

Book of Abstracts, 12th International Workshop on Microplasmas (IWM12)

Rémi Dussart, Rim Ettouri, Sylvain Iséni

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Book of Abstracts

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Contents

1	Foreword	6
2	Conference Committees and Workshop Program International Scientific Committee List of Invited Speakers Local Committee	7 7 8
Sc	chedule	10
3	Abstracts – Oral presentations Tuesday June, 4 th	11 12
	Ionization of Gas Jet Impinging onto Liquids: Stabilizing or Destabilizing?, Park Sanghoo [et al.]	12
	Influence of stray capacitances on discharge characteristics, Bröcker Lars [et al.]. Spatio-temporal development of micro-hollow cathode discharges in DC and pulsed	14
	modes: new I-V regimes, Halfaoui Abd-Almalik [et al.]	15 16
	Degradation of herbicides in water using non-thermal plasmas (NTP) at atmo- spheric pressure, Ben Othmen Cyrine [et al.]	17
	production by a micro-plasma jet for biomedical applications, Mestre Eloïse [et al.] Plasma bubbles in Oil and their applications in sterilization, Niu Jinhai [et al.]	18 19
	A nanosecond sub-atmospheric pressure plasma jet as an experimental tool and a source of excited species, Lepikhin Nikita D. [et al.]	20
	Belkacem [et al.]	21
	Effluent with Different Atmospheres and Targets, Herrera Quesada Maria [et al.] Single pulse pin-to-pin plasma discharge on levitated water droplet, Devos Alexan-	22
	dre [et al.]	23 24
	Ana [et al.]	24
	sis, Böke Marc [et al.]	26
	charges, Hoder Tomas [et al.] Investigation of excited molecular oxygen species densities produced by an atmo-	27
	spheric pressure micro plasma jet, Chur Sascha [et al.]	28
	spatiotemporal inhomogeneities and plasma dynamics, Kourtzanidis Konstantinos Numerical simulation of ionization wave propagation in an atmospheric pressure plasma jet, Murakami Tomoyuki [et al.]	29 30

	Scaling of reactive species transport towards and inside liquids for application in biocatalysis, Schöne Anna Lena [et al.]	31
		32
	to micro-discharges, Callegari Thierry [et al.]	32
	Maze-solving by micro-channel plasma and its analysis based on Boltzmann-Gibbs and Shannon entropies, Sakai Osamu [et al.]	34
	Microplasma-assisted anodic dissolution as a tool for the formation of multiele- ment perovskite oxides nanoparticles, Tarasenka Natalie [et al.]	35
	On the use of microplasma arrays for electromagnetic metasurfaces, Monti Alessio [et	
	al.]	36
	Plasma Jets and Surface Dielectric Barrier Discharges, Jeon Sang Un [et al.]	37
	Duncan [et al.]	38
	Comparison of surface-DBD dynamics sustained by sinusoidal AC and positive rectangular pulsed voltage waveforms, Giotis Konstantinos [et al.]	39
	Keisuke [et al.]	40
		41
	Viktor [et al.]	42
	alyst, Guerrero Daniel [et al.]	43
	Toward Efficient Plasma Processing of a Liquid – Several Attempts to Utilize Microplasmas in Contact with Liquid –, Shirafuji Tatsuru	44
	Plasma-assisted flow chemistry: towards new oxidation methods in organic syn- thesis, Guillermain Marie [et al.]	45
	Experimental Study of the Influence of Cathode Materials on Performance of	
		46 47
	Surface Dielectric Barrier Discharge (sDBD) for Flow Control in Plasma Conver- sion, Mohsenimehr Soad [et al.]	17
	Assisting simple optical diagnostics of an atmospheric pressure plasma via machine	
	learning, Stefas Dimitrios [et al.]	49
		50
	in Liquid Water, Bonaventura Zdenk [et al.]	51
	Ultrafast oscillation in a field emission-driven microdischarge, Chen Jiandong [et al.]	52
	Optical emission spectroscopy analysis of Hydrogen ${\rm H}\beta$ spectral line in confined	53
	Spatial 2D distribution of N-atoms absolute density in three DC MHCD se-	54
4	Stracts – Posters	55
	Absolute atomic nitrogen densities in a micro-hollow cathode discharge operating in Ar/N ₂ mixtures: DC versus pulsed modes, Halfaoui Abd-Almalik [et al.] 5 Additive Manufacturing Electronic (AME) for microplasma source production, Vasile	56
		57

Analysis of dielectric barrier discharge plasma actuators for flow control, Kim Jae	F 0
Wan [et al.]	58
lations., Lazzaroni Claudia [et al.]	59
Atmospheric-pressure air DBD treatment for plasma surface modification of glass	
and stainless Steel, Najah Aymane [et al.]	60
using Two Atmospheric Pressure Plasma Jets, Sang Un Jeon [et al.]	61
CO_2 dissociation at atmospheric pressure by micro-cathode sustained discharges, San-	
tos Sousa Joao [et al.]	62
Controlled synthesis of NO in an atmospheric pressure plasma by suppressing NO destruction channels by plasma catalysis, Yu Siqi [et al.]	63
Development of a Low-Cost, Wide-Range Power Supply for Plasma Research, Guer-	00
rero Daniel [et al.]	64
Effect of operating parameters on the propagation dynamics of fast ionization	CE
waves in a He microtube plasma jet, Agha Yanis [et al.] Electric-field-induced coherent anti-Stokes Raman scattering in visible region un-	65
der near-atmospheric-pressure hydrogen microplasma environment, Koike Takeru [et	
al.]	66
Experimental study of the gas breakdown in a controlled nanometer scale electrode	67
gap, Disson Baptiste [et al.]	67
MOSFET Pulse Power, Shirafuji Tatsuru [et al.]	68
Investigation of plasma surface modifications of wood samples by atmospheric-	
pressure air DBD and plasma torch treatments, Géraud-Grenier Isabelle [et al.] .	69 70
Laser ablation for microplasma source production, Capelli Filippo [et al.] MHCD in N ₂ -H ₂ mixtures: towards a localized plasma nitriding process?, Noel	70
Cédric [et al.]	71
Non-invasive plasma measurement in an atmospheric pressure plasma, Chung	
Chinwook [et al.]	72
Optical emission spectroscopy evidence of N atom production in surface dielectric barrier micro-discharge reactor dedicated to atmospheric pressure PECVD, Rabat	
Hervé [et al.]	73
Plasma surface modification of metals and polymers by atmospheric-pressure air	
DBD and plasma torch treatment, Liennard Marion [et al.]	74
Plasma-assisted CO ₂ conversion combined with a catalyst, Seferoglu Fatma-Nur [et al.]	75
Plasma-driven Organic Synthesis: Reducing Noble Gas Usage, Iza Felipe	76
Quantitative analysis of glasses samples and plasma diagnostics by Optical Emis-	
sion Spectroscopy and Thomson Scattering, Flaugère Robin [et al.]	77
Self-Pulsing and instabilities in silicon-based Micro Hollow Cathode Discharge operating in DC excitation, Kouadou Elane [et al.]	78
Spatial plasma configuration in plasma metamaterials, Sakai Osamu [et al.]	79
Study of a portable DBD source for surface modification and microbial inactiva-	
tion, Kostov Konstantin Georgiev [et al.]	80
Towards the realization of plasma reconfigurable metasurfaces to control electro- magnetic waves: characterization of an argon microplasma element, Laghi Giu-	
lia [et al.]	81
VOCs conversion in $\mathrm{He}/\mathrm{H_2O}$ plasma produced in a micro-capillary tube at atmo-	
spheric pressure, Santos Sousa Joao [et al.]	82

5 Sponsors

83

Author Index

1 Foreword

The twelfth International Workshop on Microplasmas (IWM 12) will take place at MUSÉE DES BEAUX-ARTS in Orléans, FRANCE from June 3^{rd} to 7^{th} 2024.

The conference will be held *in person* at the following address: MUSÉE DES BEAUX-ARTS, 1 rue Fernand Rabier, 45000 Orléans FRANCE. (Plus Codes for Google Maps: WW35+3V Orléans)

Scope of the conference:

The workshop is a gathering of enthusiastic scientists, students and engineers in the field of:

- 1. Microplasma generation/ sources
- 2. Microplasma diagnostics
- 3. Microplasma modeling
- 4. Plasmas in liquids and bubbles
- 5. Applications: material processing, plasma medicine, plasma agriculture, environmental applications, industrial contributions, etc.



2 Conference Committees and Workshop Program

International Scientific Committee

- Prof. Achim von KEUDELL (Chair), Ruhr University Bochum, GERMANY
- Prof. Osamu SAKAI (incoming Chair), The University of Shige Prefecture, JAPAN
- Prof. Jose LOPEZ (past Chair), Seton Hall University, USA
- Prof. Katharina STAPELMANN (secretary), North Carolina State University, USA
- Prof. Yi Kang Pu, Tsinghua University, CHINA
- Prof. Rémi DUSSART, GREMI University of Orléans, FRANCE
- Prof. Kazuo Terashima, University of Tokyo, Japan
- Prof. Wonho CHOE, Korea Advanced Institute of Science and Technology, REPUBLIC OF KOREA
- Dr. Matteo Gherardi, University of Bologna, Italy
- Dr. Tomáš HODER, Masaryk University, CZECHIA
- Dr. Felipe IZA, Loughborough University, UNITED-KINGDOM

Invited Speakers

The list of Invited Speakers is organized according to the following topics: Liquids and Bubbles; Modeling; Applications; Generation and Sources; Diagnostics. The timetable can be found in page 11.

- Prof. BELMONTE Thierry, Institut Jean Lamour CNRS / Université de Lorraine, FRANCE Nanosheets by Electrical Discharges in Liquids; page 16.
- Prof. BONAVENTURA Zdenek, Masaryk University, CZECHIA Electron Avalanching in Nanovoids at the Initial Stage of Nanosecond Discharge in Liquid Water; page 51.
- Dr. CALLEGARI Thierry, LAPLACE CNRS / Université de Toulouse, FRANCE Better protect our communications systems against electromagnetic attacks thanks to micro-discharges; page 32.
- Dr. KOURTZANIDIS Konstantinos, CPERI, CERTH, GREECE Two-dimensional simulations of high-pressure DBD and microwave microdischarges: spatiotemporal inhomogeneities and plasma dynamics; page 54.
- Prof. LEE Hae June, Pusan National University, REPUBLIC OF KOREA The Comparisons of Electric and Chemical Properties of Atmospheric Pressure Plasma Jets and Surface Dielectric Barrier Discharges; page 58.

- Dr. LEPIKHIN Nikita, Ruhr University Bochum, GERMANY A nanosecond sub-atmospheric pressure plasma jet as an experimental tool and a source of excited species; page 20.
- Prof. PARK Sanghoo, KAIST, REPUBLIC OF KOREA Ionization of Gas Jet Impinging onto Liquids: Stabilizing or Destabilizing?; page 12.
- Prof. SHIRAFUJI Tatsuru, Osaka Metropolitan University, JAPAN Toward Efficient Plasma Processing of a Liquid Several Attempts to Utilize Microplasmas in Contact with Liquid; page 44.
- Dr. SOBOTA Ana, Eindhoven University of Technology, THE NETHERLANDS Charging effects of a dielectric surface interacting with a plasma jet; page 24.
- Prof. TAKASHIMA Keisuke, Tohoku University, JAPAN Reactive Nitrogen Species Generation at Plasma-Liquid Column Interface; page 40.

Local Committee

Research Group in the Energetics of Ionized Media (GREMI), UMR 7344 CNRS / University of Orléans, FRANCE.



M.Sc. Baptiste Disson

Dr. Rim Ettouri

Dr. Sylvain Iséni



Dr. Olivier Aubry

Dr. Claire DOUAT

Prof. Dunpin Hong

M.Sc. Éloïne Mestre









Mrs. Sylvie JAUFFRION

M.Sc. Élane KOUADOU

M.Sc. Philippe LEFAUCHEUX

Dr. Arnaud Stolz

Dr. Thomas TILLOCHER

M.Sc. Madjid Adjabi

Dr. Augusto Stancampiano

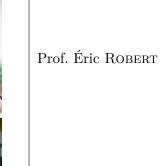
Prof. Stéphane Pellerin

Dr. Hervé RABAT

M.Sc. Tian TIAN







9













Prof. Maxime MIKIKIAN

Friday	June 07		Arrival of participants			Dimitrios STEFAS	Joao SANTOS SOUSA	Coffee Break		Yangyang FU		Kristaq GAZELI	Closing ceremony	Lunch Break (lunch box) Visit of the "musée des Beaux Arts" (optional)										
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Thursday	June 06		Arrival of participants	Inv. Thierry CALLEGARI	Ocamii SAKAI	IaN		Coffee Break			R A		Lunch Break (restaurant)			Elorens GRIMM	eoilde	qA 	- 0	- s	plicati Marie GUILLERMAIN	q		
		08:00 08:10 08:20	08:30	08:40 08:50	09:10	09:20 09:30	09:50 09:50 10:00	10:10 10:20 10:30	10:40 10:50	11:00 11:10	11:20 11:30	11:40	12:20 12:10 12:20 12:30 12:40 12:50 13:00	13:10 13:20 13:30 13:40	13:50 14:00 14:10	14:20 14:30	14:40 14:50	15:00 15:10	15:20 15:30 15:40		16:40		17:10 17:20 17:30	17:40 17:50
Wednesday	June 05		Arrival of participants	Inv. Ana SOBOTA	Marc RÖKF	Ĥ		Coffee Break	Inv. K. K				Lunch Break (lunch box)						Excursion to Chambord & Banquet (optional)					
		08:00 08:10 08:20	08:30	08:40 08:50	09:00 09:10	09:20 09:30	09:40 09:50 10:00	10:10 10:20 10:30	10:40	11:00 11:10	11:20 11:30	11:40 11:50	12:00 12:10 12:20 12:30 12:40 12:50 13:00	13:10 13:20 13:30 13:40	13:50 14:00 14:10	14:20 14:30	14:40 14:50	15:00 15:10	15:20 15:30 15:40	15:50 16:00 16:10	16:30	16:50 17:00	17:10 17:20 17:30	17:40 17:50
Tuesday	June 04	Registration		Opening ceremony	Inv Sanghoo PARK	Lare BRÖCKFR	-bdA	Coffee Break	Inv Thierry BELMONTE	Cvrino BEN OTHMEN			Lunch Break (restaurant)		Inv. Nikita LEPIKHIN	Belkacem MENACER	Maria Herrera QUESADA	Alexandre DEVOS	Coffee Break		Poster session			
		08:00 08:10 08:20	08:30	08:40			09:50 09:50 09:50	10:10 10:20 10:30	10:40 10:50 bles -		11:20 11:30 bne a		12:00 12:10 12:20 12:30 13:00 13:00	13:10 13:20 13:30 13:40	13:50 14:10 24:10			15:00 15:10	15:20 15:30 15:40	15:50 16:00 16:10	16:30 16:40	16:50 17:00	17:10 17:20 17:30	17:40 17:50
Monday June 03								Welcome		Hotel Groslot +		18:00-20:30												

3 Abstracts – Oral presentations

The abstracts (full-text) are collected in the following section. They are sorted according to the schedule shown in page 11.

08:00								
08:10		Registration	Chairmen					
08:20								
08:30								
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08:50		opening ceremony						
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09:40	or sa	Lars BRÖCKER						
09:50	Generation and sources			Jose LOPEZ				
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11:00	qn							
11:10	Liquids and bubbles Applications	Cyrine BEN OTHMEN						
11:20	nd ica	Cynne Dei Conninen						
11:30	pla	Claire DOUAT		A. STANCAMPIANO				
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14:00		Inv. Nikita LEPIKHIN						
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14:30	D L							
14:40	Diagnostics	Maria Harrara OUESADA						
14:50	ē	Maria Herrera QUESADA		Marc BÖKE				
15:00		Alexandra DEVOC		IVIAIC BUKE				
15:10		Alexandre DEVOS						
15:20								
15:30		Coffee Break						
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16:30		Poster session						
16:40		POSTEL SESSION						
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17:20								
17:30								
17:40								
17:50								

– Tuesday June, 4^{th} –

Ionization of Gas Jet Impinging onto Liquids: Stabilizing or Destabilizing?

Sanghoo Park,^{1*} Wonho Choe¹, Hyungyu Lee¹, Joo Young Park², Jinwoo Kim³, Se Youn Moon⁴, and Uroš Cvelbar⁵

¹ Department of Nuclear and Quantum Engineering, KAIST, Daejeon, Republic of Korea
 ² Korea Institute of Materials Science (KIMS), Changwon, Republic of Korea
 ³ Samsung Advanced Institute of Technology (SAIT), Suwon, Republic of Korea

⁴ Department of Quantum System Engineering, Jeonju, Chonbuk National University

⁵ Jožef Stefan Institute, Ljubljana, Slovenia

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Interfacial phenomena between gas and liquid have attracted considerable interest from both fundamental and applied perspectives. In particular, the gas-driven depression of a liquid surface is commonly observed during top-blown industrial processes and in natural processes such as the dynamic coupling of wind and ocean. Many of us are empirically familiar with the creation of a stable or unstable cavity at a water surface by a normally impinging gas jet. Here, we report an intriguing behaviour of a cavity created by an impinging 'weakly-ionized' gas jet upon the water surface in the modelled system. Typically, when a high voltage is applied to a conductive gas nozzle as gas is flowing, the gas jet becomes ionized, whose characteristic degree of ionization is very low. After the ionized gas jet (a so-called 'cold plasma jet') is formed in the gas gap and cavity, surprisingly, we find that there are significant changes in the cavity shape and its stability; certain forces exerted by the plasma jet axially elongate the cavity and make it more stable. In this presentation, the effects of weak ionization of the gas jet on the gas–liquid system and relevant principles will be discussed.

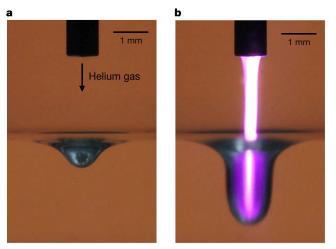


Fig. 1 Shadowgraph images presenting the depression of a free surface of distilled water by (a) a neutral helium gas jet and (b) a weakly ionized helium gas jet [1].

[1] Sanghoo Park, Wonho Choe, H. Lee, J. Y. Park, J. Kim, S. Y. Moon, and U. Cvelbar, Nature 592, 49-53 (2021).

Electrical characterization of diffuse single-filament dielectric-barrier discharges – Influence of stray capacitances on discharge characteristics

Lars Bröcker,^{1*} Claus-Peter Klages¹

¹ Institute for Surface Technology (IOT), Technische Universität Braunschweig, Braunschweig, Germany *E-mail: l.broecker@tu-braunschweig.de

Single-filament dielectric-barrier discharges (SF-DBDs) fed by argon/monomer (Ar/M) mixtures are of interest to investigate plasma-enhanced chemical vapor deposition (PECVD) at atmospheric pressure: If the duration of gas residence in the discharge is kept much smaller than the time required for diffusive transport of neutral products to the walls, only ions formed from M are deposited, as shown for mixtures of argon with hexamethyldisiloxane (HMDSO) [1] and allyltrimethylsilane (ATMS) [2], respectively. Besides the analysis of thin film properties, studies of the electrical characteristics are important to understand the influence of the discharge setup on the plasma appearance as well as plasma-chemical and -physical processes. In the present setup, a vertical tungsten rod or a copper wire (radius R, length L) glued to a borosilicate dielectric (thickness D) forms the high voltage electrode while the grounded reactor bottom is made from aluminum. Insert b of Fig. 1 shows a typical atmospheric pressure glow discharge (APGD) obtained using the mentioned SF-DBD setup with L = 30 mm and a molar fraction $x_{\rm M}$ of 50 ppm HMDSO in argon. While not much attention was initially paid to the role of the electrode length L, a closer electrotechnical inspection of the discharge setup reveals that a long electrode or an unshielded connection can be responsible for a significant stray capacity. This finding is already emerging from the analytical equation for the capacitance of an antenna consisting of a single wire perpendicular to a conducting plane, published by Grover in 1928 [3]. Numerical and experimental studies of the relation between geometric parameters (L, R, D) and the capacity C of the present discharge assembly show that C increases by more than a factor of 4 if L is increased from 1 to 80 mm.

Visual inspection of DBDs in the device shows that surface discharges emerging from deflected volume

discharges can be controlled by the electrode length L due to its strong influence on the radial field component E_r near the surface of the dielectric, see Fig. 1: For L = 1 mm, for example, the surface discharge near the dielectric (top) is radially contracted relative to the situation with L = 30 mm, and the negative glow emits much stronger (insert a). This effect can be related to a substantially larger E_r at the same maximal E_z , hindering the radial expansion of the surface discharge. Therefore, the electrode geometry influences parameters relevant for thin film formation, e. g. the transferred charge q_t and the energy dissipated per period E_g of the DBD setup.

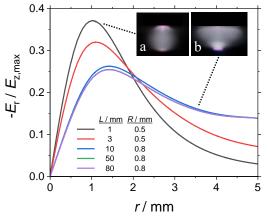


Fig. 1 - $E_r/E_{z,max}$ over *r* for combinations of *L* and *R*. Insert a: Photograph of DBD, 50 ppm HMDSO in argon, L = 1 mm. Insert b: The same with L = 30 mm. (Mirror images manually removed.)

L. Bröcker, G. S. Perlick and C.-P. Klages, Plasma Process. Polym. 17, 1-17 (2020).
 L. Bröcker, T. Winzer, N. Steppan, J. Benedikt and C.-P. Klages, Plasma Process. Polym., 21, 1-18 (2023).

^[3] F. W. Grover, Scientific Papers of the Bureau of Standards **22** (568), 569-629 (1928).

Spatio-temporal development of micro-hollow cathode discharges in DC and pulsed modes: new I-V regimes

Abd-Almalik Halfaoui*, Gérard Bauville, Pascal Jeanney, Stéphane Pasquiers and João Santos Sousa

Laboratoire de Physique des Gaz et des Plasmas (LPGP), CNRS, Université Paris-Saclay, Orsay, France *E-mail : <u>abd-almalik.halfaoui@ens-paris-saclay.fr</u>

Graphene is a material of choice for a wide range of promising technological applications in nano and optoelectronics. To prevent the hindrances of the substrate, graphene can be encapsulated in a material that preserves its properties. The search for new substrates revealed that hexagonal Boron Nitride (h-BN) buffer layers can preserve the properties of graphene [1], thus potentially leading to new disruptive technologies. Our work focuses on the development of a new deposition process using a new micro-plasma configuration based on the classical Micro-Hollow Cathode Discharge (MHCD), which has shown promising perspectives [2-4]. An experimental study of the micro-discharge spatio-temporal development has been carried out. A detailed electro-optical characterization of the different micro-plasma devices used has been performed for several operating conditions: different Ar-N2 mixtures (0-100% N2), gas pressure (few mbar to few hundreds of mbar), electrical schemes (DC vs high-voltage (few kV's)) high-frequency (few tens of kHz) nanosecond (few hundred of ns) pulses). The complementarity of electrical measurements and fast ICCD imaging, from a transverse and longitudinal perspective, along with edge-detection algorithms, allowed to highlight the characteristics of the development of the cathodic expansion, both spatially and temporally, as a function of the current (energy deposited in the plasma). In DC mode, the plasma is not confined in the hole in the abnormal regime (as it has always been stated in the literature), but it rather reaches further out of the hole vertically on the cathode side (like a rod or stem). The length of the rod depends on the gas pressure and mixture, and on the discharge current. In the normal regime, the cathodic expansion forms from the tip of the rod and extends above the surface of the cathode. This results in two distinctive parts of the plasma: a bright rod/stem sprouting out the hole of the MHCD, on which stands a homogeneous and circular expansion. It is interesting to note that the spreading rate of the cathodic expansion is higher the wider the gap between the plasma and the cathode surface (i.e. the longer the rod). When the plasma can no longer extend, limited by the electrode surface, it is forced to undergo a second abnormal regime, now extending itself in volume by increasing its thickness. In pulsed mode, at each voltage pulse, the plasma bursts out of the hole of the MHCD and spreads above the cathode, with the surface of the cathodic expansion as well as the light emission intensity varying in accordance with the oscillations of the voltage pulse. By increasing the N_2 admixture, those oscillations increase both in frequency and amplitude, giving birth to concentric circles in the cathodic expansion.

This work has been supported by the French ANR project PlasBoNG (ANR-20-CE09-0003-01).

[1] C. Dean et al., Nature Nanotech. 5, 722 (2010).

- [2] S. Kasri et al., Plasma Sources Sci. Technol. 28, 035003 (2019).
- [3] H. Kabbara et al., Appl. Phys. Lett. 116, 171902 (2020).
- [4] A. Remigy et al., J. Phys. D: Appl. Phys. 55, 105202 (2022).

Nanosheets by Electrical Discharges in Liquids

Thierry Belmonte,^{1*} Anna Nominé,¹ Frédéric Brochard,¹ Cédric Noël,¹ and Thomas Gries¹

¹ Université de Lorraine, CNRS, IJL, F-54000 Nancy, France ^{*}E-mail: thierry.belmonte@univ-lorraine.fr

The synthesis of nanoobjects through discharges in liquids appears to be an endlessly fascinating field. In addition to generating complex nanoparticles with surprising shapes and compositions, it is possible to selectively induce the 2D growth of nanoobjects by manipulating experimental conditions. This phenomenon is observed in metals such as zinc, bismuth, lead, silver, and, of course, carbon. By employing nanosecond-pulsed discharges under specific conditions, metallic nanosheets can be synthesized selectively. These conditions involve a chemical etching pretreatment, the application of weak overvoltages compared to the breakdown voltage, and the use of suitable metals, as not all metals exhibit similar behavior.

This growth mechanism remains consistent whether water or liquid nitrogen is used, indicating that the liquid medium has minimal influence on the interaction between electrodes and the metallic discharge formed in the early stages of the process. Anisotropic growth of these 2D objects is attributed to ions, but surface defects are also crucial. Chemical etching before treatments is essential to increase the probability of forming nanosheets from nearly 0% to 100%. This step is necessary to eliminate native oxides and expose surface defects. Ultrafast video analyses reveal that nanosheets are released from the cathode to the liquid through sweeping over the surface of the liquid-bubble interface, causing them to detach from their substrate. Experiments involving bismuth and lead electrodes demonstrate the potential for forming alloy nanosheets. A deeper understanding of the growth mechanism opens up new possibilities for designing 2D nanoobjects.

Oxidizing these objects in air or water subjects them to stress, which aids in stabilizing non-equilibrium oxide phases, as observed in the case of lead that produces a novel phase of lead oxide. This oxidation process may also involve carbonation, leading, for example, to the formation of the so-called BOC phase in bismuth, where BOC stands for Bismuth Oxide Carbonate ($Bi_2O_2CO_3$). This material exhibits some of the highest breakdown voltages and can be utilized as a metal oxide insulator in MOSFET transistors.

To conclude this discussion, we pose several pending questions: What conditions are necessary to cultivate 2D nanosheets from metals that still resist our persistent attempts? Can we enhance control over the number of layers in 2D nanosheets? What parameter governs their average size? And so forth.

Degradation of herbicides in water using non-thermal plasmas (NTP) at atmospheric pressure

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The intensive use of pesticides in agriculture leads to the contamination of surface water and groundwater. These persistent organic pollutants (POPs) exhibit inherent toxicity, posing environmental and health risks due to their stable molecular structures and potential to form hazardous by-products. However, conventional methods used in wastewater treatment plants remain partially effective for these pollutants. Advanced oxidation processes are introduced to degrade these toxic molecules [1].

Among the advanced oxidation processes (AOP), the use of plasma has already proven its potential to degrade persistent organic pollutants [2, 3]. Thus, this research focuses on the degradation by non-thermal plasma (NTP) processes at atmospheric pressure of the herbicides present in the water.

The main goal of the first part of this study is to perform a comparative analysis of the efficiency of three plasma reactors at atmospheric pressure (Glidarc, DBD and plasma jet) in terms of the production of key reactive species, such as hydrogen peroxide or acids/bases derived from nitrogen generated in Plasma Activated Distilled Water (PADW). Chemical analysis (spectrophotometry/UV-visible colorimetry) is performed. Furthermore, the energy efficiency of each plasma reactor is characterized.

The second part of this work is dedicated to testing the capacity of the chosen plasma reactor to treat a target herbicide.

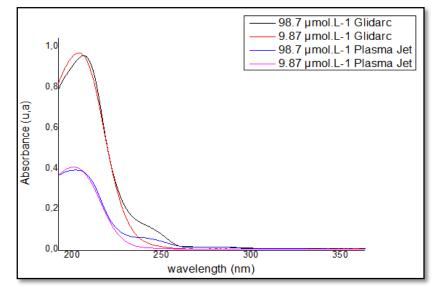


Fig.1 UV-Visible absorption spectra of Chlortoluron solutions treated by plasma jet and Glidarc for 20 minutes.

Acknowledgement: The authors are grateful to François Faubert for his guidance and experience with the Gas chromatography-mass spectrometry technique.

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Role of the carrier gas and the frequency excitation in carbon monoxide (CO) production by a micro-plasma jet for biomedical applications

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As carbon monoxide (CO) is a stable molecule and has anti-inflammatory properties, its production by plasma could be a significant advantage in the field of plasma medicine [1]. For this purpose, a small percentage of CO_2 was added in the gas mixture and was dissociated by plasma to produce CO.

The role of the nature of the carrier gas, argon or helium, has been investigated in a pulsed kHz-driven micro-plasma jet in the CO production. The concentration of CO produced was measured by absorption spectrometry via a gas analyzer, and we found that it rose from a couple of ppm to about 2000 ppm. This concentration was comparable to the one used in CO inhalation clinical trials, which means that this plasma source was safe in terms of CO production [1]. We found that two main parameters to control the CO concentration were the specific energy input (SEI) and the ratio of CO_2 in the gas mixture, but surprisingly, the nature of the carrier gas did not influence the production of CO.

This work will also present a comparative study of the CO production of two different micro-plasma jets: a MHz plasma generated by the COST jet reactor and a kHz plasma generated by a coplanar-coaxial DBD reactor. We will show that for the same SEI, the production of CO was more efficient for the kHz than the MHz-jet as shown in Fig.1.

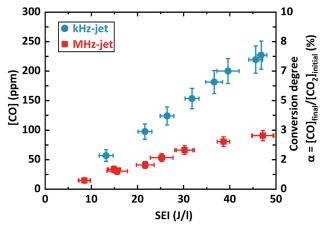


Fig.1: CO concentration (left) and the conversion degree (right) as a function of the specific energy input (SEI) for a kHz-jet (blue) and for a MHz-jet (red) at 1000 sccm of He + 0.3% CO₂ [2].

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Plasma bubbles in Oil and their applications in sterilization

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In this paper, plasma activated camellia seed oil (PACO) was prepared by wire to cylinder dielectric barrier discharge plasma interacted with camellia seed oil. Combined with the imaging by ICCD camera of the interaction process between plasma and camellia seed oil and the diagnosis of plasma active species by emission spectroscopy, as well as the analysis of PACO structure and physicochemical properties by Fourier transform infrared spectroscopy (FTIR) and chemical analysis, the bactericidal activity of PACO and its stability was explored. After discharging for 4 h at 16 kV and 6 kHz with He and O2 gas mixtures as carrier gas, the physiochemical properties of PACO prepared in the case by placing the plasma nozzle in the oil (PACO-4h) changed obviously. Compared with the untreated camellia seed oil, the iodine value of PACO decreased from 84.5 to 72 g/100g, while the peroxide value increased from 0.5 to 64.3 meq/kg and the acid value from 2.2 to 5.5 mg/g. PACO-4 h has strong bactericidal activity against E. coli and S. aureus. The diameter of bacteriostatic ring is 15.04 and 14.53 mm, respectively. Comparing of the OD600 values of PACO newly prepared with stored for 3 to 15 days, those had little change. That means the as-prepared PACO had strong bactericidal effect and good stability. According to changes of PACO OD values before and after sterilization to five common pathogens, it is easily identified that PACO has obvious bactericidal activity against P. aeruginosa, Salmonella and C. albicans besides of E. coli and S. aureus. It is of great significance for application and understanding the mechanism as well as broad-spectrum antibacterial properties of plasma activated camellia seed oil.

Keywords: Plasma activated camellia oil; ICCD imaging; Bactericidal activity; Dielectric barrier discharge.

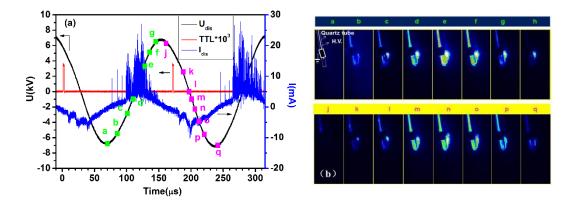


Fig. 1 Voltammetric characteristic curve of He plasma, (b) ICCD imaging of plasma propagation with the nozzle immersed in oil (U_{dis} =14 kV, f= 6 kHz, He flowrate is 1.0 L·min⁻¹)

A nanosecond sub-atmospheric pressure plasma jet as an experimental tool and a source of excited species

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The nanosecond (near) Atmospheric Pressure Plasma Jet (ns-APPJ) is demonstrated to be a convenient experimental tool for plasma kinetics studies, namely, vibrational and electronic excitation. Discharges in nitrogen and N₂:CO₂ mixtures are investigated by various experimental techniques: Optical Emission Spectroscopy (OES); Electric Field Induced Second Harmonic generation (EFISH), Coherent Anti-Stokes Raman Spectroscopy (CARS) and Quantum-Cascade-Laser Absorption Spectroscopy (QCLAS).

The observed value of the reduced electric field in the quasi-DC phase of about 100 Td is close to the optimum value for vibrational excitation of N_2 and CO_2 , as demonstrated by CARS and QCLAS. Almost all energy deposited into the plasma bulk is dissipated into the vibrational degrees of freedom, while the gas temperature is only slightly elevated. This makes the ns-APPJ an efficient source of vibrationally excited molecules, which can be used for plasma assisted catalysis studies and/or applications, including interaction with temperature sensitive substrates. Moreover, the nanosecond pulsing provides unique opportunity for separating the time scales of excitation during the active discharge and vibrational energy transfer in the afterglow, so that these processes can be studied independently, without influencing each other, see Fig.1 (a).

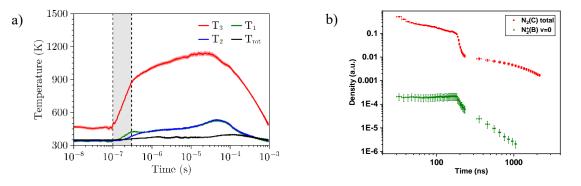


Fig. 1 a) Vibrational temperatures calculated from state-resolved CO₂ densities measured by QCLAS.
b) Relative densities of the N₂⁺(B, v=0) and N₂(C) states measured by OES.

Studies of electronic excitation in pure nitrogen performed by OES show that the ns-APPJ can be used as a source of active nitrogen species as well. For example, abnormally high population of the excited nitrogen ion, $N_2^+(B)$, has been observed during the pulse and in the afterglow of the discharge. While the expected lifetime of $N_2^+(B)$ at 200 mbar is 1 ns only, the corresponding emission is detected on a microsecond time scale, see Fig.1 (b). The mechanisms of the additional $N_2^+(B)$ population are discussed.

In summary, the ns-pulsed APPJ is a versatile tool for basic studies and applications as well. *Acknowledgements.* The work is supported by the DFG funded SFB1316 Project "Transient atmospheric plasmas - from plasmas to liquids to solids".

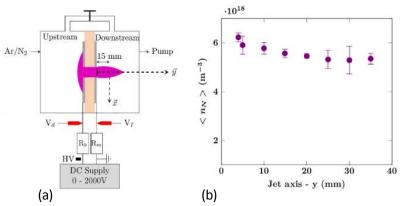
Absolute density of N-atoms using TALIF and gas temperature estimation using OES in a microplasma created by a Micro-Hollow Cathode Discharge.

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 N_2 dissociation is a challenge for the deposition of nitrides such as hexagonal Boron Nitride (h-BN). The energy required for the dissociation of N_2 is 9.7 eV, making it one of the strongest chemical bonds due to its triple covalent bonding. Micro-Hollow Cathode Discharge (MHCD) is a unique three-layer microplasma source consisting of a dielectric material sandwiched between two electrodes, with a hole (few 100s µm diameter) drilled at their center. MHCD has been shown to produce a high electron density [1] and, thus, provide a rich chemical reactivity which allows achieving dissociation of molecular nitrogen, making it a promising tool for nitride deposition. In this context, Two-photon Absorption Laser Induced Fluorescence (TALIF) and Optical Emission Spectroscopy (OES) were employed to probe an Ar/N₂ microplasma generated by a MHCD operating in DC mode (Fig.1a). TALIF was used to measure the absolute atomic nitrogen (N-atoms) density, using a krypton gas for calibration. OES was employed to determine the rotational temperature of N₂ Second Positive System N2 (SPS: $C^3\Pi_u$, $\nu' - B^3\Pi_g$, ν''). The reactor system studied consists of two chambers separated by the MHCD (400 µm diameter hole). Each chamber withstands a different pressure (P_1 and P_2). A 2.5 mm diameter aluminium electrode is positioned 15 mm away from the MHCD. For TALIF measurements, two experimental configurations were considered: i) the MHCD $(P_1=P_2)$ where no expansion is observed in the anodic chamber in contrast with the cathodic expansion that is always present, and ii) the MHCD jet $(P_1 > P_2)$ where a pressure differential is created, which drives the N-atoms out of the hole toward the aluminium electrode(Fig.1b). Both configurations were investigated with various experimental parameters, such as the percentage of argon in the gas mixture, the pressures P_1 and P_2 , and the discharge current. In addition to these two configurations, a third configuration was studied with OES. In this case, a third electrode (acting as a second anode) may favor the creation of a secondary plasma away from the MHCD. This configuration is called Micro-Cathode Sustained Discharge (MCSD). The MHCD, MHCD jet and MCSD configurations were also studied for various Ar/N_2 ratios, DC current, and pressures [2]. The rotational temperature (\approx gas temperature) was determined by numerically fitting the emission spectra to rovibrational levels of the $N_2(SPS)$. The main goal of these studies is to better understand the plasma physicochemical properties, such as gas temperature and N-atom density production pathways, and optimize the MHCD for h-BN deposition on large surfaces.



<u>Figure 1</u>: (a) The reactor used in the experiments (P1>P2). The cathode is on the left, where a negative high voltage is applied and the anode on the right (grounded). (b) N-atoms density probed with TALIF along the jet axis (conditions: 80% Ar, P_1 =50- P_2 =1 mbar, discharge current: 1.6 mA).

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Absolute LIF Measurements of 2D Spatial Distributions of OH in the COST-Jet Effluent with Different Atmospheres and Targets

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The field of microplasma technology, recognized for its ability to generate reactive oxygen and nitrogen species (RONS), is gaining interest for its applications across medical treatment, material processing, and food safety. However, the intricate chemical mechanisms inherent to plasma systems present challenges in isolating the contributions of individual RONS to the desired outcomes, especially when different substrates are introduced or varied environmental conditions are imposed. Consequently, it is essential to accurately measure and map the spatial distribution of RONS generated by microplasmas, both in the presence and absence of substrates, to facilitate the optimization of its varied applications. In this study, we utilize laser-induced fluorescence (LIF) techniques to measure absolute two-dimensional spatial distributions of hydroxyl radical (OH) concentration, a critical reactive oxygen species, within the effluent of the reference Capacitively Coupled Atmospheric Pressure Microplasma Jet (COST-jet). We analyze the effluent generated by three helium-based gas mixtures—helium-oxygen (He+O₂), helium-water vapor (He+H₂O), and helium-nitrogen-oxygen (He+N₂+O₂)—that have been previously characterized in COST-jet investigations. The resultant profiles were compared when the jet propagates into environments of pure nitrogen and ambient air, to discern the influences of ambient gas composition on OH distribution. For the helium-water mixture, we investigate how the OH distribution changes when the jet effluent impinges on solid and liquid targets. This study enhances our knowledge of the dynamics of production, consumption, and transport of OH, in the effluent of the COST-Jet, which is needed to better tailor RONS delivery.

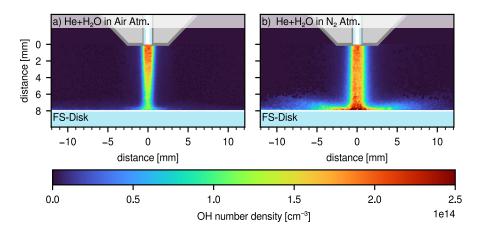


Fig. 1 Spatial distributions of OH number density in the effluent of the COST-Jet for a He+H₂O gas admixture when interacting with a solid surface located 8 mm from the COST-Jet's nozzle, in both nitrogen and air atmospheres.

Single pulse pin-to-pin plasma discharge on levitated water droplet

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Cold plasma in or on the surface of the water is widely studied nowadays for its application in several fields like medicine, agriculture or for the treatment of wastewater. The effects of plasma treated water are due to the creation, in interaction with water, of reactive oxygen and nitrogen species (RONS) during the plasma treatment. The formation of RONS and therefore the efficiency of plasma system is somewhat limited by the interface between plasma and liquid phase. The combination of plasma and micrometric droplets (ie. aerosol and spray) could greatly improve the performances of plasma-water systems [1]. Anyway, one of the key point in the study of multiphase plasmas is the understanding of all the complex physical and chemical processes occurring during the interaction [2]. In order to study those physicochemical aspects, we consider one single water micro droplet trapped in an acoustic levitator exposed to a pin-to-pin microplasma. This pin-to-pin tungsten electrodes configuration (fig 1.a), connected to a custom GREMI high voltage pulse generator creates a cold atmospheric plasma discharge pathing through or around the droplet. To be able to observe the path of the plasma and the droplet morphology, a double shutter camera coupled with a pulsed laser is used (fig 1.b-c). This combination makes it possible to take an image of the droplet interacting with the plasma as well as to follow its geometry over time (*fig 1.c*). This study investigates the effect of different parameters, like the size, the conductivity of the water and the voltage delivered to the electrode. The obtained results provide new data for the development of new plasma-aerosol devices in the fields of agriculture and medicine.

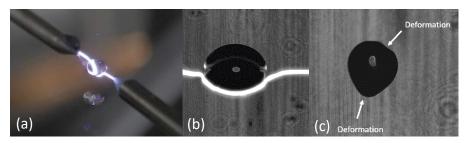


Fig. 1 : Photography (a) and high-resolution acquisition (b) of the microplasma droplet interaction between two electrodes, droplet deformation after microplasma droplet interaction.

Acknowledgements: National founded project PLASMASOL - ANR-23-CE04-0003 Keywords: Pin-to-pin discharge, Water droplet, Levitation References:

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Charging effects of a dielectric surface interacting with a plasma jet

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Non-thermal atmospheric pressure plasmas, among them plasma jets, are a focus of intense study in the recent years, due to their suitability and convenience for applications on sensitive substrates, for example polymers or living tissue. In applications, those discharges come in contact with an array of targets, most notably with varying conductivities. As these discharges are in a transient state, evolving quickly through time and space, sub-mm in characteristic size and characterized by a low ionization degree, the presence of any target affects them and the target properties determine the interaction.

This work focuses on the charging dynamics of dielectric targets while under plasma exposure. The model system consists of a plasma jet in a coaxial geometry where the inner electrode is powered and is also used as a gas inlet. The ground is placed on the outer side of a glass capillary. Sinusoidal AC at 30 kHz or pulsed voltage at 5 kHz is used to power the inner electrode. The typical power dissipated in the plasma is below 1 W. Helium is flown through the jet at rates between 500 SCCM and 1500 SCCM and allowed to expand in the room air at the exit of the glass capillary.

The diagnostics used to examine the charge dynamics in jets interacting with dielectric targets include fast imaging, Thomson scattering, Stark shift and Pockels-based Mueller polarimetry.

Charges, Fields and Species in the Micro Cavities of a Plasma Array for Catalysis

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Micro-structured plasma discharges offer great prospects for a variety of technical applications. They show great potential for applications requiring large-area treatment, catalytic conversion, or decomposition of volatile organic compounds. Therefore, arrays of dielectric barrier micro discharges in well-defined cavities are of high relevance from a scientific and technical point of view. To understand the underlying processes, fundamental knowledge about the discharge dynamics and generation of reactive species is necessary. In this work, we investigate modular constructed metal-grid micro cavity [1] plasma arrays which allow for stable operation and the incorporation of catalysts. One array consists of hundreds to thousands of small discharge cavities with dimensions in the range of 100µm each. Here, the plasma arrays are operated in helium with admixtures of reactive gases, typically in the percentage range and excited by triangular voltages between amplitudes of 400-800V with frequencies in the kHz regime.

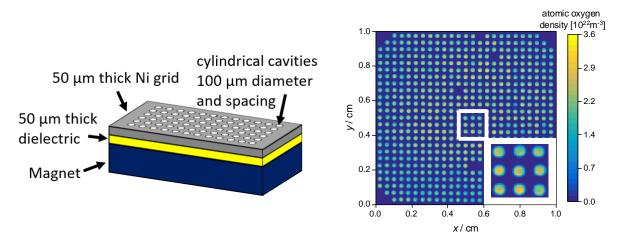


Fig. 1 Micro cavity plasma array (left) and 2D resolved oxygen densities (right)

The novel realm of plasma catalysis lacks experimental exploration regarding the impact of the fluxes of charged particles driven by electric fields and plasma-induced surface charges on catalysis. However, diagnostics in these cavities are challenging due to their small dimensions. The basic discharge behavior like discharge mode and expansion, electrical characteristics and dynamics will be discussed and accomplished by optical emission-based methods to determine electric fields (Stark shift) [2] and 2D resolved densities of reactive species (e.g. by state enhanced actinometry) [3]. Additionally, an electrical method to determine surface charges and an operando laser technique to control them will be presented.

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Intensity ratio analysis for plasma diagnostics in argon and carbon dioxide discharges

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Low temperature non-equilibrium cold plasmas found their use in multiple areas of fundamental as well as applied oriented research. Especially dielectric barrier discharges are investigated for their application in surface treatment, thin film deposition or gas conversion. While in many cases the use of barrier discharges is not the optimal solution for given purpose in selected application, their scalability and presence of various discharge mechanisms offer the possibility of fine tuning and are thus worth of detailed investigations.

Recently, interesting new results were done for homogeneous barrier discharges in the so called APTD regime (atmospheric pressure Townsend discharge) in air, CO₂ or pure nitrogen [1,2,3,4]. Advanced diagnostic techniques further deepened the understanding of the discharge mechanisms and were able to resolve their features in more details coherently with computer simulations [3], including the fine information on excited states kinetics [4]. At the same time, the wider availability of fast nanosecond pulsed high voltage sources and appropriate diagnostic techniques enabled the study of excited states kinetics on sub-nanosecond timescales [5] and most probably opened an interesting yet challenging ways how to use their relative densities for quantitative plasma diagnostics.

Relative intensities of atomic lines or spectral bands in optical emission spectra of cold plasmas were used for diagnostics for long time. Zhu and Pu summarized the attempts in [6]. Many authors proposed various methods for the use of intensity ratios for determination of electric field or electron density/temperature [6]. In this contribution we investigate the possibility to develop similar methods for plasma diagnostics also in argon or carbon dioxide plasmas. The intensity ratio of spectral lines/bands coming from different population of radiative excited states is, if used for determination of local electric field, very sensitive to the chosen radiative state excitation energy thresholds [7]. Typically, radiative states with very different excitation energy thresholds are recommended. In the case of argon and carbon dioxide excited radiative states energy thresholds however, the situation is not so straight forward if we consider also other limitations of the method. We have applied the time correlated single photon counting technique for this task and present the first results.

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Investigation of excited molecular oxygen species produced by an atmospheric pressure micro plasma jet

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Reactive oxygen species are important drivers for various chemical reactions in medicine and technological applications.

Singlet delta oxygen (O2(a1 Δ g)), a highly reactive form of molecular oxygen, crucial in various chemical processes such as sterilization, laser technology, biomarker detection, and cancer cell damage due to its elevated reactivity compared to ground state oxygen. Low-temperature plasmas serve as efficient sources of O2(a1 Δ g) through electron excitation.

However, singlet delta oxygen reacts strongly with ozone which influences the detected emission. As such the ozone density has to be taken into account when calculating the absolute singlet delta oxygen density. To overcome the low emission of O2($a1\Delta g$), a gas flow cell was utilized to gather the effluent, and 1270nm emission was captured using a density-calibrated spectrograph. The ozone density was measured via absorption spectroscopy.

This study examines the reaction dynamics of O2(a1 Δ g) in the effluent of an atmospheric pressure micro plasma jet, specifically the COST jet, and compares them to simulation results. Special attention is given to ozone (O3) and other excited molecular oxygen O2(b1 Σ 1g), both involved in the destruction of O2(a1 Δ g).

Measurements of the O2(a1 Δ g) density matched the simulation well at 10²0 m⁻³, but the measured ozone density was one magnitude lower around 10²1 m⁻³. The strong correlation between O2(a1 Δ g) and ozone in the effluent, complicates the alignment of experimental and simulation results.

The results of these measurements provide a modelling benchmark for the COST plasma jet and improve the understanding of reaction dynamics of excited molecular oxygen species.

Two-dimensional simulations of high-pressure DBD and microwave microdischarges: spatiotemporal inhomogeneities and plasma dynamics

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High-pressure discharges often take the form of filaments and streamers which present microscale characteristics. Through numerical modeling, the spatiotemporal behavior of such fine plasma structures can be elucidated but the multi-physics and multi-scale nature of plasma dynamics require dedicated numerical models and physical approximations. In this talk, we focus on numerical and physical recipes and challenges for accurate and efficient simulation of complex, high-pressure microdischarge phenomena. We'll show how both surface and volume DBDs present distinct features inside a full AC cycle, periodically transitioning from glow to streamer and microdischarge regimes [1, 2]. We'll also show how simplified plasma-wave models can reproduce characteristics of microwave discharges such as filamentation and pattern formation as well as capture microplasma formation in specific configurations such as split ring resonators and microstrips [3]. Such modeling efforts can aid the design of novel reactors and plasma actuators for various applications such as CO_2 conversion and plasma anti-icing [4].

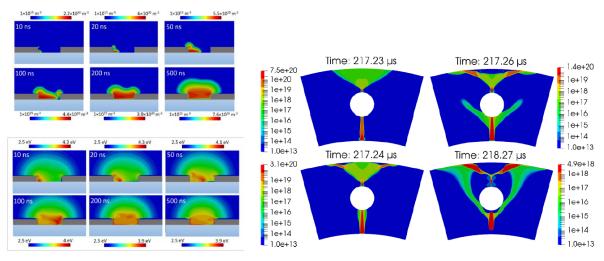


Fig. 1 Left: Microstrip excited microdischarge in Ar – electron density and temperature evolution. Right: Coaxial packed-bed DBD and formation of microdischarges in ambient air – electron density evolution

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Numerical simulation of ionization wave propagation in an atmospheric pressure plasma jet

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Atmospheric pressure dielectric barrier discharge jets are one of the typical examples of low temperature plasma sources. The plasma is ignited by a pulsed discharge and passed through a guided helium jet. The luminous zone (plasma plume) extending into the open air is not continuous, but actually consists of so-called plasma bullets [1-3]. In this research, we conduct numerical simulations with a two-dimensional axi-symmetrical model to investigate the ionizing wave propagation (streamer behavior) of a kHz-driven helium atmospheric pressure plasma jet. The two-dimensional plasma-fluid dynamics model consists of a steady-state fluid dynamics part (Navier-Stokes and heat transfer equations), a plasma mechanics part (drift-diffusion and Poisson equations) and chemical kinetics [4-7].

Figure 1 shows a numerically derived two-dimensional map of the ionization frequency of helium atoms, which allows us to understand the propagation of ionizing waves. Ionizing waves travel upward from the electrode toward the open end of the discharge tube. A "plasma bullet" forms on the outside of the tube. The propagation velocity is up to 50km/s. Numerical results are compared with experimental results obtained using optical emission spectroscopy and high-speed imaging [8].

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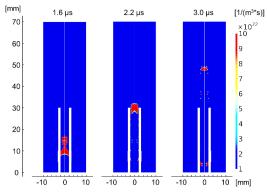


Fig. 1 Propagation of ionization waves from an atmospheric plasma jet. 2D snapshots of ionization frequency of helium atoms at 1.6, 2.2 and 3.0 μ s after starting to apply voltage.

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Scaling of reactive species transport towards and inside liquids for application in biocatalysis

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Biocatalysis, an environmentally friendly and potentially lower-cost alternative to chemical conversion, needs reactive species as a precursor for enzyme-based reactions. Small-scale radio-frequency-driven atmospheric pressure plasma jets are a suitable source for reactive species delivery in biocatalysis because they can deliver precise and controllable quantities of plasma produced reactants non-invasively to enzymes contained in a water-based solution. To achieve a selective, economical and energy-efficient process, the chemical behaviour in the gas and liquid phases is of interest as these affect the production and delivery of reactive species.

This work focusses on hydrogen peroxide production due to its ability to activate peroxygenase enzymes in the liquid component. Since the amount of each species delivered is essential to tailor the biocatalytic behaviour of the system, other plasma produced species also need to be considered. A parallel plate capillary jet with similar properties to the COST microplasma reference jet, but with a capillary between the electrodes, is studied as a hydrogen peroxide source. The capillary serves as a dielectric and allows for higher power deposition, in comparison to the COST jet, as well as for helium feed-gas containing water vapour admixtures up to saturation.

The plasma-chemical behaviour in the gas phase is investigated using a pseudo-1D plug flow model implemented in the 0D plasma chemical kinetics code GlobalKin [1] for a helium-water vapour gas phase [2]. The 1D plug flow model allows the calculation of species densities from the gas inlet, through the plasma area and the effluent, to the liquid surface. The qualitative trends in hydrogen peroxide and hydroxyl radical concentrations predicted by the model at the liquid interface have been shown to be in good agreement with their concentrations measured in the liquid [3]. As an extension of the work in [3], the species densities at the liquid surface serve as input for a 1D liquid simulation, which solves partial differential equations for species concentrations in the liquid resulting in their spatial-temporal concentration profiles. Here, the liquid simulation considers chemical reactions and diffusivity of the involved species and allows for a better understanding of reactive species scaling with depth in the liquid, and their delivery to enzymes contained inside it.

The authors thank Prof. Kushner for providing the GlobalKin code and the German Research Foundation (DFG) for financial support via CRC 1316 (project number 327886311), project B11.

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- Thursday June, $6^{\rm th}$ -

Better protect our communications systems against electromagnetic attacks thanks to microdischarges

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With the advent of planar circuit technologies, microwave wireless communication systems have become increasingly compact and integrated. However, with the accelerated development of high-power electromagnetic directed energy weapons (HP DEW) [1], their vulnerability has increased. The disruptive, even destructive, effects of these weapons on these electronic systems have for example been studied by Bäckström [2]. To protect against these threats, it is common to use microwave power limiting devices, generally based on diodes [3]. However, these semiconductor components are now showing their limits due to the increase in the power of aggression.

Recently, the authors have proposed a microstrip transmission line device integrating a microwavesustained discharge for power limiting applications, but which can also be seen as a microwave plasma source [4]. This device consists of a multilayer structure made up of two parallel planar conductors, between which there is a dielectric slab and a cavity filled with Argon at 10 Torr where the microwave plasma is generated (see Fig. 1).

In this communication, we will present the operating principle and give an overview of the performance obtained experimentally and numerically, highlighting some of the key parameters that control its performance. Based on numerical and theoretical work, we will propose an interpretation of the coupling modes of the wave to the plasma in such structures. In particular, we will show that the plasma column is sustained by a leaky wave (i.e., the microwave power propagates in the dielectric and leaks into the plasma).

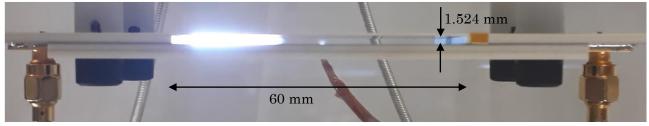


Fig. 1: Image of the plasma-based microwave power limiter in suspended microstrip technology. Argon at 10

Torr and CW signal at 3 GHz and 40 dBm (10 W).

Acknowledgments

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Maze-solving by micro-channel plasma and its analysis based on Boltzmann-Gibbs and Shannon entropies

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Maze-solving is an intelligent task of finding a suitable path among options of possible path branches. While many methods have been proposed to perform this, plasma channels are also effective to search many branch points in a maze for the optimum path. From a given starting point, all options can be quantified in probability distributions of possible paths, one of which reaches the goal [1]. After derivation of the probability distribution, Shannon entropy is calculated easily [2]. To solve a maze, in this study, we use micro-channel plasma whose cross section is 1x1 mm². Basically, as a plasma channel which is being optimized converges into the final and fixed path, the options get reduced, yielding to *decreasing* Shannon entropy.

Here, for maze-solving, we use plasma, which is a thermodynamical process; how is Boltzmann-Gibbs entropy, which should *increase* according to the Second Law of thermodynamics [3]? In fact, Boltzmann-Gibbs entropy increases due to its extensivity [3], and this discrepancy in opposite trends comes from flexibility in definition of a probability distribution that determines Shannon entropy. In comparison with free-expansion plasma, Boltzmann-Gibbs entropy is *relatively small* in the plasma channel converging into the optimized path, which corresponds to decreasing Shannon entropy.

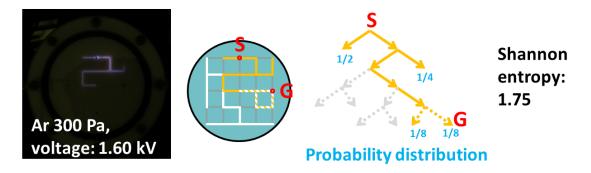


Fig. 1 Visible image of micro-channel plasma on the way to goal (G) and corresponding path from starting

point (S) to goal.

ACKNOWLEDGEMENTS

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Microplasma-assisted anodic dissolution as a tool for the formation of multielement perovskite oxides nanoparticles

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Innovations in the field of nanofabrication technologies recently resulted in a significant boost of numerous science and technological areas. Novel controllable nanoparticles (NPs) production methods allowed significant broadening of the range of nanomaterials produced, towards nanostructures of complex composition, developed surface and tunable properties tailored for specific practical applications. Therefore, further development of nanofabrication methods is still an urgent and important task. Here, we report a novel versatile plasma-assisted approach that utilizes the processes at plasma-liquid interface for the controlled production of multimetal perovskite oxide nanomaterials. Combination of distinctive properties of several metallic elements in one structure allows gaining novel electronic, magnetic, optical properties required for such rapidly developing fields as spintronics, catalysis, solar energy harvesting. The approach developed in this work (Figure 1a) allows production of NPs from the solid metal foils in distilled water without a need of any complex precursors or high temperatures. For the plasma ignition, a high voltage (1.5 kV) was applied to the combined anode consisting of pressed metallic foils and a capillary cathode with Ar gas (flow rate 60 sccm) purging through it. The method was tested on binary (e.g. GdFeO₃) as well as ternary multimetal NPs (Gd(Fe,Mn)O₃, Gd(Fe,Cu)O₃) production. In contrast to the conventional electrolysis, it allows production of NPs composed of metals having different electrode potentials while the uniform distribution of the elements in the NPs produced (Figure 1c-f) observed in the EDX mapping results proves the successful formation of NPs of the desired composition. The ratio of the elements in the NPs produced was shown to be determined by the submerged area of solid metal precursors as well as by the composition of a liquid. To sum up, the work presents a novel microplasma-assisted approach for the formation of multimetal perovskite oxide nanostructures that can be extended to a broader range of metal-based nanomaterials upon optimization of the synthesis conditions.

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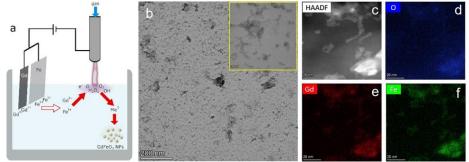


Figure 1. Scheme of the developed setup of plasma-assisted dual anodic dissolution for the production of perovskite NPs, b,c - TEM of the NPs produced, d - f - EDS mapping of the O, Gd and Fe

On the use of microplasma arrays for electromagnetic metasurfaces

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The use of plasma discharges for electromagnetic (EM) applications has been investigated in different applicative scenarios, including antennas [1], photonic band-gap structures [2]-[3] and, more recently, metamaterials [4]-[5]. In all these works, plasma is used as a bulk and homogenous material that, depending on the frequency of the impinging EM wave, exhibits either a negative or near-zero electric permittivity. However, the possibility to realize arrays of microplasma elements (such as the one shown in Fig. 1(a)) paves the way to novel and unprecedented possibilities in plasma electromagnetics. Indeed, provided that the microplasma elements are much smaller compared to the wavelength of the impinging wave, such a matrix can be engineered to behave as a metasurface [6], whose macroscopic response depends on the combination of both the plasma parameters and the geometry of the structure.

In this contribution, we describe the results of some theoretical and numerical investigations about the design of reconfigurable microplasma-based metasurfaces introducing anomalous refraction of EM waves (an example is shown in Fig. 1(b)). The EM advantages of finely structuring plasma discharges will be highlighted and several possible applications of plasma-based beam-steering devices in communication and wireless systems will be discussed.

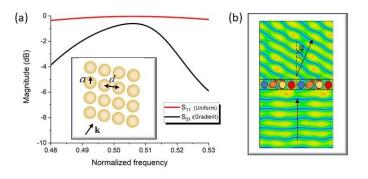


Fig. 1 (a) Transmission coefficient of different Floquet modes in a microplasma-based metasurfaces; (b) E-

field profile showing anomalous refraction of EM waves of such a device (numerical FEM simulations).

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Orléans, FRANCE

The Comparisons of Electric and Chemical Properties of Atmospheric Pressure Plasma Jets and Surface Dielectric Barrier Discharges

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Atmospheric pressure plasmas are utilized for chemical plasma applications without expensive vacuum chambers. This talk compares the He atmospheric pressure plasmas jet (APPJ) and the surface dielectric barrier discharge (SDBD) for their electric and chemical properties. At first, the electrical and chemical properties of nanopulse APPJs are tested and compared with the cases having a low driving frequency of 20 kHz. It was found that the propagation speed of the plasma bullet is affected mainly by the bias voltage rather than the pulse duration or the repetition frequency [1]. However, the optical emission spectroscopy (OES) results show that the repetition frequency dominantly controls the chemical properties [1]. The mutual interactions of two APPJs are tested by changing the injection angles by observing the Schlieren image and a high-speed camera. The OES and the surface measurement at different interaction angles gives the analysis of the chemical properties of the two APPJs. In addition to the APPJ study, we conducted the diagnostics of the electrohydrodynamics by the curved surface DBD. Neutral particle's velocity and distribution were also investigated using particle image velocimetry (PIV) to understand the neutral flow behaviors [2,3]. It was found that the interaction range of the neutral flow is much further than the plasma source size, which means that the momentum transfers by the excited species and chemical interactions are important.

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Partial Discharging in Complex Surface Dielectric Barrier Discharge Electrodes

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Surface dielectric barrier discharges (SDBDs) have recently garnered interest for applications in flow control, plasma medicine, and food processing. SDBDs can be advantageous due to their low voltage required to ignite plasma and their consistency due to the treated substrate not being part of the circuit, as in the case of volume dielectric barrier discharges. Circuit analysis on SDBDs has mainly focused on linear electrodes used for flow control.¹ Several applications, such as bacteria inactivation with SDBDs, use more complex electrode geometries that increase the generated plasma area.² To elucidate the effects of more complicated electrodes on the plasma circuit, ICCD imaging is used in conjunction with voltage and current measurements. The electrodes are powered with a 3000 Hz 2.5 kV AC signal. Time-resolved ICCD imaging is used to visualize the plasma extent within a single discharge period. The results from ICCD imaging are compared to the circuit behavior modeled with a proposed simple equivalent circuit model.³ From these measurements, it was observed that the plasma extent strongly relates to the circuit's charge voltage derivative (dQ/dV). Additionally, unlike linear electrodes previously reported in literature,¹ the measured dielectric capacitance was determined to be constant for a large majority of the on-cycle. Further, it was determined that the electrode was partially discharging during the initial phases of the on-cycle. This partial discharging had a significant impact on the circuit parameters, showing a nonlinearity in the charge vs voltage graph. Finally, it was observed that during the partial discharging period of the voltage excitation, the plasma extent of the on-sections did not continue to expand until the entire cell was ignited. The results shown here have impacts on the homogeneity and consistency of the plasma generated by the electrodes.

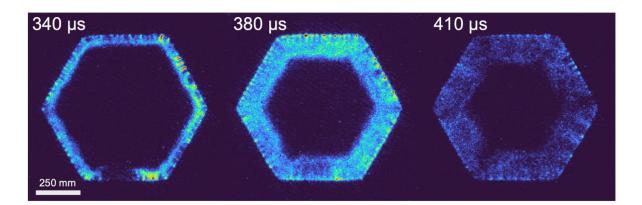


Fig. 1 ICCD images of a single electrode cell with a 2 microsecond exposure time at different times within the positive halfwave. Gate delay times of the images are shown in the upper left corner.

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Comparison of surface-DBD dynamics sustained by sinusoidal AC and positive rectangular pulsed voltage waveforms

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Surface Dielectric Barrier Discharges (SDBDs) have attracted attention in various scientific and technological fields, such as flow control and biomedicine [1,2]. The driving voltage (V) waveforms, which determine the underlying mechanism of SDBDs, may be classified into two broad categories: i) alternating current (AC) waveforms with frequencies (f) ranging from few Hz to 100 kHz, and ii) pulsed waveforms with rising/falling times of 1-100 ns (or even larger at the microsecond scale) and similar f values with AC voltages.

This work is devoted to the experimental investigation of electrical and optical features of a SDBD driven by sinusoidal AC (f=10 kHz, V=10-20 kVpp) and positive rectangular pulsed (f=0.1- 10 kHz, V=6-10 kV, t_{pulse} =160 ns-50 µs, t_{rise}/t_{fall} =50 ns) waveforms. The reactor follows a cylindrical arrangement of two annular stainless-steel electrodes separated by a quartz dielectric tube and the inner electrode is fully immersed into a transformer oil [3]. Specifically, the discharge dynamics is probed through (i) conventional photography by means of a digital camera, (ii) time-resolved images utilizing an ICCD camera, (iii) relatively calibrated space- and time-integrated emission spectroscopy, and (iv) electrical measurements of the applied voltage, the induced current and the deposited power.

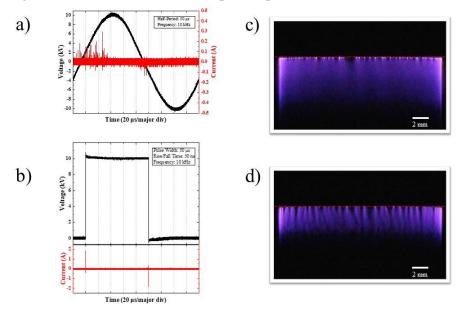


Fig. 1 Indicative oscillograms and photographs of the SDBD applying AC (a,c) and pulsed waveform (b,d).

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Reactive Nitrogen Species Generation at Plasma-Liquid Column Interface

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Exclusive use of the abundant resources for atmospheric pressure plasma generation are essential for plasma nitrogen fixation, which synthesizes nitrogen compounds exclusively from air and water [1]. It has been shown that some nitrogen oxides NO, NO₂, and N₂O₅ can be selectively generated by air plasma, recently [2, 3]. However, hydrogen containing nitrogen species ($H_xN_yO_z$) such as NH₃, HOONO, HOONO₂, are hardly selectively and efficiently produced from air and water. Further understanding of fundamental reaction process at the plasma liquid interface could be a key factor to realize selective and efficient generation of species.

Experiments have been conducted under stable liquid column flow surface to minimize the additional complexity resulted from the liquid motion. OH radical reaction decay in the liquid column jet has been experimentally demonstrated [4]. Schematic of experimental setup is shown in Fig. 1. The liquid column jet with the diameter of typically 0.13 to 0.25 mm is coaxially and colinearly guided by nitrogen gas jet through a gas nozzle. At the downstream of the nozzle, atmospheric pressure plasma is generated by a high-frequency AC power supply approximately 60 kHz, which manages plasma – liquid contact to transport nitrogen atomic radical to the liquid surface (Inset figures in Fig. 1). The high frequency discharge in a burst operation is synchronized with a pulsed gas blow at the further downstream, to selectively collect a specific part of the liquid column using the convection delay of the gas and the liquid phase products. Preliminary experiments show formation of NO_2^- and NH_3/NH_4^+ and infer the reaction products through the plasma liquid interface reaction.

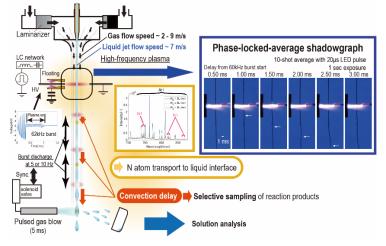


Fig. 1 Schematic of Experimental Setup.

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Zero-dimensional plasma-chemical simulations of microdischarges in bubbles during plasma electrolytic oxidation

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Plasma-liquid interactions are an important aspect for many surface treatment applications relevant to the transport and medical industries. Light metals like aluminium, titanium and magnesium, as well as their alloys are used extensively in these fields. To protect the materials from corrosion and wear, an oxide layer can be applied using plasma electrolytic oxidation (PEO). Based on conventional anodizing in liquid electrolyte solutions, PEO is in contrast operated above the breakdown voltage. This leads to transient microdischarges contained in water-vapour bubbles yielding a passivation layer on light metals. The coating properties depend on electrolyte composition and electrical parameters.

The understanding of the fundamental properties of the PEO process is limited. One such aspect is the concentrations of reactive species contained in the gas-bubble. Purely experimental approaches for the analysis of the complex nature of the microdischarge formation and sustainment prove difficult due to their stochastic and transient behaviour. But a fully consistent simulation approach for the bubble, microdischarge and the plasma-chemical kinetics is also an extreme challenge.

The approach used in this work is a 0-D plasma-chemical kinetics simulation informed by experimental data provided by a specially made single microdischarge setup (SMD) [1]. Optical emission spectroscopy is used to calculate electron temperatures and densities while a high-speed camera system, synchronized with current-voltage measurements, allows the calculation of a time resolved power per unit volume profile, which is used as input to the 0-D model.

The model solves the mass-balance equation for each included species, as well as the energy-balance equation for the electron temperature. The resulting ordinary differential equation system is solved using *DifferentialEquations.jl* [2]. The underlying chemical reaction set used in the model is adapted of that published in [3,4,5]. During the contribution, the evolution of charged and neutral species densities, as well as the electron temperature during the lifetime of typical PEO microdischarges will be shown and discussed, as well as how they scale with variable electrical parameters.

This work is supported by DFG via SFB 1316 (project number 327886311), project B5.

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Helium plasma jet for wettability alteration of microfluidic channels

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Considering the wettability in fluid-fluid mass transfer is imperative for a comprehensive study of the dissolution of CO_2 in water within carbon capture utilization and storage framework. Experimental small-scale research on mass transfer is frequently based on microfluidic devices which require adequate control over surface parameters like wettability. Plasma has already been proven to be a promising tool for the control and alteration of the wettability of solid surfaces, yet its propagation in microfluidic devices and treatment stability remains challenging. Our idea is to create and inject atmospheric pressure helium plasma jet directly into the micrometer-size channels for *in-situ* wettability treatment (see Fig. 1) and thus enable better control over the treatment parameters compared to conventional treatments in low-pressure chamber-type plasma reactors. With a homemade kHz DBD-like setup, we successfully propagated plasma through a 4 cm long rectangular microchannel of uniform depth (100 μ m) and variable width (250 - 750 μ m). Wettability results obtained by *in-situ* contact angle measurement on images indicate uniform treatment with increased hydrophilic properties after only 2 minutes of treatment. Unlike chamber-type plasma treatments, the wettability achieved with our setup offers stability for up to 70 days depending on the plasma treatment and storage parameters. Finally, we show that increased wettability affects CO₂ dissolution dynamics.

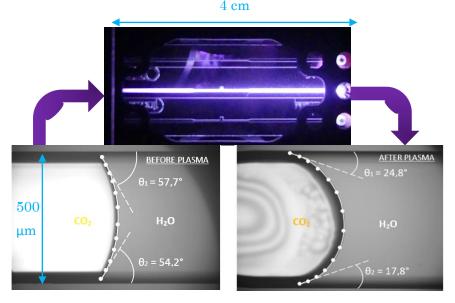


Fig. 1 Plasma jet propagating inside the glass microfluidic device and making the surface more hydrophilic (visible by the decrease of contact angle after the treatment).

Plasma-Assisted Dry Reforming of Methane Over Heterogeneous Ni/Al₂O₃ Catalyst

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 CO_2 and Methane utilization has generated much interest mainly through dry reforming of methane (DRM). DRM (Eq. 1) is a desirable reaction which can produce syngas, a binary mixture of H₂ and CO, which is used as a valuable feedstock for the Fisher Tropsch (FT) synthesis of linear olefine, while simultaneously mitigating the environmental impact of these greenhouse gasses.

 $CH_4 + CO_2 \rightarrow 2 \ CO + 2 \ H_2 \quad \Delta \ H^o \ _{25oC} = 247 \ kJ \ mol^{-1} \quad (Eq. \ 1)$

DRM, a thermo-catalytic reforming technique, generally shows a large conversion efficiency but, at the same time is accompanied by high energy consumption due to the higher temperatures in the range 400-1000°C needed for an efficient conversion of the methane. Additionally, when carrying the reaction at these relatively high temperatures, an excessive carbon deposition on the catalyst surface is frequently observed yielding a lower overall efficiency of this process and subsequently causing serious challenges to larger scale industrial applications.

In contrast to this, NTP plasma-assisted reforming technology is considered an attractive alternative approach to traditional DRM due to some significant advantages such as near atmospheric pressure operation, lower reaction temperatures, lower energy consumption and lower carbon formation. Among the several types of NTP's used for DRM, the dielectric barrier discharge (DBD) plasma is one that allows the use of various dilution gases, packing materials, and types of catalytic materials thus enhancing its energy efficiency and product selectivity.

In this ongoing work, a fixed bed reactor is modified and fitted with a proprietary DBD-based plasma generation assembly allowing for direct plasma interface with a Ni $/Al_2O_3$ catalyst material. Reaction parameters such as feed gas mixtures, operating temperatures and applied electrical energy were varied and downstream effluent was analyzed via in-line GC. Conversion efficiencies and catalyst performance are reported.



Figure 1. (LEFT) The Catalytic Low Temperature Plasma (C-LTP) reactor system developed in this research project for the reformation of methane. (RIGHT) C-LTP reactor cross section depicting atmospheric low temperature plasma formation in the gas gap.

Toward Efficient Plasma Processing of a Liquid ~ Several Attempts to Utilize Microplasmas in Contact with Liquid~

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We have investigated several methods to achieve efficient plasma processing of a liquid using microplasmas. Direct actions from plasma only reach a shallow region just below the liquid surface. Thus, it is better to employ conditions with high surface/volume ratio of a liquid. This condition is realized by making many microplasmas in liquid rather than to make a large plasma in liquid. This concept was realized as 3D integrated micro solution plasma [1], which showed efficiency higher than conventional in-liquid plasma [2]. On the other hand, we have recently investigated another method based on the concept of a micro contactor [3]. It has been successfully used for process intensification in chemical engineering involving gasliquid interfacial processes [4]. While micro contactor is a device that allows stable molecules to interact efficiently with a liquid, we have investigated potential of a micro contactor that enable radical-liquid interactions required for plasma processing of a liquid. For this purpose, we have employed an array of micro-hollow DBDs. The simplest method is to use a micro-hollow DBD as a remote plasma source for liquid processing as in the case of conventional treatments of solid surfaces. However, the distance that radicals can reach is extremely short under atmospheric pressure. Therefore, the DBD electrode and the liquid surface must be brought very close together, but it is not that easy because the liquid sticks to the electrodes owing to capillary action, and also goes into the micro hollows. We solved this problem by putting a hydrophobic micro-hollow plate on the DBD electrode as shown in Fig. 1. The methylene blue decomposition rate using this method was 1.7 g/Wh, which is 85 times higher than the conventional submerged plasma method.

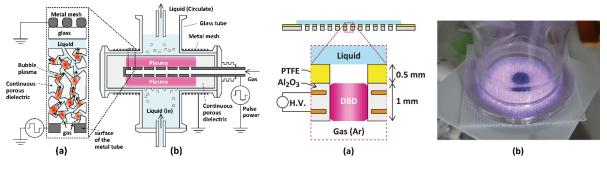
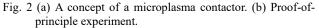


Fig. 1 A concept of many microplasmas in liquid.



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Plasma-assisted flow chemistry: towards new oxidation methods in organic synthesis

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Abstract:

Plasma can trigger reactions on organic substrates and can be used as an alternative activation source on liquids for greener and costeffective chemical processes. Based on the reactivity of radicals, this technique leads to innovative synthesis pathways.

In this work, plasma is used to induce oxidation reactions. Oxidation processes of organic compounds have direct industrial applications, since the oxidized products are used as intermediates to synthesize active pharmaceuticals ingredients, perfumes, plastics, dyes or even petrochemicals.

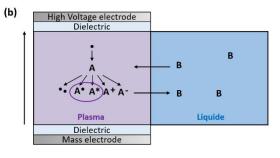
Our work is carried out in a micro-structured continuous flow reactor to easily generate DBD, thanks to small inter-electrode distance. The contact between the generated gas radicals and the liquid molecules takes place at the interface between the two phases. Controlling the plasma radical composition is crucial to favor collisions of interest.¹

This work explores how the selectivities of oxidized products are influenced by plasma parameters, flow parameters, as well as by the compositions of liquid and gas phases. To better understand the reaction mechanisms, we have used in situ and ex situ diagnostics. Optical emission spectroscopy emission has been used to identify the reactive species, and the transfer of radicals from the gas phase to liquid phase has been evidenced using ESR.² Gas chromatography coupled with mass spectrometry of the collected liquid mixture has shown that under short residence time, substrates can be functionalized to ketones, aldehydes, and epoxides.³ Promising results have been made on the oxidation of cyclohexane and olefins.

Keywords: plasma chemistry, DBD, radicals, gas-liquid interaction, microfluidic, flow chemistry, oxidation reaction

Figures:





- (a) Photography of a plasma generated in a microreactor.
- (b) Pattern of the plasma-liquid interactions.

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Experimental Study of the Influence of Cathode Materials on Performance of Micro-Cathode Arc Thruster

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Micro-cathode arc thruster (μ CAT) is a micro-Newton level thruster based on the vacuum arc with magnetic enhancement. This thruster generates plasma by ablating the metal cathode, which has the advantages of simple structure, small volume, and high specific impulse. It has broad application prospects in the field of micro-nano satellite propulsion[1]. According to previous research results, the thrust performance of μ CAT is affected by the cathode metal. In order to improve the performance of μ CAT and explore the influence mechanism of cathode materials on thrust performance, this paper carried out experimental studies on μ CAT with different cathode materials. Figure 1 shows μ CAT used in this study and discharge photos of different cathodes. Figure 2 shows the change of ion velocity and the ratio of total ion current to arc current.

The experimental results indicate that μ CAT with different cathode materials has different elemental impulse and thrust power ratio (TPR). For titanium cathode, the elemental impulse is 2.19 μ N and the TPR is 9.69 μ N/W. However, for aluminum cathode, the elemental impulse is 3.49 μ N and TPR is 16.8 μ N/W. The thrust performance of aluminum cathodes is better than titanium cathode, which maybe due to the lower cohesive energy and first ionization energy of aluminum. The ion velocity is also affected by the cathode material. With increasing external magnetic field, cathodes with smaller atomic masses have larger ion velocity increments. When the arc current is the same, cathode with lower ionization energy will produce more ions. However, as the magnetic field increases, this pattern will change. The analysis of experimental results indicates that selecting metals with lower cohesive energy, ionization energy, and relative atomic mass as cathodes may help improve the thrust performance of μ CAT.

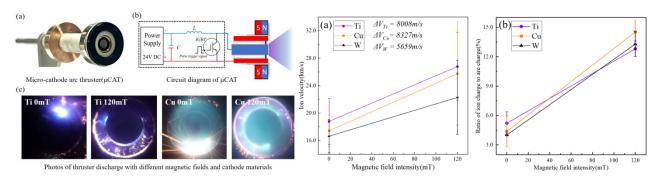


Fig. 1 Structure and discharge photos of µCAT

Fig. 2(a) Ion velocity and (b)total ion charge/arc charge of different cathode materials

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08:50 09:00	Diagnostics			Osamu SAKAI
09:10		Dimitrios STEFAS		
09:20		Joao SANTOS SOUSA		Sylvain ISENI
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10:00	Conee break			
10:10				Thierry BELMONTE
10:20	Modelling - Diagnostics	Inv. Z. BONAVENTURA		
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- Friday June, 7th -

Surface Dielectric Barrier Discharge (sDBD) for Flow Control in Plasma Conversion

<u>Soad Mohsenimehr</u>,^{1*} Achim von Keudell,¹ ¹ Experimental Physics 2, Ruhr-University Bochum, Bochum, Germany ^{*}E-mail : Soad.Mohsenimehr@rub.de

Atmospheric pressure plasmas namely dielectric barrier discharges can be used for carbon dioxide conversion or for, volatile organic compounds removal. Surface dielectric barrier discharge (sDBD) are simple sources and can be made compatible with many industrial applications. One prominent feature of the sDBD is the ionic wind, which is generated by electrohydrodynamic forces leading to the creation of upstream and downstream vortices in the vicinity of the plasma. In this study, these vortices have been investigated by means of Schlieren imaging diagnostic and fluid dynamic simulation to extrapolate the details of the flow pattern and its interaction with surface discharges. It is shown that efficient mixing of the gas flow with the plasma is essential for good plasma conversion by adjusting the residence time of species in contact with the plasma. This has been studied by monitoring the conversion of one percent CO_2 admixed to an N₂ gas stream via infrared spectroscopy in the exhaust. The results indicate the influence of gas flow rate on the conversion of CO_2 which is in good agreement with the size of vortices created by plasma to explain the phenomena [1].

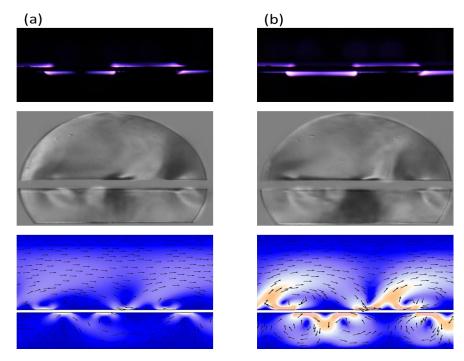


Fig. 1 First row: SDBD images of side view, second row: Schlieren images and third row: simulation images of velocity field. a) 8kVp-p and b) 10kVp-p [1].

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Assisting simple optical diagnostics of an atmospheric pressure plasma via machine learning

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Recently, the integration of machine learning (ML) into the field of plasma physics and relevant technologies has marked notable progress [1]. The coupling of powerful ML algorithms with simple conventional optical methods can shed light on various plasma features, enabling thus the control of plasma-based processes even in real time.

Accordingly, in this work, routine non-intrusive optical diagnostics assisted by unsupervised and supervised ML algorithms were used for the characterization of atmospheric pressure plasmas. Unsupervised principal component analysis (PCA) was applied to optical emission spectroscopy (OES) and charge-coupled device (CCD) imaging data originated from a cylindrical surface dielectric-barrier discharge (sDBD) (Fig.1a) [2]. This allowed to distinguish the discharge operating modes in terms of the waveform (AC or DC pulsed) as well as the amplitude of the driving high voltage (Fig.1b). Furthermore, using the OES data, a predictive model based on multilayer perceptron (MLP) neural networks was constructed with respect to the driving voltage amplitude. Finally, PCA analysis of OES data acquired around the cylindrical surface of the DBD (0°, 90°, 180°, and 270° side views) was useful to assess the discharge pattern and homogeneity. By reducing the dimensionality of the OES data via PCA and feeding it to the MLP, it was discovered that the neural network model could accurately predict the applied voltage with very low error, achieving R² values of up to 99% for the regression of the data.

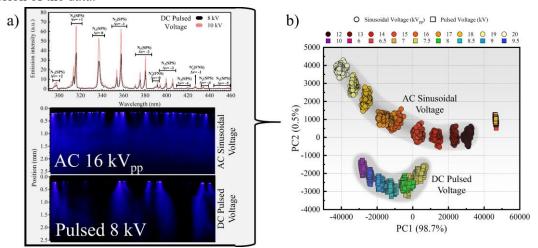


Fig. 1 a) Emission spectra and CCD images of the sDBD discharge. b) Use of PCA to detect hidden patterns in OES data

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Ar(1s₅) density in a co-axial atmospheric-pressure argon microplasma jet with N₂-O₂ shielding

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Low-temperature atmospheric-pressure microplasma jets (μ APPJs) extend plasma beyond physical barriers, providing a controlled method of plasma delivery [1]. μ APPJs applications benefit from their portability and flexibility of gas mixtures, influencing the associated chemistry. The access to non-equilibrium plasma chemistry at ambient pressure (1 atm) and close to ambient temperature renders these plasma sources attractive for a range of applications, including biomedical [2], chemical analysis [3,4], material processing [5], and other industries [6]. μ APPJs are indeed versatile sources of reactive species, namely reactive oxygen and nitrogen species (RONS), with diverse applications. However, understanding the plasma chemistry in these jets is challenging due to plasma-flow interactions in heterogeneous gas mixtures.

This work focuses on controlling the shielding gas around a μ APPJ. We use a dielectric barrier discharge (DBD) co-axial reactor where a co-flow shields the pure argon jet with different N₂-O₂ gas mixtures. A high-voltage, high-frequency microsecond squared pulse (4 kV, 1 μ s duration, 20 kHz) generates a first discharge at the pulse's rising edge and a second discharge at the falling edge. Tunable diode laser absorption spectroscopy measures the local argon metastable Ar(1s₅) density.

A pure N₂ (100% N₂ – 0% O₂) co-flow leads to less reproducible and lower peak Ar(1s₅) density (5.8×10^{13} cm⁻³). Increasing the O₂ admixture in the co-flow yields narrower Ar(1s₅) absorbance profiles and increases the Ar(1s₅) density ($6.9 \times 10^{13} - 9.1 \times 10^{13}$ cm⁻³). Furthermore, the position of the peak Ar(1s₅) density is closer to the reactor for higher O₂ fractions. Absence of N₂ in the co-flow gas mixture results in comparable Ar(1s₅) densities between the first and second discharges (maxima of 9.1×10^{13} and 9.3×10^{13} cm⁻³, respectively).

Local Ar(1s₅) density profiles from pure N_2 to pure O_2 shielding provide insights into physical and chemical processes. The spatially and temporally resolved data may contribute to optimizing argon μ APPJ reactors across the various applications and to validate numerical models.

The Portuguese FCT (Fundação para a Ciência e a Tecnologia) partially supported this work under projects UIDB/50010/2020, UIDP/50010/2020, LA/P/0061/2020, and grants PB/BD/142972/2018 and BL194/2022.

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Electron Avalanching in Nanovoids at the Initial Stage of Nanosecond Discharge in Liquid Water

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The processes of electron generation and multiplication govern the initialization and development of electrical discharges, including highly transient nanosecond discharges in liquid water produced by strongly nonuniform high electric fields applied on nanosecond time scales. The nanosecond time scale of the applied electric field does not allow bubbles to be sufficiently developed so the discharge that is observed needs to be initiated directly in the liquid environment, instead. It has been suggested [1] that nanoscopic discontinuities can be created in the liquid due to the high electric field, and these provide the needed free space for electron acceleration.

Recently, we have proposed a mechanism that allows enhanced electron multiplication in long voids, leading to the formation of the electron avalanches confined inside the voids [2], see Fig 1. The concept of electron multiplication in long cylindrical voids will be presented and discussed based on a large parametric study performed using the state-of-the-art simulation toolkit Geant4-DNA for modeling electron-liquid water interactions [2-4], supported by an overview of results from an extensive experimental campaigns [5-7].

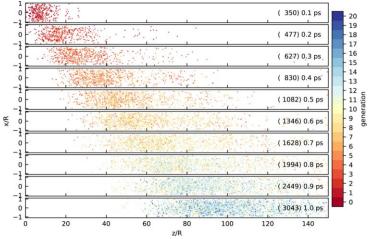


Fig. 1 Snapshots of electron positions inside electron avalanche in times $t \in [0.1, 1]$ ps for $E \cdot R = 22$ V, E is the electric field and R = 30 nm is the cavity radius. Electron population is given in parenthesis and color

bar codes electron generation. Primary electrons being generation 0.

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Ultrafast oscillation in a field emission-driven microdischarge

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Field electron emission is of fundamental importance in microscale gas breakdown when the electric field becomes sufficiently high [1-3]. In atmospheric pressure microdischarges, field emission electrons emitted from the cathode materials and positive ions due to gas ionization can lead to large amounts of space charges during the breakdown, which could largely modulate the electric field strength around the cathode and may further cause instability [4,5]. In this work, we determine the behavior of charged particles at the initial stage of microscale discharge (tens of picoseconds) using the one-dimensional particle-in-cell/Monte Carlo Collision (PIC/MCC) method. The distributions of electrons and ions in the phase space are captured, and the fundamental discharge parameters, such as electron density, ion density, and electric field distributions, are examined based on the simulation cases. The results all confirm the existence of field emission induced instability. In addition, we demonstrated the relationship between emission instability, space charge effect, and plasma frequency, which can further explain the specific physical mechanism of field emission instability. The findings provide a more precise understanding of the formation of the field emission-driven microdischarge, which informs the design and optimization of miniaturized gaseous electronic devices.

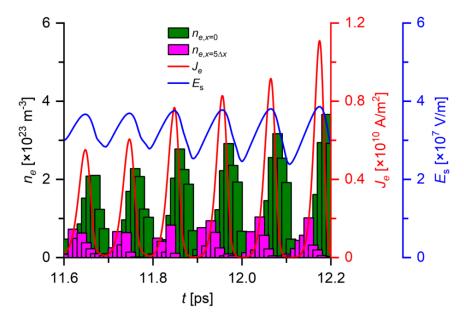


Fig. 1 Oscillating characteristics of the electron density at cathode x = 0 (green bars) and $x = 5\Delta x$ from the cathode (pink bars), emission current density (red line), and the cathode surface electric field (blue line)

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Optical emission spectroscopy analysis of Hydrogen H_β spectral line in confined plasma

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Spatially resolved Optical Emission Spectroscopy (OES) is a versatile and convenient method for investigating plasma generated in reactors with diverse geometries, such as Micro Hollow Cathode Discharge reactors produced at GREMI [1], [2]. Stark broadening, resulting from interactions between radiator atoms and the electric field produced by charged plasma particles, is a key parameter dependent on plasma particle density [3]. The Hydrogen Balmer- β line is a well-known tool in plasma diagnostics when aiming at measuring the electron density number. This is so, partly, because of the immunity of its FWHM to ion dynamics effects or to temperature changes. For a microplasma generated in a microreactor with a Through Silicon Via (TSV), ignited in He at 600 mbar with less than 1% of hydrogen, the electron density of the plasma and the gas temperature are estimated to be around 10²⁰ m⁻³ and 650K respectively for a current ranging from 0.5mA to 1.5mA. Through OES and with specific tools, we map the emission intensity of specific spectral lines across the microplasma diameter, revealing intriguing behavior. Our study shows that depending on the characteristics of the reactor, different profiles can be observed (figure 1). Whether it is a dip in the center of the line revealing the presence of a strong electric field [4] as shown in figure 1a or a significant broadening at the base of the spectral line indicating the presence of the sheath (figure 1b).

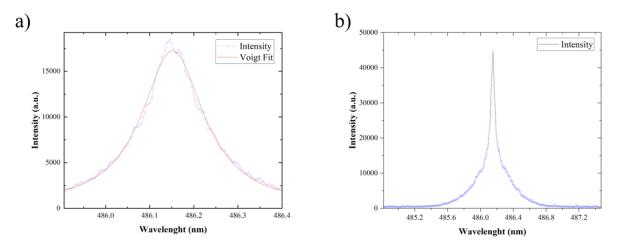


Fig. 1 Measured Balmer series H_{β} emission lines in He at 600mbar in TSV reactors: a) at 0.8mA b) at 1.2mA

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Spatial 2D distribution of N-atoms absolute density in three DC MHCD setups

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Microplasmas are promising tools for N₂ dissociation which is attractive for material deposition applications [1]. In the present study, we used ns-TALIF to measure the spatial distribution of the absolute density of N-atoms in a DC micro-hollow cathode discharge (MHCD) (Fig. 1). The MHCD used is a "sandwich" structure (molybdenum—alumina—molybdenum) with a hole of Ø400 µm at its center. The operating gas is a mixture of 20%Ar and 80%N₂. The MHCD is operated in the so-called normal regime with a discharge current of 1.6 mA. An aluminum plate, acting as a third electrode (second anode), is placed further away from the MHCD to emulate a substrate where N-atoms deposition takes place. This allows us to study the spatial profile of N-atoms in three configurations: (i) MHCD, with uniform pressure (50 mbar) on both sides of the "sandwich". Here, N-atoms simply diffuse in three dimensions from the MHCD. Their largest density is found at the hole axis, close to the MHCD, as expected. (ii) MHCD jet, with a pressure differential between the two sides of the "sandwich". Here, an unexpected density distribution is measured with largest values away from the jet axis (Fig. 1; right). A correlation between the jet width and the radial distribution of the N-atoms at different axial distances from the gap is speculated by comparing ns-TALIF with compressible gas flow simulations. (iii) Micro Cathode Sustained Discharge (MCSD), with a DC positive voltage applied to the third electrode. Two stable working regimes are identified depending on the pressure differential and current repartition between the two anodes. MCSD enables a homogenization of the density profile along the surface of the substrate, which might be suitable for nitride deposition applications.

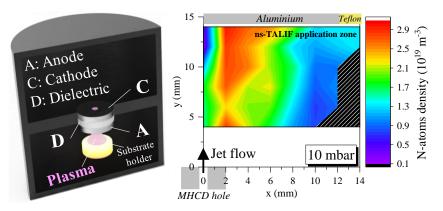


Fig. 1 (left) Indicative illustration of MHCD jet and MCSD; (right) N-atoms density mapping (MHCD jet).

Acknowledgements : Projects DESYNIB (ANR-16-CE08-0004) and SPECTRON (ANR-23-CE51-0004-01).

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4 Abstracts – Posters

The abstracts (full-text) are collected in the following section. They are sorted according to the schedule shown in page 11.

Absolute atomic nitrogen densities in a micro-hollow cathode discharge operating in Ar/N₂ mixtures: DC versus pulsed modes

<u>Abd-Almalik Halfaoui*</u>¹, Laurent Invernizzi², Gérard Bauville¹, Pascal Jeanney¹, Swaminathan Prassana², Stéphane Pasquiers¹, Kristaq Gazeli² and João Santos Sousa¹

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Graphene has shown promising applications in nano and opto-electronics thanks to its unique properties. To preserve these outstanding properties from the influence of the substrate and secure the potential applications, graphene can be encapsulated in hexagonal Boron Nitride (h-BN) buffer layers [1]. Our work aims to develop a new deposition process for h-BN films using a new micro-plasma configuration based on the classical Micro-Hollow Cathode Discharge (MHCD) technique, which has shown promising perspectives [2-4].

Atomic nitrogen (N-atoms) is a key species for the deposition and growth of h-BN films. To optimize the production of N-atoms, a detailed experimental characterization of its absolute densities using different micro-plasma devices has been performed. To this end, several operating conditions were studied: different electrical schemes (DC high-voltage (HV) versus HV (few kVs) high-frequency (HF; few 10's of kHz) nanosecond (few 100's of ns) pulses), Ar-N₂ mixtures (from 0% to 100% of N₂), and gas pressures (from few mbar to several 10's of mbar). The absolute N-atoms densities measurements have been performed using spatially resolved Two-photon Absorption Laser-Induced Fluorescence (TALIF) spectroscopy, both at the cathodic and the anodic sides of the MHCD devices.

In DC mode, the atomic nitrogen has been exclusively found on the cathodic side, with maximum densities of up to 10¹³ cm⁻³. The combination of both electrical and N-atoms density measurements allowed to shed light on the dependence of the N-atoms absolute densities on the working regime of the MHCD, showing distinctive spatial distributions and influence of the deposited energy in the abnormal and the normal regimes. In HV HF ns-pulsed mode, N-atoms have been detected both at the cathode and the anode sides of the MHCD, with maximum densities of up to 10¹⁴ cm⁻³ located on the anodic side, where there is no plasma expansion. Hence, the use of pulsed powered MHCD results in much higher N-atoms densities, showing promising perspectives as an efficient source of N-atoms for h-BN films deposition.

This work has been supported by the French ANR project PlasBoNG (ANR-20-CE09-0003-01).

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IWM-12, Orléans, France – Additive Manufacturing Electronics (AME) for microplasma source production

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The aim of this work focusses on the fabrication of microplasma sources using 3D printers for electronic devices. With size reduction of plasma sources, traditional manufacturing processes could be affected by the limitations in terms of accuracy on micrometer scale. Thanks to the efficient use of materials and the flexibility of the process, additive manufacturing can be considered as an alternative process for the production of micrometer-sized plasma sources.

Based on the work of Wang *et al* [1], we adapted the design of the source to make it similar to a surface-DBD with a grid mesh size of $500x500\mu m$ (Fig.1). The investigation undertaken in this presentation involves the optimization of printing parameters that can influence the proprieties of the plasma source, such as the size of the electrodes and the annealing time of the conductive ink. The electrical characterization of the plasma source is performed using electrical probes connected to an oscilloscope. The homogeneity of the discharge is evaluated by means of high-resolution images, while the dynamics is monitored through the use of an intensified CCD camera.

The purpose of this research is to explore additive manufacturing as a process for the fabrication of microplasma sources, identifying strengths and weaknesses to understand its potential as an alternative way of designing devices.

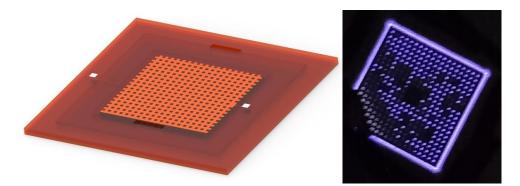


Fig. 1 On the left, a schematic view of the printed source. On the right, a first prototype with plasma on [1] Y. Wang et al. 2016, *J. Phys. D: Appl. Phys.* 49 415206

Analysis of dielectric barrier discharge plasma actuators for flow control

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A surface dielectric barrier discharge, one of the atmospheric pressure plasma devices, is utilized as a flow control device (actuator) using electro-hydrodynamics (EHD) [1,2]. Controlling turbulence on the surface of airplanes and vehicles has been studied so far [3]. The interaction of the surface DBD was observed by applying the AC sinusoidal voltage, and the effect of the spatial profiles of the plasma discharge was checked with the variation of the electrode width, dielectric thickness, electrode position, and flatness. Moreover, particle velocity and distribution were also investigated using particle image velocimetry (PIV), a method to understand the flow behavior of various fluid components [4,5].

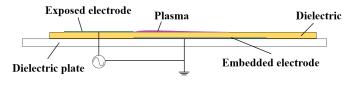
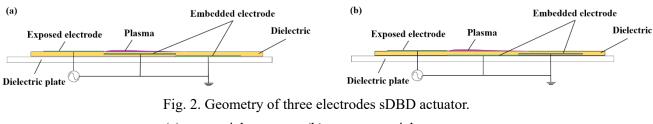


Fig. 1. Geometry of standard sDBD actuator



(a) sequential structure, (b) non-sequential structure

High voltage is applied to the exposed electrode, and the embedded electrode is connected to the ground. Plasma discharge occurs when a voltage higher than breakdown voltage is applied. A dielectric plate is placed at the bottom, through which discharge occurs only at the exposed electrode. Momentum transfer can be investigated using PIV to determine flow motion. The fluid movement of the induced flow generated through plasma discharge can be grasped. Through this research, we will confirm the difference between two-electrode case and the three-electrode case and what phenomenon occurs by each parameter and explain the change in fluid motion through the PIV system.

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Analytic model of a Micro Hollow Cathode Discharge. Comparison to PIC simulations.

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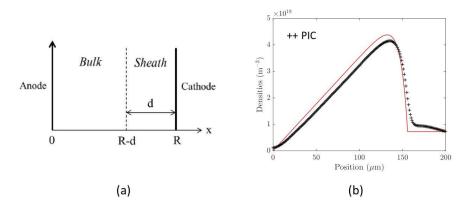
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An analytical model of the cathodic region of a Micro Hollow Cathode Discharge (MHCD) is presented. MHCDs are a particular type of microplasmas in which an electrode/dielectric/electrode structure is drilled with a hole of several hundreds micrometers in diameter.

The key feature of the model is to correctly calculate the ionization profile resulting from energetic electrons generated in the sheath and entering the plasma region with significant energy. To simplify the problem, a pure argon discharge in a 1D planar geometry is first considered. The model is decomposed into two separated regions: (i) the quasi-neutral region in the center (the so-called plasma bulk region) and (ii) the cathode sheath region near the surface. The two models are coupled at the plasma-sheath interface, where the electric field and the discharge current must be continuous. To validate the model and guide the theoretical analysis, we use Particle-In-Cell (PIC) simulations [1] for a base case (pure Ar at 100 Torr). The spatial variation of the ion density given by the analytical model and the PIC simulation is presented in fig.1b and we observe a good agreement between the two models. This indicates that the matrix sheath approximation, on which the analytic model relies, is quite appropriate for the discharge

Once the physics of this simplified geometry is understood and validated, a second symmetrical sheath is added to mimic the MHCD configuration. This complete model is then compared to experimental findings on the electron density and sheath thickness variations. The discharge expansion on the cathode backside and the role of the secondary electron emission coefficient are also discussed.



- Fig. 1 : (a) Schematic of the modeled regions for the reduced 1D model and (b) Spatial variation of the ion density given by the analytical model (solid red line) and by the PIC simulation (symbols).
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Atmospheric-pressure air DBD treatment for plasma surface modification of glass and stainless Steel

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Glass and stainless steel are materials found in numerous applications, ranging from everyday objects to advanced industrial sectors like optics, automotive and aerospace technologies. The surface properties of these materials are crucial for their performance and can be significantly altered through surface chemistry adjustments, commonly achieved via functionalization techniques. Among these latter, low-temperature plasma treatments^{1,2} stand out as a highly promising approach for enhancing and modulating surface characteristics.

In this research endeavor, our focus delves into examining the impact of a dielectric barrier discharge (DBD) plasma treatment on borosilicate glass and stainless steel surfaces under atmospheric pressure in ambient air. Our investigation entails a parametric study of the DBD plasma conditions, specifically the influence of plasma treatment duration and power, respectively. The findings unveil notable enhancements in the hydrophilicity of both glass and stainless steel surfaces by water contact angle measurements, following DBD treatment, according to the treatment time (fig.1) and the power of the DBD system. Moreover, chemical changes, occurring at the surface interface of the treated stainless steel, e.g variation of metal oxides and borosilicate glass, induced by the DBD treatment is observed by XPS. Thus, the enhancement of the hydrophilicity, along with the chemical modifications at the surface of glass and stainless steel emphasizes the cleaning effect and the oxidizing effect of the atmospheric pressure air DBD treatment.

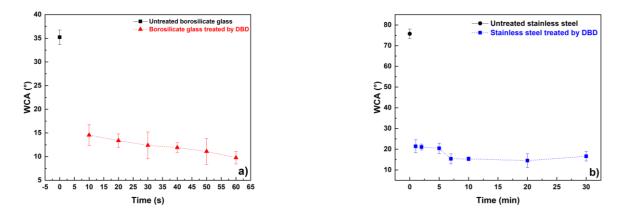


Fig. 1 variations of water contact angle (WCA) with respect to the DBD plasma treatment time of, a. glass, b. stainless steel.

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Characteristics Study of Electrical and Optical Diagnostics by Different Structures using Two Atmospheric Pressure Plasma Jets

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In recent years, atmospheric pressure plasma (APP) has been actively studied in various fields such as medicine and plasma chemistry because it can produce reactive chemical species without the need for vacuum chambers and pumps [1]. Among the many applications of APP, Atmospheric Pressure Plasma Jet (APPJ) is a popular tool used to generate plasma plumes in Ar or He gas flowed tubes. In particular, APPJ is widely used due to its lower breakdown voltage compared to air discharge [2]. In this study, two APPJ structures were placed in an anti-parallel direction and in a perpendicular direction, and the APPJs were observed Schlieren image using a high-speed camera and plasma bullet using an iCCD camera. In addition, the chemical species generated by the APPJ according to the change of voltage and flow rate were observed by optical emission spectroscopy (OES), and the difference of the observed intensity according to the power was shown. The electrical characteristics were presented by calculating the capacitance and power consumption through the Lissajous curve. Finally, We conducted add a metallic mesh and compared it to the electrical and optical properties of the original APPJ research.

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CO₂ dissociation at atmospheric pressure by micro-cathode sustained discharges

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Global warming is related to the continuous increase, since the industrial revolution, of greenhouse gases concentration in the atmosphere, especially CO₂. One potential approach to reduce CO₂ emission into the atmosphere is to capture it from waste gas streams and convert it into valuable chemicals and fuel. The dissociation of CO₂ into CO can be done via different methods, including thermolysis, thermochemical cycles, electrolysis and plasma technology [1,2]. Plasma technology has the advantage of delivering a large part of its energy to the electrons instead of heating, which allows CO₂ splitting with a reasonable energy cost [3,4]. Ideally, the plasma should have a high electron density with a low electron and gas temperatures to dissociate efficiently CO₂ [3].

Micro-cathode sustained discharges (MCSD) generate a confined plasma inside a micro-hollow cathode discharge (MHCD), which is extended to a much larger volume outside the hole with the help of a third electrode positively biased, placed some distance away (typically about 1 cm). This extended plasma is characterized by a low reduced electric field (up to few 10's Td) and a low gas temperature (up to few 1000's K), while the electron density in the hole is rather high (up to 10^{16} cm⁻³) – these values depend greatly on the gas mixture and pressure. Even if MCSD appear to be a very suitable plasma source for CO₂ splitting, there has only been one single study using MCSD to dissociate CO₂, but at low pressure [5]. Furthermore, only a few studies have been devoted to the use of MHCD to dissociate CO₂, either in pure CO₂ or diluted in Ar, up to atmospheric pressure [6-8].

In our work, we studied the CO₂ dissociation by MCSD operated in He/CO₂ mixtures at atmospheric pressure. A parametric study has been performed, varying the total gas flow, the % of CO₂ admixture, and the discharge current. We have also studied the effect of using several MCSD in series, and the individual contribution of the MHCD. To gain some insights into the chemistry taking place, the concentration in the effluent of singlet delta molecular oxygen ($O_2(a^1\Delta_g)$) and ozone (O_3) have also been monitored. We have found that the CO₂ conversion degree decreases with the CO₂ admixture and the total gas flow, while it increases linearly with the specific energy input. A maximum of CO₂ conversion of 5 % has been obtained. Furthermore, the CO₂ dissociation increases linearly with the number of MCSD used, while the contribution of the MHCD represents, no matter the operating conditions, about half of the total conversion. Interestingly, the main dissociation pathway seems to be different between the two discharges (MHCD vs MCSD).

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Controlled synthesis of NO in an atmospheric pressure plasma by suppressing NO destruction channels by plasma catalysis

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Plasma discharges containing nitrogen and oxygen have been studied by many groups due to their broad range of applications in different fields. The formation of NO is especially interesting since it can be used for the determination of the gas temperature, the analysis of plasma surface interaction, or for biological processes such as tissue/wound treatment [1]. In our experiment, NO synthesis using plasma catalysis is analyzed in a parallel-plate atmospheric pressure RF plasma from N₂/O₂ admixed to helium and using a Fe or Pt catalysts on a SiO₂ support. The NO_x species are measured by Fourier transform infrared spectroscopy (FTIR) in a multi-pass cell. The trends in species densities can be well explained by air chemistry reactions, where NO's sequential oxidation occurs with increasing oxygen admixture and ozone generation. The sequence can be controlled by the state of the surface that preferentially quenches O₃ and allows for optimum NO production. During the discharge, helium metastable species play an important role in plasma ionization and sustainment [2]. The densities of both atomic He(2³S) and molecular He₂(a³ Σ_u^+) metastable species in helium discharge are measured by broadband absorption spectroscopy.

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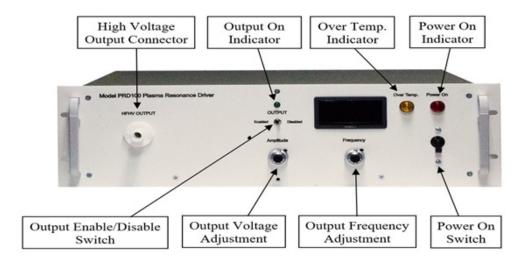
Development of a Low-Cost, Wide-Range Power Supply for Plasma Research

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A plasma generation source was designed and developed in collaboration between PlasmaTechSolutions, LLC and Amp-Line, LLC industrial electrical engineering. The plasma power supply represents the latest iterative generation device developed to aid in research conducted in the Laboratory of Electrophysics and Atmospheric Plasmas (LEAP) research facility at Seton Hall University. The goal of this collaboration was to develop an affordable power unit that could meet the wide-ranging R&D needs of academic laboratory environment working on high-pressure low temperature microplasmas.

This prototype power supply, model Plasma Resonance Driver 100 (PRD100), is a load dependent plasma driver. It was designed to provide an adjustable 0-10K V rms. (28K V peak to peak) high frequency high voltage signal for researchers to perform their plasma experiments. It covers a wide frequency range, from 7kHz to 35kHz, which fits most of the low-temperature, atmospheric pressure plasma research requirements. Designed to fit the needs of the low-temperature plasma community, the PRD100 power supply can also serve as a diagnostic instrument as it can help the researcher understand the electrical characteristics associated with their prototype reactor and assist in streamlining the iterative development process.



Effect of operating parameters on the propagation dynamics of fast ionization waves in a He microtube plasma jet

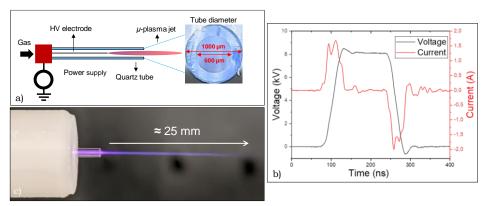
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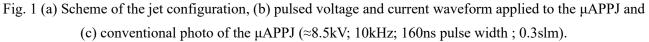
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Atmospheric pressure plasma jets (APPJ) are studied for many applications in medicine, biology, and agriculture, they also exhibit a unique potential for implementation in analytical chemistry (AC) and mass spectrometry (MS) [1,2]. Better understanding of the physics of μ APPJ is necessary for a more efficient implementation in AC/MS. Due to their small dimensions, operation at atmospheric pressure and generation with transient voltages, they exhibit steep gradients of electron density, electric field, gas temperature, discharge emission, and reactive species density, which complicates their comprehensive understanding.

This work focuses on the effects of discharge parameters (voltage amplitude (V), frequency (f), pulse width (t_{pulse}), and gas flow rate) on the spatial and temporal dynamics of a µAPPJ. Figure 1 shows the µAPPJ, which consists of a hollow micro-needle electrode (stainless-steel) inserted in a micrometric capillary tube (quartz). Helium flows through the needle acting as HV electrode, then through the tube and ejected into the surrounding air. The gas flow rate varies from 0.1 to 1 slm and the discharge is sustained by a positive pulsed voltage (fig 1.b) with the following features: V=3–10 kV, f=1–10 kHz, and t_{pulse} =0.16–10 µs. The spatial and temporal evolution of the UV–VIS plasma emission inside and outside the tube is captured using an ICCD camera (synchronized with the high voltage pulse) which is coupled to relevant electrical diagnostics. The possibility of extending the discharge propagation in different capillary tubes is investigated.





Acknowledgements

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Electric-field-induced coherent anti-Stokes Raman scattering in visible region under near-atmospheric-pressure hydrogen microplasma environment

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Electric field is one of the most important parameters for understanding and controlling microplasma. Electric-field-induced coherent anti-Stokes Raman scattering (E-CARS) in the visible region (E-CARSv) is a third-order nonlinear optical effect that generates visible light when infrared light with Raman energy and pump light are irradiated. The intensity of E-CARSv light is proportional to the square of the electric field strength, making it suitable for electric field measurements. In this presentation, we first introduce E-CARSv, which has been successfully demonstrated for electric field measurements under near-atmospheric-pressure hydrogen and nitrogen environments [1,2]. Then, we will present recent achievements in E-CARSv measurements with microplasma generation in hydrogen [3].

A non-equilibrium microplasma was generated with nanosecond-pulsed power supply with approximately 10 ns main pulse width under a 0.3 atm hydrogen atmosphere. The peak voltage was approximately 1.7 kV and the discharge gap was 1.0 mm. Collinearly aligned two nanosecond pulsed lasers, at around 2.4 μ m (1-1.5 mJ) and at 532 nm (1.4 mJ), were focused into the center region of the microplasma. The intensity of E-CARSv light was measured using a photomultiplier tube after a monochromater. The wavelength of the infrared laser was scanned in the range of 2.4–2.43 μ m to obtain the vibrational-rotational spectrum during microplasma generation. Successful acquisition of E-CARSv signals in nanosecond time resolution was achieved and rapid decrease of electric field, which should be caused by space charge accumulation, has been observed, similar to the measurements with E-CARS in the infrared region [4]. Vibrational-rotational spectrum was obtained by wavelength scanning, and the rotational temperature of hydrogen molecules could be estimated to be approximately 385 ± 15 K during the microplasma generation. By assuming the kinetic temperature is equal to the rotational temperature, the electric field strength could be estimated with the calibration measurement under known electric field strength. For example, the maximum electric field strength during the microplasma generation was estimated to be approximately 1.3 kV/mm.

Further details, including experimental details, will be presented at the workshop.

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Experimental study of the gas breakdown in a controlled nanometer scale electrode gap

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Paschen's law is a convenient analytical empirical law allowing for predicting the breakdown voltage (V_b) of a gas to be estimated relatively precisely. It is based on several assumptions, such as a uniform electric field between two electrodes of infinite size. Practically, values of V_b are directly related to the product of the pressure with the electrodes distance $(p \cdot d)$. Although this analytical approach has proven its usefulness for a large range of experimental conditions, the prediction of V_b is compromised for small inter-electrode distances, less than 1 µm. In other words, the pressure will no longer be able to compensate lower distances to keep the product $p \cdot d$ constant for a given value of V_b . Numerous experimental, theoretical and simulation studies highlight deviations from the Paschen's law for very small gap [1]. Consequently, this raises some concerns about the electrical insulation capabilities of gases for very short distances typically in the order of a micrometer and lower [2].

The experimental study follows previous work on the deviation of the Pashen's law [3] and focuses on the statistical measurement of V_b in different gases (Argon, air, etc.) for inter-electrode gap ranging from 0.1 µm to 6 µm. The experimental setup consists of a silicon wafer coated with a thin film of gold (~500 nm). It is wired to the ground potential and acts as a cathode; A sharp needle with a tip radius curvature of 20 µm is used as an anode and is fully coated with gold. A piezoelectric actuator controls the inter-electrode gap. The experiments are carried out in a closed chamber to control the pressure, the humidity and gas purity.

After showing clear deviations of V_b from the Pachen's law prediction for several gases, a statistical approach will be presented in order to identify the different regime of the breakdown with regard to the interelectrode distance. The breakdown regime will also be study at different pressures to clarify the impact of this parameter with regard to the other experimental conditions.

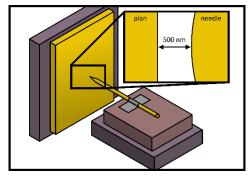


Fig. 1 Diagram of the experimental installation.

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Intensification of Surface-Launched Plasma Bullets by Employing High-dV/dt SiC MOSFET Pulse Power

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We have investigated surface-launched plasma bullets (SLPBs) [1]. The SLPBs are launched from planar surface of a dielectric plate while conventional plasma bullets are launched from a nozzle of a glass tube with DBD electrodes. The SLPBs can be applied to hydrophilic treatment of the inner surfaces of a continuous porous dielectric such as a bone-regeneration scaffold, while conventional plasma bullets cannot [2].

In our previous study, we revealed that the intensity of SLPBs increases by increasing dV/dt [3]. At that moment, however, what we could explore was to decrease the dV/dt from the maximum value $36 \text{ kV/}\mu\text{s}$ of Si MOSFET by using RC delay. It is important to investigate how higher dV/dt (than $36 \text{ kV/}\mu\text{s}$) affects the behavior of SLPBs from both academic and industrial viewpoints.

For this purpose, we employed a pulse

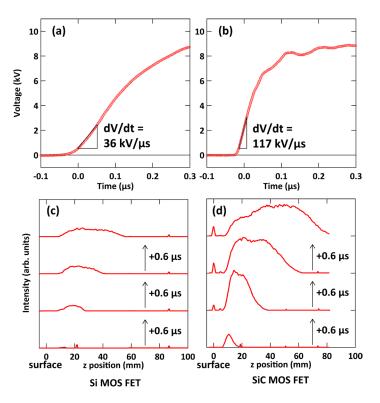


Fig. 1 Voltage-rise waveforms and intensity of a plasma bullet driven by (a) Si MOSFET and (b) SiC MOSFET.

power supply driven by MOSFETs made of cutting-edge semiconductor 4H-SiC. Since the saturation electron drift velocity $(2.7 \times 10^7 \text{ cm/s})$ of 4H-SiC is higher than that $(1 \times 10^7 \text{ cm/s})$ of Si, higher dV/dt is realized by using SiC MOSFET. The SiC MOSFET used in our study have shown dV/dt of 117 kV/µs as shown in Fig. 1(b). We confirmed that it is possible to launch SLPBs using either Si or SiC MOSFETs and observed the launched SLPBs with an ICCD imaging system. Figures 1(c) and 1(d) show optical emission profiles of the SLPBs launched by using Si and SiC MOSFETs, respectively. As can be clearly understood from these figures, the intensity of the SLPB driven by the SiC MOSFET is higher than that by the Si MOSFET.

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Investigation of plasma surface modifications of wood samples by atmospheric-pressure air DBD and plasma torch treatments

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In this study, we have investigated the effects of plasma treatments on oak wood samples in air at atmospheric pressure. Two processing techniques have been used and compared: a Dielectric Barrier Discharge (DBD) with pulsed voltage regime and a plasma torch (plasma Openair® of PlasmaTreat Company).

The DBD experimental set-up consisted of two electrodes (plane-to-plane geometry), with 2 glass plates (1 mm thick) as dielectrics placed on each electrode. The inter-electrode gap varies from 6 to 7 mm. Wood surfaces were characterized before and after plasma treatments by Water Contact Angle (WCA) measurements, Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) spectroscopy. Different experimental conditions were studied (plasma treatment time, DBD installation frequency) and the aging time after plasma treatment was evaluated. Results show a rapid decrease of WCA after both DBD and plasma torch treatments, thus indicating an improvement of surface wettability (Figure 1). SEM imaging is currently being investigated to show morphological changes on the wood surfaces and end grain images should allow us to see the effect of plasma on wood cells. The spectra obtained by Fourier Transform Infrared (FTIR) spectroscopy showed modifications in the chemical structure of wood samples treated by DBD for 15 minutes, compared with the untreated sample (Figure 2). The increase in the absorption band ranging from 1500 to 1800 cm-1 mainly results from the increase in the C–H and C=O peaks, at 1660 and 1734 cm-1 [1], respectively. Absorbance band characteristic of the O-H groups from 3100 to 3500 cm-1 slightly increases after plasma treatment. At this time, no modifications have been observed for wood samples treated with the torch plasma. Finally, wood surfaces will be coated, and mechanical pull-off tests of our treated surfaces will be carried out.

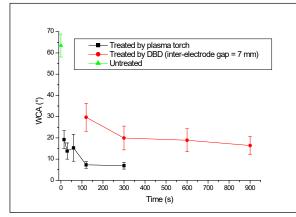
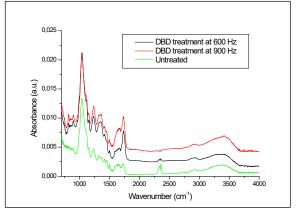
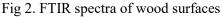


Fig 1. WCA depending on time

Orléans, FRANCE





jIWM-12, Orléans, France – Laser ablation for microplasma source production

Filippo Capelli,1* Mariachiara Grande,2 Michele Vasile,2 Giulia Laghi,2 Romolo Laurita,2 and Matteo

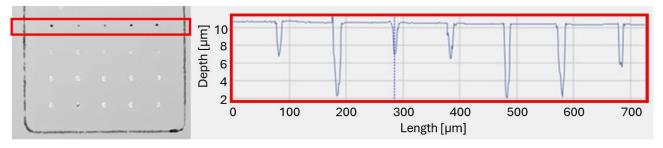
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This work focuses on the challenges of producing microplasma sources through laser ablation and how this machining technique can offer an effective solution to this problem. The adoption of laser ablation for the creation of surface micro-cavities is grounded in the research of Sallé *et alii* [1], who demonstrated the effectiveness of this technique to manipulate the surface morphology of advanced materials. Furthermore, the work of Tachibana *et alii* [2] helped define the dynamics of microplasma generation through detailed micro-cavity analysis, providing valuable information on optimal process parameters.

In this presentation, laser ablation for microplasma source production will be discussed, highlighting the typical intricacies and difficulties encountered. The experiments were conducted using a Carbide femtosecond laser; using such fast pulses simultaneously minimises the thermal effects of the machining process and provides high spatial resolution; these two effects combined allow us to speak of ablation of the material. The results obtained, based on experiments conducted on different substrates such as glass, plastic and ceramics, will be presented by means of high-resolution images of the generated micro-cavities. Through interferometer analysis, it was possible to correlate the effectiveness of the ablation process with the main operating parameters of the laser (repetition rate, number of pulses, power, focus).

Through this research, we intend not only to illustrate the effectiveness of laser ablation in the production of microplasma sources, but also to make a tangible contribution to understanding the challenges associated with this process, opening up new horizons for further developments and practical applications.



Interferometric imaging of trenches made on glass at different laser powers.

Acknowledgement: the activities pertain to the PULSE project ('Plasma reconfigurable metasurface technologies', G.A. N. 101099313) funded by the European Union under the call HORIZON-EIC-2022-PATHFINDEROPEN-01.

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- [2] K. Tachibana, IEEJ Trans., vol. 1, no. 2, pp. 145–155, 2006.

MHCD in N2-H2 mixtures: towards a localized plasma nitriding process?

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In this contribution, we report the preliminary results on the use of MHCD discharges for nitriding treatments on metallic substrates. The MHCD design employed in this study consists in a matrix made of 39 axisymmetric isotropic cavity etched on a 500 μ m thick Si wafer (100 μ m circular aperture diameter and 30 μ m depth). A thin layer SiO₂ generated by heat oxidation on the wafer surface electrically isolates the Si cavity. To serve as an electrode, the SiO₂ is partially coated with a thin Ni coating (~500nm). The second electrode is made up of a Ni metal layer produced by a PVD method at the rear of the wafer. The MHCD device is placed in a reactor chamber pumped to ~1·10⁻³ mbar and then filled with a high purity N₂-H₂ mixture (90-10%) up to 100 mbar. It is powered by a stabilized DC voltage power supply through a ballast resistor of 36 k Ω . A substrate in austenitic stainless steel (AISI 316L), previously polished like a mirror and cleaned, is facing the MHCD device (5 mm gap) and heated at 400 °C. The nitriding treatment was performed during 30 minutes by applying respectively 335 V and 1.4 mA to the MHCD system

The recorded emissions of N_2^+ ($B^2\Sigma_u^+$ - $X^2\Sigma_g^+$) and N_2 ($C^3\Pi_uB^3\Pi_g$) lead to the determination of a rotational temperature of 385(22)K and a vibrational temperature of 4064(35)K during the treatment. The results seem to indicate (i) a moderate temperature elevation of the MHCD device during the treatment and (ii) a probably high dissociation degree of N_2 [1] (favorable to nitriding processes). After treatment, a clear modification of the surface aspect of the sampled (figure 1) is observed. TEM investigations shown the formation/grow up of nitrided nanoparticles, with a nitrogen concentration up to 35 at%. These preliminary results evidenced the capability of MHCD device to produce thermochemical treatments. Further studies are necessary to improve the concept and achieve a real nitriding layer.

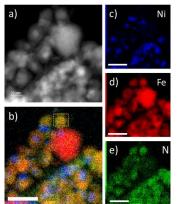




Fig. 1 (a) High angle annular dark field STEM image of nanoparticles collected after treatment. (b) EDS mapping of the area in (a). (c), (d) and (e) EDS mapping of Ni, Fe and N (scale: 50 nm). (f) Observation of sample's surface after treatment.

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Non-invasive plasma measurement in an atmospheric pressure plasma

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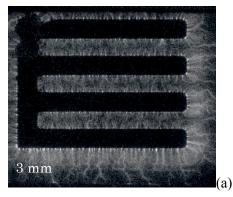
Applying electrical probe diagnostics to atmospheric plasmas is challenging due to significant perturbation caused by the probes. To address this, a probe for measuring electron temperature and ion current is indirectly connected to an atmospheric jet source. Plasma parameters are determined using floating harmonic analysis. The probe is mounted on a quartz tube surrounding the plasma. When a sinusoidal voltage is applied to a probe in contact with the quartz tube, electrons near the sheath at the dielectric tube are collected, resulting in harmonic currents in the probe current due to probe sheath nonlinearity. By the ratio of the harmonic currents at a given amplitude of the applying voltage to the probe, the electron temperature near the wall can be obtained using a collisional sheath model.

Optical emission spectroscopy evidence of N atom production in surface dielectric barrier micro-discharge reactor dedicated to atmospheric pressure PECVD

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The process of chemical vapor deposition (CVD) assisted by plasma has demonstrated its potential for obtaining thin films under an oxidizing atmosphere [1]. It enables depositions that are otherwise unattainable and facilitates a reduction in operating temperature. Within the framework of the REACTIVE project (ANR-21-CE08-0047), studies focus on thin film deposition by PECVD and PESALD (plasma enhanced spatial atomic layer deposition) under a reducing atmosphere using a plasma generated in molecular nitrogen. This contribution focuses on the study via optical emission spectroscopy and imaging of the discharge generated in the reactor designed for the process. The latter is a rectangular cavity ($lxhxw = 65x50x40mm^{3}$) containing a surface dielectric barrier discharge having electrodes in a comb shape. The gas from the plasma is available through a 1 mm slot over a length of 50 mm positioned approximately 100 µm from the substrate. The reactor box was fabricated using a 3D printer. A quartz window on top of the electrode surface enables optical diagnostic. Spectroscopic measurements were conducted using the two-stage imaging spectrometer equipped with a cryogenic CCD camera. The system has a spectral resolution down to 4 pm. The work focused on the detection and study, as a function of plasma operation's parameters, of excited nitrogen atoms. The detection of these atoms was achieved through lines identifications at wavelengths of 818.49 nm, 818.80 nm, 820.04 nm, 821.07 nm, 821.63 nm, 822.31 nm [2], while the strong emission of molecular nitrogen could be efficiently reduced in this spectral range (Figure 1). The results show that these excited atoms are only present at the electrode edge, corresponding to the roots of the filaments (micro-discharges). These results are compared to those obtained in a dry air atmosphere.



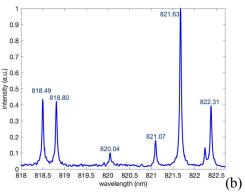


Fig. 1: (a) Image of the discharge (gate width=5 μ sec), and (b) optical emission spectrum (exposure time=60min), in N₂=100sccm.

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Plasma surface modification of metals and polymers by atmospheric-pressure air DBD and plasma torch treatment

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Many surface preparation technologies are used to improve adhesion phenomena, but traditional mechanical and chemical processes are generally polluting and expensive. In this context, plasma processes, and more particularly atmospheric-pressure plasmas, may be an interesting alternative for improving the adhesion of a material [1-2].

In this study, we were interested in the effects of plasma treatment on metals (stainless steel and aluminum) and polymers (PTFE and HDPE) in atmospheric-pressure air environment. Two types of plasma were used, Dielectric Barrier Discharge (DBD) with pulsed voltage regime and plasma torch (plasma Openair® of PlasmaTreat company). Different parameters were considered, especially the effect of processing time, frequency and electrode gap. Water contact angle (WCA) results show hydrophilization of surfaces (metals and polymers) after plasma treatment. Electrode gap affects materials differently with better results for larger space, on PTFE (fig. 1). In addition, the morphological and chemical changes, after plasma treatment, of our surfaces are performed by SEM and ATR-FTIR analyses respectively. Finally, mechanical pull-off tests of our treated surfaces will be carried out, and a comparison of the two plasmas and their impact on the treated materials will be discussed.

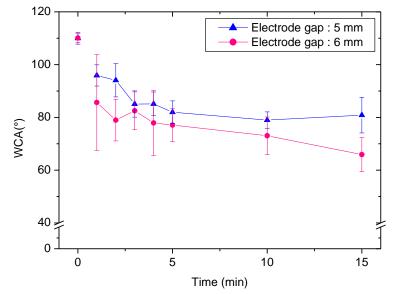


Fig 1 Electrode gap impact on WCA after plasma DBD treatment (PTFE)

 M. Kehrer, A. Rottensteiner, W. Hartl, J. Duchoslav, S. Thomas and D. Stifter. Surface and Coatings Technology **126389**, 403 (2020)
 T.S.M. Mui, L.L.G. Silva, V. Prysiazhnyi, K.G. Kostov. Surface and Coatings Technology **32-36**, 312 (2017)

Plasma-assisted CO₂ conversion combined with a catalyst

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The combination of an atmospheric pressure plasma with a catalyst is promising for environmental applications such as CO_2 conversion and the removal of volatile organic compounds (VOCs). The description of plasma catalytic systems can be very complex, in particular for in-plasma catalysis since many chemical and physical mechanisms can take place simultaneously. An atmospheric pressure plasma generated at 13.56 MHz between two plane-parallel electrodes covered with a catalytic surface is investigated by using Fourier-Transform Infrared spectroscopy, to determine the chemical composition and the concentration of the species inside the plasma channel (see Fig. 1). In previous studies [1], different reaction kinetic models for the plasma catalytic conversion of n-butane have been proposed. However, the dominant reaction mechanisms are still not well understood yet. Variation of the precursor He: CO_2 -ratio without n-butane and oxygen could help to find out whether CO_2 processes or atomic oxygen processes are more dominant on the catalytic surface [1]. In this work, the concentration of CO and CO_2 in the plasma channel has been determined, to test the validity of the proposed models from [1]. The CO_2 conversion increases with increasing specific energy input and reaches its saturation at around 60 %.



Fig. 1 Image of the plasma chamber for plasma catalysis.

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Plasma-driven Organic Synthesis: Reducing Noble Gas Usage

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Non-thermal plasmas operating at atmospheric pressure have opened the possibility of novel processing of liquids that were not possible in conventional vacuum systems due to vapour pressure limitations. Here we are interested in atmospheric pressure plasmas interacting with organic liquids, as these have the potential to be used for novel chemical synthesis. Particularly exciting are plasma-driven processes in which one can eliminate waste streams. [1] For example, the widely used oxidant oxone produces ~25 kg of waste per kg of oxygen transferred, whilst plasma-driven oxidation has the potential to completely eliminate this waste stream.

Plasmas used to treat (organic) liquids are often sustained in noble gases (typically helium or argon) as a means to control the temperature and chemistry of the interaction. Whilst this has enabled the treatment of samples with relatively high vapour pressure and the selective synthesis of valuable products, the noble gas consumption in these systems limits their applicability beyond scientific lab experimentation.

In this study, we explore the feasibility of recycling noble gas whilst harvesting oxygen from carbon dioxide in an Ar/CO_2 plasma that could be used to drive epoxidation processes. [2] A microplasma is used to split CO_2 , generating simultaneously CO that can be used for the synthesis of fuels, and atomic oxygen for the epoxidation of liquid alkenes.



Fig 1. Microplasma operating in closed-loop at 1 atm with 50sccm Ar/CO₂ through it.

The microplasma (Fig. 1) is based on a microstrip split-ring resonator, [3] and incorporates a small hole for gas to flow through the microdischarge. Mass flow/pressure controllers and a micropump are used to fill the closed-loop system with the desired gas composition, recirculate gas, maintain a constant flow through the discharge, and "top up" with fresh precursors when needed. When liquid is present in the system, vapour makes it to the gas phase and this needs to be taken into account when considering the plasma chemistry and plasma dynamics. Nonetheless, and unlike in open systems, once the solvent vapour pressure is reached, no significant evaporation is observed, with the plasma being able to treat the liquid for hours without the need for

replenishing the solvent. The microplasma has been shown to be able to operate stably in closed-loop for >12hr with virtually no noble gas consumption, thereby overcoming a barrier of previous novel plasmadriven organic synthesis processes.

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- [3] F. Iza and J. A. Hopwood, IEEE Transactions on Plasma Science 31, 782 (2003).

Quantitative analysis of glasses samples and plasma diagnostics by Optical Emission Spectroscopy and Thomson Scattering

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Laser Induced Breakdown Spectroscopy (LIBS) is an elementary analysis technique increasingly used over the past two decades in the field of quantitative analysis of matter composition. It is of particular interest to the domain of heritage glasses to know how the glasses from the past were created to be able to reproduce, among other things, the tints whose recipes are lost today [1]. LIBS satisfies this demand by allowing to determine with precision the composition and chemical concentration of a sample. Although LIBS has several advantages such as being a micro-destructive technique and being able to be performed in situ, it has the disadvantage to be dependent on matrix effects, which is a problem in quantitative analysis. To overcome this, it is necessary to use standard samples or so-called calibration-free methods [2]. When the conditions of LTE are respected, LIBS also allows us to characterize the studied plasmas. These measurements, which are often spatially integrated, can be compared to those obtained by other local plasma diagnostic methods such as Thomson Scattering (TS). However, the energy brought by the laser probe needed to induce TS might cause localized heating of the plasma which can distort the measurements of electronic temperatures [3].

The objective of this work concerns the quantitative analysis by calibration-free LIBS of laboratorymade glasses. These glasses are composed of silicon, sodium, and calcium oxides at known concentrations to investigate the matrix effects. The experiment's implementation and optimization are based on tests performed using Pyrex® glass pieces (borosilicate glass). The plasma is generated by a Nd:YAG nanosecond laser source generating a laser pulse at 532 nm (5 ns pulse width) clocked at 1 Hz to check the number of shots on the samples in an analysis chamber under a controlled atmosphere. The focusing conditions were tested beforehand to obtain the best spatial reproducibility, which is a critical parameter for optimizing the collection of plasma-emitted light [4] especially for TS. A second Nd:YAG nanosecond laser with pulse at 532 nm and pulse width of 5 ns probes the plasma and allows the acquisition of TS signals. The measurements of electron density and temperature performed with this approach are compared to those made with optical emission spectroscopy.

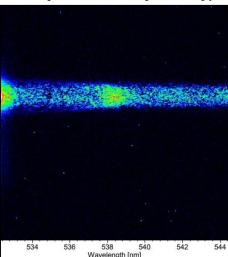


Fig.1 Right TS signal from a lab-made glass plasma after 1000 shots at a gate delay of 1000 ns.

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Self-Pulsing and instabilities in silicon-based Micro Hollow Cathode Discharge operating in DC excitation

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Non-thermal plasma generators exhibit discharge stability over a significant region and can operate at atmospheric pressure. Among the typical configurations of microplasma reactors, Micro Hallow Cathode Discharge (MHCD) are made of two electrodes separated by a thin dielectric layer [1]. Advanced techniques provide greater control over reactor shape, thereby expanding the potential applications of microplasma sources [2]. New geometries allow for the generation of plasma with unique properties, but are also limited by the inherent characteristics of its material [3]. In this study, we focus on the different electrical regimes achievable and the instabilities created as well in closed cavity shaped reactors and reactors with a Through Silicon Via (TSV).

Among them is the self-pulsing regime, in which the current and plasma voltage do not reach a steadystate. These oscillations are not a resonance and are mainly influenced by the capacitance of the reactor and the energy delivered by the power supply [4]. We investigate here the pattern behavior of two different geometries of plasma reactor operating in direct current at atmospheric pressure in He as shown Fig 1. These results are obtained using tools allowing for the observation of the voltage oscillation, the current spikes and the extinction phenomena.

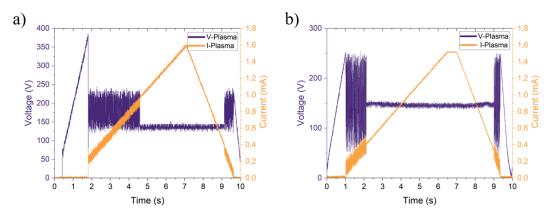


Fig. 1 Voltage and current evolution of an MHCD in He at 1bar, $R_{ballast} = 1M\Omega$: a) single hole, 150 μ m diameter closed cavity, b) single hole 150 μ m cavity with TSV.

- [1] K. H. Schoenbach, R. Verhappen, and T. Tessnow, Appl. Phys. Lett. 68, 13 (1996)
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- [3] R. Michaud et al., Plasma Sources Sci. Technol. 27, 025005 (2018)
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Spatial plasma configuration in plasma metamaterials

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Plasma is a tunable electromagnetic-wave medium that can make metamaterial properties dynamic; for instance, various functions like absorption and cloaking was verified in recent microwave experiments in which we used plasma metamaterials [1]. After almost 20-year research activities in metamaterial science, we have acknowledged accumulated achievements in both scientific and technological points of view, although its spatial design is halfway for optimization. Recently, we theoretically designed double-layer metasurfaces [2], unlike bulky configuration in other experiments (e.g., in Ref. [3]); this task to optimize its spatial configuration based on these two Dirac-cone metamaterials is quite challenging. Then, plasma (or microplasma in a tiny space) can play a key role in cases of plasma generation inside a metamaterial configuration since plasma is a thermodynamical material with functions of the wave medium. Thermodynamically, the Second Law gives us an in-depth insight of phenomenological trend observed in experiments. From spatial configuration of plasma generated in a metamaterial, we can deduce its thermodynamical role with its resultant spatial density and temperature profile.

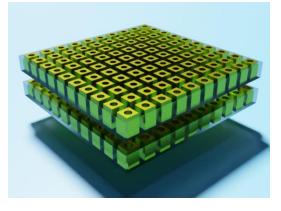


Fig. 1 One example of metamaterial design for bandgap and Dirac-cone material [2].

ACKNOWLEDGEMENTS

One of the authors (OS) thanks Prof. Francisco Pizarro-Torres at Pontificia Universidad Católica de Valparaíso, Chile, and Prof. Tsuyohito Ito at The University of Tokyo, Japan, for their useful comments on this study. This study is partially supported by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT/JSPS KAKENHI) with Grant Nos. JP18H03690, JP18K18756, JP22K18704.

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Study of a Portable DBD Source for Surface Modification and Microbial Inactivation

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Microbial contamination represents a growing concern across various fields, ranging from healthcare to food industry and everyday life [1]. Therefore, to deal with this issue cheap and effective decontamination methods should be developed. This work report on a cost-effective Dielectric Barrier Discharge (DBD) system in planar geometry designed for surface modification and decontamination. As shown in the schematic in Fig. 1 the device employs a metal mesh electrode, which allows reactive species diffusion outside the discharge region. Powered by a simple high-voltage supply adapted from a cosmetic plasma device, it operates with atmospheric air, eliminating the need for gas flux.

The device characterization includes electrical measurements and optical emission spectroscopy. The reactive species generated by the DBD system were applied for polymer surface modification, showing enhancement in the material wettability.

Tested against *Candida Albicans* and *Staphylococcus Aureus*, the device achieved over 99% reduction in microbial load with exposure times of several minutes. Simultaneously, Vero cell viability remained consistently high, between 91% and 96% across the exposure times, proving the lack of cytotoxicity.

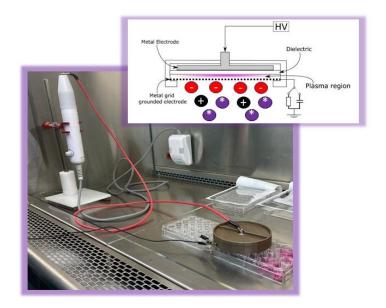


Fig. 1 Schematic of DBD arrangement and a picture of the experimental setup.

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Towards the realization of plasma reconfigurable metasurfaces to control electromagnetic waves: characterization of an argon microplasma element

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 ² AlmaPlasma s.r.l., Bologna, Italy;
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New wireless technologies, such as 5G and beyond-5G communication systems, are rapidly expanding their fields of application, thus offering concrete economic opportunities to society. [1] These technologies must meet highly demanding performance requirements (e.g. ultra-high reliability and near-zero latency) that become even more challenging considering the increasingly dynamic environments where the systems are designed to operate. [2] In the described scenario, the use of plasma reconfigurable metasurfaces appears extremely promising since it combines the ability of metasurfaces to control electromagnetic (EM) waves with the possibility to vary the characteristics of the plasma elements constituting the metasurface in real-time. [3] To properly control EM waves up to the THz range, the dimensions of the plasma elements must be comparable with those of microplasmas, fascinating discharges whose characterization is known to be far from trivial. [4]

This work proposes a detailed investigation of the behavior of a single pin-to-pin argon microplasma element in response to the variation of several parameters, such as, for example, pressure and type of voltage signal. The electrical characteristics of the plasma element are recorded using electronic probes, while the structure and the development of the discharge are monitored by means of an intensified charge coupled device (ICCD) camera. The breakdown voltage is deduced by correlating current and voltage waveforms with images from ICCD. The obtained results are also discussed in comparison with those related to similar plasma elements of lengths up to 10 cm (Figure 1). This work provides valuable insights into the realization of reconfigurable metasurfaces (composed of numerous plasma elements) to control EM waves in a wide range of frequencies.



Figure 1: Plasma elements of different lengths.

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VOCs conversion in He/H₂O plasma produced in a micro-capillary tube at atmospheric pressure

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Cold plasma micro-reactors, designed for example for chemical synthesis [1, 2] or the treatment of organic molecules in water [3], constitute a rapidly developing subject of study. This often involves using one or more dielectric barrier micro-discharge(s) (micro-DBDs) to generate a plasma with high densities of reactive species, atoms, radicals or molecular excited states, which will initiate the physico-chemistry of interest for the envisaged application. In addition, research on plasma produced by pulsed electrical discharge generating a propagating ionization wave (IW) in capillary tubes attracts increasing attention, driven in particular by applications linked to analytical chemistry [4], or to health like for instance endoscopy [5], or transport of reactive species for the treatment of cancerous tumors [6].

In our work, a plasma is created in a micro-capillary quartz tube (800 μ m of internal diameter), by a DCpulsed micro-DBD and the propagation of an IW in mixtures of He/H₂O/VOC at atmospheric pressure. The studied Volatile Organic Compounds (VOCs) are representatives of molecules belonging to different chemical families: alcohols (methanol, ethanol, isopropanol, tert-butanol), ketones (acetone), nitriles (acetonitrile), and aromatic hydrocarbons (toluene).

The conversion efficiency of these VOCs is studied as a function of the applied voltage on the micro-DBD (or the electrical energy deposited in the plasma) and of the initial concentration of the molecules in the range from 1 ppm up to 3000 ppm (depending on the molecule), with the help of high-resolution real-time mass spectrometry (CI- FTICR, using H_3O^+ as precursor ion) [7]. A variety of by-products resulting from the conversion of VOCs are identified and quantified, emphasizing that the micro-capillary plasma is able to induce a complex chemical reactivity. A qualitative analysis of the involved kinetics, based on the existing literature, reveals that helium species (ions and metastable states) and radicals coming from the dissociation of the water molecules (O and OH) are the most probable candidates to explain the formation of all compounds detected by the CI-FTICR apparatus. Quenching processes of the metastable $He(2^3S)$ by the VOCs, leading to the dissociation of the molecules, are suggested to explain some of the experimental results.

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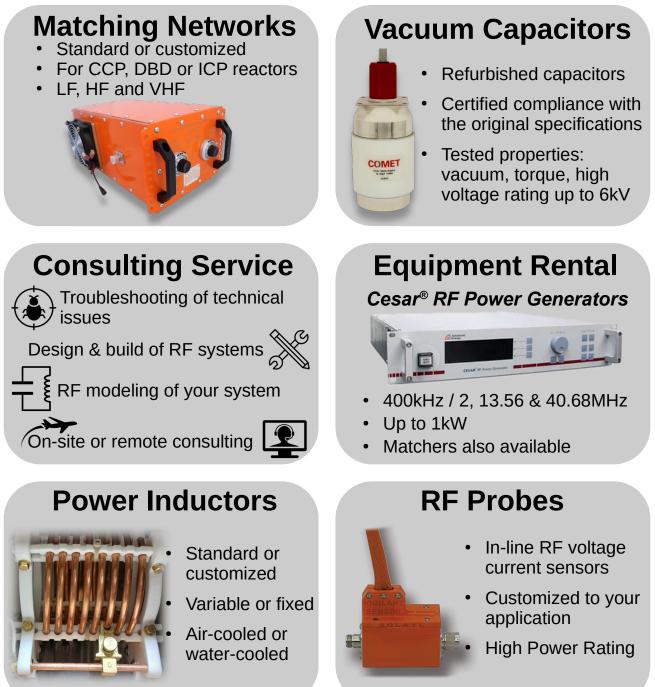








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Index

Α

Agha Yanis, 39, 65 Almeida Ana Carla De Paula Leide, 80 Alves Luis Lemos, 50 Andreazza Pascal, 60 Aubert Xavier, 21 Aubry Olivier, 73 Awakowicz Peter, 41

В

Bajon Corentin, 27 Barbuto Mirko, 36 Bauville Gérard, 15, 50, 56, 62, 82 Belmonte Thierry, 16 Ben Othmen Cyrine, 17 Bernardelli Patrick, 45 Bílek Petr, 51 Bilotti Filiberto, 36 Böke Marc, 26, 28 Bonaventura Zdenk, 51 Bonifaci Nelly, 67 Bourdon Anne, 25 Bracht Vera, 41 Brochard Frédéric, 16 Bröcker Lars, 14 Bruyere Stephanie, 71 Burhenn Sebastian, 18 Busch Christian A., 20

С

Cailhol Cyril, 33 Callegari Thierry, 33 Capelli Filippo, 57, 70, 81 Chabert Pascal, 59 Chauvet Laura, 18 Chen Jiandong, 52 Choe Wonho, 13 Chung Chinwook, 72 Chur Sascha, 28 Cvelbar Uros, 13 Czarnetzki Uwe, 20 Czerwiec Thierry, 71

D

Da Silva Diego Moraes, 80

Dap Simon, 27 De Castro Gisele Fátima Soares, 80 Devos Alexandre, 23 Dimitrakellis Panagiotis, 69 Disson Baptiste, 67 Douat Claire, 18, 42, 62 Dozias Sebastien, 18, 23, 42 Ducros Gabriel, 33 Dussart Rémi, 53, 67, 71, 78

\mathbf{E}

Escot Bocanegra Pablo, 23

\mathbf{F}

Faubert François, 60, 69, 74 Fensterbank Louis, 45 Field Thomas, 30 Flaugère Robin, 77 Foricher Yann, 45 Frank Jonathan, 22 Fu Yangyang, 52 Fuster Lucas, 33

G

Garcia-Caurel Enric, 25 Gazeli Kristaq, 21, 39, 49, 54, 56, 65 Gazeli Odhisea, 54 Gembus Jan-Luca, 41 Geraud-Grenier Isabelle, 60 Géraud-Grenier Isabelle, 69 Geraud-Grenier Isabelle, 74 Gherardi Matteo, 57, 70, 81 Gibert Titaina, 18 Gibson Andrew R., 31, 41 Giotis Konstantinos, 39, 49, 65 Golda Judith, 18, 26, 28, 31 Goncalves Duarte, 50 Grande Mariachiara, 70 Grediak Viktor, 42 Gries Thomas, 16 Grimm Florens, 41 Guaitella Olivier, 25 Guerrero Daniel, 43, 64 Guillermain Marie, 45

Η

Hae June Lee, 61 Hagelaar Gerjan, 33 Halfaoui Abd-Almalik, 15, 56 Heninger Michel, 82 Henze Daniel, 18 Herrera Quesada Maria, 22 Hoder Tomas, 27 Hoffmann Patrick, 33 Hofmans Marlous, 25 Höft Hans, 39, 49, 65 Hong Dunpin, 73

Ι

Invernizzi Laurent, 21, 39, 49, 56, 65 Iseni Sylvain, 17, 53, 67, 71, 73, 78 Itami Go, 79 Ito Tsuyohito, 66 Iza Felipe, 76

J

Jae Wan Kim, 61 Jeanney Pascal, 15, 50, 56, 82 Jeon Sang Un, 37, 58

K

Kaneko Toshiro, 40 Kaneta Takuto, 40 Karasaki Toshifusa, 34 Kawamura Emi, 59 Kawanishi Genki, 68 Kazumori Shogo, 68 Kim Jae Wan, 37, 58 Kim Jinwoo, 13 Kim Yc, 72 Kim Ys, 72 Klages Claus-Peter, 14 Kodaira Felipe Vicente De Paula, 80 Koga-Ito Cristiane Yumi, 80 Koike Takeru, 66 Kostov Konstantin Georgiev, 80 Kouadou Elane, 53, 78 Kourtzanidis Konstantinos, 29, 54 Kovacevic Eva, 74 Kuhfeld Jan, 20 Kuroda Koji, 68 Kusyn Lukas, 27

\mathbf{L}

Labenski Robin, 26 Laghi Giulia, 57, 70, 81 Laurita Romolo, 57, 70, 81 Lazzaroni Claudia, 21, 54, 59 Leal Bruno Enrique Da Silva, 80 Lee Hae June, 37, 58 Lee Hyungyu, 13 Lefaucheux Philippe, 53, 78 Lemaire Joel, 82 Lemeur Julien, 67 Lepikhin Nikita D., 20 Lesaint Olivier, 67 Liard Laurent, 33 Lieberman Michael A., 59 Liennard Marion, 69, 74 Lim Heechang, 58 Lin Chubin, 52 Lino Da Silva Mário, 50 Liu Shuda, 19 Liu Yu-Xi, 46 Lombardi Guillaume, 21, 39, 49, 54, 65 Lopez Jose, 43, 64 Lou Sam, 64 Luggenhölscher Dirk, 20

Μ

Mannion Sinead, 30 Marcos Gregory, 71 Mariotti Davide, 35 Matsumoto Atsumu, 68 Mazzeo Aaron, 38 Menacer Belkacem, 21, 54 Meoni Fancesco, 57 Mestre Eloïse, 18 Ming Yang, 19 Minke Robin, 28 Mohsenimehr Soad, 48 Monti Alessio, 36 Moon Se Youn, 13 Morand Gabriel, 45 Muneoka Hitoshi, 66 Murakami Tomoyuki, 30

Ν

Najah Aymane, 60, 69 Naude Nicolas, 27 Navratil Zdenek, 27 Ndiffo Gervais Blondel, 73 Niu Jinhai, 19 Noel Cédric, 16, 71 Nominé Anna, 16

0

Ognier Stéphanie, 45 Oh Jun-Seok, 68 Okada Shota, 30 Ollivier Cyril, 45

\mathbf{P}

Pallandre Antoine, 82 Park Joo Young, 13 Park Sanghoo, 13 Pascal Olivier, 33 Pascaud Romain, 33 Pasquiers Stéphane, 15, 50, 56, 82 Patel Praj, 38 Pellerin Nadia, 77 Pellerin Stéphane, 17, 60, 69, 74, 77 Pfaff Sebastian, 22 Pouant Clovis, 33 Poulain Christophe, 67 Prasanna Swaminathan, 21, 49, 56 Prokop David, 27

\mathbf{R}

Rabat Hervé, 73 Ramaccia Davide, 36 Remigy Alice, 21, 54, 59 Robert Eric, 23 Roman Sophie, 42

\mathbf{S}

Sakai Osamu, 34, 79 Salvi Deepti, 38 Sanami Yohei, 79 Sang Un Jeon, 61 Santos Sousa Joao, 15, 50, 56, 62, 82 Sasaki Shota, 40 Schio Laurent, 45 Schöne Anna Lena, 31 Schulz-Von Der Gathen Volker, 26, 28 Schüttler Steffen, 31 Seferoglu Fatma-Nur, 75 Shirafuji Tatsuru, 44, 68 Simek Milan, 51 Simon Antoine, 33 Slikboer Elmar, 25 Slodczyk Aneta, 42 Sobota Ana, 25 Sokoloff Jérôme, 33 Stancampiano Augusto, 23, 81 Stapelmann Katharina, 22, 38 Stefanini Luca, 36 Stefas Dimitrios, 39, 49, 65 Steuer David, 26 Steve Rudz, 77 Stolz Arnaud, 53, 78 Svarnas Panagiotis, 39, 49, 65

\mathbf{T}

Takashima Keisuke, 40 Tan Xiaokang, 19 Tanielyan Setrak, 43 Tarasenka Natalie, 35 Tatoulian Michael, 45 Terashima Kazuo, 66 Tian Tian, 73 Toscano Alessandro, 36 Trosan Duncan, 38 Tungli Ján, 51

\mathbf{V}

Van Impel Henrik, 26 Van Rooij Olivier, 25 Vasile Michele, 57, 70, 81 Vellucci Stefano, 36 Vervloedt Steijn, 63, 75 Viegas Pedro, 25 Von Keudell Achim, 48, 63, 75

W

Wang Chenjie, 19 Wang Hai-Xing, 46 Wartel Maxime, 17, 74, 77

Y

Yu Siqi, 63

\mathbf{Z}

Zhou Haifeng, 58