Non-Thermal Plasmas for Sustainable Chemistry

785. WE-Heraeus-Seminar

23 – 27 April 2023

at the Physikzentrum Bad Honnef, Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de

Aims and scope of the 785. WE-Heraeus-Seminar:

The integration of renewable electricity with fossil resources, H_2O, Air, and CO_2 resources provides unprecedented opportunities to transform the fossil energy industry to low carbon chemical manufacturing by using distributed non-equilibrium plasma catalysis. Recent studies of plasma-assisted CH_4 and CO_2 reforming, hydrogen production, NOx and ammonia synthesis (for among others fertilizer applications) have suggested that plasma can increase reactivity and plasma catalysis enables chemical selectivity. However, there are multiple scientific challenges in realizing this exciting potential of plasma (catalysis) due to the complexity of the excited and ionized states, non-equilibrium between photons, electrons, excited states, and neutral species, complex interaction and energy/mass transfer between different states and at heterogeneous interfaces, strong coupling between plasma chemistry and heterogeneous catalysis, complicated plasma catalysis mechanisms, and numerous unknown reaction pathways and elementary reaction rates. These challenges are further exacerbated by the large disparities in plasma and catalysis time and length scales as well as strong coupling between macroscopic and microscopic chemical and transport processes. Recent advances in quantum chemistry modeling, non-equilibrium energy materials and catalysts, laser diagnostics, plasma control, as well as the availability of data sciences create a great opportunity to advance the understanding of the chemistry underlying plasma (catalysis) and steer catalytic transformations in yield and selectively of low carbon chemical manufacturing.

In this seminar, world-leading experts in different research fields of plasma physics, chemistry, catalysis, quantum chemistry computation and laser diagnostics will discuss openly the challenges, opportunities, and collaborations in plasma-assisted sustainable chemistry with a focus on the following topics:

(1) Demand and technologies of energy storage technologies for a climate neutral world
(2) Non-equilibrium plasma dynamics and energy transfer
(3) Plasma-aided CO_2 hydrogenation and CO_2/methane reforming
(4) Plasma-aided NH_3 and NOx synthesis
(5) Quantum chemistry and multiscale modeling of plasma chemistry and plasma catalysis
(6) Plasma catalysis and biocatalysis for chemical production

This seminar will create an exciting platform to stimulate brainstorming discussions among the participants to discuss new ideas, inspiration, key challenges, and collaboration.

Introduction

Scientific Organizers:

Prof. Yiguang Ju	Princeton University, USA E-mail: yju@princeton.edu
Prof. Annemie Bogaerts	University of Antwerpen, Belgium E-mail: annemie.bogaerts@uantwerpen.be
Prof. Achim von Keudell	Universität Bochum, Germany E-mail: achim.vonkeudell@rub.de
Prof. Tomohiro Nozaki	Tokyo Institute of Technology, Japan E-mail : nozaki.t.ab@m.titech.ac.jp

Administrative Organization:

Dr. Stefan Jorda
Elisabeth Nowotka

Wilhelm und Else Heraeus-Stiftung
Kurt-Blaum-Platz 1
63450 Hanau, Germany

Phone +49 6181 92325-12
Fax +49 6181 92325-15
E-mail nowotka@we-heraeus-stiftung.de
Internet: www.we-heraeus-stiftung.de

Venue:

Physikzentrum
Hauptstrasse 5
53604 Bad Honnef, Germany

Conference Phone +49 2224 9010-120

Phone +49 2224 9010-113 or -114 or -117
Fax +49 2224 9010-130
E-mail gomer@pbh.de
Internetwww.pbh.de

Taxi Phone +49 2224 2222

Registration:

Elisabeth Nowotka (WE Heraeus Foundation)
at the Physikzentrum, reception office
Sunday (16:00 h – 20:00 h) and Monday
morning

Program

Program

Sunday, 23 April 2023

16:00 – 20:00	Registration	
18:00	*BUFFET SUPPER and informal get-together*	
19:30 – 19:35	Yiguang Ju	**Welcome**

Keynote lecture

Chair: Achim von Keudell

19:35 – 20:35	Dirk-Uwe Sauer	**Demand and technologies of energy storage technologies for a climate neutral world**
20:35	**Social time**	

Monday, 24 April 2023

08:00	*BREAKFAST*	
08:55	Scientific organizers	**Welcome and announcements**

Session 1: Plasma chemistry

Chair: Hyun-Ha Kim

09:00 – 09:45	Sevetlana Starikovskaia	**Plasmachemistry in pulsed nanosecond discharges: what changes at high electric fields and at high specific energy deposition**
09:45 – 10:30	Gerard Van Rooij	**Non-thermal plasmas for sustainable chemistry**
10:30 – 11:00	*COFFEE BREAK*	

Program

Monday, 24 April 2023

11:00 – 11:45	Achim von Keudell *Replacement of K. Grosse*	**In-liquid plasmas for electrolysis**

PANEL 1: Plasma chemistry

Chair Tony Murphy

11:45 – 12:30	**Panelists:** Achim von Keudell, Gerad von Rooij, Svetlana Starikovskaia
12:30 – 12:40	**Conference Photo** (in the front of the lecture hall)
12:40 – 14:00	*LUNCH*

Session 2: Multiscale modeling and plasma-chemistry interaction

Chair: Tomohiro Nozaki

14:00 – 14:45	Annemie Bogaerts	**Plasma for sustainable chemistry: A better understanding by modelling the plasma and plasma-catalyst interactions**
14:45 – 15:30	Bryan R. Goldsmith	**Atomistic modeling of plasma-assisted catalysis: Oppor-tunities and challenges**
15:30 – 16:00	*COFFEE BREAK*	
16:00 – 16:45	Yiguang Ju *Replacement of Chuan Shi*	**Plasma chemistry and thermal-chemical instability**

PANEL 2: Plasma modeling and plasma-chemistry interaction

Chair: Tony Murphy

16:45 – 17:30	**Panelists:** Annemie Bogaerts, Bryan R. Goldsmith, Yiguang Ju (or Chuan Shi)	
17:30 – 17:45	Stefan Jorda	**About the WE-Heraeus-Foundation**
18:30	*DINNER*	

Program

Tuesday, 25 April 2023

08:00	*BREAKFAST*	
08:55	Scientific organizers	**Welcome and announcements**

Session 3: CO_2 and methane Conversion-1

Chair: Richard van de Sanden

09:00 – 09:45	Tomohiro Nozaki	**In situ diagnostics of plasma catalytic conversion of CO_2: Identifying the synergistic pathways toward catalyst design**
09:45 – 10:30	Olivier Guaitella	**Role of vibrational and electronic excited states for CO_2 conversion by plasma**
10:30 – 11:00	*COFFEE BREAK*	

Session 4: CO_2 and methane Conversion-2

Chair: Annemie Bogaerts

11:00 – 11:45	Ronny Brandenburg	**CO_2 splitting in dielectric barrier discharges: Prospects to increase CO formation**
11:45 – 12:30	Richard Van de Sanden	**Non-thermal plasma conversion of CO_2, N_2/O_2 & CH_4**
12:30 – 14:00	*LUNCH*	

Program

Tuesday, 25 April 2023

PANEL 3: CO_2 and methane Conversion-1

Chair: Bryan R. Goldsmith

14:00 – 14:45 **Panelists:**
Ronny Brandenburg, Olivier Guaitella, Tomohiro Nozaki, Richard van de Sanden

Session 5: Chemical synthesis and bio-catalysts-1

Chair: Julia Bandow

14:45 – 15:30	Koichi Sasaki	**Key species in plasma-aided ammonia synthesis: atomic nitrogen versus molecular nitrogen at vibrational excited states**
15:30 – 16:00	*COFFEE BREAK*	

Co-chairs: Pia Pottkämper, Elizabeth Mercer, Chris Kondratowicz

16:00 – 17:00	**Poster flashes 1**
17:00 – 18:00	**Poster session 1**
18:30	*DINNER*

Program

Wednesday, 26 April 2023

08:00	*BREAKFAST*	
08:55	Scientific organizers	**Welcome and announcements**

Session 6: Chemical synthesis and bio-catalysts-1

Chair: Xin Tu

09:00 – 09:45	Hyun-Ha Kim	**Sustainable nitrogen fixation using spark discharge plasma for power-to-X**
09:45 – 10:30	Julia Bandow	**Plasma-driven biocatalysis – from proof of concept to improving performance**
10:30 – 11:00	*COFFEE BREAK*	

Co-chairs: Steijn Verloedt, Yury Gorbanev, Yijie Xu

11:00 – 12:00	**Poster flashes 2**
12:00 – 13:00	**Poster session 2**
13:00 – 14:30	*LUNCH*
14:30 – 18:00	**Excursion** *(Lead: Achim von Keudell)*
18:00 – 18:30	Seminar organization committee meeting (best poster awards)
18:30	*HERAEUS DINNER* *(social event with cold & warm buffet with complimentary drinks)* ***and best poster presentation awards***

Program

Thursday, 27 April 2023

07:30	*BREAKFAST*	
08:25	Scientific organizers	**Welcome and announcements**

Session 7: Plasma catalysis-1

Chair: Yiguang Ju

08:30 – 09:15	Xin Tu	**Plasma catalysis: An emerging technology for sustainable production of fuels and chemicals**
09:15 – 10:00	Leon Lefferts	**Using expertise in catalysis for understanding plasma-catalysis**
10:00 – 10:30	*COFFEE BREAK*	

Session 8: Plasma catalysis-2

Chair: Koichi Sasaki

10:30 – 11:15	Tony Murphy	**Chemical production by plasma catalysis for industrial processes**
11:15 – 12:00	Li Wang *(online)*	**Plasma catalysis for CH4/CO2 conversion to alcohols**

PANEL 4: Plasma catalysis and priorities of research

Chair: Katharina Kohse-Höinghaus

12:00 – 12:45	**Panelists:** Hyun-Ha Kim, Tony Murphy, Koichi Sasaki, Leon Lefferts, Xin Tu, Li Wang *(online)*
12:45	*LUNCH*

End of the seminar and departure

NO DINNER for participants leaving on Friday; however, a self-service breakfast will be provided on Friday morning

Posters

Posters

Sayadmahaleh Adhami	**Toluene abatement by use of non-thermal plasma and metal-free catalyst**
Matthias Albrechts	**Kinetic modeling of oxygen plasma at low and atmospheric pressure**
Margherita Altin	**The energy cost of N_2 dissociation in a microwave discharge: combining modelling and experiments**
Edmond Baratte	**Experimental and numerical study of the fundamental processes in a CO_2-CH_4 RF plasmas**
Jairo Barauna	**Plasma Catalysis for CO_2 reduction using liquid water as hydrogen source**
Yuri Barsukov	**Multiscale modeling of boron nitride nanotube synthesis and carbon nanotube synthesis and hydrogen production from natural gas pyrolysis**
Jean-Paul Booth	**Probing the kinetics of oxygen atoms and metastable molecules in oxygen-containing discharges by cavity ringdown spectroscopy: potential applications to CO_2 conversion and plasma-assisted combustion**
Yuxiang Cai	**Plasma-catalytic CO_2 hydrogenation over Fe-Cu-based perovskite catalysts**
Guoxing Chen	**A novel plasma-assisted hollow fiber membrane concept for efficiently separating oxygen from CO in a CO_2 plasma**
Richard Cimerman	**Nonthermal plasma regeneration of deactivated catalysts used for plasma-catalytic VOC/PAH removal**
Panagiotis Dimitrakellis	**Sustainable chemical synthesis through plasma-liquid interactions in a helical DBD microreactor**

Posters

Martin Drößiger Christian Koch	**CO_2 valorization via plasma catalysis**
Albert Engstfeld	**Restructuring of catalyst materials by high voltage electrolysis**
Lukas Forschner	**Electric fields during high voltage electrolysis**
Carolina Garcia Soto	**DC glow discharge - Fluidized bed reactor for CO_2 recycling**
Yury Gorbanev	**Nitrogen fixation into NO_x by plasma: Pulsed spark plasma versus arc plasma**
Vasco Guerra	**Volume and surface kinetics in CO_2 plasmas**
Karin Hansen	**Ignition and characterization of non-thermal, low-pressure plasmas in highly porous and lightweight aeromaterials**
Mery Hernandez	**Analysis of reactive species during plasma-water interaction for H_2O_2 formation using nanosecond pulsated microwaves**
Rezvan Hosseini Rad	**High pressure coaxial dielectric barrier discharge for CO_2 splitting by combined action of packed bed**
Muzammil Iqbal	**Investigation of non-thermal atmospheric pressure plasma-based nitrogen fixation using water in nitrogen arc discharge for sustainable and environmentally-friendly ammonia production**
Vít Jirásek	**Nitrogen fixation in sub-micrometer-size water aerosol using micro-hollow surface DBD reactor**
Chanmi Jung	**Plasma-induced toluene conversion into acetylene with high selectivity**

Posters

Christopher Kondratowicz	**Kinetic interaction between plasma and catalyst in plasma-assisted ammonia synthesis**
Saeed Kooshki	**Plasma-Activated Water (PAW) as a sustainable technology for wastewater treatment and agricultural development**
Konstantinos Kourtzanidis	**Numerical modeling of atmospheric pressure plasma discharge dynamics**
Victor Lafaurie	**Nanosecond surface dielectric barrier discharge: Experimental investigation of streamer to filament transition in high-pressure gases**
Shangkun Li	**One-step steam reforming of methane to methanol by plasma catalysis: experiments and DFT modelling**
Stein Maerivoet	**Effect of O_2 on the dry reforming of methane in an atmospheric pressure glow discharge**
Jean Maillard	**CO_2 conversion by NRP discharges: spotlight on two parallel CO production mechanisms**
Filippo Manaigo	**Feasibility study of plasma-based local fertilizer production**
Andrea Marchetti	**Numerical modelling of plasma assisted methane pyrolysis**
Pierre Mathieu	**Preliminary investigation of methane plasmalysis in a gliding arc plasma**
Elizabeth Mercer	**Microwave plasma conversion of martian atmosphere**
Soad Mohsenimehr	**Control of the gas flow by a surface barrier discharge**
Maria Luiza Moreira de Azevedo	**Fast pyrolysis in methane plasma**

Posters

Beatrice Musig	**Physicochemical and electrical characterization of a CeO_2-based nanostructured catalysts for plasma-assisted CO_2 methanation in a DBD reactor**
Alexander Navarrete	**Plasma-catalysis reactor concepts using microwave plasmas under nanosecond pulsation**
Christian Oberste-Beulmann	**GC-MS analysis of toluene decomposition residues formed during the plasma-assisted oxygen trace removal from synthetic coke oven gas**
Timothy Oppotsch	**Plasma-assisted removal of n-Butane from contaminated air in an SDBD reactor using $BaTiO_3$ as catalyst**
Jordyn Polito	**Investigation of reaction mechanisms for modification of organic molecules in cold atmospheric plasma activated water**
Pia-Victoria Pottkämper	**Influence of nanosecond pulsed plasmas in water on copper surfaces and on nanoparticle formation**
Rendy Prastiko	**Water decontamination using a plasma-in-liquid technique, application to per- and poly-fluoroalkyl substances (PFAS) treatment**
Dihya Sadi	**Fundamental processes in CO_2-H_2 plasmas : toward methanation in plasma catalysis**
Joao Santos Sousa	**Plasma kinetics of methane conversion in Ar/CH_4 mixtures at atmospheric pressure**
Kerstin Sgonina	**Development of plasma reactors for plasma-assisted catalysis**
Qinghao Shen	**Multitemperature model of the non-thermal plasma chemical dissociation of CO_2**

Posters

Zhan Shu	**Evolution of atomic oxygen density in the early afterglow of a nanosecond CO_2 discharge**
Lucas Silberer	**Characterization of CO_2 atmospheric pulsed microwave plasmas in Surfaguide reactor with a highly time resolved optical emission spectroscopy**
Kristina Tschulik	**Plasma treatment of nanoreactors for controlled synthesis of nanomaterials and their use in electrocatalysis and sensing**
Cas van Deursen	**Effluent nozzles in Reverse-vortex-stabilized microwave plasmas for performance enhancement**
Stijn Van Rompaey	**Diagnostics and 0D modelling of methane conversion in a ns-pulsed pin-to-pin plasma reactor**
Thomas Vazquez	**Cold atmospheric plasma and TiO_2 photocatalysis for the treatment of polluted indoor air**
Steijn Vervloedt	**NH3 synthesis in a catalytic atmospheric pressure RF discharge**
Yaolin Wang	**Shielding protection by mesoporous catalysts for improving plasma-catalytic ambient ammonia synthesis**
Yijie Xu	**Ferroelectrics-induced surface charge effect on plasma properties and instability**
Xiao Yu	**Plasma process for recycling of plastic wastes towards the productions of carbon nanomaterials and hydrogen**
Hao Zhao	**In situ identification of NNH and N_2H_2 by using molecular-beam mass spectrometry in plasma-assisted catalysis for NH3 synthesis**

Abstracts of Talks

(in alphabetical order)

Plasma-driven biocatalysis – from proof of concept to improving performance

T. Dirks[1], S. Klopsch[1], J. E. Bandow[1]

[1]*Chair of Applied Microbiology, Faculty of Biology and Biotechnology, Ruhr University Bochum, Bochum, Germany*

In plasma-driven biocatalysis, plasma-generated species dissolved in aqueous solution are used as a reactant by enzymes to produce chemicals with added value from low-value organic molecules [1]. Plasma-generated H_2O_2 was used in a reaction catalyzed by the unspecific peroxygenase of the fungus *Agerita aegrocybe* (AaeUPO) to demonstrate that regio- and stereoselectivity of enzymatic reactions can be preserved under in situ plasma-treatment conditions [1,2]. Several parameters limit enzyme performance in plasma-treated liquids. In addition to enzyme poisoning by the cosubstrate H_2O_2, limited delivery of the hydrophobic substrates to the enzyme, and product inhibition, which are common challenges observed for H_2O_2-utilizing enzymes, reactive plasma species contribute significantly to enzyme inactivation by destroying the heme cofactor, oxidizing critical amino acid residues, and even resulting in enzyme degradation [1,3,4].

Several strategies were tested to improve enzyme performance under in situ plasma treatment conditions, including the use of scavengers, enzyme-protective proteins, and the adaptation of biotechnological techniques [5]. We found that the immobilization of enzymes on solid supports and their confinement in a rotating bed reactor placed at a distance from the surface of the liquid, provides good protection of enzymes from the most reactive species [5], improves substrate delivery, and allows to replace the product-containing solution. The latter is important to overcome product inhibition. With iterative replacement of the reaction solution, enzyme performance in plasma-driven biocatalysis reached total turnover numbers greater 175,000, getting close to common in situ H_2O_2 production methods such as enzymatic cascades or electrochemical generation [6,7]. While the overall plasma biocatalysis process needs further improvement, enzyme activity is satisfactorily preserved by immobilization.

References

[1] A. Yayci et al., ChemSusChem **13**, 2072-9 (2020)
[2] A. Yayci et al., ChemCatChem **12**, 5893-7 (2020)
[3] M. Krewing et al., Plasma Processes and Polymers 2020;e2000019 (2020)
[4] M. Krewing et al., Plasma Chemistry and Plasma Processing **40**, 685-96 (2020)
[5] A. Yayci et al., Journal of Physics D: Applied Physics **54**, 035204 (2021)
[6] M. Pesic et al., Zeitschrift für Naturforschung C **74**, 101-4 (2019)
[7] A.E.W. Horst et al., Journal of Molecular Catalysis B: Enzymatic **133**, S137-42 (2016)

Plasma for sustainable chemistry: A better understanding by modelling the plasma and plasma-catalyst interactions

A. Bogaerts

Research group PLASMANT, Dept. Chemistry, University of Antwerp,
Universiteitsplein 1, BE-2610 Antwerp, Belgium

Plasma technology is gaining increasing interest for various sustainable chemistry applications, such as CO_2 and CH_4 conversion into value-added compounds, and N_2 fixation for fertilizer applications [1-4]. To improve these applications in terms of conversion, energy efficiency and product formation, a good insight in the underlying mechanisms is desirable. This can be obtained by computer modelling and experiments.

After a brief overview of the state-of-the-art in plasma-based CO_2 and CH_4 conversion and N_2 fixation, I will present some recent results obtained in our group PLASMANT, illustrating how modeling can help to better understand the underlying mechanisms, in order to improve the applications.

Examples will include: (i) reactor design improvements for enhanced performance, (ii) the effect of quenching nozzles to avoid recombination reactions, for both CO_2 splitting and N_2 fixation, (iii) placing a carbon bed after a plasma reactor for trapping the O/O_2 and thus limiting again the recombination reactions with CO back into CO_2, thereby drastically increasing the CO yield and removing O_2 from the gas mix, (iv) the effect of gas recirculation for higher CO_2 conversion, (v) plasma chemical kinetics model, surface chemical kinetics modeling, and combined plasma-surface chemical kinetics modeling for various plasma catalysis applications (including non-oxidative coupling of CH_4, partial oxidation of CH_4, NH_3 synthesis, and dry reforming of CH_4), (vi) N_2 fixation into NO_x in various plasma reactors, supported by chemical kinetics modeling, also followed by lean-NO_x trap conversion into NH_3, and (vii) the combined CO_2 and N_2 fixation for in-situ resource utilization of the Martian atmosphere.

References

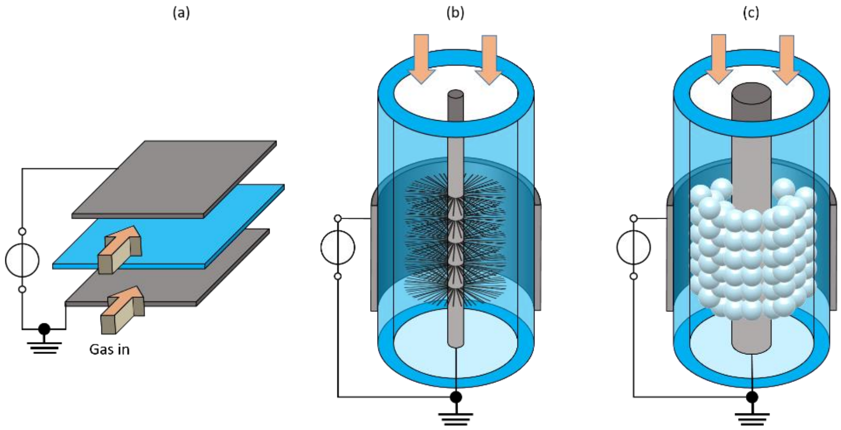
[1] R. Snoeckx and A. Bogaerts, Chem. Soc. Rev. **46**, 5805-5863 (2017).
[2] A. Bogaerts and E. Neyts, ACS Energy Lett. **3**, 1013-1027 (2018).
[3] K.H.R. Rouwenhorst, Y. Engelmann, K. van ‘t Veer, R.S. Postma, A. Bogaerts and L. Lefferts, Green Chemistry, **20**, 6258-6287 (2020).
[4] K.H.R. Rouwenhorst, F. Jardali, A. Bogaerts and L. Lefferts, Energy Envir. Sci., 14, 2520-2534 (2021).

CO_2 Splitting in Dielectric Barrier Discharges: Prospects to Increase CO Formation

R. Brandenburg[1,2], **M. Schiorlin**[1], **R. Hosseini Rad**[1],
H. Mahdikia[1], **D. Adrianto**[1] **and V. Brüser**[1]

[1]Leibniz-Institute for Plasma Science and Technology, Greifswald, Germany
[2] University of Rostock – Institute of Physcis, Rostock, Germany

Dielectric barrier discharges (DBDs) as robust and well-scalable nonthermal plasma reactors are one option for a plasma-based conversion of carbon dioxide by using intermittent renewable energy for new power-to-X approaches [1]. Although a direct combination with catalysts can be realized in this type of discharge, their energy efficiency is significantly inferior to that of microwave plasmas or gliding arcs. This contribution will evaluate how the energy yield of carbon monoxide (CO), a component of the chemical feedstock syngas, can be improved by the parameters of DBD reactors. Inter alia, the role of the barrier material and thickness, the discharge gap, the operation pressure and gas composition as well as the discharge geometry will be investigated. The variation of the parameters is accompanied, in addition to the study of CO formation, mainly by extensive electrical investigations taking into account non-fully electrode coverage by plasma and parasitic capacitances in the electrical circuit. This is necessary to accurately determine the plasma power and to derive correlations between discharge physics and plasma chemistry.



The studies compare three different discharge geometries, namely (a) plane parallel volume DBDs; (b) coaxial barrier corona discharges and (c) coaxial packed-bed DBDs with and without catalysts [2].

References

[1] A. Bogaerts and G. Centi, Front. Energy Res. **8**, 111 (2020)
[2] R. Hosseini Rad et al. Chem. Eng. J. **456**, 141072 (2023)

Atomistic Modeling of Plasma-Assisted Catalysis: Opportunities and Challenges

Bryan R. Goldsmith

Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA

Low-temperature plasma (LTP)-assisted catalysis is a growing field of research that has reported a variety of synergistic effects for increased activity, yield, or selectivity compared to conventional thermocatalytic processes. The effect of LTP on many surface-catalyzed reactions is multi-faceted and not well-understood at an atomistic level. Atomistic modeling via quantum chemical methods have provided numerous insights into catalyst structure-property relations and reaction mechanisms for thermocatalytic and electrocatalytic systems, but much progress remains to bring understanding of LTP-assisted catalysis to the same level. Modeling LTP-assisted catalysis by quantum mechanical, molecular simulation, and microkinetics approaches has the capability to elucidate underlying structure-property-mechanism relations of catalysts as a function of the LTP conditions. In this talk, I will discuss the state-of-the-art in terms of atomistic modeling of LTP-assisted catalysis, on-going challenges, and opportunities for progress. I will also highlight some recent research from our lab on modeling LTP-induced surface charge effects on small molecule activation by metal catalysts supported on metal oxides.

Role of vibrational and electronic excited states for CO_2 conversion by plasma

O. Guaitella[1], E. Barrate[1], D. Sadi[1], C.A. Garcia Soto[1],
T. Silva[2] and V. Guerra[2]

[1] Laboratoire de Physique des Plasmas (UMR 7648), CNRS, Univ. Paris-Saclay,
Sorbonne Université, École Polytechnique, France
[2]Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Univ. de Lisboa,
Portugal

The role of CO_2 vibrations is often mentioned as being crucial for efficient CO_2 conversion by plasma, whether for methanation, dry reforming or even methanolization. The role that excited electronic states could play is much less often mentioned. Both vibrational and electronic states can carry a significant amount of energy and therefore it is essential to take them into account if one wants to describe the energy of the electrons in the plasma correctly [1].

The lifetime of these excited states is very short at atmospheric pressure, and therefore it is very difficult to measure their density. In order to elucidate their role, experiments dedicated to the comparison with 0D kinetic models have been conducted for several years [2]. They are measurements carried out in glow discharge or radiofrequency reactors at a few mbar, in open or closed reactor. In these reactors, it is possible to carry out measurements with many techniques, in particular infrared absorption, allowing determining not only the absolute densities of molecules but also their vibrational temperature, as well as the electric field and the gas temperature. Thanks to these "benchmark" systems, it is then possible to constrain step by step kinetic models that allow to highlight the role played by the vibrations of CO_2 and CO, but also of excited electronic states like $CO(a^3\Pi)$ or $O(^1D)$. These studies were first carried out in pure CO_2 [3] but they are now performed in other mixtures such as CO_2/H_2 or CO_2/CH_4. When the chemical kinetics of the plasma phase is sufficiently well understood, it becomes possible to use the same plasma but this time to expose catalytic surfaces, which can in turn be studied by infrared absorption spectroscopy. The combination of *in situ* and time-resolved measurements of the gas phase and the adsorbed phase in a single system offers unique information to try to understand the plasma/catalyst interaction.

This work was partially supported by the European Union's Horizon 2020 research and innovation programme under grant agreement MSCA ITN 813393.

References

[1] L. D. Pietanza, O. Guaitella *et al*, *Eur. Phys. J. D* **75** (2021) 237
[2] Klarenaar, B. L. M., et al. *Plasma Sources Sci. and Tech.* **26** (2017): 115008
[3] A.S. Morillo-Candas, et al. *The Journal of Physical Chemistry C* **124**.32 (2020): 17459-17475

Plasma chemistry and thermal-chemical instability

Yiguang Ju[1] and Hongtao Zhong[1]

[1]*Princeton University, Princeton, USA*

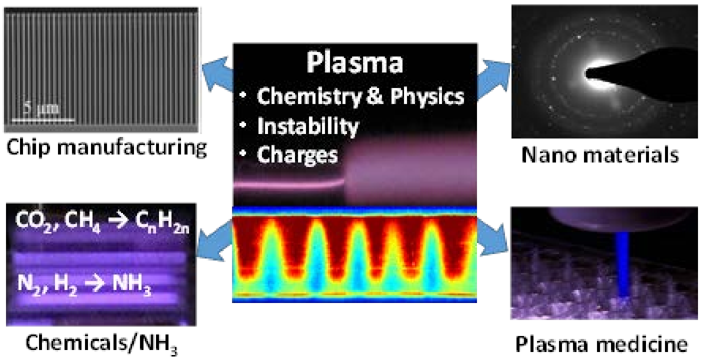


Fig. 1 Schematic of understanding and control of plasma chemistry, properties, instability, and surface and space charges for advanced plasma manufacturing and bio-applications.

Non-equilibrium plasma provides new reaction pathways and reduces activation energies via excited states and active species to enhance chemical reactions and enables higher efficiency and selectivity in energy and chemical conversion. Unfortunately, at elevated pressures and with strong plasma-surface interaction, plasma becomes intrinsically unstable and thus leads to a critical challenge for chemical manufacturing [1, 2]. Recently it has been found that plasma instability is not only affected by the thermal mechanism but also by plasma chemistry. A new concept of plasma themal-chemical instability was proposed [1-3]. Therefore, it is important to understand the mechanisms and selectively control the plasma chemistry and plasma thermal-chemical instability at elevated pressures in plasma catalysis for advanced plasma manufacturing of materials and chemicals (Fig. 1). This lecture will present an overview of the recent development in the studies of plasma chemistry and thermal-chemical instability and their impact in plasma assisted combustion as well as chemicals and materials synthesis. The lecture will first discuss the phenomenon and theory of plasma thermal-chemical instability. Then, experimental and computational studies of thermal chemical instabilities with different reactants and diluents will be examined. Finally, control of plasma chemistry and thermal-chemical instability using fractal electrode, aerosols, and surface charge will be discussed.

References

[1] Zhong H, Shneider M, Mao X, Ju Y.. Plasma Sources Science and Technology. 2021;30:035002.

[2] Zhong H, Yang X, Mao X, Shneider MN, Adamovich IV, Ju Y., Plasma Sources Science and Technology. 2022;31:114003.

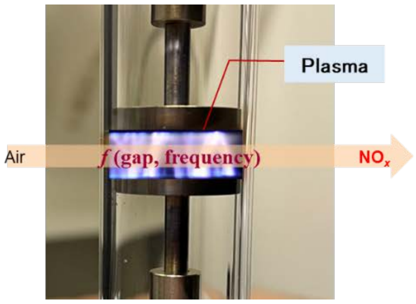
[3] Zhong H, Shneider MN, Mokrov MS, Ju. Journal of Physics D: Applied Physics. 2019;52:484001.

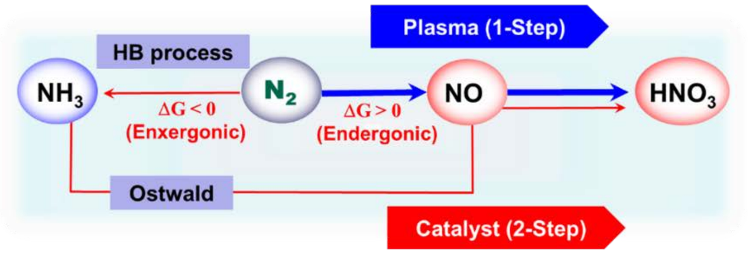
Sustainable nitrogen fixation using spark discharge plasma for power-to-X

Hyun-Ha KIM[1] **and Ayman A. Abdelaziz**[1]

[1]*National Institute of Advanced Industrial Science and Technology (AIST),*
Tsukuba Ibaraki, Japan

Plasma nitrogen fixation is one of the promising processes for electricity-driven valuable compounds which is also referred to as power-to-X (X = H_2, NH_3, NOx, alcohols, etc) processes. Haber-Bosch process has been the key technology of nitrogen fixation over 100 years, which is also representative chemical processing based on high temperature and high pressure. In this work, we aimed to present a deep understanding of NO_x formation by nonthermal plasma and to unveil the most crucial parameters to reduce energy cost. To this end, NOx formation in DBD and spark discharge reactors was investigated under various operating conditions. Rotational and vibrational temperatures were estimated using optical emission spectroscopy and theoretical fitting. The spark discharge is more efficient due to its ability to generate more vibrational excitation, which is pivotal to reduce the energy cost. Moreover, the proper design of the plasma reactor to provide larger plasma-air processing is important. Meanwhile, the gas flow rate and temperature have an influence on the selectivity and no effect on reducing the energy cost, as the energy cost follows the energy density.





References

[1] HH Kim *et al*, Plasma Chem. Plasma Process. **36**, 45-72 (2016)
[2] HH Kim *et al*, Int. J. Plasma Environ. Sci. Technol. **15**, e01004 (2021)
[3] A. Abdelaziz *et al*., J. Phys. D: Appl. Phys **53**, 114001 (2020)
[4] A. Bogaerts *et al*., J. Phys. D: Appl. Phys **53**, 443001 (2020)
[5] I. Adamovich *et al*., J. Phys. D: Appl. Phys **55**, 373001 (2022)

Using expertise in catalysis for understanding plasma-catalysis

Leon Lefferts

University of Twente, Faculty of Science and Technology, P.O. Box 217, 7500AE, Enschede, the Netherlands

This presentation discusses how expertise in testing of heterogeneous catalysts can be translated to plasma catalysis, aiming at strengthening the interpretation of steady-state experimental results. In addition, we will discuss the relationship between kinetics and thermodynamics, which is essentially different for plasma catalysis compared to thermal catalysis. We will exploit relatively straightforward conceptual theory generally accepted in the field of catalysis, i.e. Langmuir-Hinshelwood and Eley-Rideal reaction mechanisms, to improve qualitative understanding of plasma catalysis.

Determination of activity of catalysts for plasma-enhanced catalytic reactions requires independent determination of plasma-catalytic and plasma-chemical contributions. Non-porous catalyst particles are preferred with active sites, e.g. surface metal atoms in the surface of supported nanoparticles, exclusively at the outer surface in order to have an accurate number of active sites. Appropriate characterization to determine the number of active sites is required. Active sites within nm-sized pores cannot contribute because plasma cannot form in such confined space and because of sluggish diffusion inside pores compared to the life-time of plasma-activated species. Size, shape and packing of catalyst particles and bare support particles should be identical in order to minimize any changes in plasma chemistry via physical effects of the solids on the plasma.

Experiments at low conversion and far from thermodynamic equilibrium are even more important for plasma catalysis than for thermal catalysis because of plasma-enhanced reversed reactions, which would lead to underestimation of the rate of the forward reaction.

Using a plasma in combination with a catalyst influences the conversion and reaction rates in three ways:

- via decreasing the activation barrier of the forward reaction
- via the surface coverage of adsorbed species on the catalyst surface
- via decreasing the activation barrier of the backward reaction, especially when surpassing equilibrium of molecules in ground-state

Chemical production by plasma catalysis for industrial processes

A. B. Murphy[1], B. E. Ashford[1], Y. Yang[2], S. Ullah[2], J. Hong[3,4], R. Zhou[3], T. Zhang[3], R. Zhao[3,4], P. J. Cullen[3], K. Ostrikov[4]

[1]CSIRO Manufacturing, P.O. Box 218, Lindfield NSW 2070, Australia
[2] CSIRO Energy, Private Bag 10, Clayton South VIC 3169, Australia
[3] School of Chemical and Biomolecular Engineering,
University of Sydney NSW 2006, Australia
[4] School of Chemistry and Physics and Centre for Materials Science,
Queensland University of Technology, Brisbane QLD 4000, Australia

Plasma catalysis is being developed for several chemical processes, including ammonia production, dry reforming of methane and CO_2 hydrogenation. Its advantages over thermal catalysis include operating at ambient conditions and small scales, using electrical power, and turning on and off rapidly, all of which increase compatibility with renewable energy sources [1].

Plasma catalysis processes are all at low TRL (technology readiness level), and some fundamental problems have emerged. Probably the most critical is the limited energy efficiency, which is a consequence of the high electron energies typical of dielectric barrier discharges. These favour high-energy (gas-phase dissociation of molecules followed by surface adsorption) over low-energy reaction pathways (vibrational and electronic excitation of molecules followed by dissociative adsorption) [1].

These and other limitations will be discussed, as well as novel approaches that may assist in overcoming the difficulties. Strategies under investigation include choosing different reactants [2] and novel catalysts, implementing hybrid reactor designs [3], and pulsed reactor excitation. The prospects for industrial application of plasma catalysis will be assessed. The talk will focus on ammonia production, but other processes will be considered.

References

[1] A. Bogaerts, E. C. Neyts, O. Guaitella, A. B. Murphy, Plasma Sources Sci. Technol. **31** 053002 (2022)
[2] J. Hong, T. Zhang, R. Zhou, L. Dou, S. Zhang, R. Zhou, B. Ashford, T. Shao, A. B. Murphy, K. Ostrikov, P. J. Cullen, Green Chem. **24** 7458 (2022)
[3] R. K. Sharma, H. Patel, U. Mushtaq, V. Kyriakou, G. Zafeiropoulos, F. Peeters, S. Welzel, M.C.M. van de Sanden, M. N. Tsampas, ACS Energy Lett. **6** 313 (2021)

In situ diagnostics of plasma catalytic conversion of CO_2: identifying the synergistic pathways toward catalyst design

<u>T. Nozaki</u>, D.-Y. Kim, X. Chen

Dept of Mechanical Engineering, Tokyo Institute of Technology
2-12-1 O-okayama, Meguro, Tokyo, Japan

This paper describes the plasma-catalyst hybrid reaction of reverse water-gas-shift reaction ($CO_2 + H_2 = CO + H_2O$). The intermetallic Pd_2Ga/SiO_2 alloy catalyst was studied for this purpose. CO_2 conversion was doubled when dielectric barrier discharge (DBD) was applied, which exceeded the thermodynamic equilibrium limit. *in situ* transmission infrared (*in situ* TIR) spectroscopy was employed, showing both the formation and decomposition of monodentate formate (m-HCOO) were promoted by DBD: first, vibrationally excited CO_2 promotes m-HCOO formation via Eley-Rideal (E-R) mechanism. Second, DBD increases surface hydrogen which induces H-assisted decomposition of m-HCOO. Such microscopic reaction behavior was verified by the fluidized-bed DBD reactor [1]. The apparent activation energy for the thermal reaction was E_t = 75 kJ/mol, while that for plasma catalysis was E_p = 44 kJ/mol [2]. The difference between activation energy (75–44 = 31 kJ/mol) is greater than the activation energy to bending mode vibration of CO_2 (ca. 8 kJ/mol). This is explained by the molecular orbital change of bending mode CO_2 in which the LUMO level of CO_2 decreases, promoting the interaction with surface hydrogen. Moreover, the surface hydrogen is increased by DBD. This kind of drastic reaction promotion is possible with a polyatomic molecule such as CO_2 [2] and CH_4 [3], but may not occur with a diatomic molecule because only stretching vibration is possible which does not change molecular orbital significantly.

The activity of Pd_2Ga/SiO_2 alloy catalyst was compared with the monometallic Pd/SiO_2 catalyst. Formation of m-HCOO with Pd/SiO2 is explained by the Langmuir-Hinshelwood mechanism due to the significant energy barrier for the E-R path. This indicates the Ga alloy intrinsically promotes E-R pathway which is further facilitated by bending mode CO_2. Meanwhile, the activation barrier for m-HCOO decomposition for Pd and Pd2Ga is essentially the same and this process is unrelated to CO_2. Therefore, Ga-alloyed does not play a role, but the H-rich surface induced by DBD promotes hydrogen-assisted m-HCOO decomposition rather than spontaneous m-HCOO decomposition.

Ack: The project is supported by JST CREST (JPMJCR19R3).

[1] X Chen, H-H Kim, T Nozaki, *Plasma Process. Polym.*, e2200207, 2023.
[2] D-Y Kim, H Ham, X Chen, S Liu, H Xu, et al, *JACS*, **144**, 14140–14149, 2022.
[3] Z Sheng, Y Watanabe, H-H Kim, S Yao, T Nozaki, *Chem. Eng. J.*, **399**, 125751, 2020.

Key species in plasma-aided ammonia synthesis: atomic nitrogen versus molecular nitrogen at vibrational excited states

Koichi Sasaki

Division of Applied Quantum Science and Engineering, Hokkaido University, Sapporo, Japan

It is believed that the key step in the catalytic synthesis of ammonia is surface adsorption of nitrogen. The difficulty in the adsorption of nitrogen is basically due to the high dissociation potential of molecular nitrogen, and it is expected that the generation of a plasma is helpful to enhance the adsorption rate by transporting atomic nitrogen from the plasma gas phase. However, because of the toughness of molecular nitrogen, the degree of dissociation in a nitrogen plasma is usually less than 0.1%. On the other hand, it is also known that the probability of dissociative adsorption of molecular nitrogen is enhanced if it is excited vibrationally. Since vibrational temperatures are usually higher than gas temperatures in nonequilibrium plasmas, it is possible that the production of vibrationally excited molecular nitrogen is the mechanism for the plasma-assisted catalytic synthesis of ammonia. In this talk, we will try to show correlations among the flux of atomic nitrogen, the flux of molecular nitrogen at vibrational excited states, and the synthesis rate of ammonia.

We employed three plasma sources: a helicon-wave excited high-density plasma, a miniature electron cyclotron resonance (ECR) plasma, and an atmospheric-pressure plasma jet. In the helicon-wave plasma, in which both the densities of atomic nitrogen ($n_N=10^{13}$ cm^{-3}) and vibrationally excited molecular nitrogen ($T_v=0.3$ eV with $n_{N2}=10^{14}$ cm^{-3}) were high, we observed linear correlation between the conversion from nitrogen to ammonia and the density of vibrational excites states, whereas the conversion was saturated when it was plotted as a function of the atomic nitrogen density. In the miniature ECR plasma ($n_N=10^{11}$ cm^{-3}, $T_v=0.1$ eV, and $n_{N2}=10^{14}$ cm^{-3}), the correlations were rather ambiguous and it was speculated that both atomic nitrogen and vibrationally excited molecular nitrogen contributed to the ammonia synthesis. In the atmospheric-pressure plasma jet ($n_N=10^{14}$ cm^{-3}, $T_v=0.1$ eV, and $n_{N2}=10^{21}$ cm^{-3}), we observed the correlation between the synthesis rate and the density of vibrational excites states, but the synthesis rate did not correlate with the density of atomic nitrogen. These results suggest that the probability of surface adsorption of atomic nitrogen is much higher than that of vibrationally excited molecular nitrogen. However, vibrationally excited molecular nitrogen can play a leading role if its density exceeds the density of atomic nitrogen by orders of magnitude.

This work was supported by JST CREST Grant No. JPMJCR19R3.

Demand and technologies of energy storage technologies for a climate neutral world

Dirk Uwe Sauer[1, 2, 3]

[1] Center for Ageing, Reliability and Lifetime Prediction for Electrochemical and Power Electronic Systems (CARL), RWTH Aachen University, Germany,
Campus Boulevard 89, 52074 Aachen, Email: sr@isea.rwth-aachen.de
[2] Helmholtz Institute Münster (MEET), Aachen, Germany
[3] E.ON Energy Research Center @ RWTH Aachen University, Aachen, Germany

The advancing climate change makes a rapid restructuring of the energy supply to reduce and ultimately completely avoid fossil CO_2 emissions worldwide imperative. Thanks to successful scientific work and comprehensive market introduction programmes in some countries of the world, two technologies are available today in the form of wind power technology and photovoltaics, which can already generate electricity at unrivalled low cost in many places in the world. In order to realise a reliable supply with the fluctuating power generation from wind and sun, storage facilities are necessary on a large scale in addition to comprehensive load management and the flexible use of controllable renewable power generators such as biogas or hydropower.

A distinction must be made between storage systems that feed electricity back into the grid when they are discharged ("power-to-power energy storage") and the transfer of energy to other application sectors ("power-to-X"), in which storage systems must then be used again. The latter includes, for example, heat storage, fuels or basic materials for industrial production such as methanol, ammonia or other liquid or hydrocarbons.

The lecture will present the various technologies and discuss their development status and market introduction as well as the need for further research and development. It will also be considered which technology will most likely be dominant in the market in the next 15 years.

In addition, in the area of storage for the electricity system, it must be considered which system services must be provided by storage and where in the structure of the hierarchically organised electricity grid they should be integrated. The requirements for storage facilities are derived from this. It becomes clear that in the area of storage for the electricity grid, the investment and life cycle costs as well as the ecological footprint play a role, while in the case of battery storage in mobility, the gravimetric and volumetric energy density play an important role in addition to the costs. It will also be considered where battery-based storage and where gas-based storage (hydrogen and its derivatives) will be the means of choice, and how the availability of raw materials and concepts of the circular economy may affect the choice of technologies.

Plasmachemistry in pulsed nanosecond discharges: what changes at high electric fields and at high specific energy deposition

S. Starikovskaia[1]

[1]lLaboratoire de Physique des Plasmas (LPP), CNRS, Sorbonne Université,
Université Paris-Saclay, École Polytechnique, Institut Polytechnique de Paris,
route de Saclay, Palaiseau, 91128 France

Nanosecond pulsed discharges allow operation in a wide range of pressures: from parts of mbar to tens of bar. Stability of the discharge in such a wide pressure range is a reason of a long list of potential industrial applications: from non-destroying treatment of plastics or polymer samples to plasma-assisted medicine, aerodynamics, combustion and detonation. At moderate pressures, units – to tens of mbar, easy control of specific energy deposition (SED) and reduced electric field is possible and proved experimentally. The SED can be within the range of 0.001 to 10 eV/molecule at high electric fields, hundreds of Td. The discharges are (i) uniform at low and moderate gas densities; (ii) naturally synchronized in time in the case of a multi-streamer configuration at high gas densities; (iii) provide efficient excitation and dissociation of the gas at a time scale shorter than the typical time scale of "conventional" kinetics not related to plasma chemistry [1,2].

The talk will review the work done by the group of kinetics of nanosecond discharges in the direction of studying of plasma parameters and optimizing plasma chemistry, as well as available picosecond and nanosecond plasma diagnostic. In particular, the kinetics with participation of electronically excited molecules and atoms, explaining complete dissociation of O_2 in moderate pressure discharge in air and 10% dissociation degree of N_2 in the discharge in nitrogen, as well as experimental confirmation by ns-TALIF (two-photon absorption laser induced fluorescence) measurements, will be presented. A brief analysis of plasma parameters in nanosecond discharges, from fast ionization waves (FIWs) at moderate pressure to filamentary nanosecond surface dielectric barrier discharges (nSDBDs) at tens of bars will be given. Consequences of developed chemistry of excited species for plasma diagnostics and necessary precautions when treating the data will be discussed.

References

[1] S.M. Starikovskaia, J. Phys. D: Appl. Phys. **47**, 353001 (2014)

[2] N.A.Popov and S.M. Starikovskaia, Progress in Energy and Combustion Science **91,** 100928 (2022)

Plasma catalysis: An emerging technology for sustainable production of fuels and chemicals

X. Tu

Department of Electrical Engineering and Electronics, University of Liverpool, Liverpool, UK

The the synthesis of value-added fuels and chemicals from inert molecules with strong chemical bonds (e.g., CO_2, CH_4, and N_2) has generated significant interest [1-5]. However, these molecules are thermodynamically stable and require a significant amount of energy for activation, making their conversion a challenge. Non-thermal plasma (NTP) is an emerging technology that shows promise for gas conversions under ambient conditions. Combining NTP with heterogeneous catalysis has the potential to generate a synergistic effect from interactions between the plasma and catalysts, which can activate catalysts at low temperatures and improve their activity and stability of the catalysts. This can result in a remarkable increase in conversion, selectivity, and yield of target products, as well as the energy efficiency of the process. Moreover, plasma processes can be turned on and off instantly, providing great flexibility in decentralised chemical production using renewable energy sources, particularly intermittent renewable energy. This presentation will focus on the latest advances in the use of plasma catalysis for the synthesis of fuels and chemicals through various chemical processes such as biogas conversion [1], CO_2 conversion [2][3], and ammonia synthesis [4][5].

References

[1] Wang et al., *Angew. Chem. Int. Ed.* 56, 13679-13683 (2017).
[2] Wang et al., *ACS Catal.* 8, 90-100 (2018).
[3] Sun et al., *JACS Au*, 2, 1800-1810 (2022).
[4] Wang et al., *ACS Catal.* 9, 10780-10793 (2019).
[5] Wang et al., *J. Am. Chem. Soc.* 144, 12020-12031 (2022).

Non-thermal plasma conversion of CO_2, N_2/O_2 & CH_4

Richard van de Sanden[1,2]

[1]DIFFER), Eindhoven, The Netherlands
[2]Department of Applied Physics, EIRES, Eindhoven, The Netherlands

In this talk I will give an overview of the status of non-thermal plasma conversion of CO_2, N_2/O_2 and CH_4 using microwave generated plasmas. The background is renewable energy driving chemistry in which the non-thermal properties of plasma (difference in temperatures between the electrons, the molecules and their vibrational degrees of freedom), possibly with the assistance of catalysts, can drive chemical conversions beyond the thermodynamic limit. Important aspects as energy and conversion efficiency and the chemical conversion processes at play, as determined using several (in situ) diagnostics will be highlighted. In addition, some novel approaches in which plasma are combined with electrochemical conversion using hydrogen or oxygen transporting membranes and their potential advantgaes, will be discussed.

Non-Thermal Plasmas for Sustainable Chemistry

G.J. van Rooij

Department of Circular Chemical Engineering, Faculty of Science and Engineering,
Maastricht Unversity
g.vanrooij@maastrichtuniversity.nl

A carbon neutral and circular economy requires utilization of waste materials and biomass as feedstock for the production of new materials. Moreover, the energy input must be of zero carbon footprint, which currently implies that it concerns electric energy input that is intermittently available. Plasma technology carries distinct advantages and/or promises that make it suitable to make an impact in the transition to a circular economy such as compatibility with (intermittent) sustainable energy and unique opportunities for efficiency and/or selectivity in reactions with CO_2, N_2, and CH_4 [1].

Vibrational excitation effects were invoked to explain the very high energy efficiencies reported in the 80s and are still being embraced by the research community as key to success. This work invokes vibrational laser excitation to determine the limits of CO_2 dissociation by vibrational excitation alone [3]. In situ plasma temperature and species measurements in dynamic experiments confirm short timescales for the vibrational non-equilibrium [4]. The main opportunity that we recognize for vibrational excitation enhanced CO_2 dissociation occurs due to excitation transport to the plasma edges and recombination with oxygen atoms [5]. These results are extrapolated to opportunities for industrial application of plasma that are currently researched in the context of the Brightsite consortium, the knowledge center aiding the transition of the process industry at Chemelot in the southeast of the Netherlands [6].

References

[1] G. J. Van Rooij et al., Plasma Phys. Control. Fusion **60**, 014019 (2018)
[2] V. D. Rusanov et al., Soviet Physics Uspekhi **24**, 447 (1981).
[3] Q. Ong, PhD thesis, Eindhoven University of Technology (2022).
[4] A.W. van de Steeg et al., Plasma Sources Sci. Technol. **29**, 115001 (2020).
[5] A. van de Steeg et al., ACS Energy Letters 6, 2876 (2021).
[6] https://brightsitecenter.nl/

In-Liquid Plasmas for Electrolysis

K. Grosse, P. Pottkämper, and A. von Keudell

Chair for Experimental Physics II, Ruhr University Bochum, Bochum, Germany

Plasmas inside and in contact with liquids have been a highly promising field for plasma medicine or electrolysis. The understanding of the physics of the plasma ignition and sustainment is, however, still in its infancy due to the complexity of the phenomenon. For example, in the case of nanosecond high voltage pulses applied to a sharp tungsten electrode, electrostriction is very large so that rupture of the liquid occurs at a negative pressure of at least 24 MPa. Cavitation voids are formed and ignition inside these voids may occur. However, also field effects inside the liquid or at the tungsten liquid interface may cause ignition. Ignition converts the liquid spontaneously in the plasma state, which then expands this initial void to form a bubble. This creates a pressure pulse of the order of 10s of GPa depending on the HV voltage and the emission of acoustic waves that can be observed via shadowgraphy. The plasmas are observed with emission spectroscopy using a temporal resolution of 2 ns [1,2,3]. This reveals a broad continuum consisting of black body radiation and line radiation of the hydrogen Balmer series. The hydrogen emission lines are significantly broadened from Stark broadening and affected by self-absorption. It is shown that the plasma behave very similar for positive and negative polarity applied to the tungsten electrode. The plasma induced chemistry is used to activate a copper oxide surface used for as a catalyst for electrolysis. This activation process is monitored with in-situ infrared spectroscopy revealing a complex interplay between plasma and electrochemical activation of the interfaces.

References

[1] K. Grosse, M. Falke, A. von Keudell, J. Appl. Phys. **129**, 213303 (2021)

[2] K. Grosse, V. Schulz-von der Gathen, A. von Keudell, Plasma Sources Sci. Technol. **29**, 095008 (2020)

[3] A. von Keudell, K. Grosse, V. Schulz-von der Gathen, Plasma Sources Sci. Technol. **29**, 085021 (2020)

Plasma catalysis for CH_4/CO_2 conversion to alcohols

Y. Zhao[1], H. Xu[1] , X. Tu[2] and L. Wang[1]

[1]*Dalian Maritime University, Dalian, China*
[2] *University of Liverpool, Liverpool, UK*

Plasma catalysis is a promising way for CH_4/CO_2 conversion into high-value chemicals under mild conditions[1], eliminating the need for a two-step high-temperature and high-pressure process via syngas. However, the resulting products are complex, containing CO, hydrocarbons and oxygenates (e.g., alcohols, acids, ketones, and aldehydes). In our group, different strategies were exploited to tune the distribution of oxygenates (Fig.1)[2,3]. Results reveal that the valence state and acid type of catalysts are crucial for this reaction. Specifically, Cu^{2+} species are favorable to the formation of alcohols, whereas Cu^{+} species favors to produce acetic acid. Furthermore, in the condition of avoiding the interference of copper, the correlations of alcohols and acetic acid versus Lewis acid site (LAS) and Brønsted acid site (BAS) have been experimentally confirmed. The X zeolite with only LAS exhibits superior activity toward alcohols production. The HZSM-5 possessing rich BAS, however, significantly contributes to the generation of acetic acid. Very recently, high selectivities of methanol (> 90%) and ethanol (~85%) were individually achieved over the well designed catalysts.

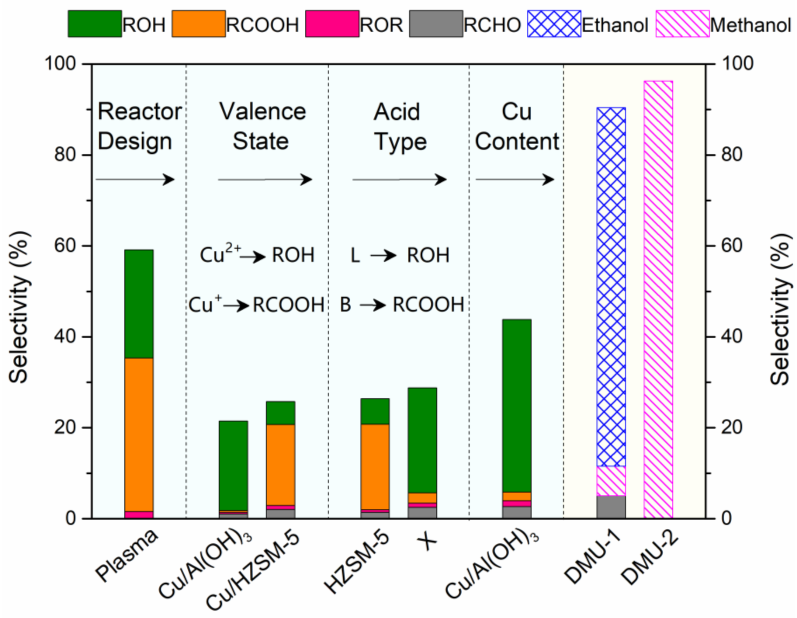


Fig. 1 Tuning the distribution of oxygenates in the plasma-catalytic CH_4/CO_2 reaction

References

[1] A. Bogaerts, et al. J. Phys. D: Appl. Phys. 53 (2020) 443001.
[2] L. Wang, et al. Angew. Chem. Int. Edit. 56 (2017) 13679
[3] Y. Wang, et al. Appl. Catal. B: Environ. 315 (2022) 121583.

Abstracts of Posters

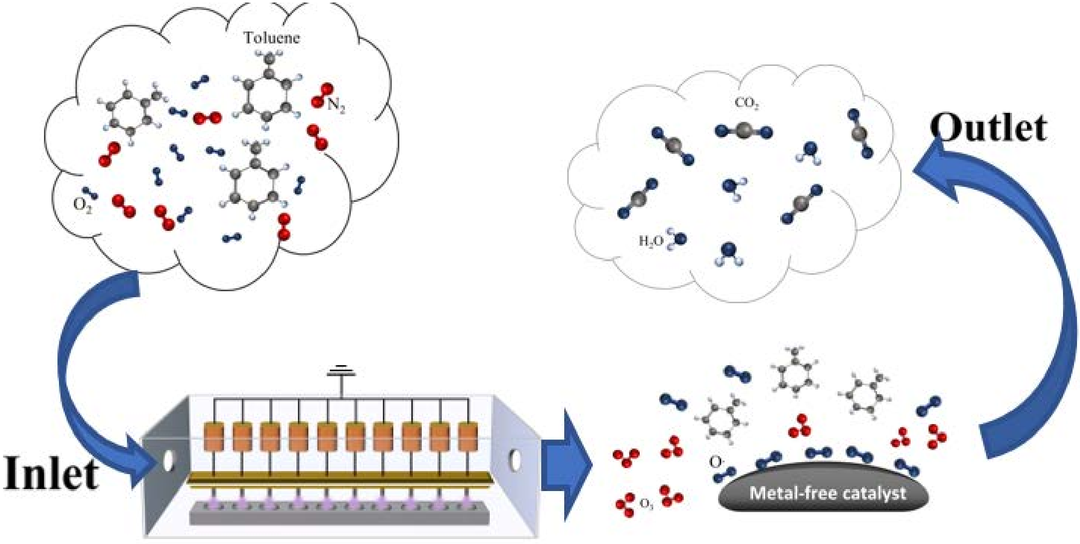
(in alphabetical order)

Toluene abatement by use of non-thermal plasma and metal-free catalyst

Moazameh Adhami[1] , Maryam Nilkar[1], Sara Abednatanzi[2], Pascal Van Der Voort[2], Rino Morent[1], Nathalie De Geyter[1,*]

[1] *Research Unit Plasma Technology, Department of Applied Physics, Ghent University, Belgium*
[2]*Center for Ordered Materials, Organometallics and Catalysis, Department of Inorganic and Physical Chemistry, Ghent University, Belgium*

Non-thermal plasma is a commonly studied method for the removal of volatile organic compounds (VOCs). However, this technique lacks selectivity and generates unwanted by-products. To overcome this limitation, combining non-thermal plasma with various catalysts has been explored as an alternative technology for efficient VOC abatement due to their promising selectivity and activity across different temperature ranges [1,2]. This study presents the development of a highly selective metal-free catalyst through a post-plasma catalysis process for removing low concentrations of toluene. The impact of electrical parameters and temperature on



References

[1]. T. Chang, Y. Wang, Y. Wang, Z. Zhao, Z. Shen, Y. Huang, S. K. P. Veerapandian, N. De Geyter, C. Wang, and Q. Chen, Science of The Total Environment 154290 (2022).
[2]. A. A. Adelodun, Journal of Industrial and Engineering Chemistry **92**, 41 (2020).

The energy cost of N_2 dissociation in a microwave discharge: combining modelling and experiments

M. Altin[1], P. Viegas[2,], L. Vialetto[3], A. W. van de Steeg[4], S. Longo[5], G. J. van Rooij[1] and P. Diomede[1]

[1]Faculty of Science and Engineering, Maastricht University, 6211 KH Maastricht, The Netherlands

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

[3]Theoretical Electrical Engineering, Faculty of Engineering, Kiel University, Kaiserstraße 2, 24143 Kiel, Germany

[4]DIFFER - Dutch Institute for Fundamental Energy Research, 5612 AJ Eindhoven, The Netherlands

[5]Dipartimento di Chimica, Università degli Studi di Bari, 70126 Bari, Italy

The production of N radicals in microwave (MW) plasma discharges is investigated through both experiments and modeling. Particular attention is given to establish the effect of vibrational excitation to enhance radical production with respect to thermal equilibrium conditions.

A self-consistent 0D global model of the plasma core is developed for this purpose, including the novel Fokker-Planck approach to describe N_2 vibrational kinetics. Simulated values of gas, vibrational and electron temperature, and electron density are compared with experimental results, obtained through in-situ laser scattering diagnostics in the pressure range between 50 and 400 mbar, yielding good agreement.

Simulations show that dissociation is mostly reliant on the reaction $N_2(X,v) + N_2(A) \rightarrow N_2(v=0) + N + N$, and hence is strongly dependent on the population of vibrational levels. At 50 mbar, the production rate of N is increased by 4 orders of magnitude with respect to the thermal case. Above 100 mbar, the production rate of N matches the thermal prediction.

The sensitivity of the model to transport parameters and power density input has been investigated. The deposited power density drives the deposition of energy into different degrees of freedom, with high value of power density favoring initial fast heating of the plasma and reducing the non-equilibrium properties of the plasma discharge.

The energy cost of N_2 dissociation in a microwave discharge: combining modelling and experiments

M. Altin[1], P. Viegas[2,], L. Vialetto[3], A. W. van de Steeg[4], S. Longo[5], G. J. van Rooij[1] and P. Diomede[1]

[1]Faculty of Science and Engineering, Maastricht University, 6211 KH Maastricht, The Netherlands

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

[3]Theoretical Electrical Engineering, Faculty of Engineering, Kiel University, Kaiserstraße 2, 24143 Kiel, Germany

[4]DIFFER - Dutch Institute for Fundamental Energy Research, 5612 AJ Eindhoven, The Netherlands

[5]Dipartimento di Chimica, Università degli Studi di Bari, 70126 Bari, Italy

The production of N radicals in microwave (MW) plasma discharges is investigated through both experiments and modeling. Particular attention is given to establish the effect of vibrational excitation to enhance radical production with respect to thermal equilibrium conditions.

A self-consistent 0D global model of the plasma core is developed for this purpose, including the novel Fokker-Planck approach to describe N_2 vibrational kinetics. Simulated values of gas, vibrational and electron temperature, and electron density are compared with experimental results, obtained through in-situ laser scattering diagnostics in the pressure range between 50 and 400 mbar, yielding good agreement.

Simulations show that dissociation is mostly reliant on the reaction $N_2(X,v) + N_2(A) \rightarrow N_2(v=0) + N + N$, and hence is strongly dependent on the population of vibrational levels. At 50 mbar, the production rate of N is increased by 4 orders of magnitude with respect to the thermal case. Above 100 mbar, the production rate of N matches the thermal prediction.

The sensitivity of the model to transport parameters and power density input has been investigated. The deposited power density drives the deposition of energy into different degrees of freedom, with high value of power density favoring initial fast heating of the plasma and reducing the non-equilibrium properties of the plasma discharge.

Experimental and numerical study of the fundamental processes in a CO2-CH4 RF plasmas

E.Baratte[1] ,**T. Silva**[2], **V. Guerra**[2] **and O.Guaitella**[1]

[1]Laboratoire de Physique des Plasmas, Ecole Polytechnique-CNRS 91128, Palaiseau, France
[2]Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Portugal

Despite the strong applicative potential of CO_2-CH_4 plasmas, their understanding remains challenging because of their complexity. This work aims at bringing insights on the fundamental processes taking place in a low-pressure RF discharge by comparing experiment and models. A pulsed RF discharge is ignited in a cylindrical pyrex reactor at a pressure of 5Torr in a closed reactor (without any flow). Trains of plasma pulses (typically 5 to 10 pulses per train) are sent and an FTIR measurement yielding the densities of IR active species is taken after each train, as done in [1]. The evolution of the densities as a function of the time of plasma are obtained. A modelling of the system is done using the LoKI simulation tool. The kinetic scheme previously validated in the glow discharge [2] is completed with reactions including the C2HY species. LoKI is used to compute the evolution of the densities through the balance equations after each discharge and post-discharge. A relatively good agreement between modelling and experiment highlights several important pathways, such as the reaction between the excited O(1D) and the CH_3, already observed in [2]. The behaviour of the CH_4, which undergoes a decrease during the first seconds of the experiment followed by a reincrease, is attributed to surface processes.

References

1. A.S. Morillo Candas, *J. Phys. Chem. C*, 124, 32, 17459–17475 (2020)
2. E.Baratte, in preparation (2023)

Plasma Catalysis for CO2 reduction using liquid water as hydrogen source

Jairo Barauna[1,2*], Tomás Garcia[2], Olivier Guaitella[3], Monica Magureanu[4], Vasile I. Parvulescu[1]

[1]University of Bucharest - Department of Organic Chemistry, Biochemistry and Catalysis, Bucharest, Romania.
[2]CSIC, Instituto de Carboquímica, Zaragoza, Spain.
[3]LPP, CNRS, École Polytechnique, Sorbonne Université, Université Paris-Saclay, IP-Paris 91128, Palaiseau, France.
[4]National Institute for Laser, Plasma Radiation Physics, Magurele, Romania.

Reacting CO2 with H2O is an interesting way to obtain valuable compounds from available and cheap sources while at the same time recycling carbon dioxide. This is specially promising if liquid compounds can be generated since those are easier to transport and store. Plasma is a suitable technique to convert CO2, but using gaseous CO2 + H2O it does not lead to liquid products [1], while the use of liquid water proved to be able to achieve molecules as long acetic acid [2]. To further study this system, we bubbled CO2 either into pure water or into water with suspended catalyst particles (a slurry), catalysts chosen were MnO, Mn2O3, Mn3O4 and MnO2. The needle where the CO2 is added into the system also works as the high voltage electrode and plasma discharges form in the interior of the bubble. Using a high-speed camera, it was possible to obtain images from plasma developing in different stages of the raising bubble and to properly correlate those with the amount of power injected. Furthermore, the outlet gas was analyzed by Fourier-transform infrared spectroscopy (FTIR), the liquid after the discharge was analyzed by Total Organic Carbon, Time-of-flight mass spectrometry (TOFMS) and by evaporating the water it was able to collect a solid-like substance that was also analyzed by FTIR. Those confirmed the conversion of CO2 to CO in gas-phase and long-chain organic products as Tridecanoic Acid remaining in the liquid phase. Also, it was possible to observe the effect of the discharge on the catalysts, where the lower oxidation states of manganese in the oxides were less stable and were more prone to be partially converted into MnCO3.

Acknowledgments: The authors would like to thank MSCA ITN grant N° 813393.

References

[1] Ma et al. Plasma Chemistry and Plasma Processing **39.1**:109-124 (2019).
[2] Yang et al. ACS Energy Letters **6.11:** 3924-393 (2021).

Multiscale modeling of boron nitride nanotube synthesis and carbon nanotube synthesis and hydrogen production from natural gas pyrolysis

Yu. Barsukov[1], A. Khrabry[2], S. Jubin[1,2], S. Ethier[1] and I. Kaganovich[2]

[1]Princeton Plasma Physics Laboratory (PPPL), Princeton, NJ, United States
[2] Princeton University, Princeton, NJ, United States

The research focus of this work is on high temperature synthesis of boron nitride (BNNT) and mass production of carbon nanotubes (CNT) and hydrogen from natural gas with participation of metal catalyst nanoparticles. We performed multiscale modeling[1,2] using several kinetic approaches, such as transition state theory for quantum chemistry calculations of probabilities of chemical reactions, ab-initio and classical molecular dynamics, and thermodynamics analysis, which allow for the exploration of equilibrium mixture composition on a surface and inside the volume[1,3]. The research goal is to identify the critical factors that determine the appropriate process windows for BNNT and CNT growth. Namely, we identified a rate limiting step of N_2 fixation[1], i.e., incorporation into boron clusters, and determined that the low rate of this key step is the main impediment to large scale production of BNNTs. It is well known that BNNTs are synthesized from a B/N_2 mixture in a cooling reactor at temperature ranges below 4100 K (the boron condensation point) and above 2400 K, where boron exists in the form of liquid droplets. We showed that the processes of N_2 fixation and boron consumption leading to the formation of BNNT precursors do not occur on liquid boron droplets but through the N_2 dissociative chemisorption on small boron clusters in gas phase. The low effectiveness of the whole process is due to the low density of small boron clusters in the cooling reactor. Therefore, large scale BNNT synthesis can only be achieved in a reactor where generation of small boron clusters is maximized. In addition, we performed a complex chemical kinetic modeling of CNT growth from natural gas pyrolysis in the presence of metal catalyst particles with the goal of finding a process window for cost-effective methane conversion into CNT and H_2. We are identifying the optimal conditions where CNT forms without the formation of undesirable soot byproduct.

References

[1] Yu. Barsukov et al., Nanotechnology **32**, 475604 (2021)
[2] S. Jubin et al., Frontier in Physics **10** (2022)
[3] A. Khrabry et al., Phys. Chem. Chem. Phys. **21**, 13268 (2019)

Probing the kinetics of oxygen atoms in oxygen-containing discharges by cavity ringdown spectroscopy: potential applications to CO_2 conversion and plasma-assisted combustion

J.P.Booth[1] , S. Zhang[1], E. Baratte[1] , A-S Morillo-Candas[1], O.Guaitella[1] and T. Dias[2]

[1]LPP-CNRS, Ecole Polytechnique, Palaiseau, France
[2]IPFN, IST Lisbon, Portugal

Oxygen atoms play a key role in many plasma systems important for energy, including combustion and CO_2 conversion. Therefore, it is important to develop techniques to measure the absolute density of this species, ideally with spatial and temporal resolution. Two-photon LIF[1] is widely used, due to its excellent sensitivity and spatial and temporal resolution. Nevertheless, it requires a complex laser system, and absolute calibration of the results is complicated and imprecise. Recently a cavity ringdown spectroscopy (CRDS) technique has been developed for oxygen using the forbidden $O(^3P_2)\rightarrow O(^1D_2)$ transition at 630nm[2, 3], allowing calibration-free measurements of absolute oxygen atom densities and translational temperatures. We have applied this technique to DC positive glow discharges in O_2 and CO_2, in the pressure range 1-8 Torr, as well as in radiofrequency capacitively-coupled plasmas in O_2. These measurements highlighted the importance of surface processes in determining the steady-state atom densities, and in particular how these can drift significantly with time, causing difficulty in the comparison of results unless these effects are fully characterised.

References

[1] K. Niemi, V. Schulz-von der Gathen, and H.F. Dobele, Plasma Sources Science & Technology, **14**, 375, (2005)
[2] R. Peverall, S.D.A. Rogers, and G.A.D. Ritchie, Plasma Sources Science and Technology, **29**, 045004, (2020)
[3] J.P. Booth, A. Chatterjee, O. Guaitella, D. Lopaev, S. Zyryanov, A. Volynets, T. Rakhimova, D. Voloshin, A. Chukalovsky, Y. Mankelevich, and V. Guerra, Plasma Sources Science and Technology, **31**, 065012, (2022)

Plasma-catalytic CO_2 hydrogenation over Fe-Cu-based perovskite catalysts

Yuxiang Cai [1, 2], **Guoxing Chen** [3], **Annemie Bogaerts** [2, *], **Xin Tu** [1, *]

1 Department of Electrical Engineering and Electronics, University of Liverpool,
Liverpool, L69 3GJ, UK
2 Research group PLASMANT, Department of Chemistry, University of Antwerp,
Wilrijk-Antwerp, BE-2610, Belgium
3 Fraunhofer Research Institution for Materials Recycling and Resource Strategies IWKS,
Brentanostraße 2a, 63755 Alzenau, Germany

CO_2 is a greenhouse gas that contributes significantly to global warming and climate change. Its transformation into value-added fuels and chemicals is a topic of considerable interest, but the activation of CO_2 remains a major challenge due to its thermodynamic stability and high energy requirements. In this study, a plasma-catalytic approach was employed to hydrogenate CO_2 via the reverse water-gas shift (RWGS) reaction in a dielectric barrier discharge (DBD) reactor at low temperatures. A series of $LaMO_3$ (M = Mn, Ni, Fe, Ce, Co) perovskite catalysts were evaluated, and $LaFeO_3$ was found to have the best RWGS performance. Subsequently, a range of B-site partial substitution $La_{0.5}Sr_{0.5}Fe_xCu_{1-x}$ (x = 1, 0.9, 0.8) perovskite catalysts were developed and tested. All perovskite samples exhibited high stability, with $La_{0.5}Sr_{0.5}Fe_{0.9}Cu_{0.1}O_{3+\delta}$ demonstrating the greatest potential for promoting selective CO_2-to-CO conversion (with a selectivity of 97.2%) while suppressing CH_4 generation. This excellent catalytic performance can be attributed to modification in the catalyst's surface structure, including increased metal dispersion, smaller particle size, and stronger metal-support interaction. Additionally, the formation of the Fe-Cu alloy resulted in an electronically richer Fe state that facilitated CO_2 adsorption and conversion, while the remaining $La_{0.5}Sr_{0.5}FeO_{3+\delta}$ perovskite structure led to more oxygen vacancies and higher oxygen mobility, promoting the selective conversion of CO_2 to CO. To investigate the mechanism of plasma-induced surface reactions, a 0D plasma kinetics model was combined with in-situ Fourier transform infrared (FTIR) analysis. The results indicate that perovskite catalysts change the dominant pathway, with CHO radicals and surface COOH playing a critical role in the plasma-catalytic RWGS process.

A novel plasma-assisted hollow fiber membrane concept for efficiently separating oxygen from CO in a CO_2 plasma

Guoxing Chen[1], Marc Widenmeyer[2], Gert Homm[1], Anke Weidenkaff[1,2]

[1]Fraunhofer Research Institution for Materials Recycling and Resource Strategies IWKS, Alzenau, Germany
[2]Department of Materials and Earth Sciences, Technical University Darmstadt, Darmstadt, Germany

Plasma-based technologies providing extremely flexible ‘turnkey’ applications are increasingly attracting interest in renewable energy usage and CO_2 conversion into carbon neutral fuels [1-2]. Here, we report a breakthrough concept combining plasma and mixed ionic-electronic conductor, hollow fiber membranes for significantly enhancing the oxygen permeability which may stimulate the CO_2 conversion by direct product separation. Several CO_2-tolerant oxygen transport membrane (OTM) materials with high oxygen permeation fluxes have been developed in our previous studies [3-8]. In this work, structure and composition of $La_{0.6}Ca_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ (LCCF) hollow fiber membranes were characterized before and after oxygen permeation tests in a CO_2 plasma. The oxygen permeation flux can be increased by one order of magnitude via this new plasma-assisted hollow fiber membrane concept, reaching up to 4 ml min^{-1} cm^{-2} in a CO_2 containing atmosphere. A constant high oxygen permeation flux was maintained during long-term operation, which is of major importance for commercial application. The applied rapid switching between operation and stand-by demonstrated the additional strength of the setup to cope with a potential unstable supply when using renewable electricity. These results show that plasma-assisted CO_2 conversion combined with a LCCF hollow fiber membrane allows to simultaneously enhance oxygen permeation and CO_2 conversion by inhibiting the reverse reactions. Therefore, it may be considered as a future industrial procedure for the autarkic formation of C_1 platform chemicals from CO_2 and (excess) regenerative energy.

References

[1] A. Bogaerts et al., *ACS Energy Lett*. 3 (2018), 1013.
[2] G. Chen et al., *Appl. Catal. B: Environ*. 214 (2017), 114.
[3] G. Chen et al., *J. Membr. Sci*. 590 (2019), 117082.
[4] G. Chen et al., *J. Membr. Sci*. 595 (2020), 117530.
[5] G. Chen et al., *Chem. Eng. J.* (2019), 123699.
[6] G. Chen et al., Adv. Funct. Mater. 32(2022), 2105702.
[7] G. Chen et al., *Front. Chem. Sci. Eng*. 14 (2020),405
[8] G. Chen et al., *J. Membr. Sci*. 639 (2021),119783

Nonthermal plasma regeneration of deactivated catalysts used for plasma-catalytic VOC/PAH removal

R. Cimerman[1], J. Kšanová[1], L. Satrapinskyy[2] and K. Hensel[1]

[1]Division of Environmental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina, 842 48 Bratislava, Slovakia
[2] Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina, 842 48 Bratislava, Slovakia

A combination of nonthermal plasma with catalysis, i.e., plasma catalysis, usually provides higher energy efficiency and product selectivity than either nonthermal plasma or catalysis alone [1]. Therefore, plasma-catalytic processes are generally characterised by a lower yield of undesired by-products. However, the plasma-catalytic removal of complex volatile organic compounds (VOCs) or polycyclic aromatic hydrocarbons (PAHs) may lead to significant formation of the by-products deposited on the surface of the catalysts, eventually leading to their deactivation and, thus, to an overall reduction in process efficiency.

In this work, the cylindrical DBD reactors packed with various catalysts (Pt/γAl_2O_3, Pd/γAl_2O_3, TiO_2, $BaTiO_3$) were firstly employed for plasma-catalytic removal of toluene (VOC) or naphthalene (PAH) with synthetic air as a carrier gas [2]. Removal of the pollutants resulted in formation of several gaseous and solid by-products, some of them were found as undesired carbon deposits on the surface of the catalysts. Secondly, deactivated catalysts were regenerated by DBD reactors of the same geometry for several hours with oxygen as a carrier gas at ambient or elevated temperature (100°C). Regeneration of the catalysts led to formation of gaseous products (CO_2, CO and HCOOH) as a result of oxidation of solid carbon deposits and their concentration as a function of time was evaluated. A level of the catalyst regeneration strictly depended on the material of the catalysts. The analysis of regeneration products was performed by FTIR. Surface of the catalysts was analysed by SEM and optical microscopy. Finally, regenerated catalysts were reused for toluene removal experiments for several cycles. The results obtained with regenerated catalysts were compared with those non-regenerated.

This work was supported by grants of Slovak Research and Development Agency APVV-20-0566 and Slovak Grant Agency VEGA 1/0822/21.

References

[1] H.-H. Kim, et al., *Int. J. Plasma Environ. Sci. Technol.* **15**, e01004 (2021)
[2] R. Cimerman, M. Cíbiková, L. Satrapinskyy, K. Hensel, *Catalysts* **10**, 1476 (2020)

Sustainable chemical synthesis through plasma-liquid interactions in a helical DBD microreactor

P. Dimitrakellis[1,2], **F. Cameli[1]**, **D. Nguyen[1]** **and D. G. Vlachos[1]**

[1] Delaware Energy Institute (DEI), University of Delaware, Newark, Delaware, USA
[2] Centre for Research and Technology Hellas / Chemical Process and Energy Resources Institute (CERTH/CPERI), Thessaloniki, Greece
Email: p.dimitrakellis@certh.gr

Plasma processing is gaining momentum as a novel and greener chemical synthesis route due to its ability to perform reactions at ambient conditions using electrical energy. Plasma microreactors integrate microflow with discharges in submillimeter scale, enabling a highly reactive environment at mild operating conditions and low energy input. This unique combination is particularly beneficial for plasma-liquid interactions due to the enhanced interfacial area between phases and mass transfer at the microscale [1]. Biphasic microreactors are usually complex. We present a simple and modular microreactor design based on a helical dielectric barrier discharge (DBD) that enables high interfacial area, adjustable residence time, and high productivity of valuable molecules [2]. We have applied our technology to the synthesis of hydrogen peroxide from water using inert gas plasma, as well as the synthesis of valuable gases like hydrogen and ethylene and high-value liquid oxygenates from abundant feedstocks.

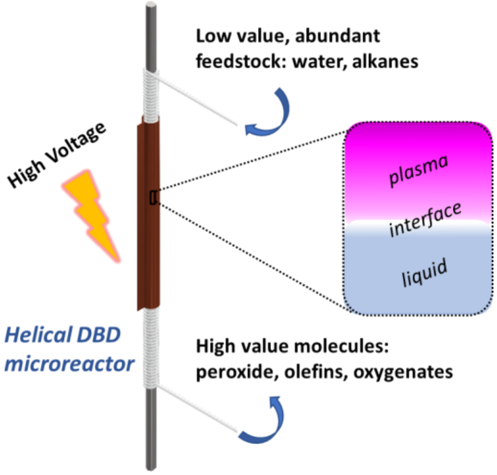


Figure 1: Helical DBD microreactor for sustainable chemical synthesis.

References

[1] T-Y. Chen, Y. W. Hsiao, M. Baker-Fales, F. Cameli, P. Dimitrakellis, D. G. Vlachos, Chemical Science **13** 10644 (2022)

[2] F. Cameli, P. Dimitrakellis, T-Y. Chen, D. G. Vlachos, ACS Sustainable Chemistry and Engineering **10** 1829 (2022)

CO_2 VALORIZATION VIA PLASMA CATALYSIS

Christian Koch[1], **Juliane Titus**[1,2], **Martin Drößiger**[1], **Torsten Lorenz**[1]
[1]*enaDyne GmbH, Turmhofstraße 1, 09599 Freiberg*
[2]*Institute of Chemical Technology, Universität Leipzig, Linnéstr. 3, 03103 Leipzig*
Email: CK@enaDyne.de

Methane and carbon dioxide are two main contributors to the greenhouse effect. A feedstock of both gases is biogas, from which recently the methane is thermochemically used. The activation of thermodynamically highly stable molecules is challenging, hence, elevated temperatures are needed for their conversion in the so called dry reforming of methane in which CO_2 and CH_4 are converted to form synthesis gas. An alternative pathway to thermal catalysis is the excitation of the reactants in a plasma [1] which would allow a one-step synthesis of valuable hydrocarbons, e.g. alcohols or ethylene, with a negative carbon footprint.

By using a novel electrode material, a plasma can be ignited which is indicated to be in a highly diffusive plasma-mode (Fig. 1). Within the "Carbon to Value Challenge" of SprinD, the electrode material was adjusted to improve the plasma-active properties. Here, a data-driven optimization allowed an accelerated adjustment of the materials composition and properties. Compared with the equivalent non-optimised material composition and the identical operating parameters such as gap width, pressure, frequency, pulse width, volume flow and stoichiometric ratio of CO_2 and CH_4, a reduction of the ignition voltage by more than 52 % was achieved. As a consequence, a reduction of the reduced electric field (E/n) can also be expected. In this manner, a vibration ("ladder-climbing dissociation") based activation of CO_2 [2] and CH_4 is pursued, resulting in a highly energy-efficient and reaction-selective synthesis of valuable hydrocarbons. [3]. It should be noted that in the applied set-up, a specific cooling is applied to reduce the influence of the plasma induced thermal catalysis. Hence, the influence of solely the non-thermal plasma onto reactant conversion and product selectivity is investigated.

Fig. 1: *Image of the plasma generated using the novel electrodes in presence of a catalyst.*

Not only the electrode material is adjusted to stir the reaction pathway towards hydrocarbons, but also the addition of a catalyst within the plasma. Even in presence of a catalyst, the determined energy input needed to ignite the plasma in a stream of CH_4 and CO_2 suggest, that the excitation of reactants follows the so "ladder-climbing" pathway. Hence, the dissociative pathway is expected to be suppressed. Not only is the energy input into the plasma reduced, the reaction product distribution is expected to be limited. The species produced tent to favor, e.g. C-C coupling, as short chained (≤ C4) hydrocarbons are found in the product gas stream. The presence of alcohols leads to the conclusion, that not only CH_4 is converted, but also the CO_2 is fixated within the reaction products.

By carefully selecting the electrode material and catalyst, enaDyne is able to valorize two challenging greenhouse gases via plasma catalysis.

References

[1] R. Michiels, Y. Engelmann, A. J. Bogaerts, *J. Phys. Chem. C* 124, 25859-25872 (2020)
[2] R. Snoeckx., A. J. Bogaerts, *Chem. Soc. Rev.*, 46, 5805-5863 (2017)
[3] A. J. Bogaerts, G. Centi, *Front. Energy Res.*, 8, 1-23 (2020)

Restructuring of Catalyst Materials by High Voltage Electrolysis

E. Artmann, T. Schmider, L. Forschner, T. Jacob, and A.K. Engstfeld

Institute of Electrochemistry, Ulm University, Ulm, Germany

The performance of an (electro)catalyst material is determined by its intrinsic activity, selectivity as well as stability during operating conditions. These aspects strongly depend on the structural properties of the catalysts (surface). To tune the structural properties of a catalyst or to understand the degradation of the catalyst, a fundamental atomic scale level understanding is required. Such information is hardly accessible from complex three-dimensional materials but can be derived from studying low-index single-crystal electrodes. For several decades, this approach has been successfully explored in electrocatalysis, where the applied potential is in the range of mV to a few volts (within or slightly above the stability range of the electrolyte). Performing electrolysis at significantly higher voltages, a plasma can be ignited in a gas sheath surrounding the plasma working electrode (contact glow discharge electrolysis - CGDE). This approach allows preparing catalyst materials (from the electrode or species in the solution) and induces (electro)chemical reactions in the solution.

Here, we study the evolution of the structural properties of (electro-)catalytically relevant materials such as Pt and Au during high voltage electrolysis, from normal electrolysis (NE) up to CGDE in an aqueous alkaline electrolyte.[1] From studies on wire electrodes, we will show that Au and Cu restructure significantly during these conditions, whereas Pt seems primarily stable. We performed similar experiments on poly-oriented single-crystal electrodes to gain more detailed insights into the structural changes on an atomic scale level. The electrodes are characterized using XPS, SEM, optical microscopy, and electrochemical methods. Overall, we show how to tune complex three-dimensional structure formation (specifically nanoporous Au formation), discuss facet-dependent restructuring, and discuss the difference between NE and CGDE on restructuring processes.

References

[1] E. Artmann, *et al.*, ChemPhysChem **22**, 2429 (2021)

Electric Fields During High Voltage Electrolysis

L. Forschner, E. Artmann, T. Jacob, A. K. Engstfeld

Institute of Electrochemistry, Ulm University, Ulm, Germany

In-liquid plasmas can for example be generated by applying a sufficiently high voltage between two gas-evolving electrodes with different sizes in an electrolyte. Under these conditions, normal electrolysis (NE) breaks down concomitant with the ignition of a plasma within a stable gas sheath which surrounds the smaller electrode. This effect is denoted as Contact Glow Discharge Electrolysis (CGDE).[1] Both NE and CGDE can be used to modify the (near) surface regions of an electrode.[2] To understand the mechanism of electrode (re)structuring, the influences of several parameters have to be considered, including the electrode and electrolyte temperature, reactive species such as H_2O_2, as well as the electric fields inside the electrolyte and the plasma sheath.

In this work, we focus on the electrolyte potential distribution between the two driving electrodes. The distribution has been measured during NE using reversible hydrogen reference electrodes.[3] We will show that the total cell voltage is dominated by the voltage drop inside the electrolyte, which depends significantly on the cell geometry. Similar experiments were conducted in the presence of CGDE, where the formation of a continuous gas sheath around the working electrode leads to a sudden drop in the current. Thus, the electrolyte voltage drop is smaller during CGDE than during NE. Instead, the majority of the voltage now drops within the plasma layer. To gain more detailed insights on the plasma sheath thickness, we recorded high-speed camera images of the plasma working electrode. Based on this complementary experimental approach, we discuss the shape of the potential distribution within the CGDE electrolysis cell.

References

[1] Hickling, A.; Ingram, M. D., Trans. Faraday Soc. **60**, 783-793 (1964)

[2] Artmann, E. et al., ChemPhysChem **22**, 2429-2441 (2021)

[3] Forschner, L. et al., submitted, DOI: 10.26434/chemrxiv-2022-nw4sp (Preprint, 2022)

DC glow discharge - Fluidized bed reactor for CO2 recycling

C. Garcia-Soto[1,2], P. Thevernet[1], D. Sadi[1], M. Fondaneche[1], E. Baratte[1], V. I. Parvulescu[2], O. Guaitella[1]

[1] Laboratoire de Physique des Plasmas, École Polytechnique, CNRS, Sorbonne Université, Palaiseau, France

[2] Department of Organic Chemistry, Biochemistry and Catalysis, University of Bucharest, Bucharest, Romania

The increase in global temperature is attributed to the greenhouse gas effect especially from carbon dioxide (CO_2) emissions. Non-thermal plasmas can provide the highly energetic environment needed for CO_2 conversion. Therefore, a plasma-catalysis approach could offer a significant advantage by improving conversion, selectivity and energy efficiency. Fluidized bed reactors increase the surface contact area with the gas phase and improve the heat transfer [1-3]. A DC glow discharge ignited in a fluidized bed with and without Alumina (Al_2O_3) particles is investigated with aid of Optical Emission Spectroscopy at low pressure. It is observed a decay in Oxygen atom density through the fluidization of the material and an increase in the intensity of CO systems, specifically Angstrom band system which could be due CO density, electron density and/or electric field, in comparison to the plasma alone. This indicates that fluidized particles indeed cause a reduction in the O presence and could lead to an increase in CO density. In addition, temperature of rotation was calculated by CO Angstrom system [4]. The temperature does not increase significantly although the presence of Al_2O_3 particles seems to constrain the plasma spatially. The plasma-assisted catalytic behavior was further investigated by FTIR spectroscopy for the characterization of the downstream gas from glow discharge/FBR resulting on superior performance than the glow discharge alone. The performance data obtained by Dielectric Barrier Discharge (DBD)-FB reactor is compared and it is concluded that the presence of alumina improves the dissociation of CO_2. Despite the very low catalytic activity of alumina alone yet it has a physical effect changing the chemistry. The development of this innovative route is crucial to understanding the enhancement of plasma-surface interaction for CO2 recycling.

References

[1] Wang et al., Catal. Today, **148**, pp. 275–282 (2009)
[2] Chen et al. J. CO2 Utilization, **54**, p. 101771 (2021)
[3] Pou et al, J. CO2 Utilization, **27**, pp. 528–535 (2018)
[4] Yamada et al, Jpn. J. Appl. Phys., **60** (2021)

Nitrogen fixation into NO_x by plasma: Pulsed spark plasma versus arc plasma

E. Vervloessem[1,2], I. Tsonev[1], C. O'Modhrain[1], A. Nikiforov[2], N. De Geyter[2], A. Bogaerts[1] and Y. Gorbanev[1]

[1] *Research group PLASMANT, Department of Chemistry, University of Antwerp, Wilrijk, Belgium*

[2] *Research Unit Plasma Technology, Department of Applied Physics, Ghent University, Ghent, Belgium*

Industrial nitrogen fixation is not only unsustainable due to non-environmentally benign operating conditions, high energy demand, and the need for centralised production, but also due to its heavy use of fossil energy carriers. Among the proposed substitutes, plasma-based N_2 fixation is of high interest due to the flexibility of its use and synergy with sustainable energy sources, i.e., renewable electricity [1].

To gain a feasible industrial potential, a plasma process must have a feasibly low energy consumption (EC) [2]. A pulsed spark plasma used in our work on N_2 fixation exhibited a very low EC for NO_x generation, close to the thermodynamic limit – 0.4 MJ/mol. To elucidate the mechanisms leading to this unprecedentedly low value, we performed electrical and optical analysis of the plasma jet, and developed a chemical kinetic model. We demonstrated that the plasma power and the corresponding gas temperature are the reason for the very low EC: they provide a strong vibrational-translational non-equilibrium and promote the non-thermal Zeldovich mechanism reactions. The ratio of pulse/interpulse times are critical for finding a balance between the drop in temperature and the fraction of gas treated by the plasma [3].

Notably, several factors hinder the applicability of such pulsed plasma, e.g. the commonly observed inverse correlation between EC and production rates (PR), or the necessity to enhance the selectivity towards NO_2 - the desired product for a more facile generation of nitrate-based fertilisers. Other plasma systems can aid in reaching these prerequisites - specifically, arc plasmas which operate in a regime close to thermal equilibrium.

However, the said inverse correlation between EC and PR often remains. To enhance the performance of such process, we investigated for the first time the use of a rotating gliding arc plasma for N_2 fixation at elevated pressures, at different feed gas flow rates and compositions. Our results demonstrate a dramatic increase in the NO_x yield, with a near-exclusive NO_2 production (which is beneficial for downstream absorption and hence the overall fertiliser production), and a record-low EC of 1.8 MJ/mol at a high PR of 69 g/h. The performed reaction rate constant analysis let us ascribe this improvement to the enhanced direct thermal Zeldovich mechanism, and to the increased rate of NO oxidation over the back-reactions of Zeldovich mechanism due to the elevated pressure [4]. This identifies pressure as an important parameter to enhance the plasma performance, which is largely overlooked by researchers. Plasma operation at slightly elevated pressures does not require equipment any different than that used at atmospheric pressure, but improves the process, thus making plasma N_2 fixation an even more appealing technology.

References

[1] H. Chen, D. Yuan, A. Wu, X. Lin, X. Li, Waste Dispos. Sustain. Energy **3**, 201 (2021)

[2] K. H. Rouwenhorst, F. Jardali, A. Bogaerts, L. Lefferts, Energy Environ. Sci. 1**4**, 2520 (2021)

[3] E. Vervloessem, Y. Gorbanev, A. Nikiforov, N. De Geyter, A. Bogaerts, Green Chem. **24**, 916 (2022)

[4] I. Tsonev, C. O'Modhrain, A. Bogaerts, Y. Gorbanev, ACS Sustainable Chem. Eng. DOI: 10.1021/acssuschemeng.2c06357 (2023)

Volume and surface kinetics in CO_2 plasmas

T. Silva,[1] C. Fromentin,[1] T. C. Dias,[1] P. Viegas,[1] J. Afonso,[1]
J. Silveira,[1] V. Guerra[1], L. Vialetto[2], A. S. Morillo-Candás[3],
E. Barrate[3] and O. Guaitella[3]

[1]Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Portugal
[2] Theoretical Electrical Engineering, Faculty of Engineering, Kiel University, Germany
[3] Laboratoire de Physique des Plasmas (UMR 7648), CNRS, Univ. Paris-Saclay, Sorbonne Université, École Polytechnique, France

In the last decade a vast effort has been dedicated to the development of models to study CO_2 activation in non-equilibrium plasmas, due to their interest in various applications [1]. Several models have been used to study in detail the volume kinetics of CO_2 plasmas, including the role of electron impact reactions, vibrational excitation, and electronically excited states. In turn, the study of heterogeneous processes is often limited to specific aspects of the plasma-surface interaction. However, the actual coupling of volume and surface kinetics and a description of their mutual influence is still missing [1].

This contribution presents recent advances in the development of “reaction mechanisms” for CO_2-containing plasmas [2], based on the comparison of the simulations from a 0D self-consistent kinetic model with experimental data obtained in low-pressure plasmas. Moreover, deterministic and kinetic Monte Carlo methods are used to simulate surface kinetics [3], including the surface modifications induced by the production and destruction of metastable chemisorption sites. The proposed formulation generalises the common surface recombination models by incorporating effects of plasma-surface interactions and allows the coupled description of the complex volume plasma chemistry and surface kinetics in CO_2 plasmas.

This work was partially supported by Portuguese FCT-Fundação para a Ciência e a Tecnologia, under projects UIDB/50010/2020, UIDP/50010/2020, PTDC/FIS-PLA/1616/2021 and grant PD/BD/150414/2019, by the European Union's Horizon 2020 research and innovation programme under grant agreement MSCA ITN 813393, and by the European Space Agency under Project I-2021-03399.

References

[1] L. D. Pietanza, O. Guaitella *et al*, *Eur. Phys. J. D* **75** (2021) 237
[2] C. Fromentin *et al*., *Plasma Sources Sci. Technol*. **32** (2023) 024001
[3] D. Marinov *et al*., *Plasma Process. Polym*. **14** (2017) 1600175

Ignition and characterization of non-thermal, low-pressure plasmas in highly porous and lightweight aeromaterials

K. Hansen[1], L. M. Saure[2], R. Adelung[2] and F. Greiner[1]

[1]Institute of Experimental and Applied Physics, Kiel University, Kiel, Germany
[2] Institute for Materials Science, Kiel University, Kiel, Germany

Environmental protection plays an important role in our everyday life. A promising research field in respect of these challenges is catalysis and more specific plasma catalysis. The efficiency of the chemical processes depends on the interplay between the plasma and the catalyst surface. An optimal material has a large reactive surface, low flux resistance and a good plasma penetration ability. Therefore, we investigate multi-scale aeromaterials, micron-sized frameworks with nano-sized walls in non-thermal, low-pressure plasmas. These aeromaterials are highly porous (> 99,8 %) and lightweight (< 3 mg/cm^3) and are synthesized at Kiel University. Different materials provide different porosities and conductivities.

We investigate the interaction of aeromaterials with low-pressure, radio-frequency argon plasmas. The plasma is ignited in cylindrical cavities in aeromaterial cylinders. Optical emission spectroscopy (OES) and electrostatic probes are used to study the influence of the aeromaterial surface on the plasma.

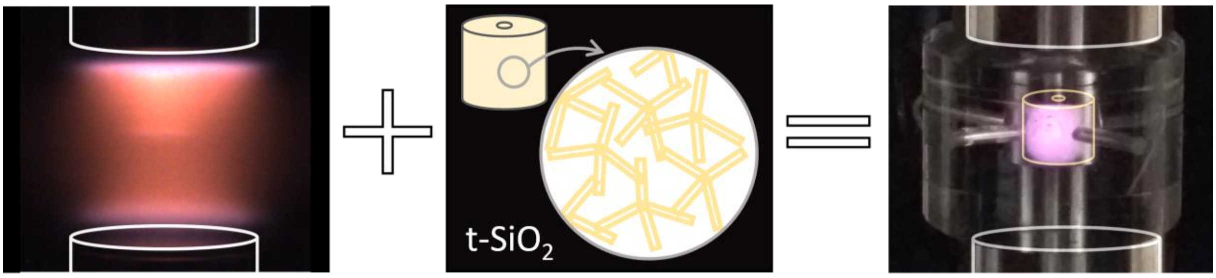


Figure 1: Concept of our project: *Left box:* A low-pressure plasma is ignited between cylindrical electrodes (white-rimmed) at 250 Pa. *Middle box:* The aeromaterial cylinder (8 mm diameter and 8 mm height with a 1 mm bore) consists of an interconnected tetrapodal micro-structure (here for Aeroglass, t-SiO$_2$). *Right box*: The Aeroglass cylinder is placed between the electrodes with an adapter and the plasma can be ignited in the bore. The photograph is taken at 250 Pa with 26 W RF-power.

Analysis of reactive species during plasma-water interaction for H_2O_2 formation using nanosecond pulsated microwaves

M. Hernandez[1], **L. Iglesias**[1], **S. Soldatov**[2], **G. Link**[2], **A. Navarrete**[1],

R. Dittmeyer[1]

[1] *Institute for Micro Process Engineering, Karlsruhe Institute for Technology, Karlsruhe, 76344, Germany*

[2] *Institute for Pulsed Power and Microwave Technology, Karlsruhe Institute for Technology, Karlsruhe, 76344, Germany*

Hydrogen peroxide is the preferred green oxidant reagent since it decomposes into water and oxygen, and therefore it is widely used in green chemistry applications. It has been demonstrated that plasma-based synthesis of H_2O_2 is influenced by plasma-water interactions, but the factors involved in the reaction mechanisms and synthesis are still a matter of investigation. Previous studies proposed that plasma-water interface phenomena as sputtering, OH ion emission, and evaporation controlled the H_2O_2 synthesis at atmospheric pressure.[1] Furthermore, the direct cooling of the plasma-liquid zone, and the use of spray water, has been related to the enhancement of the H_2O_2 yield in the aqueous phase because of quenching of radicals and side undesired reactions.[2,3]

Among plasma configurations, microwave plasmas have been less studied for H_2O_2 production given the higher temperatures of operation leading to H_2O_2 decomposition. Nevertheless, they are interesting for handling higher gas flow rates and do not require complex electrodes. In this work, we directly use water in combination with argon/oxygen mixtures to produce H_2O_2 by means of a microwave plasma reactor. The reactor consists of a coaxial torch based on microwaves modulated with nanosecond pulsations, which would allow a better control of the temperature[4]. We compared the behaviour of the system using a water spray adaption and argon/oxygen mixtures as carrier gases obtaining H_2O_2 concentrations up to 6 mM. Through OES we could identify atomic oxygen lines, OH region and the typical Balmer lines for H. The differences of reactive species observed by OES gave a hint of reaction pathways for the H_2O_2 formation. Decrease in water drop size and increment of contact area between plasma-water is studied and its influence on the H_2O_2 yield.

References

1. Liu, J., et al. Scientific reports, **6**(1), 1-7 (2016)
2. Lin, J., et al. The European Physical Journal D, **74**(4), 1-7 (2020)
3. Burlica, R., Shih, K. Y., & Locke, B. R. Industrial & Engineering Chemistry Research, **49**(14), 6342-6349 (2010)
4. Soldatov, S., et al. Journal of CO2 Utilization **58,** 101916 (2022)

High Pressure Coaxial Dielectric Barrier Discharge for CO_2 Splitting by Combined Action of Packed Bed

Rezvan Hosseini Rad[1], Milko Schiorlin [1], Volker Brüser [1], Ronny Brandenburg[1,2]

[1] Leibniz Institute for Plasma Science and Technology, Felix-HausdorffStraße 2, 17489 Greifswald, Germany
[2] University of Rostock, Institute of Physics, Albert-Einstein-Str. 23-24, 18059 Rostock, Germany

Global warming and climate change is one of the main concern in the world. In this regard, CO_2 conversion is more and more in the focus, while this greenhouse gas is considered as a source of carbon for value added chemicals production by renewable energies [1]. The CO_2 splitting to CO as a platform chemical in coaxial Dielectric Barrier Discharge (DBD) is investigated in this work. In particular, the effect of the process pressure as a parameter that has hardly been investigated so far is examined. The effects of bed particles without and with CeO_2 coating are compared. The admixture of Ar to CO_2 is used to reduce the breakdown voltage and enable full discharging of the gas at elevated pressures at still moderate high voltage amplitudes. Although increasing the pressure increases the breakdown voltage in our reactors, it is enhancing the CO_2 dissociation and yield of CO formation significantly in the Ar/CO_2 gas mixture 4:1. The electrical characterization reveals that at each voltage amplitude, a maximum plasma power is obtained at a specific pressure. It is shown, how the ratio between the pressure and gas mixture dependent discharge or breakdown voltage and the high voltage amplitude determines the plasma power. The addition of glass beads seem to support the plasma formation at elevated pressures, e.g. in the voids of the packed bed. The packed bed also increases the CO formation at 2 bar, even more when CeO_2 is coated on the bed particles. It will be discussed whether (1) a higher rate of collisions between electrons and gas molecules, (2) an enhancement of ion formation by 3-body processes and (3) the suppression of back reactions at the CeO_2 surface enable a more economic CO formation in DBDs [2].

References

[1] A. George et al. Renewable and Sustainable Energy Reviews 135 (2021): 109702.
[2] R. Hosseini Rad et al. Chem. Eng. J 456 (2023) 141072.

Investigation of Non-Thermal Atmospheric Pressure Plasma-Based Nitrogen Fixation Using Water in Nitrogen Arc Discharge for Sustainable and Environmentally-Friendly Ammonia Production.

Muzammil Iqbal[1], **Majeed Muhammad**[2], **Dae Hoon Lee**[2]

[1] *Circular Chemical Engineering, Faculty of Science and Engineering, Maastricht University, Netherlands*

[2] *Department of Plasma Engineering, Korea Institute of Machinery and Materials, South Korea*

The growing demand for fossil-free energy has prompted extensive research into new, clean, and sustainable methods of meeting global energy needs. One promising approach is the production of green, sustainable fuels such as ammonia from base molecules like water and nitrogen using renewable electricity. Non-thermal atmospheric pressure plasma-based NH_3 synthesis has been shown to have significant potential for the production of carbon-free fertilizer using renewable electricity. In this study, we developed an atmospheric pressure rotating gliding arc discharge reactor in conjunction with a catalyst to achieve a higher ammonia production rate. Our research involved a two-step ammonia production process, including the facile production of NOx and hydrogen from nitrogen discharge in water and the highly selective catalytic reduction of NOx to ammonia in the presence of hydrogen. The plasma technique we studied yielded an ammonia concentration of approximately 0.84% with a selectivity of 95% and a production rate of 120 µmol/s, by integrating a catalytic reduction system with plasma. These results are notable as they represent a 300-400-fold increase in ammonia yield compared to previous studies on ammonia synthesis from nitrogen. These promising findings represent a significant advancement in the transition towards sustainable and environmentally friendly ammonia production.

References

[1] I. Muzammil, ACS Energy Letters 2021 6 (8), 3004-3010

[2] I. Muzammil, RSC Advances, 2021, 11, 12729-12738

Nitrogen fixation in sub-micrometer-size water aerosol using micro-hollow surface DBD reactor

V. Jirásek, T. Homola, J. Fujera, V. Prukner, and M.Šimek

Institute of Plasma Physics AS CR, Prague 8, Czech Republic

Ammonia and nitrogen fertilizers are essential components for plant growth. Since the 1960s, the application of various fertilizers has increased more than five-fold, and the ammonia currently produced using the Haber–Bosh process has a massive carbon footprint owing to the production of hydrogen, an ammonia precursor, from fossil fuels. Furthermore, because fossil fuel supplies have become geopolitically destabilized, alternative methods for producing ammonia and fixing nitrogen in water are becoming extremely important for sustainably producing fertilizers and, thus, preventing global food crises. Non-thermal plasma reactors, which enable electrical discharges to be generated in various gases and both liquid and gaseous water, have attracted considerable attention as an alternative method for producing ammonia and fixing nitrogen. Here we used a multihollow surface dielectric barrier discharge (MSDBD) to generate plasma in synthetic air and nitrogen containing admixtures of very fine (< 300 nm) water aerosols. The combination of MSDBD plasma with water aerosols enabled fast solvation of gaseous plasma products in water and production of plasma-activated water (PAW) with the admixture of ammonia. The plasma interaction with the water aerosols was studied using optical emission spectroscopy and a scanning mobility particle sizer to provide information about the size and distribution of the water particles entering and exiting the plasma reactor. The gas exiting the plasma reactor was analyzed using Fourier-transform infrared spectroscopy, and the PAW collected in an ice-cooled vessel was analyzed for nitrogen products and H_2O_2. The MSDBD shows promise as a catalyst- and H2-free method for fixing nitrogen in water. Moreover, because MSDBD consumes very little energy (<5 W) and the plasma unit is simple to construct, the proposed method for producing PAW is a promising alternative toward building a decentralized sustainable economy.

Plasma-induced toluene conversion into acetylene with high selectivity

C. Jung[1], D.K. Dinh[2], Y.N. Kim[2], and D.H Lee[1,2]

[1]Korea University of Science and technology, Daejeon, Republic of Korea
[2]Korea Institute of Machinery and Materials, Daejeon, Republic of Korea

Toluene conversion process was investigated using rotating arc plasma with hydrogen-nitrogen mixture carrier gases at atmospheric pressure. Toluene is a major component of various by-products generated in the chemical industry. Most of previous studies on plasma conversion of toluene aims hydrogen production in high concentration condition or removal in low concentrations [1,2]. In this study, the conversion process was designed to convert toluene into valuable product or acetylene with high selectivity. A parametric study was conducted to investigate the effects of residence time, specific power input, and reactant concentration on product selectivity. The optimal and maximum conditions for toluene conversion were determined through each experiment in the designed reactor. The results showed the highest acetylene selectivity among ever reported studies. Additionally, the results were compared with the thermal pyrolysis of toluene under the same reactant condition. The findings suggest that rotating arc plasma is a suitable plasma source for converting toluene into acetylene efficiently and can be applied to the conversion process of other light hydrocarbons.

References

[1] F. Saleem, Energy & Fuels **32**, 5164 (2018)
[2] S. Liu, Chemical Engineering Journal **307**, 793 (2017)

Kinetic Interaction between Plasma and Catalyst in Plasma-Assisted Ammonia Synthesis

Christopher Kondratowicz[1], Ning Liu[1], Yiteng Zheng[2], Zihan Lin[2], Bruce E. Koel[2], and Yiguang Ju[1]

[1]*Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey, USA*
[2] *Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey, USA*

In the search for viable clean energy solutions due to growing demands for eco-friendly power generation, various hydrogen carriers such as ammonia have been explored for more efficient energy storage, higher energy density, and safer transportation[1]. The Haber-Bosch process has been the primary industrial production method for ammonia since the 1920s, involving high temperatures and pressures in conjunction with a fused iron catalyst. Using non-thermal plasmas, it is possible to use energetic electrons to excite stable molecules such as N_2 to generate radicals as well as electronically and vibrationally excited states. This could potentially reduce the activation energy by forming ammonia through new reaction pathways due to strong heterogeneous kinetic interactions between plasma chemistry and catalyst. As a result, it is possible to lower the synthesis temperatures and pressures required to produce ammonia.

One of the major challenges in achieving plasma assisted ammonia synthesis is understanding and quantifying the relationship between the surface and gas chemistry in an N-H plasma system. The roles of both gas and surface chemistry are analyzed through a variety of product and surface characterization techniques. The atomic concentrations of N and H radicals are measured in-situ using two-photon absorption laser induced fluorescence (TALIF), which provides an understanding of the gas phase chemistry and the reactions in gas-phase plasma. The presence of plasma-surface interaction is evident from surface nitrogen formation on the electrode surface after plasma discharges using X-ray photoelectron spectroscopy (XPS). These techniques will provide insights into the reaction mechanism through analysis of the formation and stability of nitrogen species on the catalytic surface. This work will lay the groundwork for future study targeting maximizing surface performance.

References

[1] A. Patonia et al, The Oxford Institute for Energy Studies, **EL 42** (2020)

Plasma-Activated Water (PAW) as a Sustainable Technology for Wastewater Treatment and Agricultural Development

S. Kooshki[1] , P. Pareek[1] and Z. Machala[1]

[1] *Faculty of Mathematics, Physics, and Informatics, Comenius University, Bratislava, Slovakia*

Nowadays, more than two billion people around the world use drinking water sources contaminated by fecal matter and microbial contamination and nearly 6 billion people will suffer from clean water scarcity by 2050. In the meantime, the global water demand for agriculture is increasing. One of the possible solutions is wastewater treatment and recycling as an efficient resource for balancing water demand for agriculture. However, all conventional wastewater treatment methods have numerous disadvantages, such as low efficiency against some organic pollutants, high running costs, and pollutants emission into the environment [1]. To address this issue, we demonstrate that the atmospheric-pressure Non-Thermal Plasma (NTP) treatment of wastewater can be a new potential low-energy alternative to conventional water treatment method and a green route [2]. NTP interactions with water not only cause biological pollutant disinfection in Plasma-Activated Water (PAW) thanks to the production of Reactive Oxygen and Nitrogen Species (RONS) in PAW, but can also improve seed germination and plant growth.

In this study we focused on the effects of the NTP as a sustainable technology for the treatment of waste water contaminated with *Staphylococcus epidermidis* bacteria and the use of such produced PAW for seed germination enhancement. Chemical and bactericidal effects induced by air plasma in the bacteria suspensions using a new dielectric barrier discharge reactor with liquid film covering one electrode were investigated. The effects of the generated PAW on the barley seed germination percentage cultivated in vitro conditions were evaluated. Inactivation of the bacteria suspensions were determined in dependence on pH, Oxidation-Reduction Potential (ORP), and correlated with chemical RONS generated in the PAW. Using Responses Surface Methodology (RSM) the optimum parameter area in the plasma treatment time as the main parameter in the experiments was obtained to minimize the electric power consumption by the system in the bulk quantity water treatment. This study shows the ability of cold plasma technology for sustainable recovery of clean water and sustainable agriculture.

This work was supported by Slovak Research and Development Agency APVV-17-0382 and Slovak grant agency VEGA 1/0596/22 grants.

References

[1] P. Gururani, P. Bhatnagar, B. Bisht, V. Kumar, Environmental Science and Pollution Research **28**, 65062 (2021)

[2] A. Barjasteh, Z. Dehghani, P. Lamichhane, N. Kaushik, E. Choi, Applied Sciences **11**, 3372 (2021)

Numerical modeling of atmospheric pressure plasma discharge dynamics

Konstantinos Kourtzanidis[1]

[1]Centre for Research and Technology-Hellas (CERTH) -
Chemical Process & Energy Resources Institute (CPERI)
6th km Harilaou - Thermis, Thermi
57001, Thessaloniki, Greece

Atmospheric pressure plasma (APP) discharges present exciting features for electrified, on-demand and decentralized chemical processing as they do not require expensive and complex vacuum systems while presenting high reactivity due to multiple and high species production in various background gas environments [1]. In this work, the spatiotemporal dynamics of microwave, ns-pulsed and Dielectric Barrier Discharge (DBD) APPs are studied with in-house advanced numerical models [2-4] revealing the importance of applied conditions and design parameters as well as plasma-surface-wave interactions on various discharge aspects such as: breakdown, glow-to-streamer transition, streamer propagation and steady state power balance. Special focus is given on numerical assumptions, bottlenecks, and guidelines for performing efficient simulations retaining accuracy.

References

[1] Keidar, Michael, Klaus-Dieter Weltmann, and Sergey Macheret. "Fundamentals and applications of atmospheric pressure plasmas." *Journal of Applied Physics* 130.8 (2021): 080401.

[2] Kourtzanidis, K., & Raja, L. L. (2017). Three-electrode sliding nanosecond dielectric barrier discharge actuator: modeling and physics. *AIAA Journal*, *55*(4), 1393-1404.

[3] Kourtzanidis, K., Dufour, G., & Rogier, F. (2020). Self-consistent modeling of a surface AC dielectric barrier discharge actuator: in-depth analysis of positive and negative phases. *Journal of Physics D: Applied Physics*, *54*(4), 045203.

[4] Konstantinos Kourtzanidis 2023. Full-wave and plasma simulations of microstrip excited, high-frequency, atmospheric pressure argon microdischarges. *Plasma Sources Sci. Technol.* **32** 025002

Nanosecond Surface Dielectric Barrier Discharge: Experimental investigation of streamer to filament transition in high-pressure gases

V. Lafaurie[1], S. Starikovskaia[1]

Laboratory of Plasma Physics, UMR764, Ecole Polytechnique, Palaiseau, France[1]

A common feature of high-pressure nSDBD is the two different discharge propagation modes that exist depending on the pressure and applied voltage, referred to here as the diffuse/streamer mode and the filament mode. For a fixed pressure, the diffuse/streamer mode with a diameter of roughly 200-300μm is usually observed at lower applied voltages. With increasing voltage, filament of roughly 20μm channels appear for every 4 or 5 diffuse streamer observed. This transition is abrupt, typically taking 1 to 2 ns, and accompanied with a sharp rise of electron density from 10^{15} cm^{-3} to 10^{19} cm^{-3}. A transition point was defined as the voltage for which formation of 2 to 5 filaments is observed in the first 12 ns of the discharge.

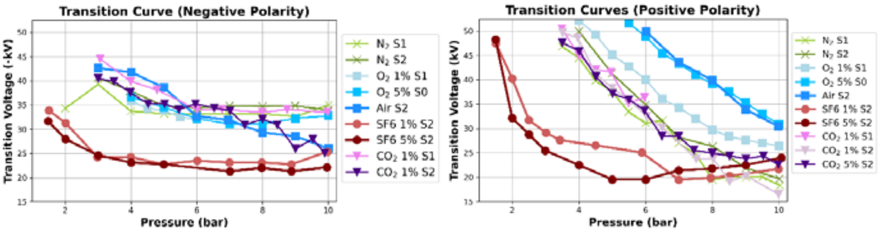


Figure 2: Transition curves in positive and negative polarities for different gas compositions

In the positive polarity, the variation of the transition threshold with gas composition is large. Using N_2 as the reference, the addition of fractions of O_2 to the mixture appears to increase the transition voltage for a given pressure. This can be attributed to photoionisation of the O_2 by electronically excited N_2. Indeed, in N_2:O_2 mixtures ionization of O_2 molecules occurs due to the absorption of the emission produced by highly excited N_2 and N-atoms, both produced by direct electron impact [5,6]. For comparison, measurements with CO_2 fractions cannot be differentiated from N_2 transition. At the negative polarity, all curves for N_2:O_2 mixtures and CO_2 are collapsed together.

Finally, looking at the highest possible electronegativity, that is at the SF_6 fractions, the transition voltage is noticeably lower than all other mixtures. It is of importance to note that in the highest pressures in both polarities, the SF_6 discharges are immediately in filamentary mode, no diffuse mode existing and no discharge lighting before the transition. The trend of transition is somewhat maintained although shifted left, and the addition of even 1% of SF_6 is sufficient to still transition at pressures where, in pure N_2, it would be impossible to get a filament.

Acklowledgements

The work was partially supported by the French General Directorate of Armaments (DGA) under the EP-DGA convention, PPRINCE Project.

References

[2] Ding, Ch, et al. "Fine structure of streamer-to-filament transition in high-pressure nanosecond surface dielectric barrier discharge**." Plasma Sources Science and Technology** 31.4 (2022): 045013.
[3] Starikovskaia S et al. Surface discharges: possible applications for plasma-assisted ignition and electric field measurements. **In 48th AIAA Aerospace Sciences Meeting Including the New Horizons Forum and Aerospace Exposition** (2010) (p. 1587).
[6] Pancheshnyi S. Photoionization produced by low-current discharges in O_2, air, N_2 and CO_2. **Plasma Sources Sci. Technol. 24** (2015) 015023.

One-step steam reforming of methane to methanol by plasma catalysis: experiments and DFT modelling

<u>Shangkun Li,</u>[1] Yanhui Yi, [2*] Yingzi Hao,[2] Kristof M. Bal,[1] Nick Gerrits,[1] Erik C. Neyts,[1] Annemie Bogaerts[1*]

[1] Research Group PLASMANT, Department of Chemistry, University of Antwerp,
Universiteitsplein 1, BE-2610, Wilrijk, Antwerp, Belgium

[2]State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian
University of Technology, Dalian
*Corresponding Author's E-mail address: shangkun.li@uantwerpen.be;
yiyanhui@dlut.edu.cn; annemie.bogaerts@uantwerpen.be

The selective activation and targeted conversion of methane into value-added chemicals is considered a holy grail in catalysis. Plasma technology is a promising approach to activate gas molecules by energetic electrons instead of heat, it can be operated at mild conditions and allows easy upscaling.[1,2] Our previous study revealed that plasma-catalytic direct oxidation of methane to methanol (DOMTM) could realize 81 % liquid oxygenates selectivity and 50 % CH_3OH selectivity promoted by Ni-based catalysts, at low temperature and atmospheric pressure.[3]

Recently, we found that one-step steam reforming of methane to methanol (SRMTM) via a combination of $CH_4/H_2O/Ar$ plasma with copper-containing zeolite can further increase the CH_3OH selectivity to 82 %, with 4.7 % CH_4 conversion. Catalyst characterization and plasma diagnostics reveal that the excellent reaction performance is attributed to Cu-O active sites confined by the pore of Cu-MOR zeolite. Furthermore, by dedicated experiments and DFT calculations, we demonstrate that the existence of a redox process from Cu^{2+} to Cu^{+} on Cu-MOR plays an important role in plasma-catalytic SRMTM in a continuous flow reactor. This study provides a fundamental understanding of radical-involved processes taking place and the mutual interactions between plasma and zeolite-confined copper catalyst.

References

[1] R. Snoeckx; A. Bogaerts, Chem. Soc. Rev.46 (2017), 5805-5863.
[2] S. Li, R. Ahmed, Y. Yi, A. Bogaerts, Catalysts, 11 (2021) 590.
[3] Y. Yi, S. Li, Z. Cui, Y. Hao, Y. Zhang, L. Wang, P. Liu, P.; X. Tu, X. Xu; H. Guo, A. Bogaerts, Appl. Catal. B: Environ. 296 (2021) 120384.

Effect of O_2 on the Dry Reforming of Methane in an Atmospheric Pressure Glow Discharge

S. Maerivoet[1], B. Wanten[1], S. Van Alphen[1] and A. Bogaerts[1]

[1] Research group PLASMANT, University of Antwerp, Antwerp, Belgium
E-mail: stein.maerivoet@uantwerpen.be

Syngas is an important precursor in chemical industry. Currently natural gas is used to prepare syngas for industrial usage. [1] In accordance with the shift towards a green, circular industry, syngas could be produced using plasma and CO_2. The process combining CO_2 and CH_4 is called the dry reforming of methane (DRM) and has been a focus of plasma research for a long time. Unstable plasmas are observed at high CH_4 fractions [2], therefore we studied the effect of O_2 on the DRM plasma.

A confined Atmospheric Pressure Glow Discharge (cAPGD) is experimentally optimized for conversion, energy cost and product output when converting CO_2 and CH_4 along with O_2. Optimal results are obtained at 42.5/42.5/15 $CO_2/CH_4/O_2$, with a total conversion of 53 %, and 49 % CO_2 conversion and 75 % CH_4 conversion. Mostly syngas is produced with a ratio of 0.80 (H_2/CO), whilst having an energy cost of 2.47 eV molecule^{-1}. Further increase of the CH_4 fraction leads to unstable plasma, including abundant coke formation. Further increase of the O_2 fraction would surpass the lower explosion limit.

A fluid model was developed to understand the effect of O_2 on the macroscopic properties of the plasma, as well as to gain insight into the chemistry. A reduced chemistry set was developed including 21 species with 57 reversible reaction pairs, describing the thermal chemistry of DRM with O_2. A heat source was modelled based on the experimental shape recorded by Trenchev et al. [3] and the experimentally obtained power.

References

[1] Sun, P.; Young, B.; Elgowainy, A.; Lu, Z.; Wang, M.; Morelli, B.; Hawkins, T. Criteria Air Pollutants and Greenhouse Gas Emissions from Hydrogen Production in US Steam Methane Reforming Facilities. ACS Publ., **53 (12),** 7103–7113 (2019)

[2] Wanten, B.; Maerivoet, S.; Vantomme, C.; Slaets, J.; Trenchev, G.; Bogaerts, A. Dry Reforming of Methane in an Atmospheric Pressure Glow Discharge: Confining the Plasma to Expand the Performance. J. CO2 Util., **56** (2022)

[3] Trenchev, G.; Nikiforov, A.; Wang, W.; Kolev, S.; Bogaerts, A. Atmospheric Pressure Glow Discharge for CO2 Conversion: Model-Based Exploration of the Optimum Reactor Configuration. Chem. Eng. J., **362**, 830–841. (2019)

CO2 conversion by NRP discharges: spotlight on two parallel CO production mechanisms

J. Maillard[1], T. van den Biggelaar, E. Pannier, C. O. Laux

[1]*laboratoire EM2C, CNRS, Université Paris-Saclay, France*

The CO2 conversion by Nanosecond Repetitively Pulsed (NRP) discharges is investigated using Optical Emission Spectroscopy (OES) and nanosecond optical imaging. The measurements depict a highly heterogeneous and fluctuant plasma. They bring to light a highly-ionized, micron-sized, thermal filament developing from the electrodes. The filament reaches the Local Thermodynamic Equilibrium (LTE) at about 30,000 K and 40 bar under the effect of a secondary pulse 70 ns after the breakdown. This is the first identification of the thermal-spark NRP regime in CO2. In parallel, a colder molecular, non-equilibrium, region coexists with the filament. The non-equilibrium region matches the previous experimental and numerical descriptions of NRP discharges in CO2. We show that both regions consume a significant part of the energy. While they may both contribute to CO production, they underlie utterly different mechanisms.

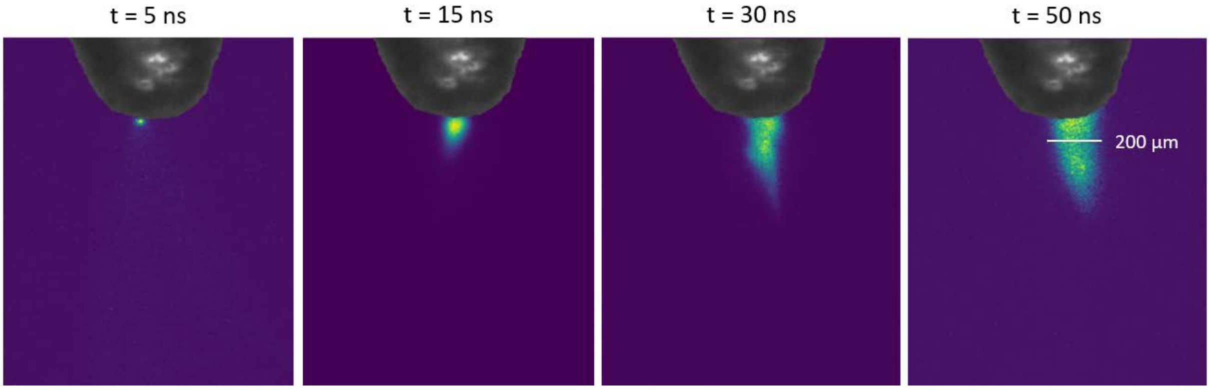


Figure 1. Evolution of the visible emission in the first 50 ns of the discharge. The emission is imaged with a telescope and an ICCD camera. For consistency, we choose images from type-a pulses.

Feasibility study of plasma-based local fertilizer production

Filippo Manaigo[1,2], Annemie Bogaerts[2], Rony Snyders[1,3]

[1] Chimie des Interactions Plasma-Surface (ChIPS), CIRMAP, Université de Mons, 7000 Mons, Belgium;
[2] Research group PLASMANT, Department of Chemistry, University of Antwerp, Universiteitsplein 1, BE-2610 Antwerp, Belgium;
[3] Materia Nova Research Center, Parc Initialis, 7000 Mons, Belgium

The Haber Bosch (HB) is the dominant process responsible for the production of nitrogen based fertilizers on an industrial scale. It is estimated that more than 40% of the world population is fed thanks to it [1] and that it contributes to approximately 1% of the global CO_2 emission. In its most commonly spread design, the HB requires large scale production and facilities to provide high pressures (around 100 bar) and high temperatures (650K – 750K) with little economic drawbacks [2-3].

Plasma driven nitrogen fixation is thus gaining interest as a local, downscaled and cleaner alternative. This work presents a feasibility study for a lower scale plasma based production of ammonium nitrate fertilizers. A comparison with the state of the art production facilities based on the HB process in the European Union framework is presented highlighting the repercussions on the production cost of a metric ton of ammonium nitrate due to:

- The differences in the capital expenditures of a state of the art fertilizer production facility and its plasma based alternative
- The influences of the variation of the natural gas pricing
- The costs for energy production both with renewable sources and combined cycle fossil fueled power plants
- The costs for H_2 production with steam methane reforming, plasma pyrolysis and electrolysis
- The transport costs within the European Union

References

[1] Erisman, J. W. et al, Nature Geosci 1, 636–639 (2008)
[2] Rafiqul, I.; Weber, C.; Lehmann, B.; Voss, A. Energy 2005, 30, 2487–2504
[3] Cherkasov, N.; Ibhadon, A.; Fitzpatrick, P. Chem. Eng. Process 2015, 90, 24-33

Numerical modelling of plasma assisted methane pyrolysis

A. Marchetti[1], E. Salzano[2], M. Gherardi[1]

[1] Department of Industrial Engineering, Alma Mater Studiorum—University of Bologna, Bologna, Italy

[2] Department of Civil, Chemical, Environmental, and Materials Engineering, Alma Mater Studiorum—University of Bologna, Bologna, Italy

Due to the global climate crisis, there is growing interest directed toward the production of new environmentally sustainable fuels. In this context, hydrogen represents one of the most promising solutions, especially in the class of green hydrogen, produced in a process not emitting greenhouse gases (GHG). Methane pyrolysis can be a valuable alternative to the most common production strategies of hydrogen (such as methane steam reforming) because it does not emit GHGs according to its chemical reaction. The main issue with the process is that it requires high temperatures to operate, traditionally reached by the combustion of fractions of the methane fed to the process. To enable the chemical reactions without involving any combustions, an electrical power source can be supplied, leading to a plasma assisted methane pyrolysis process. Plasma, being a ionized, quasi-neutral gas, is characterized by non-equilibrium traits, due to the lower inertia of electrons related to the heavier particles, that influence its chemical pathways. According to these properties, pyrolysis of methane in a plasma environment can occur due to the plasma temperature or to the promotion of reaction pathways by reactive species introduced by the non-equilibrium chemistry. In order to optimize the process yields, an in depth understanding of the chemical processes must be achieved. This can be done by numerically modelling the plasma assisted methane pyrolysis chemistry, highlighting the most relevant reaction pathways, and favouring the conditions required to obtain those reactions. Typically, detailed plasma chemistry is modelled through zero-dimensional time dependent modelling involving the solution of the electron Boltzmann equation and particle balances equations so a similar approach can be adopted to model the plasma assisted methane pyrolysis chemical pathways. In order to obtain the process optimization, the preliminary step that I am focusing on is to use a Boltzmann solver to model just the electron interactions. This allows to identify the operating conditions favouring the most valuable electron collisions for the chemical process. Nonetheless, this approach presents some limits regarding its validity that I plan to evaluate through a comparison of the Boltzmann solver computations with empirical measurements deriving from scientific literature together with the results obtained from the whole chemistry simulation.

Preliminary investigation of methane plasmalysis in a gliding arc plasma

Pierre MATHIEU[1], Abhyuday CHATTERJEE[1], Nepal CHANDRA ROY[1], Rony SNYDERS[1, 2]

[1] *Chimie des Interactions Plasma-Surfaces, University of Mons, Mons, Belgium*
[2] *Materia Nova Research Center, Mons, Belgium*

Steam methane reforming (SMR) is the current conventional industrial process for hydrogen production. It is reasonably efficient but also energy-intensive and environmentally detrimental as it emits about 12 kg of CO_2 per kg of H_2. [1] This makes the development of cleaner H_2 production routes mandatory as H_2 is foreseen to be a key player in the energetic transition that our societies have to carry out. Water electrolysis (WE) and plasma-assisted methane pyrolysis (also known as methane plasmalysis, MP) constitute two very promising alternatives to SMR, though the WE reaction requires more energy than SMR (+ 285 kJ/mol and + 165.12 kJ/mol, respectively), while MP only requires +74.58 kJ/mol.

The objective of the present work is to contribute to a better understanding of the physical and chemical mechanisms of MP in an atmospheric pressure gliding arc discharge by applying a set of plasma diagnostic tools. The gliding arc reactor was designed to optimize the gas residence time in the plasma region and therefore the conversion rate of methane.

The injected gas mixture consisted in CH_4 carried by Ar (the CH_4 to Ar ratio varied from 0.2 to 0.4). Optical emission spectroscopy was used to evaluate the impact of the plasma power, the total injected gas flow and the CH_4/Ar ratio on the rotational and vibrational temperatures (T_{rot} and T_{vib}) of the C_2 species and the electronic density (n_e) of the plasma. The observed correlation between n_e and T_{rot} suggests that in our experimental window, the average amount of energy brought to heavy particles by an electronic impact allows rotational excitations (implying more gas heating), but does not promote vibrational excitations (activating a more energy-efficient chemistry).

Finally, the CH_4 conversion rate and H_2 selectivity of the process were determined through gas chromatography. Maximum values of 30% and 57.6% were achieved for these parameters, respectively. The lowest energy cost obtained was about 150 kJ/L_{CH4}.

REFERENCES

[1] M. Gautier *et al.*, *International Journal of Hydrogen Energy*, ***42*****(47)**, 28140–28156 (2017)

Microwave Plasma Conversion of Martian Atmosphere

Elizabeth Mercer[1], Sean Kelly[1,2], Yury Gorbanev[1], and Annemie Bogaerts[1]

[1] Research group PLASMANT, Department of Chemistry, University of Antwerp, Universiteitsplein 1, 2610 Antwerpen, Belgium

[2] School of Biosystems and Food Engineering, University College Dublin, Belfield, Dublin 4, Ireland

Human curiosity and imagination have led to a unique discussion among fantasy writers and scientists alike- can we colonize outside of Earth? The potential for microwave plasma-based *in-situ resource utilization* (ISRU) of Martian atmosphere is explored in this work, where the conversion of Martian mixture (ca. ~96% CO_2, 2% N_2, and 2% Ar) into life-sustaining chemicals is a crucial step towards realizing the extension of human exploration.

In February 2021, the Perseverance rover landed on Mars. It was a mission full of firsts, and on April 20th, Mars OXygen In-Situ resource utilization Experiment (MOXIE) completed its first test in converting Marian atmosphere into subsequent molecules, including O_2 [1]. Using 300 W of power, atmospheric gas mixture was brought through a Solid OXide Electrolyzer (SOXE) to produce ~6-8 g/h of O_2. In total, it is estimated that bringing four astronauts home from the Martian surface would require over 25 metric tons of O_2. MOXIE is a huge step forward and shows what is possible for future experiments on converting Martian atmosphere.

Microwave plasma reactors house the ability to convert CO_2 into CO and O_2, much like MOXIE, but without the use of electrodes [2], [3]. This method has been proven effective here on Earth through various research and has shown encouraging results at sub-earth-atmospheric conditions [4]–[6]. The Martian atmosphere is about 7% of Earth's atmosphere, making it an ideal environment for gas conversion using microwave plasma reactors. Here, we take it a step further toward ISRU on Mars. Our measurements at 1000 W and 10 nlpm produced ~75 g/h of O_2 and ~3 g/h NO_x species using a 2.45 GHz waveguided reactor at ~3.5 x Martian atmosphere (25 mbar). The energy cost required to produce O_2 was ~0.038 kWh/g and showed promising results when compared to MOXIE experiments currently underway on the surface of Mars.

References

[1] J. A. Hoffman *et al.*, “Mars Oxygen ISRU Experiment (MOXIE)—Preparing for human Mars exploration,” *Sci. Adv.*, vol. 8, no. 35, p. eabp8636, Mar. 2023, doi: 10.1126/sciadv.abp8636.

[2] R. Snoeckx and A. Bogaerts, “Plasma technology – a novel solution for CO2 conversion?,” *Chem. Soc. Rev.*, vol. 46, no. 19, pp. 5805–5863, 2017, doi: 10.1039/C6CS00066E.

[3] V. A. Legasov *et al.*, “A nonequilibrium plasma-chemical process of CO2 dissociation in high-frequency and ultrahigh-frequency discharges,” *Sov. Phys. Dokl.*, vol. 23, p. 44, Jan. 1978.

[4] P. Viegas *et al.*, “Insight into contraction dynamics of microwave plasmas for CO2 conversion,” 2020.

[5] A. J. Wolf, T. W. H. Righart, F. J. J. Peeters, W. A. Bongers, and M. C. M. van de Sanden, “Implications of thermo-chemical instability on the contracted modes in CO2 microwave plasmas,” *Plasma Sources Sci. Technol.*, vol. 29, no. 2, p. 25005, Feb. 2020, doi: 10.1088/1361-6595/ab5eca.

[6] A. Van De Steeg, P. Viegas, A. Silva, T. Butterworth, A. Van Bavel, and J. Smits, “Redefining the Microwave Plasma Mediated CO 2 Reduction Efficiency Limit : The role of O-CO2 Association,” pp. 1–15.

CONTROL OF THE GAS FLOW BY A SURFACE BARRIER DISCHARGE

S. Mohsenimehr[1]**, A. Von Keudell** [1]

[1]*Experimental Physics II, Ruhr-University Bochum, Bochum, Germany*

Keywords: dielectric barrier discharge, plasma aerodynamics, flow pattern, vortices

Surface Dielectric Barrier Discharges (SDBD) are well-known plasma sources for gas stream purification and gas conversion due to their easy scalability in various applications [1]. In addition, SDBDs with versatile electrode configuration are used as plasma actuators to generate thrust and to manipulate, thereby, the flow pattern, to reduce the drag and to control the transition from laminar to turbulent flow [2]. The aim of this project is to combine plasma chemistry and plasma-based flow control concepts. The plasma-flow interaction and its contribution to the chemistry of transported species is evaluated.

In this work, a twin SDBD is employed, which consists of an aluminium oxide plate (190x88x0.63 mm) that is covered by nickel metallic grid (comb design with 10mm electrode width and 10mm gap distance between coated electrodes) printed on both sides asymmetrically. The SDBD is generated at atmospheric pressure using damped sinusoidal voltage waveforms (G2000 Redline Technologies). To investigate the flow pattern, the Schlieren technique was carried out to visualize the refractive index gradients in the medium and to compare this with a fluid dynamic simulation in two dimensions performed by COMSOL. The fluid simulation uses the 2D Navier Stokes equations for compressible Laminar flow assuming small Reynolds numbers. This simulation model is used to predict the plasma aerodynamic and how it could influence the surrounding fluidic flow. The formation of distinct vortices in the flow pattern in both simulation and experiment is observed. The electrode design of the SDBDs is optimized to maximize the plasma-induced thrust on the species conversion.

References

[1] F. Kogelheide., et al. Plasma Processes and Polymers **17.6** (2020): 1900126.

[2] L. Sergey B., et al. Plasma Sources Science and Technology **25.6** (2016): 063001.

Fast pyrolysis in methane plasma

M.L. Azevedo[1], D. Del Cont-Bernard[1], T.W.H. Righart[1], G.J.J. Van Rooij[1] and T.D. Buttwerworth[1]

[1]*Plasma Chemistry, Department of Circular Chemical Engineering, Faculty of Science and Engineering, Maastricht University*

Plasma technology offers the potential to electrify high-temperature processes, being in line with the chemical industry's transition towards renewable energy. This project will focus on optimizing methane (CH_4) pyrolysis process to directly produce ethylene (C_2H_4) using high temperatures, short residence times, and fast quenching.

Since the 1940s, the industrial-scale Hüls process has applied arc plasma to convert natural gas into acetylene (C_2H_2). However, when we consider the reaction enthalpies of CH_4 pyrolysis to C_2H_2 and C_2H_4, it is more energy-efficient to directly produce C_2H_4:

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \quad \Delta H = 378 \frac{\mathrm{kJ}}{\mathrm{mol}\,(C_2H_2)}$$

$$2CH_4 \rightarrow C_2H_4 + 2H_2 \quad \Delta H = 202 \frac{\mathrm{kJ}}{\mathrm{mol}\,(C_2H_4)}$$

In this project, we will investigate CH_4 pyrolysis using a microwave (MW) plasma discharge, which allows fine temporal control over the plasma input power. In order to obtain direct C_2H_4 production, we will explore sub-millisecond residence time in high temperatures.

To understand how different regimes can effect conversion and product distribution, we initially compared different pressures. We could see that with increasing pressure, CH_4 conversion is higher and selectivity shifts from C_2H_4 to C_2H_2. In higher pressure, the plasma volume decreases, suggesting a higher power density and a higher local temperature, promoting increasing dissociation rates.

In order to obtain further insights into how residence time and temperature influence selectivity of hydrocarbons, we want to investigate different plasma configurations: forward vortex and reverse vortex. With reverse vortex, we expect less gas recirculation, thus a smaller residence time.

With a gas chromatographer, we will analyze how different parameters and plasma regimes influence our product distribution.

Physicochemical and electrical characterization of a CeO_2-based nanostructured catalysts for plasma-assisted CO_2 methanation in a DBD reactor

B. Musig[a,b], **O. Guaitella**[c], **M.E. Gálvez**[b], **M.V. Navarro**[a]
[a] *Instituto de Carboquímica ICB-CSIC, Zaragoza, Spain*
[b] *Institut d'Alembert, CNRS UMR 7190 Sorbonne Université,Saint-Cyr l'Ecole, France*
[c] *Laboratoire de Physique des Plasmas, Ecole Polytechnique, Palaiseau, France*

Among the different processes for the chemical utilization of CO_2, its methanation stands as a promising technology allowing both the synthesis of a carbon-neutral fuel and the storage of off-peak renewable electricity (power-to-gas concept). The methanation reaction is exothermic but strongly hindered by kinetics. It has been recently demonstrated that the use of a non-thermal plasma in combination with a Ni-containing catalyst results in an enhanced methane yield even at atmospheric pressure and mild reaction temperatures (around 200°C) [1]. Plasma-catalyst coupling still represents one of the biggest challenges. Two different efforts for catalyst optimization should be developed side by side to improve performance and energy efficiency: first, tailoring the physicochemical properties, such as area and basicity of the surface; secondly, considering the conductivity and electrical behaviour of the material packed in the dielectric barrier discharge (DBD) reactor when in contact with plasma. In the present study, different Ni catalysts supported on synthesised nanostructured CeO_2, were used to pack a DBD reactor and tested for plasma-assisted CO_2 methanation. The focus was on the contribution of physicochemical properties and conductivity of the packing material to the electrical behaviour in plasma characterized by Q-V Lissajous figure analysis and plasma current amplitude. The catalyst selection paradigm in plasma catalysis changes compared to thermal CO_2 methanation. The Ni/CeO_2 catalyst that possesses optimized surface area (70 m^2/g), basic sites (medium strength), and particle size (smallest Ni and CeO_2 particle), which are the ideal properties for thermal catalysis according to literature, is not the most efficient in the plasma-assisted reaction. This is due to the electrical behaviour and conductivity properties, as this packing material leads to higher capacitance and larger charge transferred, conditions that are unfavourable for the reaction in plasma.

References

[1] R. Dębek et al., Renewable Sustainable Energy Reviews **116** 109427 (2019)

Acknowledgements: *This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 813393.The authors would like to acknowledge the Departamento de Ciencia, Universidad y Sociedad del Conosciemiento of the Gobierno de Aragón for the project No LMP151_21.*

Plasma-Catalysis reactor concepts using microwave plasmas under nanosecond pulsation

Alexander Navarrete[1], **Sergey Soldatov**[2], **Mery Sheryll Hernandez**[1], **Guido Link**[2], **John Jelonnek**[2,3], **Roland Dittmeyer**

[1] Institute for Micro Process Engineering (IMVT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

[2] Institute for Pulsed Power and Microwave Technology (IHM), Karlsruhe Institute of Technology, Karlsruhe, Germany

[3] Institute of Microwaves and Electronics (IHE). Karlsruhe Institute of Technology, Karlsruhe, Germany

Opportunities for the development of innovative materials and scalable technologies for the future energy infrastructure in Germany and other connected regions are explored in the Helmholtz program "Materials and Technologies for the Energy Transition". As part of this initiative, KIT has contributed to several of these developments in the area of "chemical energy carriers" using unique infrastructure such as the Energy Lab 2.0 and developments in the area of efficient, compact reactors powered by renewable energy.

At the Karlsruhe Institute of Technology (KIT), two institutes, IHM and IMVT joined forces in order to overcome this challenge from a multidisciplinary perspective. As a result, we have developed the first nanosecond pulsated microwave plasma [1, 2]. This route allows to control the delivery of energy and progress of the reactions at atmospheric pressure.

In order to take advantage of this new approach, novel suitable reaction systems are being developed. Two examples will be highlighted:

- The activation of CO2 under a plasma activated chemical looping concept.
- The synthesis of hydrogen peroxide with microwave plasma.

References

[1] Soldatov et al., ACS Energy Letters, **6**, 124 (2021)

[2] Soldatov et al, Journal of CO2 Utilization **58**, 101916 (2022)

GC-MS Analysis of Toluene Decomposition Residues formed during the plasma-assisted Oxygen Trace Removal from Synthetic Coke Oven Gas

C. Oberste-Beulmann[1], **T. Oppotsch**[1], **M. Muhler**[1]

[1]*Laboratory of Industrial Chemistry, Ruhr-University Bochum, Bochum, Germany*

In order to reduce greenhouse gas emissions from steel production, a promising approach is the utilization of exhaust gases for chemical synthesis. The high CO/CO_2 and H_2 content make them valuable resources in a carbon-neutral economy [1]. However, in order to allow for subsequent usage as synthesis gas, different cleaning and conditioning steps are required. One of these steps is the removal of oxygen traces. In this work, this process step was carried out using a surface dielectric barrier discharge (SDBD). Besides the main components H_2 (60%), CH_4 (20%), N_2 (10.5%), CO (7.5%), CO_2 (2%), and O_2 (< 1%), 100 ppm – 200 ppm of toluene were used as a model contamination substance present in the gas stream. During several hours on stream, toluene decomposition residues accumulated on the electrode surface and reactor walls. The residue was dissolved in isopropanol and acetone and was subsequently analyzed by gas chromatography coupled with mass spectrometry (GC-MS). A variety of different reaction products was found. Identified products were either directly functionalized toluene containing hydroxy or amine groups or originated from ring opening followed by functionalization.

From the observed reaction products, a tentative reaction mechanism can be postulated, as shown in Figure 1. However, the identified substances represent a subset of the molecules formed in the discharge: compounds that are too volatile do not accumulate on the surface, whereas some solid substances cannot be dissolved and are therefore not analyzed by GC-MS.

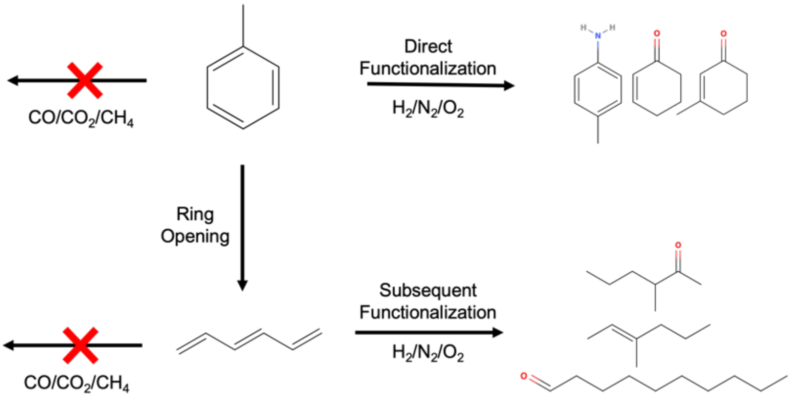


Figure 1. General reaction mechanism of toluene traces in an $H_2/N_2/O_2$ plasma.

References

[1] M. Bender et al. Chemie Ingenieur Technik 2018, **90**, 1782–1805.

Plasma-assisted removal of n-Butane from contaminated air in an SDBD reactor using BaTiO3 as catalyst

T. Oppotsch[1], **C. Oberste-Beulmann**[1], **M. Muhler**[1]

[1]*Laboratory of Industrial Chemistry, Ruhr-University Bochum, Bochum, Germany*

A variety of industrial processes leads to the formation and release of volatile organic compounds (VOCs).[1] These compounds are detrimental even in low concentrations and require effective removal. Conventionally, thermal approaches are applied. However, high energy demand and a non-economic operation for low VOC concentrations led to an investigation of alternatives, such as plasma-catalytic oxidation.

In this study, *n*-butane was chosen as a model VOC, because it is not easily oxidized, and its handling is less demanding than other VOCs, e.g., toluene.[2,3] The surface dielectric barrier discharge (SDBD) reactor used in the study utilizes a thin alumina plate imprinted with a metal grid on each side.[4] The plasma ignites next to the grid. $BaTiO_3$ is applied as a catalytic coating onto the electrode configuration. It is either applied as partial coating with a gap of 1 mm separating electrode grid and catalyst coating or as full coating.

Loadings of 0.3 mg cm^2 and 3 mg cm^2 for the full coated electrode configuration, 3 mg cm^2 and 8 mg cm^2 for the gap coated electrode configuration were investigated. An uncoated electrode configuration was studied for reference. Measurements were carried out at room temperature and at 160 °C.

The previously reported inability to ignite the fully coated SDBD was not observed with $BaTiO_3$ instead of MnO2 as catalyst material. Moreover, $BaTiO_3$ seems to have a positive effect on the discharge as the applied voltage that is required to reach a certain dissipated power was reduced, especially for lower values. The selectivity ratio of CO and CO_2 as main products was not altered, and both are formed equally. In contrast, $BaTiO_3$ showed a slightly positive influence on conversion of n-butane, which was increased at elevated temperature. For the partial coating, the conversion enhancement due to the catalyst is up to 1.5% and 2.5% at room temperature and at 160 °C, respectively; whereas the full coating increases conversion by up to 2.3% at room temperature and up to 5.7% at 160 °C.

References

[1] J. Kesselmeier, et. al., Journal of Atmospheric Chemistry, 33 (1999) 23–88.

[2] M. S. Gandhi, et. al., Journal of the Taiwan Institute of Chemical Engineers, 44 (2013) 786–794.

[3]N. Peters, et. al., Plasma Processes and Polymers, (2021); 18:e2000127.

[4] B. Offerhaus, et. al., Plasma Processes and Polymers (2017); 14:e1600255.

Investigation of reaction mechanisms for modification of organic molecules in cold atmospheric plasma activated water.

Jordyn Polito[1], Maria J. Herrera Quesada[2], Katharina Stapelmann[2], and Mark J. Kushner[3]

[1]Dept. of Chemical Engineering, University of Michigan, Ann Arbor, MI, USA

[2]Dept. of Nuclear Engineering, North Carolina State University, Raleigh, NC, USA

[3]Dept. of Elect. Eng. and Comp. Sci., University of Michigan, Ann Arbor, MI, USA

Plasma activated water (PAW) has gained attention as an environmentally friendly source of reactive oxygen and nitrogen species (RONS) for use in plasma medicine, smart agriculture, and food processing. Plasma sources for production of PAW are generally cold atmospheric plasma (CAP) sources such as plasma jets having various electrode configurations (point-to-plane, point-to-point, wire-cylindrical) [1]. RONS formed in the plasma solvate into the water and can interact with and modify organic material in solution (i.e., bacterial cell membranes and viruses for disinfection, amino acids in plant roots or sprouts as part of the nitrogen fixation process). However, the reaction mechanisms behind RONS interactions with organics in PAW are still unclear. RONS are generally believed to interact with organic molecules in solution by abstracting hydrogen molecules from the organic backbone to create radical sites that are susceptible to reaction with other RONS. Reaction mechanisms for similar reactions of RONS with gas-phase alkanes are well established and can be used as analogs for liquid-phase reactions, though reaction rates must be adjusted. Better understanding of the reaction mechanisms between RONS and organic molecules in PAW can aid in better design of PAW-producing systems as sources for green chemistry. Computational plasma models, when validated against experimental data, can be used to develop these mechanisms for more efficient design of PAW-producing systems.

In this work we develop reaction mechanisms for CAP treatment of organic molecules in solution to aid in better understanding of PAW as a source of green chemistry. Global Kin, a zero-dimensional plasma chemistry module capable of addressing interactions across a gas-liquid interface, was used to predict densities of functionalized organic products in solution after CAP treatment. RONS contributions to functionalization, cross-linking, or chain scissions of organics to achieve desired products will be discussed. Differences in RONS production leading to desired outcome (i.e., cell death, functionalization) as a function of reactor configuration and inlet gas composition will be presented. Comparison to available experimental data will be provided where possible.

References

[1] R. Zhou et. al. J. Phys. D. Appl. Phys. 53, 50 (2020).

Influence of nanosecond pulsed plasmas in water on copper surfaces and on nanoparticle formation

P. Pottkämper[1], K. Laake[1], O. Krettek[1], E. Jüngling[1], P. Cignoni[1], and A. von Keudell[1]

[1]*Ruhr-University Bochum, Bochum, Germany*

Discharges in liquid, so called in-liquid plasmas, enable a variety of applications. When ignited by voltage pulses with fast rise times and nanosecond pulse lengths applied to a small electrode wire, yield a high degree of dissociation of the liquid, a high mass transport and efficient reaction rates. Through the plasma treatment a variety of reactive species, e.g. solvated electrons, hydroxide (OH^-) and hydrogen peroxide (H_2O_2) species can be created from the liquid medium. These species can react with surfaces placed in the liquid, possibly inducing surface changes with useful applications.

In this work, in-liquid plasma treatment is used to modify a copper surface. Copper oxide nanocubes possess catalytic properties and, for instance, are being used in the electrochemical reduction of CO_2. The activity of the nanocubes decreases over time with use. Therefore a method to re-activate these catalytic properties is needed. By the in-liquid plasma treatment, the reactive species in the liquid such as H_2O_2 might induce an oxidation of copper and the growth of such copper oxide nanoparticles. In previous experiments with the setup used in this work, it has been found that the electrode degrades over time, dissolving the electrode material into the liquid. In this work, tungsten is used as an electrode material due to its high melting point, leading to its high durability during the experiments. It has been found by Lukes et al. [1] that the electrode material of an in-liquid plasma has an influence on the concentration of H_2O_2 in the treated liquid. As a result the choice of electrode material might affect the modification of the treated surface. Therefore another focus of this project is to investigate the production of nanoparticles from the electrode material.

References

[1] P. Lukes et al., Plasma Sources Sci. Technol. **20,** 034011 (2011)

[2] K. Grosse et al. J. Appl. Phys. **129**, 213302 (2021)

[3] K.Grosse et al. Plasma Sources Sci. Technol. **29** 095008 (14pp) (2020)

[4] K. Grosse et al. Plasma Sources Sci. Technol. **28** 085003 (2019)

Water decontamination using a plasma-in-liquid technique, application to per- and poly-fluoroalkyl substances (PFAS) treatment

R. Prastiko[1], **A. Vega-González**[1] **and X. Duten**[1]

[1]*CNRS, UPR 3407, Laboratoire des Sciences des Procédés et des Matériaux, LSPM,*
Université Sorbonne Paris Nord, F-93430 Villetaneuse, France

Hundreds of everyday products from non-stick cookware, cosmetics, cleaning products, food packaging, and many others are made with highly toxic chemicals called PFAS. Poly- and perfluoroalkyl substances (PFAS) are a large family of fluorinated organic anthropogenic chemicals that are resistant to degradation due to their stability and strength of the C-F bonds which is the strongest covalent bond in organic chemistry [1]. The massive use and non-degradable properties of PFAS have not only resulted in contamination in the environment such as surface water, seawater, groundwater, and potable water but also health issues. Thus, the European Union has set a directive for drinking water at 0.1 µg/L for individual PFAS and 0.5 µg/L for total PFAS, while the United States Environmental Protection Agency has established a health advisory level for drinking water at 70 ng/L for PFOA and PFOS combined. Today, non-equilibrium plasma has been deemed an eco-friendly alternative technology in wastewater treatment. Non-equilibrium plasma can generate many reactive chemical species like reactive oxygen species (ROS) such as H_2O_2 and O_3, reactive nitrogen species (RNS) such as peroxynitrite and peroxynitrate, radicals H•, O•, OH•, NO•, NO_2•, as well as hydrated electrons [2] which can degrade PFAS. Thus, the objective of this research project is to use the interaction of non-equilibrium plasma with liquids for the treatment of PFAS-polluted waters, taking advantage of the possibilities offered by this technology of allowing rather complex chemistry, while limiting the use of solvents and other chemical products. It is especially this last point which justifies the adoption of this technique for PFAS degradation, a water pollution which constitutes a worldwide public health emergency.

References

[1] D. O'Hagan, Chem. Soc. Rev. **37**, 308-319 (2008)
[2] C. A. Aggelopoulos, J. Chem. Eng. **428**, 131657 (2022)

Fundamental processes in CO2-H2 plasmas : toward methanation in plasma catalysis

D. Sadi[1], E. Baratte[2], O. Guaitella[3]

[1,2,3]*Laboratoire de Physique des Plasmas, Ecole Polytechnique, Palaiseau, France*

Hydrogen produced by electrolysis can be combined with the CO2 coming from the natural gas network and converted in CH4 via the reaction $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$. It is proven that plasma can actively dissociate CO2, however the main product of plasma CO_2 hydrogenation is carbon monoxide, therefore a plasma process is not selective for CH_4 production which is why the presence of a catalyst is needed.

To combine the plasma with a catalyst we need first to understand the gas phase. The study focus on the different properties of CO_2–H_2 plasmas in various percentages and various kind of plasmas – glow discharge, RF discharge, pulsed discharge – all at low pressure (from 1 to 6 Torr) and various currents from 10 to 50 mA, using complementary and crossed diagnostics.

To do so we use absorption spectroscopy in the infrared range where the line strength of such molecules as CO_2 and CH_4 are particularly strong using an FTIR 1) in a « Single pulse » configuration [1] which allows us to get the evolution of vibrational characteristics of the plasma within a 5ms pulse such as vibrational temperatures, 2) in a « Building up » configuration [1] in a closed reactor in static configuration (no gas flux) on a RF pulsed discharge allowing us to follow the long-term temporal evolution of gas densities until we reach a pseudo stationary state and is crucial to put constraints on the cross sections of the different process at stake to go toward a modelling of CO_2–H_2 chemistry and 3) studying the downstream gas composition of the glow discharge.

We combine those diagnostics with emission spectroscopy using USB-spectrometers from which we can derive rotational and vibrational temperature of CO from the fitting of the third positive and Angström system of the CO. We can also derive from the emission spectrum the atomic densities of H and O through actinometry.

Finally we begin to investigate on plasma-surface interaction through a fluidized bed [2] coupled with emission spectroscopy and downstream absorption measurements in order to move on next to plasma-catalysis interaction.

References

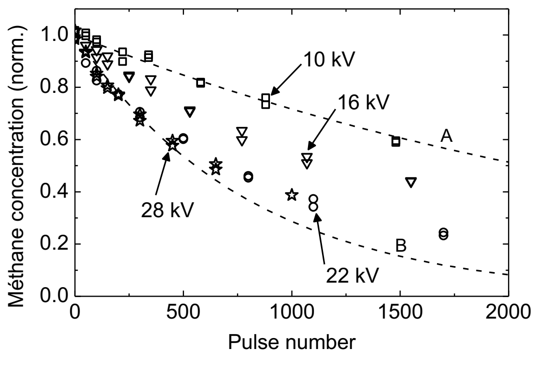
[1] E. Baratte et al., PSST, in writing

[2] C. Garcia-Soto et al., PSST, in writing

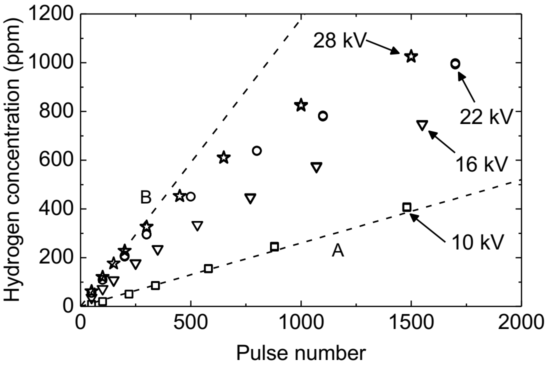
Plasma kinetics of methane conversion in Ar/CH_4 mixtures at atmospheric pressure

N. Blin-Simiand, P. Jeanney, L. Magne,
S. Pasquiers and J. Santos Sousa
Université Paris-Saclay, CNRS, Laboratoire de Physique des Gaz et des Plasmas, 91405 Orsay, France

Methane conversion has become an important research topic and has attracted a lot of attention, in particular in what concerns environmental issues. In that respect, non-thermal plasmas have proven their effectiveness with the use of several types of electrical discharges. Mixtures of CH_4 diluted in Ar have been subject of numerous works [1], with development of detailed kinetic modellings. The present work aims to contribute to the understanding of the processes involved in the Ar/CH_4 mixture.
A UV photo-triggered discharge reactor is used, in which the plasma (50 cm^3) is homogeneous, the electric field uniform and the deposition of electric energy in the plasma controllable. The moderate values of the reduced field E/N, associated with the preceding properties, allows a 0D self-consistent physical and chemical modelling in the frame of the local field approximation. It will be then possible to propose an accurate detailed kinetic scheme by comparing experimental results to calculations (work in progress), as previously performed for other organic molecules [2,3]. The figures below present some experimental results, CH_4 and H_2 (main product) concentrations measured in the volume of the device (9 L, with a closed gas circuit including a tank), as function of the number of current pulses, N. The decrease of the CH_4 concentration is described by the simple law: $[CH_4]=[CH_4]_0.\exp(-N/N_C)$.



Methane concentration, normalized to the initial value of 1000ppm, for different values of the applied voltage at the time of the pre-ionisation.
Lines: A, N_C=3000 ; B, N_C=800 (see text).



Hydrogen concentration.
Lines: A, 0.26 ppm/pulse ; B, 1.18 ppm/pulse.

[1] H. Bai et al., J. Phys. D: Appl. Phys. **54**, 424002 (2021), and references therein.
[2] N. Moreau et al., J. Phys. D: Appl. Phys. **43**, 285201 (2010).
[3] W. Faider et al., J. Phys. D: Appl. Phys. **46**, 105202 (2013).
Work supported by the French ANR project PlasBoNG (ANR-20-CE09-0003-01).

Development of plasma reactors for plasma-assisted catalysis

K. Sgonina[1], A. Quack[1], and J. Benedikt[1,2]

[1]Institute of Experimental and Applied Physics, Kiel University, Kiel, Germany
[2] Kiel Nano, Surface and Interface Science KiNSIS, Kiel University, Kiel, Germany

The energy efficient and decentralized performance of catalytic reactions, such as for the production of ammonia, has become even more important nowadays. Plasma-assisted catalysis can help to achieve these goals as it is available on demand and works without enormous external heating. Nonequilibrium atmospheric pressure plasmas are used to dissociate gaseous molecules, which can then react at the surface of the catalyst to form the desired products [1]. Plasma-assisted catalysis reactors at atmospheric pressure are often realized by packed bed reactors, in which the catalyst is packed into or deposited on millimeter-sized spheres [1-3]. However, these millimeter-sized spheres are not feasible for all types of possible catalysts.

Therefore, different plasma reactors for plasma-assisted catalysis were developed and tested with and without different catalysts for in-plasma catalysis, where the catalyst is in direct contact with plasma, and post-plasma catalysis, where only reactive species from the plasma are reaching the catalyst. Dielectric barrier discharges operated at kHz-frequencies are used for ammonia synthesis using N_2 and H_2 as working gas as well as for methane formation experiments using CO_2 and H_2. Depending on the reactor-type and working gas, the gas temperature during plasma operation ranges from room temperature up to 200 °C.

Acknowledgements

The inorganic catalysts are synthesized by and chosen in cooperation with Jihao Wang, Sharif Najafishirtari, and Malte Behrens of the Institute of Inorganic Chemistry of the Kiel University. The metal-organic-frameworks are synthesized by and chosen in cooperation with Hauke Rohr and Norbert Stock of the Institute of Physical Chemistry of the Kiel University.

References

[1] Annemie Bogaerts *et al.* 2020 J. Phys. D: Appl. Phys. **53** 443001.
[2] Jungmi Hong *et al.* 2018 ACS Sustainable Chemistry & Engineering **6(1)**, 15-31.
[3] Prateek Mehta *et al.* 2019 ACS Energy Letters **4 (5)**, 1115-1133.

Multitemperature model of the non-thermal plasma chemical dissociation of CO_2

Qinghao Shen[1] , **Floran Peeters**[2] **and Richard van de Sanden**[1,3]

[1] *Dutch Institute for Fundamental Energy Research, Eindhoven, The Netherlands*
[2] *Leyden Jar company, Eindhoven, The Netherlands*
[3] *Eindhoven University of Technology, Eindhoven, The Netherlands*

In this paper, a non-thermal zero-dimensional reaction kinetics model considering the Boltzmann vibrational distribution for CO_2 decomposition is presented. The model is characterised by vibrational temperatures different from gas temperatures to simulate non-thermal conditions. The entire vibrational manifolds of CO_2, CO and O_2 are included, and a new procedure to calculate the reaction rate constants under the non-thermal conditions is proposed. In addition, the required energy to obtain a non-thermal condition, often not included in other work, is included and its effect on the CO_2 conversion and energy efficiency is studied. In all cases the Boltzmann distribution is assumed for the vibrational states and the effect of activation barrier is taken into account using Fridman-Macheret expression [1]. The results illustrate the beneficial effect of higher vibrational than gas temperature on the CO_2 conversion and energy efficiency. The model predicts a maximum efficiency of about 86 % under non-thermal conditions when all molecules are considered to be vibrationally excited with a temperature higher than the gas temperature. This work aims to provide more insights into the dissociation and recombination reactions in CO_2 conversion under non-thermal conditions and aims to offer an opportunity for multi-dimensional non-thermal model in the future.

References

[1] Fridman A A, Plasma chemistry, Cambridge University Press (2008)

Evolution of atomic oxygen density in the early afterglow of a nanosecond CO_2 discharge

Z. Shu[1], G.V. Pokrovskiy[1] and S.M. Starikovskaia[1]

[1]Laboratoire de Physique des Plasmas (LPP), CNRS, Sorbonne Université,
Université Paris-Saclay, Observatoire de Paris, PSL Université, École Polytechnique,
Institut Polytechnique de Paris, 91120 Palaiseau, France

In low temperature nonequilibrium plasmas, the dominating channel of CO_2 conversion is usually the dissociation of mixture molecules by electron impact under high electric field and high deposited energy, which can be provided by nanosecond discharges. It is important to apply time-resolved measurements of major species like atomic oxygen in the CO_2 discharges to better understand the dynamic processes.

The nanosecond discharge was initiated in the capillary tube with 2.0 mm of internal diameter and 52.89 mm of inter-electrode distance. High-voltage pulses (9 kV of amplitude, 30 ns of FWHM and 10 Hz of repetitive frequency) were delivered via the coaxial cable. CO_2 under 19.5 mbar flowed at the rate of 10 sccm so that each discharge was initiated in the new gas portion.

Two-photon absorption laser-induced fluorescence (TALIF) was used to measure the absolute density of atomic oxygen in the afterglow. The ground-state O atoms were excited by a 225.7 nm focused laser pulse, and 845 nm fluorescence signal was detected by a photomultiplier (PMT). An optical pulse slicer was used to narrow the bandwidth of the laser pulse to determine the effective decay rates of the excited O atoms. Calibration was taken by Xe-TALIF under the pressure of 2 mbar.

The measured electrical parameters of the CO_2 discharge show that the reduced electric field reaches 700 Td and the specific deposited energy is almost 1 eV/particle immediately after the first nanosecond pulse. The TALIF measurements indicate a temporal profile of $O(3p\ ^3P_{0,1,2})$ effective decay rates between 0.3 to 0.9 ns^{-1} and ground-state O-atom absolute density between 10^{16} to 10^{17} cm^{-3}, which gives the dissociation rate up to 20 % in a single pulse.

Acknowledgements

The work was partially done in the framework of activity of E4C Interdisciplinary Center of IPP.

References

[1] G.V. Pokrovskiy, PhD Thesis, l'Institut Polytechnique de Paris (2021)
[2] G.V. Pokrovskiy, N.A. Popov and S.M. Starikovskaia, Plasma Sources Sci. Techn., **31(3)**, 035010 (2022).

Characterization of CO_2 atmospheric pulsed microwave plasmas in Surfaguide reactor with a highly time–resolved optical emission spectroscopy

Lucas Silberer[1], **Sergey Soldatov**[1], **Guido Link**[1], **John Jelonnek**[1,2]

Karlsruhe Institute of Technology (KIT), [1]IHM, [2]IHE, 76131, Karlsruhe, Germany

Carbon dioxide capture and conversion is a promising tool to mitigate the man-made CO_2 emissions into the atmosphere and save the surpluses of renewable electric energy in the form of liquid hydro carbonates. One of the most efficient reactors for direct CO_2 splitting to date are plasma reactors [1]. In particular, surface wave-based reactors, e.g. the Surfaguide [2] feature a simple, robust design and high energy densities coupled into the plasma. With operation at vacuum conditions, such reactors show maximum energy efficiencies up to 80% [1]. Operation at atmospheric pressure is favourable for industrial deployment, but its efficiency deteriorates at this pressure significantly [3]. To improve the efficiency, fast gas quenching [4] or fast modulation of the supplied microwave power [5] are considered as a mean. The earlier publications from KIT indicate that the pulsing of the microwave power sustaining the CO_2 atmospheric plasma in coaxial torch advances the efficiency and conversion of the process by more than two times [5]. In present experiment we utilize a novel microwave solid-state power generator (SSPG) with a maximum power of 8 kW to investigate CO_2 atmospheric microwave plasmas in the Surfaguide reactor. The SSPG enables us to supply the microwave power in short pulses with ON and OFF times from 50 ns to 20 μs. By manipulating the ON and OFF times, we control the CO_2 conversion and efficiency of the process. For detailed characterization of pulsed plasmas, a highly time-resolved optical emission spectroscopy (OES) is utilized [5]. With this advanced OES diagnostic, for different duty cycles of power pulsation and different ON and OFF times, the C_2 Swan-band emissions and CO emissions from 420 nm to 520 nm are recorded. The highly time-resolved OES measurements enable to estimate the rotational- and vibrational temperatures of CO and C_2 species within a period of the microwave power modulation.

References:

[1] Annemie Bogaerts and Erik C. Neyts; ACS Energy Letters 2018 3 (4), 1013-1027, DOI: 10.1021/acsenergylett.8b00184

[2] Moisan, Michel; Nowakowska, Helena (2018): Plasma Sources Sci. Technol. 27 073001, https://doi.org/10.1088/1361-6595/aac528.

[3] F A D'Isa et al (2020): Plasma Sources Sci. Technol. 29 105009, https://doi.org/10.1088/1361-6595/abaa84.

[4] Ante Hecimovic, Federico A. D'Isa, Emile Carbone, Ursel Fantz (2022): Journal of CO2 Utilization, Volume 57, 101870, ISSN 2212-9820, https://doi.org/10.1016/j.jcou.2021.101870.

[5] Soldatov, S.; Link, G.; Silberer, L.; Schmedt, C. M.; Carbone E.; D'Isa, F.; Jelonnek, J.; Dittmeyer, R.; Navarrete, A. (2021): ACS Energy Lett. 2021, 6 (1), 124−130, https://doi.org/10.1021/acsenergylett.0c01983.

Plasma treatment of nanoreactors for controlled synthesis of nanomaterials and their use in electrocatalysis and sensing

Gabriel Boitel-Aullen[1], Paolo Cignoni[1], Andriana Loukovitou[1], Steffen Schüttler[2], Thais Schroeder Rossi[1], Maximilian Gerwin[1], Judith Golda[2], Kristina Tschulik[1]

[1] *Ruhr University Bochum, Faculty of Chemistry and Biochemistry, Chair of Analytical Chemistry II, Electrochemistry and nanoscale materials, ZEMOS, Universitätsstraße 150, 44801 Bochum, Germany*
[2] *Ruhr University Bochum, Faculty of Physics and Astronomy, Chair of Experimental Physics II, Plasma interface physics, NB 5, Universitätsstraße 150, 44801 Bochum, Germany*
e-mail : kristina.tschulik@ruhr-uni-bochum.de

The development of environment-friendly and efficient materials for applications in the domains of energy has now become a major challenge. To this purpose, nanomaterials, which exhibit enhanced physical properties at the nanoscale while reducing the quantity of active material, constitute an appropriate answer to these issues. Gold nanoparticles (NPs) and gold-based bi-metallic NPs are well-known systems for applications in the fields of electrocatalysis or sensing. In this work, we propose an original bottom-up synthesis route of these systems, in which the metallic precursors are encapsulated inside reverse micelles. They consist of aqueous microemulsions dispersed in organic phase, which is stabilized by molecular or polymeric surfactants.[1] The spatial confinement induced by this method allows to better control NPs formation and configuration, and thus, to better tailor target properties.

Reduction of the metallic salts inside the reverse micelles has already been achieved thanks to chemical agents, or by electrochemistry.[1,2] Here, we propose to take advantage of the highly reactive species produced by a plasma source. Several ambient pressure plasma sources are tested, with different admixtures, on the Au mono and bi-metallic NPs samples, in which the precursor can be either in solution, or deposited onto a surface prior the plasma treatment. The plasma-synthesized NPs are subsequently compared with the ones obtained by chemical or electrochemical methods, in terms of efficiency for hydrogen evolution reaction (HER). The preliminary results obtained on these systems are promising, showing the possibility of a control over NPs concentration and configuration (alloy or core-shell structures for bi-metallic NPs), and increased catalytic activity over HER, even with low amounts of metal.

References

[1] M. V. Evers, M. Bernal, B. Roldan Cuenya, K. Tschulik, Angewandte Chemie, 58, 8221–8225 (2019)
[2] M. Jaugstetter, N. Blanc, M. Kratz, K. Tschulik, Chemical Society reviews, 51, 2491–2543 (2022)

Effluent nozzles in Reverse-vortex-stabilized microwave plasmas for performance enhancement

C. van Deursen[1], H.M.S. van Poyer[1], Q. Shen[1], W.A. Bongers[1], F.J.J. Peeters[2],
F.M.A. Smits[1,3], M.C.M. van de Sanden[1,4]

[1]DIFFER, de Zaale 20, Eindhoven, The Netherlands

[2]TU Eindhoven, Dept. Of Mechanical Engineering, Eindhoven, The Netherlands

[3]Leiden Institute of Physics, Leiden University, The Netherlands

[4] TU Eindhoven, EIRES and Dept. Applied Physics, The Netherlands

Efficiency and conversion in a reverse vortex microwave plasma utilized for CO_2 dissociation are enhanced by considering and optimizing the thermal trajectory of the plasma effluent using a converging diverging nozzle. The nozzle mixes the cold, non-converted gas on the outside of the flow with the hot, active gas in the middle of the flow and to force the gas to accelerate, thereby cooling the effluent. The temperature profile of the plasma is determined at 2 axial positions: at plasma height and just before the gas enters the nozzle. The temperature of the gas exiting the nozzle is determined by a thermocouple.

Diagnostics and 0D modelling of methane conversion in a ns-pulsed pin-to-pin plasma reactor.

S. Van Rompaey[1,2], E. Morais[1], M. Gromov[2], A. Nikiforov[2], R. Morent[2] and A. Bogaerts[1].

[1]Research group PLASMANT, University of Antwerp, Antwerp, Belgium
[2] Research Unit Plasma Technology (RUPT), Ghent University, Ghent, Belgium

With the world striving for a carbon-neutral society, sustainable alternatives are being investigated as energy sources, aiming to slow fossil fuel exploration and emissions of greenhouse gases. Hydrogen (H_2) is an interesting energy source because it can supply more energy per kilogram than fossil fuels.[1] However, the production of H_2 currently faces a few drawbacks. For example, H_2-production by steam methane reforming is very energy-intensive, heavily reliant on fossil fuels and it generates large amounts of CO_2.[1] On the other hand, water electrolysis comes with a high energy cost, resulting in its limited application for H_2-production.[2] A promising solution is plasma-assisted pyrolysis of hydrocarbons as it has a low energy cost compared to its competitors and produces no CO_2.[3]

In this contribution, we describe how nanosecond pulsed plasma discharges are used to generate high electron densities and a strong non-equilibrium medium, which stimulates methane conversion, resulting in a high energy efficiency.[4] These nanosecond pulses are applied to a pin-to-pin plasma reactor that uses a feed gas of 100 % methane (CH_4) at different applied pressures from 0.5 to 2 bar. The plasma is characterised in several ways. I/V-traces are collected to obtain the applied power and the dimensions of the plasma discharge are gleaned from time-resolved ICCD-images. Subsequently, the power density can be derived from the applied power and plasma volume. Moreover, optical emission spectroscopy is employed to acquire information on electron density and gas temperature in the plasma. The results from the experiments are then used as input parameters for the 0D-model, allowing for an accurate understanding of the gas-phase chemical kinetics in the reactor. Thus, we try to bridge this gap of fundamental knowledge in the process of methane dissociation, laying a solid basis for green H_2-synthesis via plasma technology.

References

[1] M. Gautier, V. Rohani, L. Fulcheri, Int. J. Hydrog. Energy **42**, 28140-28156 (2017).
[2] E. Tatarova, N. Bundaleska, J. P. Sarette, C. Ferreira, PSST **23**, 063002 (2014).
[3] L. Fulcheri, N. Probst, G. Flamant, F. Fabry, E. Grivei, X. Bourrat, Carbon **40** (2002).
[4] H. Taghvaei, A. Jahanmiri, M. R. Rahimpour, M. M. Shirazi, N. Hooshmand, J. Chem. Eng. **226** (2013).

Cold atmospheric plasma and TiO_2 photocatalysis for the treatment of polluted indoor air

T. Vazquez[1], **D. Wiedermann**[2], **J. Babic**[2], **Z. Machala**[1]

[1]*Faculty of Mathematics, Physics, and Informatics, Comenius University Bratislava, Slovakia*
[2]*IQ Capital s.r.o., Banská Bystrica, Slovakia*

Indoor air contains many harmful compounds (chemical pollutants, bacteria, pathogenic aerosols, tobacco smoke, etc.) that can cause respiratory, cardiovascular, and oncological diseases. It is an important health issue as it might be responsible for an excess of millions of deaths each year [1]. Achieving a high indoor air quality would be therefore a major advance for public health.

In this study, we used cold atmospheric plasma and photocatalysis for the treatment of indoor air at large gas flow rates (>100 L/min). The main advantage using these technologies is the capability to destroy the pollutants contrary to traditional filters that just trap them. In addition, cold atmospheric plasma and photocatalysis have shown to be efficient for the decomposition of a wide range of pollutants, and they have also recently proved to be effective for inactivation of viruses such as SARS-CoV-2 [2].

We designed an air decontamination device that combines a surface Dielectric Barrier Discharge (DBD) for the plasma generation, and a TiO_2 coating which is activated by UV-A LEDs. The main goal of this stage of our work is to decompose chemical pollutants (formaldehyde, acetone and acetaldehyde) to form CO_2 and H_2O. The overall efficacy of the device is promising given the very short residence time of the pollutant in the reactor (single-pass method and a large gas flow). We also monitored the concentration of ozone generated by the DBD, which is a strong oxidant of the pollutants but its excess is well decomposed by the photocatalytic process to prevent its outflow from the device. Electrical parameters of the DBD are key components to find the best compromise between the species produced by the plasma, the interaction with the photocatalysis process, and the overall efficiency of the device.

This work was supported by Slovak Research and Development Agency APVV-17-0382, and APVV-20-0566, and a postdoctoral support of Comenius University Bratislava.

References

[1] World Health Organization, WHO guidelines for indoor air quality: selected pollutants, Regional Office for Europe (2010)
[2] H. Mohamed *et al*, Frontiers in Physics, **9**, 683118 (2021)

NH_3 synthesis in a catalytic atmospheric pressure RF discharge

S.C.L. Vervloedt[1], **C. Stewig**[1], **A. von Keudell**[1]

[1]*EP2, Department of Astronomy and Physics, Ruhr-University Bochum, Bochum, Germany*

Since the beginning of the last century, a growing fraction of the population depends on the availability of artificial fertilisers. Ammonia is one of the main ingredients for the nitrogen-based fertilisers. At the moment, this substance is synthesised with the Haber-Bosch process, which uses a significant amount of the global energy consumption. A potential alternative would be plasma catalysis, since such a reactor can be easily turned on/off depending on the on-site demand and the supply of renewable energy.

This contribution will present on the experimental results of the NH_3 synthesis in an N_2+H_2+He atmospheric catalytic homogenous RF discharge. The goal of the project is to observe and characterise plasma-catalytic synergism. The NH_3 concentration is obtained with Fourier transform infrared (FTIR) absorption spectroscopy – using the HITRAN database [1] – and the excitation of N_2 by the plasma is characterised with optical emission spectroscopy (OES). The reactor is optimised for studying this synergism by maximising the surface-to-volume ratio in a rectangular configuration of parallel oriented electrodes. These electrodes are covered from the plasma with glass plates, which act as a dielectric barrier resulting in a homogenous plasma. The plasma side of these glass plates will be modified to contain the catalytic materials, thereby creating a catalytic-plasma reactor.

The plasma synthesis of NH_3 is studied to benchmark the reactor before introducing a catalytic material. The highest conversion is achieved at nitrogen-deficient conditions, i.e. 5% $N_2/(N_2+H_2)$. This could be explained by considering a reduced N_2 excitation with a increasing N_2 admixture. The dissociation of the stable N_2 molecules is a bottle neck in the formation of NH_3 [2]. Characterising the excitation of N_2 with the vibrational temperature of the $N_2(C)$ state – which is created through excitation by electron impact – shows that increasing the N_2 admixture reduces this temperature, thus the overall excitation of N_2 as well.

References

[1] Gordon et al, J. Quant. Spectrosc. Radiat. Transf. **277**, 107949 (2022)
[2] Mehta et al, Nat. Catal. **1**, 269-275 (2018)
[3] Ceppelli et al , Plasma Sources Sci. Techn. **30**, 115010 (2021)

Shielding protection by mesoporous catalysts for improving plasma-catalytic ambient ammonia synthesis

Yaolin Wang[1] and Xin Tu[1]

[1] Department of Electrical Engineering and Electronics, University of Liverpool,
Liverpool, L69 3GJ, UK

Plasma catalysis is a promising technology for decentralized small-scale ammonia (NH_3) synthesis under mild conditions using renewable energy and shows great potential as an alternative to the conventional Haber-Bosch process[1]. To date, this emerging process still suffers from a low NH_3 yield due to limited knowledge in the designing of highly efficient catalysts and the *in situ* plasma-induced reverse reaction (i.e., NH_3 decomposition). Here we show that a bespoke design of supported Ni catalysts using mesoporous MCM-41 could enable efficient plasma-catalytic NH_3 production at 35 °C and 1 bar with >5% NH_3 yield at 60 kJ/L. Specifically, the Ni active sites were deliberately deposited on the external surface of MCM-41 to enhance plasma-catalyst interactions and hence improve NH_3 production. The desorbed NH_3 could then diffuse into the ordered mesopores of MCM-41 to be shielded from decomposition due to the absence of plasma in the mesopores, that is, shielding protection, thus driving the reaction forward effectively. A unique integrated plasma/FTIR cell for in situ probing of plasma-induced surface reactions over different Ni/MCM-41 catalysts, together with comprehensive catalyst characterisation and plasma diagnostics, was applied to clearly demonstrate and elucidate this catalytic mechanism for enhanced plasma-catalytic ammonia synthesis at ambient conditions with solid and convincible evidence. This strategy sheds light on the importance of a rational design of catalysts specifically for improving plasma-catalytic processes[2].

References

[1] Y. Wang, M. Craven, X. Yu, J. Ding, P. Bryant, J. Huang, X. Tu, **ACS Catal.**, 9, 10780-10793 (2019).

[2] Y. Wang, W. Yang, S. Xu, S. Zhao, G. Chen, A. Weidenkaff, C. Hardacre, X. Fan, J. Huang, X. Tu, **J. Am. Chem. Soc.**, 144, 12020-12031 (2022).

Ferroelectrics-induced Surface Charge Effect on Plasma Properties and Instability

Yijie Xu[1], Ning Liu[1] and Yiguang Ju[1]

[1]Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey, United States of America

As more renewable energy enters the market, plasma-assisted manufacturing is one way to utilize electrical power in a turnkey process. Compared to the traditional high-temperature equilibrium process, plasma-assisted methods are pursued as promising techniques for manufacturing under energy-efficient conditions and possibly changing the reaction pathways. However, there are scientific challenges in simultaneously manipulating plasma discharge and surface reactions directly and efficiently, which are critical parameters in plasma-assisted chemical manufacturing.

Here the possibility of experimentally manipulating plasma properties and instability by controlling the surface charge introduced by ferroelectrics materials will be explored. Ferroelectric materials are presented due to their unique feature of spontaneous polarization, which will generate surface charge to interact with electrons in the plasma, increasing the energy density in the reactor. It has been understood that in most plasmas, the role of the electrons is so crucial that they not only ionize species but also dissociate and excite the reactant gas through electron-impact collisions. The surface charge is expected to influence the electron properties in the plasma, resulting in plasma performance changes. Furthermore, the previous simulation shows surface charge can affect the electric field, electron number density and electron temperature in DBD plasma, as well as significantly improve surface reaction by increasing adsorption energy when it comes to reaction kinetics.

Laser diagnostic approaches such as Thomson scattering and electric-field-induced second-harmonic generation will be employed to evaluate plasma properties and instability in this work. In a word, the effect of surface charge, introduced by ferroelectrics materials, on plasma properties and instability will be investigated with laser diagnostics to better understand and control the plasma-assisted chemical manufacturing process.

Plasma process for recycling of plastic wastes towards the productions of carbon nanomaterials and hydrogen

Xiao Yu[1], Guoxing Chen[1], Marc Widenmeyer[2], Isabel Kinski[1], Xingmin Liu[2], Dominique Schüpfer[1], Xin Tu[3], Gert Homm[1], Anke Weidenkaff[1,2]

[1]Fraunhofer Research Institution for Materials Recycling and Resource Strategies IWKS, Alzenau, Germany
[2]Department of Materials and Earth Sciences, Technical University Darmstadt, Darmstadt, Germany
[3]Department of Electrical Engineering and Electronics, University of Liverpool, Liverpool, UK

With the development of modern industry and population expansion over the last few decades, global demand and consumption of plastic materials have expanded substantially. The COVID-19 pandemic further enhanced the consumption of medical plastic materials, which are used to produce single-use health protection products. The current disposal routes for the post-customer wastes are mainly thermal utilization and landfill, which is environmentally unfriendly. More efficient and sustainable recycling methods are highly needed. Non-thermal plasma technologies have gained a lot of attention and are particularly appealing for quickly and efficiently converting waste plastics into valuable chemicals and materials. In this study, an atmospheric pressure microwave plasma was combined with perovskite-type pre-catalysts [1] for the co-production of H_2 and value-added carbon composite materials. Different types of real-word plastic wastes have been tested with and without a pre-catalyst including high-density polyethylene, low-density polyethylene, polypropylene and polystyrene. For both thermal catalytic [2] and plasma catalytic processes, the effect of different process parameters and pre-catalyst types on gas production and carbon species was thoroughly investigated. The physicochemical characteristics of the produced carbon nanomaterials were comprehensively characterized by the state-of-the-art techniques to investigate the relationship between the quantity and quality of carbon materials and plastic wastes types. Coupling thermal catalytic process with microwave plasma discharge resulted in a significant improvement of the H_2 yield. The presented findings demonstrated that the developed pre-catalyst is a promising candidate for the productions of H_2 and the carbon nanotube composites for energy storge applications from plastics in an atmospheric pressure microwave discharge.

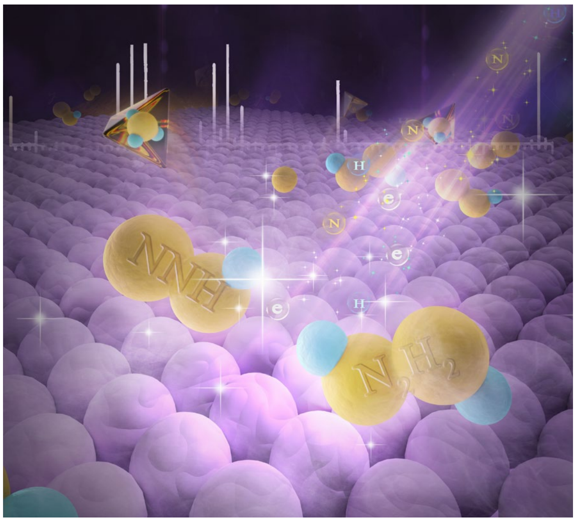
References

[1] G. Chen, et al., J. Membr. Sci., **590**, 117082 (2019)
[2] X. Yu, et al., Appl. Catal. B Environ. 2023 (submitted)

In situ identification of NNH and N_2H_2 by using molecular-beam mass spectrometry in plasma-assisted catalysis for NH_3 synthesis

<u>Hao Zhao</u>[1,2], Guohui Song[2,3], Zhe Chen[1], Xiaofang Yang[4], Chao Yan[2], Shota Abe[1], Yiguang Ju[2], Sankaran Sundaresan[1], Bruce E. Koel[1]

[1]Department of Chemical and Biological Engineering,
Princeton University, Princeton, NJ 08544, USA
[2]Department of Mechanical and Aerospace Engineering,
Princeton University, Princeton, NJ 08544, USA
[3]School of Energy and Power Engineering,
Nanjing Institute of Technology, Nanjing 211167, CN
[4]Princeton Nuenergy Inc., Princeton, NJ 08540, USA



ABSTRACT: Ammonia synthesis at 533 K and atmospheric pressure was investigated in a coaxial dielectric barrier discharge (DBD) plasma reactor without packing and with porous γ-Al_2O_3, 5 wt% Ru/γ-Al_2O_3, or 5 wt% Co/γ-Al_2O_3 catalyst particles. Gas-phase species were monitored in-situ using an electron impact molecular-beam mass spectrometer (EI-MBMS). Gas-phase species NNH and N_2H_2 were first identified under common conditions of plasma-assisted ammonia synthesis and were present at levels comparable to NH_3 in the plasma discharge. Concentrations of NNH, N_2H_2, and NH in a reactor packed with γ-Al_2O_3 or other particles were lower than those observed in an empty reactor, while NH_3 increased. These observations point to the importance of NNH and N_2H_2 in plasma-assisted surface reactions in ammonia synthesis. Reaction pathways of direct adsorption of gas-phase NNH and N_2H_2 on solid surfaces and subsequent reactions were proposed. This study demonstrated that in-situ identification of gas-phase species via EI-MBMS provides a powerful approach to study the kinetics of plasma-assisted catalysis.

References

[1] H. Zhao, G. Song, Z. Chen, X. Yang, C. Yan, S. Abe, Y. Ju, S. Sundaresan, B.E. Koel, ACS Energy Lett., 7 (2022) 53–58.