational excitation in molecular dissociation and so in the NO formation.

In the second part, we share our recent results related to the performances of an atmospheric pressure GAP discharge, especially in term of discharge stability which today is most of the time ensured by using external ballast resistors. Although this indeed allow for an enhancement of the plasma stability, very little is reported about how it impacts the process efficiency both in term of chemical yield and energy cost. In this work, both the performances and the stability of the plasma are evaluated as a function of the utilisation of ballast resistors. The results confirm that if the use of a ballast resistor indeed allows for a strong stabilization of the plasma without impacting the conversion yield, especially at low plasma current, it dramatically increases the energy cost of the process from 2.82MJ/mol to 7.9MJ/mol. As an alternative approach, we demonstrate that the replacement of the ballast resistor by an inductor is promising since it allows to decently stabilize the plasma while it does not affect neither the energy cost of the process nor the conversion yield.

This work is supported by the FNRS project “NITROPLASM”, EOS O005118F.

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Understanding nitrogen fixation while studying volume and surface kinetics in N₂-O₂ plasmas

T. Silva^{1(*)}, C. D. Pintassilgo^{1,2}, A. Herrmann³, S. Bera³, S. Welzel³, M. N. Tsampas³, M. C. M. van de Sanden^{3,4} and V. Guerra¹

¹*Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal*

²*Departamento de Engenharia Física, Faculdade de Engenharia, Universidade do Porto, Portugal*

³*Dutch Institute for Fundamental Energy Research (DIFFER), Eindhoven, The Netherlands*

⁴*Eindhoven Institute for Renewable Energy Systems (EIRES), Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands*

(*) tiago.p.silva@tecnico.ulisboa.pt

Plasma-assisted nitrogen fixation is considered a very promising alternative to the well-established but environmentally harmful Haber-Bosch process. Motivated by the possibility of having an efficient NO synthesis in plasmas, many recent efforts have been targeted at describing the chemistry of N₂-O₂ plasmas through experiments and modelling studies. While experimental works are often focused on the tuning of plasma conditions that optimize NO production (see e.g. [1]), recent modelling studies have been targeted at calculating new and more refined rate coefficients for the Zeldovich mechanism through quasi-classical trajectory (QCT) methods [2].

In this work, we investigate the volume and surface kinetics of N₂-O₂ plasmas while assessing the role of the main mechanisms leading to the production of interesting species, including not only NO, N₂O or NO₂ (often measured in experiments) but also atomic species with special relevance to the understanding of the Zeldovich mechanism, namely atomic oxygen O(³P) and atomic nitrogen N(⁴S). This work leverages upon extensive modelling studies published over the past years (see e.g., the review in [3]) and very recent experimental campaigns devoted to the observation and rationalization of nitrogen oxidation enabled only by coupled plasma (produced by an inductive coil and connected to a matching network of a radio frequency generator) and catalyst [4]. We are particularly interested at understanding the flow of relevant species towards the post-discharge region of the reactor, where a catalyst can be placed. Our study demonstrates a good agreement between model and experiment, indicating that our computational approach accurately captures the relevant chemistry and can be used to unveil the dominant mechanisms in the plasma. This work represents an important first step towards developing of a reaction mechanism specifically tailored to the production of NO.

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Path to Selective Generation of Excited Species and Radicals in High-Pressure Nonequilibrium Plasmas

Caleb Richards¹, Sai Raskar¹, Keegan Orr¹, Xin Yang¹, and Igor Adamovich^{(*)1}

¹ Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH, USA

(*) adamovich.1@osu.edu

”Hybrid” plasmas sustained by a repetitive ns pulse discharge overlapped with a sub-breakdown DC or RF waveform offer selectivity in the generation of excited vibrational and low-energy electronic states of diatomic and small polyatomic molecules [1-3]. Unlike a ns pulse / DC discharge, a ns pulse / RF plasma can be sustained using a single pair of electrodes external to the plasma flow reactor. Measurements of the electric field in a ns pulse / RF discharge show that the peak reduced electric field during the ns pulses, up to 400 Td, is much higher compared to the reduced electric field in the RF plasma, 15-25 Td, which is optimum for the efficient vibrational excitation of N₂ by electron impact.

Measurements of N atoms, metastable electronic states, N₂(A³Σ_u⁺), and vibrationally excited molecules in the ground electronic state, N₂(X¹Σ_g⁺,v), in the ns pulse / RF plasma in nitrogen demonstrate that these species are generated selectively. N atoms and N₂(A³Σ_u⁺) are produced by the ns pulses, while N₂ vibrational excitation is enhanced by the RF waveform (see Fig. 1). IR emission spectra of the hybrid plasmas in CO-N₂ and CO₂-N₂ mixtures show that this approach also generates strong vibrational excitation of CO and CO₂, suggesting an enhancement of CO₂ dissociation. Sustaining hybrid plasmas in reacting molecular gas mixtures may isolate the plasma chemical reaction pathways dominated by vibrationally excited molecules from those of excited electronic states and atoms. The targeted vibrational excitation of molecular species in hybrid discharges is scalable to high pressures, electron densities, and discharge powers. This approach can be extended to the vibrational excitation of other molecular species where the vibrational relaxation is relatively slow, such as CO, CO₂, and H₂.

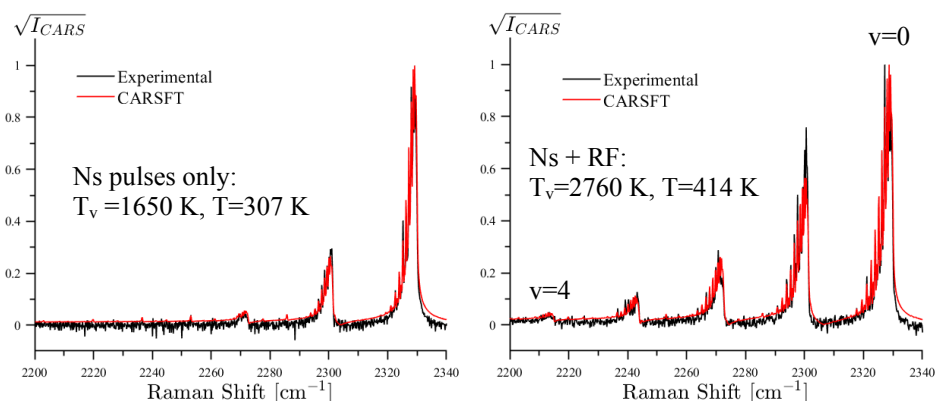


Fig. 1: N₂ CARS spectra in a ns pulse discharge (left) and in a ns pulse / RF discharge in nitrogen. P=100 Torr, pulse peak voltage 24 kV, repetition rate 10 kHz, peak RF voltage 1 kV.

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Abstracts

Poster communications

Breakdown in axisymmetric device with dielectric spacer at 1 atm

Rui Almeida^{(*)1,2}, Pedro Almeida^{1,2}, George Naidis³, Mikhail Benilov^{1,2}

¹ Departamento de Física, FCEE, Universidade da Madeira, Funchal, Portugal

² IPFN, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

³ Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow, Russia

(*) email of corresponding author

In this work we study the dependence of the ignition voltage (IV) and breakdown voltages (BDV) with regard to the proximity of a dielectric surface to the active discharge path. The studied device consists of a dielectric disc spacer of 4 mm height close-stacked between two disc electrodes of 7.5 mm radius in air at 1 atm. Below the BDV the discharge would extinguish and above it, the current increases rapidly by more than 5 orders of magnitude. The IV was investigated for different dielectric radii and boundary conditions over the dielectric surface, by means of the resonance method [1].

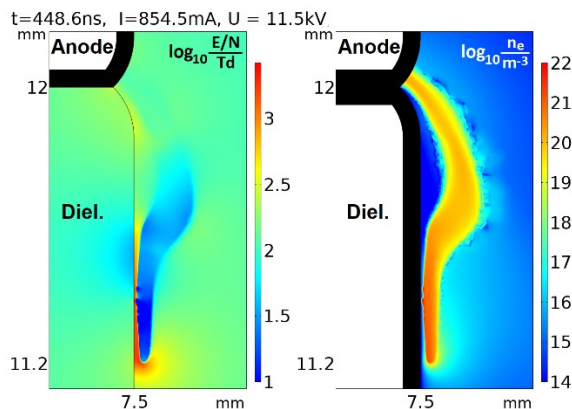
The dependence of the BDV was investigated using time-dependent simulations, for three dielectric radii (R), two dielectric constants (ϵ_D) and against two initial surface charge distributions, using the model described in [1] with the boundary condition of surface charge accumulation on the dielectric surface. The simulation's initial conditions were the Laplace solution for the electric field, uniform species densities of order 10^{10} m^{-3} and vanishing photoionization terms. Results are presented in the table below.

	$\epsilon_D = 1$	$\epsilon_D = 12$	
$R(\text{mm})$	$U(\text{kV})$	$U(\text{kV})$	$IV(\text{kV})$
3	10.0	10.0	9.9
7.5	9.5	12.0	6.8
8.2	14.5	—	11.5

Table: Minimum breakdown voltages belong to interval $[U-0.5, U]$ in kV, for three dielectric radii R and two values of the dielectric relative permittivity ϵ_D . No initial surface charge on dielectric surface. The last column shows the device's IV in kV.

In all cases, breakdown was seen to occur as a result of the gradual development of a near-cathode volume streamer that would eventually strike the cathode surface. For $\epsilon_D=12$ and $R=8.2$ mm, the calculation of the BDV still has to be validated. The figure below shows how the presence of surface charge leads to a reduction of the BDV .

Figure: Case of dielectric radius of 7.5 mm, $\epsilon_D=12$ and initial surface charge distribution of the IV state. Detail of a positive surface streamer propagating along dielectric. At the shown instant the electron density trailing behind the streamer head is seen to be collapsing the distance to the dielectric surface at several points. This attraction, between charge and dielectric, is expected on the basis of electrostatics.



Acknowledgments

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An extended Townsend criterion for multidimensional geometries

Rui Almeida^{1,2}, Pedro Almeida^{1,2}, George Naidis³, Mikhail Benilov^{(*)1,2}

¹ Departamento de Física, FCEE, Universidade da Madeira, Funchal, Portugal

² IPFN, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

³ Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow, Russia

(*) email of corresponding author

In this work we validate the Townsend self-sustainment criterion as it is extended to include the effect of negative ions and non-homogeneous electric fields in multidimensional geometries. The formulated extended criterion is validated against the exact solution of the eigenvalue problem describing the ignition of self-sustained discharges.

The ignition voltage (IV) of electrical discharges in gases is governed by an eigenvalue problem describing the ion and electron transport in the applied electric field [1]. At ignition of a self-sustained discharge, the discharge current is very low, multistep processes are irrelevant, and the charged particle conservation equations are linear. If diffusion, photoionization, and detachment reactions are neglected, and the local-field approximation adopted, then a partial integration of the system of conservation equations along the electric field lines gives a necessary condition for existence of a non-trivial solution,

$$e^{K(z_a)} + \int_0^{z_a} \eta e^{K(z)} dz = 1 + \frac{1}{\gamma'}, \quad \text{with } K(z) = \int_0^z (\alpha - \eta) dz \quad (1)$$

where α is the ionization coefficient, η is the electron attachment coefficient, γ' an effective secondary electron emission coefficient, coordinate z is measured along a field line from the cathode ($z = 0$) to the anode ($z = z_a$), and both integrals are evaluated along a field line. Equation (1) represents the extended Townsend criterion. It is reduced to the classical Townsend expression if no negative ions are considered, $\eta = 0$ (and uniform electric field).

The approach was validated against the exact solution of the eigenvalue problem describing the ignition of a self-sustained discharge computed by the resonance method [1]. The kinetic and transport coefficients are the same as in [1]. The extended Townsend criterion gives a very good result for the IV if η is replaced with the effective attachment coefficient [2]. The table below shows validation for the coaxial geometry.

p (atm)	Eigenvalue problem			Townsend criterion		
	a	b	c	Extended	Classical	d
0.117	5.60	5.72	5.68	5.77	5.73	5.73
0.996	26.16	26.69	26.10	26.73	26.14	26.16
9.063	153.21	163.12	148.39	163.15	148.42	152.77

Table: Inception voltage of coaxial negative corona (in kV) with inner radius of 0.1195 cm and outer radius of 4.875 cm, for different values of pressure. a) Full model. b) No photoionization and no detachment. c) No photoionization and no attachment. d) Equation (1) with η replaced with the effective attachment coefficient introduced in [2].

Acknowledgments

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Modelling low-current periodic pulses in corona discharges

Nuno Ferreira^{(*)1,2}, Ataollah Eivazpour^{1,2}, Pedro Almeida^{1,2}, George Naidis³,
Mikhail Benilov^{1,2}

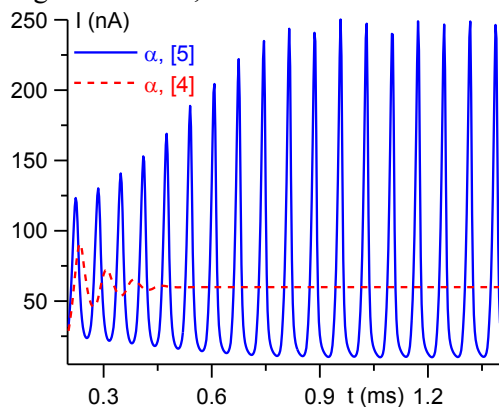
¹ Departamento de Física, FCEE, Universidade da Madeira, Funchal, Portugal

² IPFN, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

³ Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow, Russia

(*) email of corresponding author

In this work we study numerically the effect of small changes in the ionization coefficient on the loss of stability in negative corona discharges. These discharges are self-sustained and appear in nonuniform electric fields. Although very useful in several applications (e.g., medicine and environmental science), these discharges are undesired in high-voltage power transmission lines due to energy losses and/or device damage. For negative polarity, one observed regime is the so-called Trichel pulse regime, where periodic pulses in current appear. Another possible regime is stationary glow corona, which can evolve into the Trichel pulse regime by applying a finite perturbation (e.g., increasing the voltage by 1V). Experiments to reveal the mechanism of formation of such pulses were performed in several works, e.g. [1], and simple and detailed numerical models were employed, e.g. [2] [3]. In the literature, the proposed physical models of the formation of Trichel pulses can differ substantially [1]. Modelling has revealed sensitivity, in terms of the pulse frequency, DC current and rise time, to variation of kinetic coefficients [2]. This work shows results of modelling for a negative corona discharge, in a needle-to-plane geometry, like that presented in [1] but with a needle having a tip radius of 200 μm , and a 5 mm gap in atmospheric air. Using two different ionization coefficients, we applied a 1V perturbation to a stationary glow corona at 25 nA, and simulated current evolution in time, as seen in Fig. 1. We have also performed simulations in conditions of [2] with similar results. For higher currents, there is streamer formation and propagation. The discharge character



(oscillatory decay into stationary glow, formation of periodic pulses – of lower current than that seen on Trichel pulses, or streamers) is strongly dependent on the ionization coefficient, even with a small variation (less than 4%).

Fig. 1: Current oscillogram with different ionization coefficients after perturbation of 1 V. Initial condition was the stationary glow corona at $I = 25$ nA.

Acknowledgments

This work was supported by European Regional Development Fund through the program Madeira 2014–2020 under Project No. PlasMa-M1420-01-0145-FEDER-000016 and FCT of Portugal under Project No. UIDP/50010/2020 (UMa).

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Stability of negative corona discharges at inception

Ataollah Eivazpour^{(*)1,2}, Nuno Ferreira^{1,2}, Pedro Almeida^{1,2}, George Naidis³,
Mikhail Benilov^{1,2}

¹ Departamento de Física, FCEE, Universidade da Madeira, Funchal, Portugal

² IPFN, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

³ Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow, Russia

(*) email of corresponding author

In this work, the stability of negative DC corona discharge is investigated numerically. Atmospheric pressure ambient air in needle-to-plane configuration is treated as an example. The appearance of Trichel pulses is an inevitable phenomenon in negative corona discharges in electronegative gases. It is clear that the transition of the discharge between pulseless and pulsed modes is a matter of loss of stability of quasi-stationary negative DC corona discharge. This topic is investigated using as an example a corona in air at atmospheric pressure in a needle-to-plane electrode configuration with 5mm gap [1]. Following [2], a linear stability analysis of the trivial (no-discharge) solution was performed by means of an eigenvalue solver. The trivial solution loses stability when the applied voltage reaches the corona ignition voltage, in agreement with [2]. This occurs on a real eigenvalue, which means that the negative corona must be stable at low currents. This conclusion was confirmed by investigation of stability of the negative corona discharge against finite perturbations: perturbations in the form of small increments of the applied voltage (about 0.5V) are imposed and the evolution of the discharge over time is followed by means of a time-dependent solver.

The computed current-voltage characteristics of the stationary negative corona discharge is shown in figure 1. As a perturbation is imposed, the discharge evolves into a stationary state at currents below $\approx 0.05 \mu\text{A}$ (2.2V above the inception voltage). At higher currents, the discharge becomes unstable by appearance of current pulses. At currents higher than 100 μA , the stationary discharge evolves into its stable mode. The conclusion that the negative corona is stable at low currents is interesting and promises a further insight into the nature of the Trichel pulses.

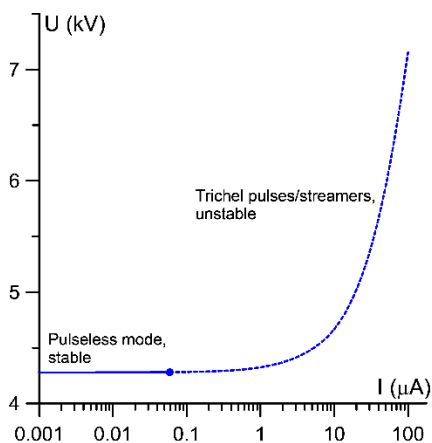


Figure 1: CVC of stationary negative corona discharge. Solid line: stable states. Dashed line: unstable states (computed by means of a stationary solver). Circle: point of neutral stability.

Acknowledgments

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Nitrogen fixation by an arc plasma at elevated pressures

Ivan Tsonev, Colin O'Modhrain, Annemie Bogaerts, Yury Gorbanev (*)

Research group PLASMANT, Department of Chemistry, University of Antwerp, 2610 Antwerpen, Belgium

(*) yury.gorbanev@uantwerpen.be

The main factor hindering the application of plasma-based nitrogen fixation for fertiliser production is the often-observed inverse correlation between energy consumption (EC) and production rates (PR). Likewise, there is a necessity to enhance the selectivity towards NO_2 - the desired product for a more facile absorption in aqueous scrubbers and hence for the formation of nitrate-based fertilisers [1].

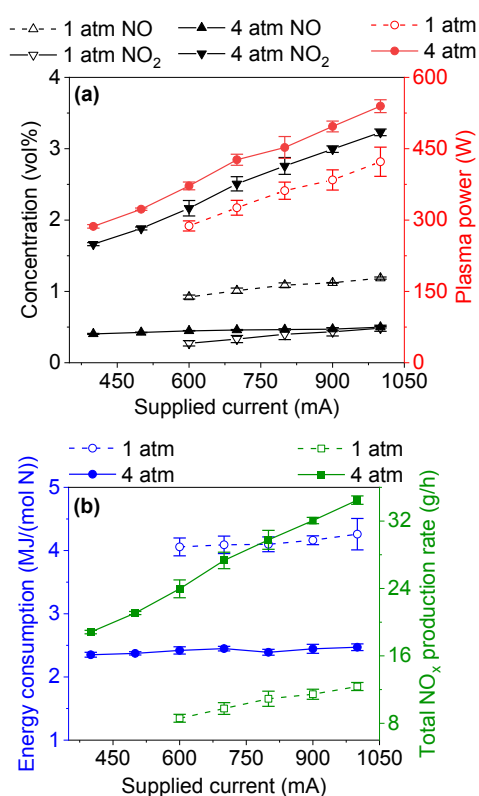


Fig. 1: Arc plasma nitrogen fixation, 8 Ln/min air, 1 and 4 atm: (a) concentration of the produced NO_x and plasma power; (b) EC and PR.

We used a negative DC rotating gliding arc plasma at elevated pressures (1-4 atm), at different feed gas flow rates and composition (air and oxygen-enriched air). We demonstrate a dramatic increase in the amount of NO_x produced as a function of increasing pressure (hence higher PR) and NO_2 as the near-exclusive end product, while the power scales differently than PR with increasing pressure, resulting in a lower EC (Fig. 1).

Under optimised conditions (with oxygen-enriched air), we obtained a PR as high as 69 g/h and an EC of 1.8 MJ/(mol N), the lowest reported for this high PR. By comparing the kinetic rate coefficients of the Zeldovich mechanism (direct and back reactions) and the oxidation of NO to NO_2 as a function of pressure, we ascribe this improvement not only to the enhanced thermal Zeldovich mechanism, but also to the increased rate of NO oxidation. The latter becomes more dominant over the back Zeldovich reaction at elevated pressures [2].

Evidently, pressure is an important parameter to enhance the performance of plasma nitrogen fixation. This parameter is scarcely studied in

the field of plasma gas conversion, although plasma-based processes at high pressures have been identified as highly industry-appealing [3].

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On reaching the strong $T \ll T_{vibr}$ vibrational non-equilibrium in CO₂

Vladislav Kotov¹

¹ *Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung - Plasmaphysik (IEK-4), Partner of the Trilateral Euregio Cluster (TEC), 52425 Jülich, Germany*

(*) v.kotov@fz-juelich.de

To date, the mechanism of plasma chemical conversion of CO₂ into CO which is most promising for industrial applications is thermal quenching in high frequency discharges. In theory dissociation from high vibrational states at relatively low translational-rotational temperature $T < 1000$ K may lead to conversion with higher energy efficiency than the thermal process. However, so far the vibrationally non-equilibrium process has not been undoubtedly detected experimentally.

Numerical calculations performed with the approximate ‘2-modes’ model of the CO₂ vibrational kinetics [1] suggest that to obtain significant dissociation by that mechanism the effective vibrational temperature T_{vibr} around 3000 K or higher is required. The criterion for reaching the corresponding level of non-equilibrium between T and T_{vibr} can be expressed in terms of the parameter Q/p^2 , where Q is the specific volumetric power input into vibrational excitations, and p is the gas pressure. The critical value $(Q/p^2)_{crit}$ above which efficient dissociation is possible can be estimated on the basis of empiric vibrational relaxation times measured in shock tube experiments. For $T=300$ K this estimate yields $(Q/p^2)_{crit} \approx 40$ (Pa·s)⁻¹, and $(Q/p^2)_{crit}$ is increased with increased T .

The peak magnitude of Q/p^2 reached in microwave CO₂ convergence experiments is almost always smaller than even the room- T $(Q/p^2)_{crit}$, or at best only marginally above this theoretical threshold. This observation is consistent with the fact that in those experiments no significant T/T_{vibr} non-equilibrium has been detected. At the same time, increasing Q/p^2 by decreasing p inevitably leads to reduced electric fields E/n which are too high to selectively direct the electron energy into vibrational excitations rather than into other channels. The necessity to fulfil simultaneously at least both Q/p^2 and E/n conditions makes it difficult to achieve the presumed non-equilibrium process even in specially designed low pressure laboratory experiments with high voltage glow discharges or ns-pulse discharges.

Nevertheless, achieving the non-equilibrium state with $T < 1000$ K and $T_{vibr} \approx 3000$ K in low- p experiments could be possible in CO₂ diluted in CO (or N₂). Opposite to CO₂ the vibrational-translational losses from CO are known to be very slow in this T -range. At the same time, a very fast near-resonant vibrational coupling is expected between CO and asymmetric modes of CO₂. The diatomic gas can thus serve as accumulator of vibrational energy for CO₂. Preliminary calculations with two temperature T/T_{vibr} model show that the required conditions may be realized in the experimental device of [2] (ns-pulse discharge) at $p=10$ Torr and initial concentration CO₂ of the order of 1 %. No high conversion energy efficiency can be achieved in such experiments because of too much energy spent for heating of the ballast gas, but they could enable experimental study of vibrational kinetics of CO₂ in $T \ll T_{vibr} \approx 3000$ K conditions.

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Green H₂ synthesis from NH₃ cracking using plasma: Comparison between the performance of different plasma reactors

Igor Fedirchyk ^{(*)1}, Laura Boelen ¹, Annemie Bogaerts ¹

¹ PLASMANT, Department of Chemistry, University of Antwerp, 2610 Antwerp, Belgium

(*) igor.fedirchyk@uantwerpen.be

H₂ is often considered a primary medium for storing and carrying energy produced from renewable sources. However, storage and long-distance transportation solutions for gaseous and liquid H₂ are inefficient and expensive [1]. Among the alternative H₂ carriers, NH₃ is a compelling carbon-free option [2], with an extensive logistics and storage infrastructure. A significant obstacle to using NH₃ in this role is the high energy requirement for its decomposition into H₂ and N₂. Plasma reactors have shown promising results in gas conversion, and some studies have already investigated their application to NH₃ decomposition [3–5]. However, only a limited number of plasma reactors were considered. Most studies focused on dielectric barrier discharge reactors, alone or combined with various catalysts.

In our work, we aimed to evaluate the performance of several different plasma reactors and compare them against each other and thermocatalytic ammonia cracking. We tested plasma reactors with a background in gas conversion: rotating gliding arc [6] and atmospheric pressure glow discharge [7]. Other reactors, such as gliding arc plasmatron [8], dielectric barrier discharge and pin-to-pin reactor, will be tested in the coming months. The main controllable design factors during the experiments are the discharge current, feed gas composition and flow rate. In the atmospheric pressure glow discharge, we also varied the distance between the electrodes, which impacts the gas residence time in the reactor and the plasma power, as an additional factor. The reactor performance was evaluated based on the NH₃ conversion and energy cost of NH₃ decomposition as main benchmarks.

In tests with undiluted NH₃, the rotating gliding arc and atmospheric pressure glow discharge plasma reactors achieved similar NH₃ conversion and NH₃ decomposition energy costs of approximately 50% and 320 kJ/mol. Reaching comparable NH₃ conversion in the thermocatalytic process with Ru or Fe catalysts requires 50-100 kJ/mol [9], showing that we still need to improve the plasma process to be competitive.

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Atomic wall recombination in oxygen plasmas

Pedro Viegas^{1(*)}, José Afonso¹, Jorge Silveira¹, Ana Sofia Morillo-Candás², Luca Vialletto³, Tiago Dias¹ and Vasco Guerra¹

¹ *Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa Portugal*

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

³ *Theoretical Electrical Engineering, Faculty of Engineering, Kiel University, Germany*

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

Heterogeneous surface kinetics plays a role in most plasma processes where surfaces interact either with active discharges or their afterglows. It can affect both the plasma and surface properties. In particular, in oxygen-containing discharges the adsorption and recombination of atomic oxygen on reactor surfaces determine the gas composition, the availability of O for important volume reactions (e.g.: $\text{CO}_2 + \text{O} \rightarrow \text{CO} + \text{O}_2$; $\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M}$) and eventually the flux of reactive oxygen species (ROS) towards target surfaces.

In Booth et al. (2019) [1], the wall loss frequencies of O atoms have been measured in the positive column of an oxygen DC glow discharge in a Pyrex tube (borosilicate glass) of 10 mm inner radius, for several pressures and discharge currents. However, the surface mechanisms determining recombination are not fully known yet. In particular, the increasing recombination with decreasing pressure below 1 Torr has not been described to date.

In this work we employ the LisbOn Kinetics simulation tool [2,3], including the description of surface kinetics of atomic oxygen to simulate self-consistently the evolution of atomic oxygen in both gaseous and adsorbed phases in the experimental conditions of Booth et al. (2019) and highlight the most relevant mechanisms. The description of surface kinetics proceeds via the kind of mesoscopic modelling employed in the past [4-6]. Through the self-consistent approach, the fluxes of species from the plasma directly affect the surface, and the surface processes directly affect the available densities in the gas phase, as well as the gas temperature.

The coupled model describes the experimental dependence of the atomic oxygen recombination probability on pressure, current, gas temperature and wall temperature, and allows to identify the most important recombination mechanisms for each operating condition. Moreover, this work demonstrates that the plasma has important effects on the surface at low pressures.

Acknowledgements

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Investigation of cold atmospheric plasma for environmental remediation/sanitation and materials activation/regeneration

Christos A. Aggelopoulos^{(*)1}, Irene-Eva Triantaphyllidou¹, Maria Hatzisymeon¹, Stauros Meropoulis¹, Stefania Giannoulia¹, Konstantia Papalexopoulou¹, Oxana Dolinski¹, Dimitris Tsokanas¹

¹ Laboratory of Cold Plasma and Advanced Techniques for Improving Environmental Systems (PlaNET), Institute of Chemical Engineering Sciences, Foundation for Research and Technology Hellas (FORTH/ICE-HT), 26504, Patras, Greece

(*) caggelop@iceht.forth.gr

Cold atmospheric plasma (CAP) is a novel technology that has shown significant potential in environmental remediation, materials processing and medical applications. The efficiency of CAP lies in the generation of high energy electrons (up to 1–10 eV) and the subsequent production of a significant number of energetic and chemically reactive species (e.g. free radicals, excited atoms, ions, and molecules) which act as the driving force for the initiation and propagation of plasma chemical reactions. One of the main advantages of the method is that it does not require high temperatures, reducing energy consumption. Since different types of plasma discharges or working gases may be used, different plasma properties may result and thus a variety of applications may arise.

The main goal of PlaNET laboratory is to develop novel cold plasma-based and plasma-catalytic systems in order to exploit at a maximum level the benefits of CAP towards the highly energy-efficient remediation of contaminated environmental sites (i.e. water, soil, groundwater) by persistent and recalcitrant pollutants such as dyes, antibiotics, pesticides, PFAs, etc. [1,2]. In-depth investigation is carried out on both laboratory and scale-up basis in order to determine all critical parameters. Water sanitation (bacteria and viruses removal) through CAP is also within the scope of PlaNET, including both direct plasma exposure and indirect via the production of plasma-activated water. A parallel goal is the use of CAP for the efficient activation/regeneration of materials used as adsorbents of pollutants present in water [3,4]. Finally, the application of CAP to induce apoptosis in cancer cells, falls under the scope of PlaNET, since CAP can selectively induce apoptosis of cancer cells, leaving healthy cells largely unaffected [5].

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CO₂ splitting in atmospheric microwave plasma sustained with ultra-fast energy pulsations

Sergey Soldatov^{(*)1}, Lucas Silberer¹, Guido Link¹, Alexander Navarrete³,
Roland Dittmeyer³, John Jelonnek^{1,2}

Karlsruhe Institute of Technology (KIT), ¹IHM, ²IHE, ³IMVT, 76131, Karlsruhe, Germany

(*) sergey.soldatov@kit.edu

One of the most efficient long-term storage of surplus renewable electrical energy is its use for conversion of stable molecules e.g. CO₂ and H₂O into chemical energy carriers, such as hydrocarbons and other valuable commodities. The conversion of CO₂ to CO in microwave plasmas so far demonstrated the highest efficiency (over 80%) for the low pressure conditions [1]. However, for future large-scale industrial applications a vacuum operation is not desirable. Despite the atmospheric pressure plasma systems are more welcome for

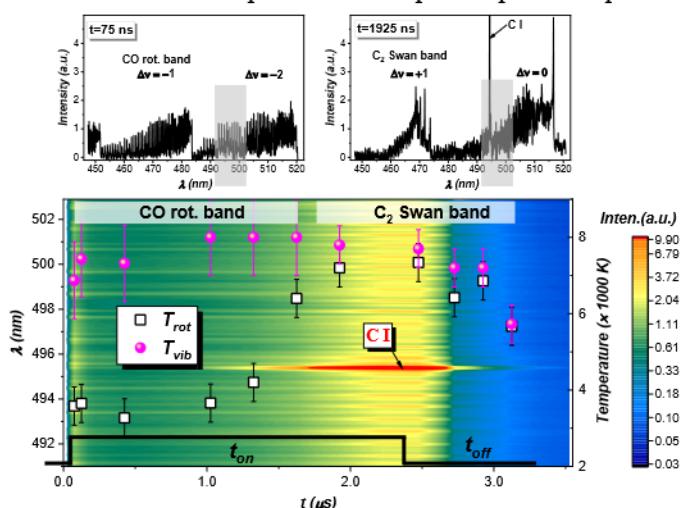


Fig. 1: Microwave CO₂ plasma emission and related rotational (T_{rot}) and vibrational (T_{vib}) temperatures (a). Parameters: $P_{peak}=220$ W, $t_{on} = 2.5$ μ s, $t_{off} = 7.5$ μ s, flow rate 12 slm [3].

industrial scale applications, the efficiency of the process degrades because much of the supplied energy is wasted through excessive heating of the gas [2]. A promising approach was found in recent experiments in compact coaxial plasma torch by supplying the microwave energy in short pulses rather than continuously [3]. It was shown that pulsations with duration of several microseconds and a duty cycle of about 0.25 promote the conversion and efficiency of the CO₂ splitting. Moreover, due to fast gas temperature quenching between pulses, the effective gas temperature control by variation of pulse parameters was demonstrated (see Fig. 1).

In present work, a review of recent experimental activities on the CO₂ splitting in both coaxial torch and Surfaguide microwave reactor is given. The conversion and efficiency of the process are studied both in pulsed and continuous wave (CW) plasmas. The diagnostics system features fast power meters for monitoring absorbed power, a gas analyser to measure concentration of reaction products as well as an ultra-fast optical emission spectrometer for estimating vibrational and rotational temperatures of the plasma.

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Plasma diagnostics for oxygen separation experiments

Aleksandr Pikalev^{(*)1,2}, Xingyu Chen^{1,3}, Richard van de Sanden^{1,4}, Vasco Guerra²

¹ *Dutch Institute for Fundamental Energy Research (DIFFER), 5612AJ Eindhoven, The Netherlands*

² *Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal*

³ *School of Electrical Engineering, Xi'an Jiaotong University, Xi'an 710049, China*

⁴ *Eindhoven Institute for Renewable Energy Systems (EIRES), Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands*

(*) a.pikalev@diffier.nl

The Mars exploration needs in situ resource utilization (ISRU), in particular, production of oxygen for life support and as a fuel oxidizer. The Martian atmosphere consists mostly of CO₂ (95%) and has low pressure (~600 Pa) and low temperature (-63°C in average). In such conditions, low temperature low pressure plasma is one of the most promising techniques for the CO₂ conversion [1]. After the conversion, oxygen needs to be separated, which can be done using a solid oxide electrolyte cell (SOEC). Integration of the SOEC with the plasma could have a synergetic effect [2-3].

We investigate the plasma-SOEC interactions in the BAri Brush Electrode (BABE) reactor [4] with four DC glow discharges and an afterglow region between their ring anodes. The tubular SOEC consisting of yttria-stabilized zirconia (YSZ) electrolyte and lanthanum strontium manganite (LSM) electrodes is situated in the afterglow region. The SOEC-plasma interactions are investigated in He-O₂ gas mixture. Preliminary experiments demonstrated that the plasma can enhance the oxygen pumping at lower SOEC working temperatures (350°C).

The effect could be related to the oxygen dissociation in the plasma, presence of excited states and the surface charging. For more insights, we need to know the plasma conditions. For lower pressures (up to a few Torr) the discharge region fully consists of cathodic parts with non-local electron energy distribution function (EEDF), making it difficult to describe properly the electron kinetics with a global model without further input from experiment. In this contribution we present measurements of the plasma conditions in the discharge and afterglow regions using optical emission spectroscopy and a Langmuir probe. The experiments are conducted with the oxygen concentration of 20% and with almost pure helium with a small impurity of air. The measurements provide dependences of the ionization degree, excited states densities and electron energies on the gas pressure (0.5-10 Torr) and the discharge current. The obtained EEDF can be used for plasma chemical modelling.

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Nitric oxide and O atomic density kinetics in a low pressure N₂-O₂ surfaguide microwave using Laser Induced Fluorescence

Abhyuday Chatterjee¹, Omid Samadi Bahnamiri², Claudia Verheygen³, Nikolay Britun⁴, Annemie Bogaerts³, Rony Snyders¹

¹ ChIPs, University of Mons, 7000 Mons, Belgium

² Department of Circular Chemistry Engineering, Maastricht University, The Netherlands

³ PLASMAN, University of Antwerp, Campus Drie Eiken
Universiteitsplein 1 2610 Antwerp, Belgium

⁴ Nagoya University: Nagoya, Aichi, 464-8601, Japan

(*) abhyuday.chatterjee@umons.ac.be

Kinetics of nitric oxide (NO) in the plasma driven oxidative nitrogen fixation is a crucial study to understand the reaction mechanism and optimization. Nitric oxide ground state, NO(X) absolute density and kinetics in a low pressure (2-5 Torr) pulsed (50% duty cycle, 500Hz) 13.6 GHz microwave surfaguide discharge of 50% N₂-50% O₂ mixture at 0.7 kW average power is determined with laser induced fluorescence (LIF). These are the optimum conditions for NO formation previously determined in this system by O.S. Bahnamiri et al [1]. Two-photon Absorption LIF (TALIF) is used to determine the density and kinetics of O atom kinetics in parallel which is a crucial precursor of NO formation. Counter intuitive trend of decrease in NO(X) and O^{3P} has been observed in the 'On' time of the pulse where the density increases in the 'Off' time (Figure 1). Increment of contribution from the reversible reaction of NO₂ formation in the 'II' phase 'On' time and annihilation to form back NO in the 'Off' time was determined to be the responsible reaction for the behaviour for both the NO and O kinetics with a 0D kinetic model. A connection between the experimental and modelling results are the focus of the work in understanding the NO kinetics in low pressure microwave discharge.

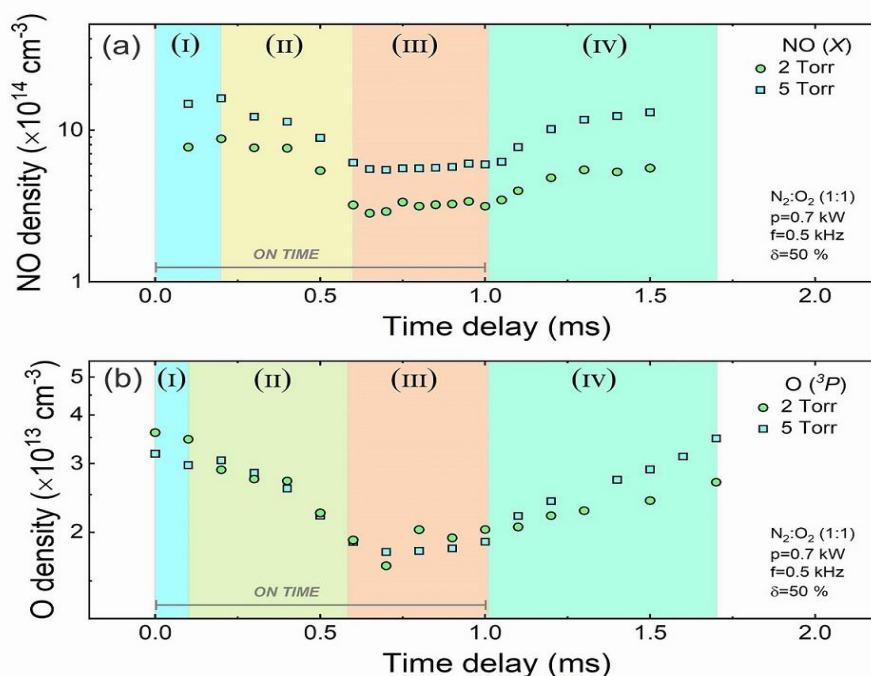


Figure 1: NO(X) and O atomic density kinetics in a pulsed low pressure MW discharge

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Determination of atomic oxygen density and reduced electric field in oxygen-containing plasmas through OES methods

L. Kuijpers^{1,4}, T. Silva^{(*)2}, V. Guerra², E. Baratte³, O. Guaitella³, D. Sadi³ and M.C.M. van de Sanden^{1,4}

¹ Dept. Applied Physics, Eindhoven Institute for Renewable Energy Systems, Eindhoven Univ. Techn., Eindhoven, The Netherlands

² Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Univ. de Lisboa, Portugal

³ Laboratoire de Physique des Plasmas (UMR 7648), CNRS-Univ.Paris Sud-Sorbonne Université - Ecole polytechnique 91128 Palaiseau, France

⁴ Dutch Institute For Fundamental Energy Research, Eindhoven, The Netherlands

(*) tiago.p.silva@tecnico.ulisboa.pt

Plasma diagnostics in CO₂ and O₂ plasmas are often expensive, active, complex, and highly sensitivity to noise. In this work two non-intrusive diagnostic approaches have been investigated: oxygen actinometry [1] and the line ratio method for the reduced electric field [2]. Both methods are based on optical emission spectroscopy (OES) which is a powerful characterization tool based on the measurement and analysis of light emitted by the spontaneous relaxation of excited species in the plasma.

The methods are based on the comparison of measured and simulated emission line intensity ratios. This is done for a DC glow discharge in oxygen with trace argon and xenon, operating at pressures in the range of 0.55-5 Torr and a current of 40 mA. The investigation starts with the direct calculation of the emission line intensities. The EEDF is calculated using the LisbOn KInetics Boltzmann solver (LoKI-B) [3], from which line intensities can be calculated assuming an extended corona model.

The calculated line intensities are tested against measured line intensities from OES. Best agreement is found using the Tayal and Zatsarinny electron impact excitation cross sections [4, 5]. The results exhibit excellent trend for the evolution of the line intensities as a function of discharge pressure. A correction factor is suggested to achieve agreement in the absolute values of the line intensities of different species.

The calculated reduced electric field is compared with the reduced electric field from experiment. The atomic oxygen density is found using actinometry and results are compared against Cavity Ring Down Spectroscopy measurements. For both methods the results based on consistent line intensity calculations give good agreement with experimental values. Sensitivity to O₂(a¹Δ_g) and O(³P) populations is tested to be low, allowing for the use of approximate or literature values.

The line ratio method and actinometry prove to give accurate results if the underlying line intensity calculations are good and consistent. Both absolute values and trend of the reduced electric field and atomic oxygen density over discharge pressure have been reproduced appropriately.

Acknowledgements

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Mapping the density of Nitrogen radicals in RF inductively coupled flow reactors

A. Herrmann^{1*}, P. Krebaum², S. Bera¹, M.N. Tsampas¹ M.C.M. van de Sanden^{1,3}

¹Dutch Institute for Fundamental Energy Research (DIFFER), Eindhoven, The Netherlands

²Fontys Hogeschoolen Technische Natuurkunde, Eindhoven, The Netherlands

³Eindhoven Institute for Renewable Energy Systems (EIRES), Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

(*) a.herrmann@diffier.nl

The fixation of Nitrogen has a large energy demand as high temperature and pressure is needed for the reactions. Nowadays fossil fuels are used to obtain these conditions, causing a production of CO₂ summing up to 1% of the world's emission. These conditions are necessary, as the Nitrogen triple bond is very strong, requiring high energy input to activate the molecules. One possibility for making the shift to renewable energy sources for nitrogen fixation is through Plasma catalysis, as plasma can be used to transfer electric energy to the Nitrogen molecule, creating highly reactive species.

For characterization of the reaction and improvement of the reactor, knowledge of the flux of activated species is necessary. In RF inductively coupled flow reactors, the density of highly reactive species varies with distance from the plasma glow. We are developing a probe to map the density of Nitrogen radicals at varying distance from the plasma glow in an N₂ plasma. The probe (depicted in the schematic in Fig. 1) consists of two thermocouples mounted through an adjustable feedthrough, giving a range of motion of approximately 18 cm. One of the two thermocouples coated with a thin catalytic layer (Copper) on which radicals exothermically recombine, while the other acts as a reference, obtaining information on other plasma interactions and heat fluxes. The radical density can be deduced from the measured temperature difference using a few assumptions on recombination rate, -heat and heat fluxes from other sources [1],[2].

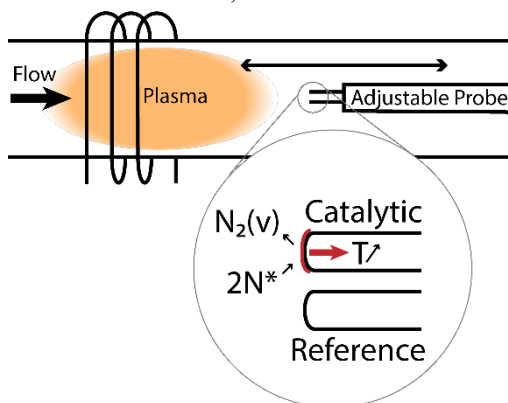


Fig. 1: Schematic of the catalytic probe

In our work, we conduct a thorough analysis, gaining the radical density, by first determining the heat flux at the catalyst surface through a heat flux analysis of the system and subsequently using optical emission spectroscopy to gain the recombination coefficient of the catalytic surface and energy dissipated by the recombination.

Acknowledgements

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Numerical Modeling of Plasma Reactors for CO₂ Conversion with Applications to Mars In-Situ Resource Utilization

Lanie McKinney^{1*}, Tiago Silva², Vasco Guerra², Carmen Guerra-Garcia¹

¹ *Department of Aeronautics and Astronautics, Massachusetts Institute of Technology, Cambridge, MA, USA*

² *Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal*

* laniemck@mit.edu

Nonthermal plasmas are an attractive technology for CO₂ splitting as the plasma nonequilibrium can be leveraged to break the stable bonds of CO₂ through selective excitation of electronic and vibrational modes, as well as vibrational energy exchanges. Because carbon dioxide comprises 96% of the Martian atmosphere, a nonthermal plasma CO₂ conversion reactor is a promising oxygen-generation technology that could enable human exploration of Mars [1]. Such a reactor needs two stages: a plasma source, for the splitting phase, and a separation stage, to produce a pure stream of oxygen. Primary considerations and driving factors for engineering such a reactor are dissociation fraction, energy efficiency, temperature, and reactor geometry which can be initially explored through a numerical model to inform later reactor design. In particular, the temperature of the reactor has implications for the coupling with the separation stage as separation membranes of interest, mixed-ionic electronic conducting membranes and solid-oxide membranes, typically require an operating temperature of ~800-1000 K [1].

In this work we present a 0D model that uses BOLSIG+ as the Boltzmann solver and ZDPlasKin as the chemical kinetic solver. We then extend the 0D model to 1D by solving the species, momentum, and energy conservation equations of the reactive flow, to explore fluid and transport effects and better improve the predictions of efficiency and dissociation fraction in a physical system. The separation stage is considered as a boundary condition in this reactor. To better understand the coupling of operating conditions and chemical heating in the plasma, we put particular emphasis on the energy balance of the reactor by including the heat transport equation in the model and tracking energy conservation. The chemical kinetic model used is based on prior work in [2], and utilizes a subset of CO₂ vibrational chemistry to capture CO₂ vibrational excitation and energy exchanges, while also maintaining a reduced chemical kinetic model to efficiently solve the 1D case. The emphasis is put on nanosecond repetitively pulsed discharges (NRPD) and parametrically explores Earth and Martian conditions. A wide range of operational parameters are tested, in temperature, pressure and electrical settings, to map dissociation fraction and efficiency and inform future reactor design.

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Reforming of methane in a DBD reactor: A reaction kinetics model

G. Vieira¹, C. Bacariza¹ N Pinhão^{(*)2}

¹ Centro de Química Estrutural - Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

² Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

(*) npinhao@ctn.tecnico.ulisboa.pt

Biogas, mainly composed by CH₄ and CO₂, represents an attractive renewable carbon source to address the global energy demand and, simultaneously, reduce waste and greenhouse gases emissions [1]. In this way, dry reforming of methane (DRM, CH₄ + CO₂ → 2CO + 2H₂) constitutes a promising pathway for biogas valorization. However, the highly endothermic nature of the reaction, requiring excessive energy consumption, increasing the operating and investment costs and inducing severe catalysts deactivation, limits its industrial implementation. Non-thermal plasmas offer an attractive alternative, allowing to operate at a lower gas temperature, atmospheric pressure and lower energy input, and leading to a reduction in carbon formation, increased products selectivity and prolonged catalysts stability [2].

The optimization of plasma DRM requires a detailed knowledge of the reactions processes and modeling plays an important role on this. In this work, we discuss the results of a 0D kinetic model for a dielectric barrier discharge plasma-assisted methane dry reforming, solving the equations for the particle balance, the electron energy conservation and the gas temperature. The model adopts the same reaction scheme as in [3] but takes into account the gas heating and the temperature dependence of reactions. The concentration profiles of the species along the reactor, estimations for the conversion and selectivity values and the contribution of each reaction for the formation and loss of each species were obtained.

Acknowledgments

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Probing the dynamics of a gliding arc discharges in air

Davide del-Cont Bernard¹, Francesco Mazza², Leonardo Castellanos Gonzales²,
Tom Butterworth^{1(*)}, Alexis Bohlin^{2,3}

¹ *Circular Chemical Engineering, University of Maastricht, 6167 RD, Geleen, Netherlands*

² *Aerospace Engineering, TUDelft, 2629 HS, Delft, Netherlands*

³ *Department of Computer Science, Electrical and Space Engineering, Luleå University of Technology, Bengt Hultqvists väg 1, 981 92 Kiruna, Sweden*

(*) email of corresponding author

Gliding arc discharges are a potential means to drive strongly endothermic chemical reactions, such as CO₂ reduction, or nitric oxide synthesis from air. Moreover, it is hypothesised that such endothermic chemical reactions can occur at energy efficiencies that exceed the thermal equilibrium limit due to vibrationally enhanced chemical kinetics. The existing knowledge on the topic is divided - some literature claims a role of vibrational non-equilibrium, whilst others claims the chemistry is thermal [1,2].

Herein, we show experiments where we determine the thermodynamic state of a gliding arc operating in air during the development and extinction phases of the discharge cycle. This is achieved by probing the gliding arc using the state-of-the-art laser technique ultra-broadband fs/ps hybrid-CARS, which we apply in combination with tomographic tracking of the filament location. This system allows us to perform spatially and temporally resolved single-shot measurements of ro-vibrational temperature and gas composition within a gliding arc at 1 kHz. We track the arc filament path as it transits through the CARS probe volume, such that we can determine when and where we are acquiring spectra relative to the filament position. With this, we use statistical analysis of many CARS spectra to assess the rovibrational state of the discharge. Finally, we are able to determine unequivocally – can we generate vibrational-translational non-equilibrium in a gliding arc?

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Insights into methane reforming to olefins via nanosecond pulse plasma

Gromov Mikhail^{(*)1}, Stijn Van Rompaey^{1,2}, Gregory Smith², Rino Morent¹, Anton Nikiforov¹

¹ *Research Unit Plasma Technology (RUPT), Department of Applied Physics, Ghent University, Sint-Pietersnieuwstraat 41, 9000-Gent, Belgium*

² *Research group PLASMANT, Department of Chemistry, Antwerp University, Universiteitsplein 1, 2610 Wilrijk, Belgium*

(*) mikhail.gromov@ugent.be

The development of unconventional hydrocarbon production methods mined from the ocean floor (the US shale revolution) brought a major structural shift in the hydrocarbon market. The shale gas production chain is a complex, multistage process and includes production, processing, transportation, etc., which unavoidably are accompanied by natural gas leaks into the environment. Considering the fact that methane (CH_4) is ~ 25 times more maleficent greenhouse gas than carbon dioxide (CO_2), the environmental performance of shale gas production and managing its supply chain are of great concern and interest [1]. In this situation, one of the possible solutions to minimize the environmental footprint associated with CH_4 production and to make the process even more economically profitable is on-site production of the final, highly valuable hydrocarbons, as shown in Figure 1. In light of this, plasma technology has again been considered to be a helpful tool for synthesizing products such as ethylene (C_2H_4) or hydrogen (H_2) owing to its potential selectivity, “on/off” operation control, and relatively small scale system designs.

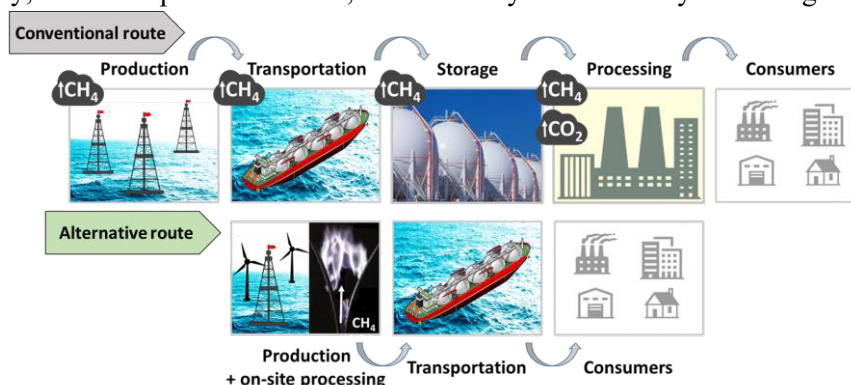


Figure 1. Conventional and alternative route of methane reforming

Considering the endothermic nature of the methane reforming process, a nanosecond pulse plasma is regarded as a good match, specifically due to a tremendous instantaneous power density, lying in the range of GW/cm^3 ; meanwhile, the time-averaged power is only W/cm^3 . Therefore, in this work, we focus on the diagnostics of $\text{CH}_4:\text{H}_2$ (1:1) plasma operated within a wide pressure range from 0.5 to 2.5 bar. The plasma physical characteristics such as power density, gas temperature, and electron density are coupled with the plasma-induced chemistry of the primary intermediates measured via laser-induced fluorescence spectroscopy. The results of this work allowed us to deduce the main fundamental reasons for the successful implementation of such nanosecond plasma reported earlier in the literature [2, 3].

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Plasma/surface interaction for efficient CO₂ recycling: plasma-membrane coupling

Dihya Sadi^{1*}, Olivier Guaitella¹

¹ *Laboratoire de Physique des Plasmas, Ecole Polytechnique, Palaiseau, France*

(*) dihya.sadi@lpp.polytechnique.fr

CO₂ recycling aims at using CO₂ from industrial emissions as a raw material rather than treating it as a waste product. To achieve this, it is necessary to convert chemically CO₂ with a low energy cost, despite the stability of this molecule. Non Thermal plasmas properties allow this, however an inherent difficulty in most plasma chemical synthesis processes is to control the selectivity into the products formed. In particular it is important to prevent reverse reaction processes reforming CO₂ from CO and O or O₂. This work proposes a novel solution to this problem by placing ceramic mixed electronic and ionic membranes in direct contact with the plasma to continuously extract the oxygen atoms formed [1],[2].

Most membranes used for gas separation needs partial pressure difference between both sides of the membrane and relatively strong heating to enhance their permeation properties [3]. By coupling the membrane with plasma we expect to obtain

- 1) an improvement in the membrane permeation properties when used with a plasma due to the presence of an electric field as well as atomic oxygen [2],
- 2) an improvement in CO₂ plasma conversion due to the removal of the oxygen atoms from the medium shifting the balance between recombination and dissociation.

In this work, we study the permeation properties of membranes at the center of a low-pressure glow discharge ignited at few mbar in a quartz tube. In order to compare the permeation induced by heating or by plasma, the glow discharge reactor is also placed inside a cylindrical oven.

First, the influence of the membrane material and the gas heating by the furnace on the physical characteristics of the glow discharge (temperature, conversion, etc...) are analysed. Rotational and vibrational temperature of CO are deduced from the fitting of the third positive and Angström system of CO, as well as rotational temperature of O₂(b) system. Downstream gas composition is analysed by FTIR comparing the conversion with and without membrane.

Then, to evaluate the permeation properties of the membranes, a mass spectrometer is used to identify and quantify the different species going through the membrane. By closing the pumping inside the membrane and monitoring the pressure increase, the permeation flux can be determined for various plasma/heating conditions. These measurements are performed with CO₂ and O₂ gas, at 2 and 5 torr with either just heating or with plasma. The effect of the plasma on the permeation properties can then be studied.

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Experimental and numerical study of the conversion mechanisms in the low-pressure CO₂-CH₄ glow discharge

E.Baratte^{(*)1}, T.Silva², V.Guerra², O.Guaitella¹

¹ Laboratoire de Physique des Plasmas (LPP), École Polytechnique, Institut Polytechnique de Paris, 91128 Palaiseau, France

²Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Portugal

(*) edmond.baratte@lpp.polytechnique.fr

The simultaneous recycling of CO₂ and CH₄ through the Dry Reforming of Methane (DRM, CO₂ + CH₄ → 2CO + 2H₂) by plasma produces the base components necessary for biohydrocarbons production and is, therefore, a promising lead for energy storage [1]. However, understanding the fundamental processes of CO₂-CH₄ plasmas remains challenging because of the numerous species and reaction pathways. This work aims to shed light on the mechanisms driving these plasmas. To this aim, a low-pressure glow discharge was ignited in a dedicated pyrex reactor. Several mixtures, ranging from pure CO₂ to 50:50 CO₂:CH₄ were studied between 1 and 7 Torr at a current of 40mA. The gas composition was monitored downstream of the discharge by FTIR spectroscopy [2], while the reduced electric field and the gas temperature were measured in situ.

The homogeneous glow discharge was modelled using the 0D LoKI simulation tool, following the method from [3]. Based on the experimental results, a kinetic scheme including only molecules with up to one carbon atom was developed. A relatively good agreement is obtained between the measurements and the model on the fractions of the main species of the plasma as shown on Figure 1. The self-consistent E/N obtained from Loki is also in good agreement with the measurement, allowing to draw insights into the fundamental mechanisms.

The excited states appear to play a crucial role in the plasma chemistry, in particular the excited O(1D) state. A good description of these states can avoid resorting to the vast chemistry of the C_xH_y molecules to describe the plasma. The present model also allowed to describe an RF discharge in similar conditions.

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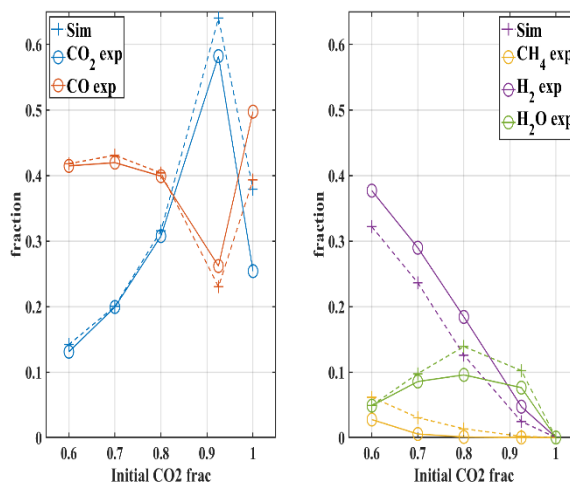


Figure 1: comparison of the measured and simulated fractions of the main species (CO₂, CO, CH₄, H₂ & H₂O) in a CO₂:CH₄ glow discharge at 5 Torr as a function of the initial gas composition

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An assessment on vibrational rate coefficients with interest to chemistry of CO₂ plasmas

Tiago Silva^{1(*)}, Edmond Baratte², O. Guaitella², Vasco Guerra¹

¹*Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal*

²*LPP, Ecole Polytechnique, UPMC, Université Paris Sud-11, CNRS, Palaiseau, France*

(*) tiago.p.silva@tecnico.ulisboa.pt

The development of green technologies that accelerate the transition towards a more sustainable and resilient world requires long-term and large-scale energy storage solutions. A very promising and environmentally friendly solution to this problem relies on the development of a suitable energy storage scheme in which the excess of renewable power is used to convert feedstock of pollutant gases such as CO₂ into chemical fuels. In this context, non-thermal plasmas have gained much attention regarding CO₂ decomposition due to their potential to activate CO₂ at reduced energy cost, while exciting CO₂ vibrations that efficiently contribute to overcome the dissociation barrier. This has led to a growing field of research aimed at combining renewable electricity with plasmas to convert pollutant gases into synthetic fuels for energy storage pathways. In relation to this point, the understanding of vibrational kinetics in plasmas is of major importance given the influence of the vibrations on molecular conversion, gas heating and electric energy distribution functions.

In this work we do an assessment on vibrational rate coefficients in different molecular systems, which include CO-CO₂, CO-CH₄, CO-H₂, CO₂-CO, CO₂-CH₄ and CO₂-N₂. For each case we solve a system of zero-dimensional rate balance equations considering volume and surface mechanisms associated to the creation and loss of vibrational species. These modelling results are compared against experimental data obtained in pulsed DC glow discharges, operated under single-pulse environment, at pressure of 3 Torr and discharge current of 40 mA. Overall, we observe a good agreement between model predictions and experimental results in terms of vibrational temperatures. In a few cases some differences between the model predictions and the experimental data are observed, that are explained by considering the impact of surface modifications.

Acknowledgments

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Rising EU climate targets to 55% GHG emissions reduction: Exploitation of emerging plasma-assisted sustainable resources for energy production

Gregor Primc^{1*}, Kaja Primc²

¹ *Department of Surface Engineering, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia*

² *Institute for Economic Research, Kardeljeva ploščad 17, 1000 Ljubljana, Slovenia*

(*) gregor.primc@ijs.si

In 2018, the EC adopted the Regulation on the Governance of the Energy Union and Climate Action (EUGR; Regulation (EU) 2018/1999) as part of the Clean Energy for all Europeans Package (CEP) to facilitate the implementation of the Energy Union. The purpose of the EUGR was to develop a transparent governance process and help deliver on the new 2030 climate and energy targets. Under the EUGR, member states were required to develop integrated National Energy and Climate Plans (NECPs) by the end of 2019, covering five dimensions of the Energy Union: energy efficiency, renewables, greenhouse gas emissions reductions, interconnections and research and innovation, which replaced the previous National Energy Efficiency Action Plans (NEEAPs) for monitoring the progress in achieving national targets in the period 2021–2030. As part of the European Green Deal, in July 2021, the EC adopted a package of legislative proposals called “Fit for 55”, redefining the decarbonisation targets set before to 40% to at least 55% by 2030 compared to 1990 levels. These proposals aim to “fundamentally transform our economy and society for a fair, green and prosperous future” (EC, 2021). This new ambition requires both a rapid increase in the utilization of renewable energy resources and the exploration of emerging technologies for sustainable energy production.

The overall assessments of the existing NECPs show that for renewable energy the combined commitment by EU Member States is above the existing renewable energy target of at least 32% (estimated at 33.1%–33.7%). It proves that renewables are becoming cost-effective and that more potential can be tapped through more equal efforts amongst the EU member states. However, to meet the higher 2030 climate target of at least 55% greenhouse gas (GHG) emissions reduction, substantial research efforts will be needed to develop environmentally friendly technologies that will enable a just transition (i.e. moving to a more sustainable economy in a way that is fair to everyone). In recent years, plasma technologies are emerging as environmentally friendly technologies, replacing other energy- or chemical-intensive techniques. Lately, much attention from the scientific community has been focused on the development of green energy sources utilising plasma-assisted technologies. Therefore, the main focus of this poster is to present the potential of plasma technologies for use in energy production to enable access to affordable, reliable and safe energy services while meeting the 55% decarbonisation target by 2030.

Effect of the magnetic field on the electron kinetics under AC/DC electric fields

T. C. Dias¹, C. D. Pintassilgo^{1,2}, V. Guerra¹

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

² Departamento de Engenharia Física, Faculdade de Engenharia, Universidade do Porto, Portugal

(*) Email: tiago.cunha.dias@tecnico.ulisboa.pt

Electrons play a major role in the reactivity of low-temperature plasmas (LTP), since they transfer the energy gained from the electric field to the heavy species through various collisional channels. Thus, an accurate solution of the electron kinetics is necessary for a precise description of an LTP.

The LisOn KInetics Monte Carlo solver (LoKI-MC) [1] was recently developed by our group, aiming to provide the community a general and flexible electron kinetics solver that does not depend on the two-term approximation. Some interesting features are the straightforward insertion of gas internal levels, anisotropic scattering and inclusion of the thermal motion of the gas molecules.

The first version of LoKI-MC addressed only configurations with constant electric field and null magnetic field [1]. Here, we extend the formulation to AC/DC electric fields together with DC magnetic fields. The implementation of this significant feature requires an extensive benchmark/verification.

The purpose of this work is threefold: (i) verify LoKI-MC against previous independent benchmark calculations, reinforcing the confidence on the present code and on the past calculations; (ii) extend the set of benchmarks available in the literature to consider the influence of other physical parameters, specially in conditions of coexistent AC electric fields and DC magnetic fields; (iii) gain insight into the underlying physics of the electron swarm kinetics in these configurations, with special emphasis on the phenomenon of electron-cyclotron resonance.

With respect to point (i), LoKI-MC passed with distinction several benchmark tests available in the literature, using the well-known Reid-ramp and Lucas-Saelee gas models, and this will be shown in the conference. Figures 1 and 2 concern the points (ii) and (iii) above mentioned. Figure 1 presents the electron mean energy ($\langle\epsilon\rangle$) and reduced Townsend coefficient (α/N) in N_2 for DC electric and magnetic fields. An increase of the magnetic field significantly reduces the fraction of high-energy electrons, leading to a decrease of $\langle\epsilon\rangle$ and α/N . Figure 2 shows $\langle\epsilon\rangle$ in Ar for an AC electric field and a DC magnetic field, and different AC frequencies. In this case, when the cyclotron frequency is near the excitation angular frequency, the magnetic field may increase the electron energy due to the well-known electron-cyclotron resonance, where there is an enhancement of electron acceleration caused by a synchronization of the cyclotron motion with the electric field.

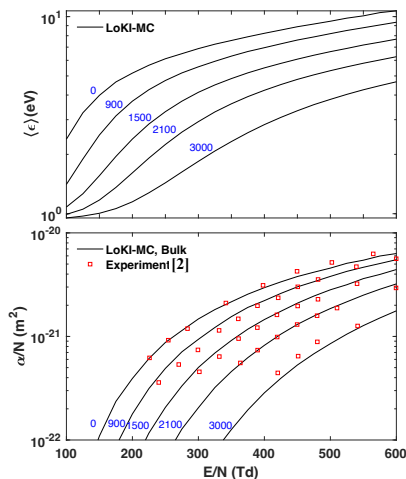


Figure 1: $\langle\epsilon\rangle$ and α/N coefficient in N_2 , as a function of E/N (DC) and varying B/N from 0 to 3000 Hx.

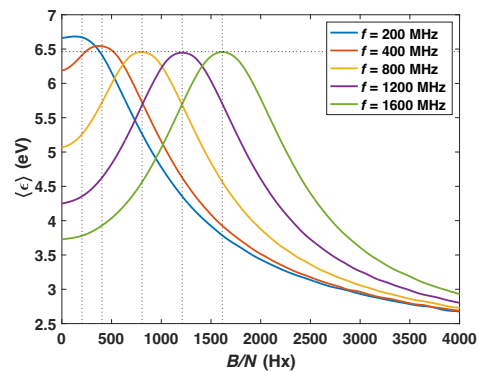


Figure 2: $\langle\epsilon\rangle$ in Ar, for $E_{rms}=100$ Td, as a function of B/N and varying the AC frequency of E .

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