KEROGREEN Workshop

Plasma catalysis for renewable Fuels and Chemicals

15 November 2019

This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under grant agreement No 763909.

Towards sustainable and green aviation fuel production

KEROGREEN Workshop
Plasma catalysis for renewable Fuels and Chemicals

15 November 2019

Location: Dutch Institute for Fundamental Energy Research (DIFFER) - *Collegezaal*
De Zaale 20, 5612 AJ Eindhoven, The Netherlands
Chair: Prof. Roland Dittmeyer, Karlsruhe Institute of Technology, DE

KEROGREEN is a Research and Innovation Action (RIA), financed by the European Commission under the Call Topic "Competitive low-carbon-energy - new knowledge and technologies" (H2020-LCE-06-2017) in the H2020 Work programme "Secure, Clean and Efficient Energy".

The main goal of this 4-years project is the development and testing of an innovative conversion route for the production of sustainable aircraft grade Kerosene from water and air powered by renewable electricity. The KEROGREEN conversion route is based on plasma driven dissociation of air captured CO_2, solid oxide membrane oxygen separation and Fischer-Tropsch (F-T) kerosene synthesis.

Plasma technology offers new prospects for the activation of molecules, atoms, radicals and ionised particles interacting with electrochemically active materials, resulting in enhanced productivity and reduced energy consumption. This workshop solicits contributions in the development of new fuel synthesis techniques based on novel materials, both experimental and theoretical, leading to commercially attractive production routes. The technology should be consistent with future decentralised electricity production sites, often remote and spread out over large areas, with individual units at the MW scale, as opposed to the high energy density plants of today localised in urbanised areas. Long distance transport of the gaseous and liquid fuels produced is by pipeline, rather than by expensive high voltage powerlines.

Towards sustainable and green aviation fuel production

Programme

9:00	**Registration**
10:00	**Welcome** Prof. Richard van de Sanden, director of DIFFER, NL
10:15	**EU Project KEROGREEN: Main Challenges** Adelbert Goede, DIFFER, NL
10:35	**Progress on CO$_2$ plasmolysis at DIFFER** Prof. Richard van de Sanden, DIFFER, NL
10:55	**Synergistic combination of solid oxide electrolyte cells with plasma processes** Dr. Michalis Tsampas, DIFFER, NL
11:15	**Coffee break**
11:30	**Plasma-assisted CO$_2$ conversion: Computer modelling for a better understanding of the underlying mechanisms** Prof. AnnemieBogaerts, University of Antwerp, BE
12:00	**Development of an all-ceramic cathode for highly efficient CO2 electrolysis** Prof. Hennie Bouwmeester, University Twente, NL
12:30	**POSTER SESSION with walking Lunch**
14:30	**Conversion of CO$_2$ into added-value chemicals like CO using microwave generated plasmas – a collaborative project within KIT-IGVP-IPP** Prof. UrselFantz, Max Plank Institute for Plasma Physics, DE
15:00	**A pathway to a CO$_2$-neutral mobility: Plasma Fuel** Stephan Renninger, Stuttgart University, DE
15:30	**The quest for CO$_2$-free hydrogen - challenges & opportunities of plasma-based methane pyrolysis** Dr. Frederik Scheiff, BASF SE, DE
16:00	**Coffee break**
16:15	**Plenary discussion on the way forward** All Speakers interacting with Audience, **Chair**Prof. Roland Dittmeyer, Karlsruhe Institute of Technology, DE
16:45	**Closing remarks** Prof. Roland Dittmeyer, Karlsruhe Institute of Technology, DE
17:00	**End of workshop**

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Speakers

and resp. abstracts

Prof. Dr. Annemie Bogaerts

Annemie Bogaerts has a PhD in chemistry (1996), and is full professor at the University of Antwerp (BE). She is head of the interdisciplinary research group PLASMANT, which he founded after her own PhD work, and which counts about 35 scientists.
Her research interests include studying plasmas by modeling and experiments, for various applications, but with main emphasis on plasma-based gas conversion and plasma catalysis (CO_2 conversion, CH_4 conversion, and N_2 fixation), as well as plasma medicine (cancer treatment). The modeling for plasma-based gas conversion includes modeling plasma chemistry, plasma reactor design and plasma-catalyst interactions. The experimental work focuses on gliding arc plasmas, dielectric barrier discharges (for plasma catalysis) and atmospheric pressure glow discharges.

During the KEROGREEN workshop on Plasma catalysis for renewable Fuels and Chemicals, Bogaerts will give a brief overview of the performance of various plasma reactors for CO_2 splitting and dry reforming of methane, and present the results of modeling and experiments on plasma chemistry (with main emphasis on the role of CO_2 vibrational levels in energy efficient CO_2 conversion) and plasma reactor design.

Abstract

Plasma-assisted CO_2 conversion: Computer modelling for a better understanding of the underlying mechanisms

Authors: Annemie Bogaerts, Antonin Berthelot, Vincent Vermeiren, Ramses Snoeckx, Marleen Ramakers, GeorgiTrenchev

Plasma-based CO_2 conversion is gaining increasing interest. To improve this application in terms of conversion, energy efficiency and product formation, a good insight in the underlying mechanisms is desirable. We try to obtain this by computer modelling, supported by experiments. We will first provide a brief overview of the state of the art in plasma-based CO_2(and CH_4) conversion, with different types of plasma reactors. Subsequently, we will present some recent results obtained in Antwerp in this domain, including experiments and modelling for a better understanding of the underlying mechanisms. This includes modelling the plasma chemistry as well as the reactor design, in different types of plasma reactors commonly used for gas conversion, i.e., dielectric barrier discharges (DBDs), gliding arc (GA) discharges, microwave (MW) plasmas and atmospheric pressure glow discharges (APGDs). For the plasma reactor design, we use 2D or 3D computational fluid dynamics modelling. For the plasma chemistry, we make use of zero-dimensional chemical kinetics modelling, which solves continuity equations for the various plasma species, based on production and loss terms, as defined by the chemical reactions. We will focus especially on the the role of vibrationally excited CO_2 levels, which are the key species for enhanced energy efficiency of the CO_2 conversion. Our model reveals the relative importance of various processes, responsible for the CO_2 conversion, in a range of different conditions, and this is linked to the energy efficiency in the various types of plasma reactors. We have also studied the plasma chemistry in CO_2/CH_4 and in CO_2/H_2O mixtures, with the purpose of producing value-added chemicals. The main products formed are a mixture of H_2 and CO, or syngas, with a tuneable H_2/CO ratio depending on the gas mixing ratio. The production of oxygenated compounds, such as methanol, formaldehyde, etc, is very limited, showing the need for combining with a catalyst. A detailed chemical kinetics analysis allows to elucidate the different pathways leading to the observed results, and to propose solutions on how to further improve the formation of value-added products. Finally, we also try to elucidate whether plasma can be formed inside catalyst pores, for different pore sizes and materials, of interest for plasma catalysis.

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Speakers

and resp. abstracts cont'd

Prof. Henny J.M. Bouwmeester

Henny J.M. Bouwmeester, member of the advisory board of KEROGREEN, heads the Electrochemistry Research group, part of the Membrane Science Technology cluster, at the University of Twente, Enschede, The Netherlands, and is part-time professor at the University of Science and Technology of China (USTC) in Hefei, China. His research interests include solid state thermodynamics, ionic transport and interfacial/electrode kinetics closely related to applications such as oxygen transport membranes, solid oxide fuel cells, solid oxide electrolysis cells and sensors. At the KEROGREEN workshop on Plasma catalysis for renewable Fuels and Chemicals, he will lecture about recent investigations towards development of an all-ceramic cathode for direct CO_2 electrolysis.

Abstract

Development of an all-ceramic cathode for highly efficient CO_2 electrolysis

Authors: Yunan Jiang, Yang Yi, Changrong Xia and Henny J.M. Bouwmeester

High-temperature solid oxide cells afford chemical storage of renewable electricity. In particular, the electrochemical conversion of the greenhouse gas CO_2 is attracting increasing interest to facilitate a sustainable energy technology. In this paper, we will present results of investigations towards the use of perovskite-structured $Sr_2Fe_{1.4}Mn_{0.1}Mo_{0.5}O6\text{-}\delta$(SFMM0.1) as cathode material for CO_2 electrolysis. Both parent $Sr_2Fe_{1.5}Mo_{0.5}O6\text{-}\delta$ (SFM) and SFMM0.1 are redox stable in air and 5%H_2/Ar at 850 °C. When dual-phase SFMM0.1-SDC (samaria-doped ceria) is incorporated as cathode in an electrolyte-supported SOEC for electrolysis of pure CO_2 , a current density of 1.35 A/cm^2 is achieved at 800 °C under an applied bias of 1.5 V, without the addition of a reducing gas such as H_2.

The enhanced cell performance relative to that achieved when using SFM-SDC as the cathode can be accounted for by data from electrical conductivity relaxation experiments and first-principle calculations, revealing that oxygen transport, CO_2 adsorption and reduction kinetics are all enhanced upon doping of parent SFM with Mn. The SFMM0.1-SDC composite electrode furthermore exhibits excellent coking resistance. This work shows that SFMM0.1-SDC is a promising alternative to replace metal-based electrodes for direct CO_2 electrolysis.

Prof. Dr-Ing. Ursel Fantz

Ursel Fantz studied physics and got her PhD in Electrical Engineering at the University of Stuttgart, followed by a habilitation in the field of experimental plasma physics at the University in Augsburg. Since 2004 she is at the Max-Planck-Institute for Plasma Physics (IPP) in Garching, where she became division head of the ITER Technology & Diagnostics division in 2010.

Her expertise is in the field of low temperature plasmas physics and diagnostics for industrial applications, ion sources for negative and positive hydrogen ions for neutral beam injection and particle accelerators, and in the cold edge of fusion plasmas.

During the KEROGREEN workshop on Plasma Catalysis for renewable Fuels and Chemicals she will give an overview of the recently started activities on CO_2 conversion by microwave plasmas, performed within a collaborative work of IPP, KIT (Karlsruhe Institute of Technology) and the IGVP (Institute of Interfacial Process Engineering and Plasma Technology) of the University of Stuttgart.

Abstract

Conversion of CO_2 into added-value chemicals like CO using microwave generated plasmas – a collaborative project of KIT-IGVP-IPP

Authors: Ursel Fantz on behalf of the KIT, IGVP and IPP teams
(KIT: J. Jelonnek, G. Link, S. Soldatov; IGVP: M. Walker, A. Schulz, I. Kistner;
IPP: E. Carbone, A. Hecimovic, F. D'Isa, U. Fantz)

The challenge to establish non-equilibrium plasmas as an alternative route for the activation of low-energy molecules into value added chemicals requires competences in plasma technology, plasma physics and diagnostics, plasma chemistry and also engineering aspects for system optimisation and upscaling. The German activities in this collaborative work focus on plasmas close or at atmospheric pressure generated by a microwave field. In order to cover a wide parameter range several sources are used: at atmospheric and sub-atmospheric pressure, the microwave plasma torch (2.45 GHz, up to 3 kW) and a coaxial plasma jet, which are supplemented by a surfaguide system working at lower pressure. Besides developing a process for CO_2 conversion into CO by direct conversion in the plasma or by activation of chemical processes at surfaces (plasma catalysis) admixtures of CH_4 or nitrogen fixation are envisaged as well. Furthermore, the gas separation in the effluent is explored by optimising the structure of the oxygen separation membranes.

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Dr. Adelbert Goede

Adelbert Goede conducted and first published the DIFFER CO_2 plasma dissociation work in 2012. Trained as plasma physicist at AMOLF Amsterdam, he worked at the world leading EU fusion project JET from 1975 to 1988. From 1988 he set up and lead the Earth Observation Division at Space Research Organisation Netherlands, acting as Co-PI of the SCIAMACHY spectrometer launched in 2002 on ESA ENVISAT, producing an invaluable 10 year global dataset of atmospheric CO_2 and other GHGs.He returned to his old field in 2006 to work on the solution rather than the problem of climate change. He coordinates the H2020 KEROGREEN project, the EERA Chemical Energy Storage program, is Advisor to the Director of DIFFER and the German Kopernikus program P2X.

Abstract

EU project KEROGREEN; Main challenges

Author: A P H Goede for the KEROGREEN consortium

Aviation, one of the least tractable of sectors to de-carbonise, has been treated most leniently, so far. Due to its severe mass and volume constraints, kerosene remains the only fuel option insight that enables long haul flight. KEROGREEN CO_2 neutral kerosene, synthesised from air and water, powered by renewable electricity, offers a tantalising way out. CO_2 feedstock is converted by plasma driven dissociation, solid oxide membrane O_2 separation, CO purification by pressure swing adsorption, Water Gas Shift production of Syngas (H_2 and CO) followed by synthesis of kerosene through the Fischer-Tropsch process purified by Hydrocracking. The fuel cycle is closed by re-capturing CO_2 emitted during flight by ground based air capture. Because the synthesised kerosene contains no sulphur and produces no soot (no aromatic compounds), it meets future air pollution standards. Synergism between plasma activated species and novel perovskite electrodes of the oxygen selective membrane is expected to increase productivity. Innovative system integration, including heat integration and CO_2 recirculation, fits the entire system into a container sized pilot to produce 0.1 kg/hr kerosene by 2022. Specific challenges include the oxygen separation and the system integration, both breaking new ground. The overall challenge is to increase conversion yield and energy efficiency of both the synthesis chain and the carbon capture from air, resulting in reduced cost and allowing upscaling to the size of a decentralised and remote production plant, close coupled and sized to the renewable electricity source, with transportation and storage of the renewable energy produced to point of use by pipeline rather than expensive HV power lines.

Stephan Renninger

Stephan Renninger has a Master's degree in Sustainable Electrical Energy Supply, with a specialization on Electrical Energy Storages. He is leading the execution of the Plasma Fuel project at the Chair for Electrical Energy Storage Systems, Institute for Photovoltaics, University of Stuttgart since 2018.
Besides his university background he has industry experience in energy storage development, as well as power engineering.

During the KEROGREEN workshop on Plasma catalysis for renewable Fuels and Chemicals, he will represent the University of Stuttgart and their partners to give an overview of the pursued process for sustainable fuel production.

Abstract

A pathway to a CO_2-neutral mobility: Plasma Fuel

Authors: Stephan Renninger, Maike Lambarth, Peter Birke

The challenge to establish non-equilibrium plasmas as an alternative route for the activation of low-energy molecules into value added chemicals requires competences in plasma technology, plasma physics and diagnostics, plasma chemistry and also engineering aspects for system optimisation and upscaling. The German activities in this collaborative work focus on plasmas close or at atmospheric pressure generated by a microwave field. In order to cover a wide parameter range several sources are used: at atmospheric and sub-atmospheric pressure, the microwave plasma torch (2.45 GHz, up to 3 kW) and a coaxial plasma jet, which are supplemented by a surfaguide system working at lower pressure.
Besides developing a process for CO_2 conversion into CO by direct conversion in the plasma or by activation of chemical processes at surfaces (plasma catalysis) admixtures of CH_4 or nitrogen fixation are envisaged as well. Furthermore, the gas separation in the effluent is explored by optimising the structure of the oxygen separation membranes.

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Dr. Frederik Scheiff

Frederik Scheiff has a PhD in chemical engineering from TU Dortmund University, where he worked 3 years in the field of micro reaction engineering research. He then joined BASF in 2014, working in a team on high temperature reactions. In 2017 he took over the lead of this team, which is embedded in BASF's reaction engineering research group.

Besides his background in industrial reaction engineering, he gained experience in decarbonization technologies and has spent several years of research on renewable hydrogen by methane pyrolysis.

During the KEROGREEN workshop on Plasma catalysis for renewable Fuels and Chemicals he gives an overview on current plasma research for methane decomposition.

Abstract

The quest for CO_2-free hydrogen - challenges & opportunities of plasma-based methane pyrolysis

Authors: Dr. Frederik Scheiff, Dr. Kai Rainer Ehrhardt, Dr. Stephan Schunk

The response to global climate change will foster a fundamental change from fossil to renewable energies in all industries. Electrification is seen as important pillar for many sectors, such ase-mobility, renewable fuels and sustainable chemistry. However, production of chemicals and synthetic fuels with low CO_2-footprint is only feasible with new CO_2-avoiding or CO_2-utilizing production technologies. As CO_2 avoidance and utilization are energy-intensive exercises,the efficient use of renewable electricity will be a key task in the future. That raises the need for new e-reactor technologies and plasma-reactors are aspired as one promising approach.

Besides the plasma-based activation of CO_2, as in the KEROGREEN project, plasma reaction technologies for CO_2 avoidance also gain importance. This presentation will elaborate on methane decomposition for hydrogen generation as one example for current research on plasma-reactor technology in the framework of CO_2 debate.

Today, hydrogen is mostly produced by methane steam reforming, which produces about 9 t of CO_2 per ton of H_2. A potentially CO_2-free electric hydrogen generation route is the thermal decomposition of methane to hydrogen and solid carbon, called methane pyrolysis. This route requires less energy than water electrolysis and could be CO_2-free in case of electric energy supply. The plasma-route is currently one approach for methane decomposition. However, it competes with other thermal, catalytic and non-catalytic routes. To this end, current activities on methane pyrolysis as well as challenges and opportunities of plasma-based methane decomposition will be review in this presentation.

Dr. Mihalis N. Tsampas

Mihalis Tsampas has a PhD in catalysis and electrochemistry and since 2014 he is a senior researcher and group leader of Catalytic and Electrochemical Processes for Energy Applications (CEPEA), at the Dutch Institute for Fundamental Energy Research (DIFFER). Before joining DIFFER, he was appointed as a postdoctoral researcher in the CNRS institute for Catalysis IRCELYON in France and in the Energy, environment and water research center at the Cyprus institute, while he obtained his PhD from the Department of Chemical Engineering of the University of Patras in Greece (2010). He is the co-author of more than 40 scientific articles, one book chapter and holds a patent. His activities are focused on the development of efficient electrochemical systems

Abstract

Synergistic combination of solid oxide electrolyte cells with plasma processes

Authors: A. Pandiyan, V. Kyriakou, R. Sharma, D. Neagu, A. Goede, S. Welzel,
M.C.M. van den Sanden, M.N. Tsampas

High-temperature solid oxide electrolysis cells (SOCs) are advanced electrochemical energy storage and conversion devices with high conversion/energy efficiencies. They offer attractive high-temperature electrolysis routes which can convert CO_2 or CO_2/H_2O into valuable chemical feedstock, enabling large-scale energy storage/conversion and facilitate the integration of renewable energies into the electric grid. SOCs typically consists of an ion conducting electrolyte, an anode and a cathode where electrolysis reactions take place. The high operating temperature and difficult activated carbon–oxygen double-bond of $CO_2$2 put forward strict requirements for SOC cathode. Great efforts are being devoted to develop suitable cathode materials with high catalytic activity and excellent long-term stability for CO_2/H_2O electro-reduction.

CO_2 valorisation can also be realized via plasma processes, in which gasses are activated by energetic electrons instead of heat. This allows thermodynamically difficult reactions, such as CO_2 splitting, to occur with reasonable energy cost. The main bottleneck of this process is that CO remains mixed with O_2 and residual CO_2. Therefore, efficient gas separation and recuperation are essential for obtaining pure CO, which can be used to produce CO_2-neutral fuels using water gas shift (WGS) and Fischer-Tropsch reactions. In this contribution, we examine the synergistic combination of SOCs and plasma processes where CO_2 activation is used to relax the SOCs material requirements. For the realization of this scope we follow a two pathway approach, in the first one SOCs are connected downstream with a plasmolysis reactor and in the second one an integrated approach is examined, where SOCs and plasma activation occurs in a single unit.

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Prof. Dr. Ir. M.C.M (Richard) van de Sanden

Richard van de Sanden is the Director of the Dutch Institute for Fundamental Energy Research (DIFFER) and Professor in Plasma Physics and Chemistry at the Department of Applied Physics, Eindhoven University of Technology.
At DIFFER he focuses on the plasma physics/chemistry/-surface interaction during renewable energy driven gas conversion into CO_2 neutral fuels and chemicals. He has authored and co-authored over 500 papers in peer-reviewed journals and is the co-inventor of over 20 patents. In 2008 he won the European William Crookes Plasma Prize and in 2009 he received the FOM Valorisation Prize. He is a member of the Royal Netherlands Academy of Sciences and was awarded with the Plasma Prize of the AVS Plasma Science and Technology in 2014.

Abstract

Plasma activation of carbon dioxide: status and outlook

Authors: R. van de Sanden, W. Bongers, P. Diomede, F. Peeters, P. Viegas, B. Wolf, T. Righart, G. van Rooij, A. van de Steeg, Q. Ong, A. Goede, S. Welzel, M. Tsampas

In this presentation I will summarize the status of the plasma activation of carbon dioxide work at DIFFER using the vortex stabilized microwave plasma flow reactor at 2.45 GHz. We will present the fundamental studies to establish the main CO formation mechanism. It is observed (varying flow and pressure at constant power) that in the pressure range where optimal energy efficiencies are reached, the plasma undergoes several transitions. A diffuse glow at low pressure transitioning to a confined elongated mode at higher sub-atmospheric pressures is observed using imaging techniques. This also results in a steep increase in the electron density from 10^{17} to larger than 10^{19} m^{-3}, in the low pressure regime after which the electron density saturates as a consequence of the skin depth limitation of the plasma formation in the higher pressure regime (150-600 mbar), as determined from microwave interferometry measurements. The translational temperature as determined from the spectral width of the atomic oxygen at 777 nm clearly tracks the mode transitions and electron density, clear evidence for a local chemical equilibrium, with temperatures in the range 2500-6500 K. The observed high translational temperatures exclude a significant contribution of the proposed nonequilibrium pathway of ladder climbing to obtain high energy efficiencies. The energy efficiency behaviour as function of pressure shows a very steep increase in the low pressure regime (up to 150 mbar), but the maximum is reached before the translational temperature reaches its maximum. The efficiency in the low pressure regime is weakly flow dependent whereas at higher sub-atmospheric pressures the flow strongly influences the energy efficiency and conversion. Detailed flow modelling and a simplified 1.5D model, representing the plasma by a heat source shows that flow pattern and (turbulent) diffusion mechanism are as essential for a quantitative understanding of the energy and conversion efficiency as function of pressure and flow.

Poster programme

and resp. abstracts

Towards sustainable and green aviation fuel production

Poster programme (alphabetic order)

ID	Last name	First name	Affiliation	Title
1	Guerra	Vasco	Instituto Superior Técnico, Lisbon/DIFFER	Vibrational energy relaxation in CO_2 and CO_2-N_2 pulsed discharges
2	Hecimovic	Ante	Max Planck Institute for Plasma Physics (IPP)	CO_2 dissociation from low to high pressures in plasma torch and surfaguide
3	Mushtaq	Usman	DIFFER	Protonic Ceramic based Electrochemical Cells for the Generation of Renewable Fuels : Development and Characterization
4	Rana	Surjyakanta	University of Antwerp	Plasma catalytic reforming of CO_2 over supported CuO-based materials in a dielectric barrier discharge reactor
5	Schulz	Andreas	University of Stuttgart, IGVP	Microwave plasma reactor for CO_2 decomposition
6	Slaets	Joachim	University of Antwerp	Gliding Arc Plasma: A Promising Approach for CO_2 and CH_4 Conversion into Value-added Chemicals
7	Soldatov	Sergey	Karlsruhe Institute of Technology	Sustaining atmospheric plasma with nanosecond microwave pulses to increase the efficiency of CO_2 splitting
8	Sorkun	Murat Cihan	DIFFER	Discovering two-dimensional materials via artificial intelligence
9	Tezsevin	Ilker	DIFFER	High-throughput computational screening of CO_2 reduction and O transport materials
10	van de Steeg	Alex	DIFFER - NFC	In-situ measurements of temperatures and species densities in contracted CO_2 microwave plasma for solar fuel production
11	Viegas	Pedro	DIFFER	Self-consistent Fokker-Planck approach to vibrational kinetics of CO_2 plasma
12	Viswanathan	Narasimhan	DIFFER	Automated screening of single atom catalysts for solar fuel conversion
13	Zhang	Qi	DIFFER	A multi-scale computational framework for electroactive materials discovery for redox flow batteries
14	Zhou	Xuan	DIFFER	A multi-scale computational framework for organic electrode materials discovery for Li batteries

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1

Vibrational energy relaxation in CO_2 and CO_2-N_2 pulsed discharges

Authors: V. Guerra, L. Terraz, A. S. Morillo-Candas, P. Ogloblina, M. Grofulović, C. D. Pintassilgo, O. Guaitella and T. Silva

This work addresses the influence of N_2 on the CO_2 vibrational distribution and the corresponding effect on the gas heating mechanisms in DC pulsed discharges at pressures 1-5 Torr and discharge currents 10-50 mA. The populations of ~70 individual vibrational levels of CO_2 and 10 levels of N_2 are self-consistently calculated by coupling the electron Boltzmann equation with a system of rate-balance equations describing the most important vibrational-energy exchanges. A gas thermal balance equation is further added to the model. The theoretical investigation is complemented with a series of time-resolved in situ Fourier transform infrared spectroscopy measurements providing the time-evolution of the different CO_2 vibrational temperatures and of the gas temperature, as well as the concentration of CO molecules. It is shown that V-T deactivation by O atoms can have a strong influence on the vibrational kinetics, by affecting directly the relaxation of N_2 vibrational excited states and, as a result, the very important energy transfers between vibrationally excited $N_2$2 and CO_2. It is verified that wall deactivation of vibrationally excited states can play an important role at the lower pressures, modifying the vibrational distribution functions and contributing directly to the gas heating. The experimental results reveal a larger conversion of CO_2 when N_2 is added to the plasma, that could not be attributed to enhanced dissociation by direct electron impact.

This work was partially funded by the Portuguese FCT (Fundação para a Ciência e a Tecnologia), under Projects UID/FIS/50010/2019 and PTDC/FIS-PLA/1420/2014 (PREMiERE).

2

CO_2 dissociation from low to high pressures in plasma torch and surfaguide

Authors: Federico D'Isa, Ante Hecimovic, Emile Carbone, Ursel Fantz

In this work we report on investigation of conversion and energy efficiency of 2.45 GHz microwave plasma torch and 2.45 GHz surfaguide. The two plasma sources are studied in the pressure range from 5-1000 mbar (surfaguide 5-60 mbar, plasma torch 60-1000 mbar). Rotational and vibrational temperatures of the emitting species are determined from fitting of molecular spectra (C_2 Swan band, and CO Angstrom band). In surfaguide, the gas temperature increases with pressure (5-35 mbar) in the range 1400-2000K. In the plasma torch, two different modes are observed and their effects in terms of plasma performance on CO_2 conversion are analysed. The low pressure regime (below 120 mbar) exhibits the gas temperature comparable to the gas temperature observed in the surfaguide for the same pressure. Above 120 mbar (exact pressure depends on the power input), a sudden but reproducible transition from a radially diffuse to a contracted plasma regime is reported. The latter is accompanied by a sharp increase of gas temperature from 3000 to 6000 K in the plasma core.

Conversion and energy efficiency are determined using relatively calibrated mass spectrometer. It is found that conversion is strongly influenced by the discharge parameters, exhibiting peak values in the 100-200 mbar range, and usually increase with power. The measured CO_2 conversion and energy efficiency are compared to the conversion expected for a hot CO_2 gas at thermal equilibrium (at measured temperatures). A detailed analysis of plasma sources performance allows determining plasma conditions at which either electron driven dissociation or thermal driven dissociation dominate.

3

Protonic Ceramic based Electrochemical Cells for the Generation ofRenewable Fuels: Development and Characterization

Authors: Usman Mushtaq, Rakesh Sharma, Stefan Welzel, M.C.M. van de Sanden,
Mihalis Tsampas

Conventional O_2- ion based solid oxide cells (SOCs) are attractive energy conversion devices because of high conversion efficiency and excellent fuel flexibility. However, the high operating temperature of SOCs (650~850°C) causes critical issues such as material degradation due to thermal stresses, sealing failures, high maintenance costs etc. In this regard, protonic solid oxide cells (PSOCs) offer advantages compared to more traditional SOCs, such as lowering of the operating temperatures to 450-650°C due to fast proton conduction and low proton activation energy, as well as better fuel utilization and reduced operating voltage. PSOCs have also been reported to achieve higher efficiencies at lower temperature ranges (450 - 650°C) as well. Despite their advantages over SOCs, design, development and optimization, including practical application of such proton conductors remain a challenge.

In this work, the design, architecture, processing and electrochemical performance of the PSOCs will be presented.

4

Plasma catalytic reforming of CO_2 over supported CuO-based materials in a dielectric barrier discharge reactor

Authors: Surjyakanta Rana, Neda Hafezkhiabani, Inne Michielsen, Annemie Bogaerts,
Vera Meynen

Plasma catalysis is an emerging field of conversion technology, particularly focused on converting (relatively stable) greenhouse gases such as CO_2 and CH_4 to basic chemical building blocks by using electrical energy for gas ionization and dissociation at non-equilibrium conditions. The influence of different supports and supported copper oxide catalysts ($CuO/\gamma\text{-}Al_2O_3$, $CuO/\alpha\text{-}Al_2O_3$, and CuO/ZrO_2) on the non-thermal plasma-catalytic dry reforming of methane (DRM) has been investigated in terms of the conversion of reactants, selectivity and yield of specific products, energy efficiency and (resistance to) coke formation on the catalyst surface. The interplay of the plasma with the copper oxide supported materials and vice versa enhances the performance of the dry reforming of methane at ambient temperature and pressure in a coaxial dielectric barrier discharge (DBD) plasma reactor. A clear difference in selectivity can be observed, depending on the applied support materials. In addition, all the copper oxide supported materials resulted in an enhanced conversion, and energy efficiencies compared to the empty reactor using the same flow rate, as well as the same residence time. The supported copper oxide catalysts were fully characterized by various techniques, such as: UV-DR for metal dispersion, XRD for crystal phases and size, N_2 sorption for surface area and porosity, TPR for metal-support interaction and type of copper species, TGA and Raman analysis for evaluation of coke deposition.

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5

Microwave plasma reactor for CO_2 decomposition

Authors: Andreas Schulz, Irina Kistner, Katharina Wiegers, Matthias Walker, Günter Tovar, Frederic Buck, Thomas Schiestel

A modular microwave plasma unit for CO_2 conversion has been set up and investigated. This plasma torch enables a self-ignition and stable operation of the CO_2 plasma over a wide range of parameters. The electric field distribution and the gas flow inside the plasma torch were modelled with an FEM simulation to optimize the configuration. Another important point is the separation of oxygen from the CO_2 plasma to obtain pure CO for the syngas. For this purpose a tubular reactor was constructed, which is connected to the plasma torch and that contains a ceramic capillary, which acts as a permeation membrane for the oxygen. The oxygen permeation was investigated for a variety of capillary material compositions to identify the best operating conditions for the conversion of CO_2.

6

Gliding Arc Plasma: A Promising Approach for CO_2 and CH_4 Conversion into Value-added Chemicals

Authors: Joachim Slaets, Maryam Aghaei, Stef Stollenwerk, Sara Ceulemans, Annemie Bogaerts

Gliding arc plasmas have interesting characteristics for efficient gas conversion, creating opportunities for both the reduction of CO_2 emissions and the conversion of CO_2 and CH_4 into chemicals and fuels. They operate at mild conditions, while still achieving high electron densities. They could also be implemented into industrial installations because of their ease of operation and simple design. We present results on two types of gliding arc reactors, the gliding arc plasmatron (GAP) and the rotating gliding arc reactor (RGA). The GAP reactor design creates an outer vortex that isolates the reactor wall from the inner vortex through which the plasma arc is located. This reactor was tested for dry reforming of methane (DRM) with the addition of N_2 and O_2 to the gas stream, which is common in industrial facilities. Therefore, the combination of these gasses is interesting for implementation into real-world applications. The best performance is achieved for a mixture of 15 % CH_4, 10 % CO_2, 61.5 % N_2 and 13.5 % O_2, for which a total conversion of 19% could be reached at an energy cost of 2.6 eV/molecule. Chemical kinetics modelling could reveal the underlying chemical pathways. The RGA has a different flow design with only one forward flow through which the arc is established. We explored a range of flow rates and currents for pure CO_2-splitting. A maximum conversion of 7.5 % could be achieved with an energy cost of 4.5 eV/molecule. For DRMa higher total conversion of 25.6 % was reached with a lower energy cost of 3.5 eV/molecule. Both reactors show promising and competitive results that will be further explored in future work.

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Sustaining atmospheric plasma with nanosecond microwave pulses to increase the efficiency of CO_2 splitting

Authors: S. Soldatov, A. Navarrete, J. Jelonnek, G. Link, C. Schmedt, R. Dittmeyer

An atmospheric CO_2 plasma sustained in a coaxial torch with short, nanosecond microwave pulses is compared with a plasma sustained with continuous microwave power. The use of a novel, advanced solid state microwave generator enables to supply pulsed microwave energy with ON and OFF times from 50 ns to 200 μs. Analysis of both CO_2 conversion and energy efficiency made for different pulse lengths, duty cycles and gas flows has shown the advantage of pulsed energy supply against CW operation. The work also features the accurate measurement of the absorbed microwave power in the plasma, which is demanding for the correct estimation of process efficiency.

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Discovering two-dimensional materials via artificial intelligence

Authors: Murat Cihan Sorkun, Severin Astruc, Süleyman Er

With exotic and tunable properties, two-dimensional (2D) materials are offering novel opportunities in various fields, including energy conversion and storage, electronic and opto-electronics, and catalysis. Despite only a few 2D materials have been experimentally synthesized, hundreds of 2D materials have been predicted to be stable by density functional theory (DFT) calculations. Accordingly, materials repositories based on accurate DFT calculations are emerging. Still, the high computational cost of DFT calculations restrains the number of new compounds that can be calculated and it curbs the speed of explorations in a vibrational composition search space of 2D materials. To overcome this challenge, we developed an artificial intelligence (AI) algorithm that can screen an extremely large chemical space of 2D materials compositions within a few seconds. Using the algorithm and a brute-force elemental substitution strategy, we generated approximately 72,000,000 candidate materials using 22 prototype 2D structures. We applied different, multi-step, physics-based filters to identify the most promising 2D candidates. Using artificial neural networks, we predicted approximately 300,000 new 2D materials that are stable. Additionally, we predicted the key electronic and magnetic properties of these 2D materials that will be interesting for various material applications. To our knowledge, we developed the largest ever AI-based 2D materials database, by incorporating the AI predicted structure-composition-property data of virtual 2D materials.

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High-throughput computational screening of CO_2 reduction and O transport materials

Authors: Ilker Tezsevin and Süleyman Er

A serious challenge, also for the KEROGREEN project, is the separation of oxygen from a gas mixture that is produced by the plasma-activated dissociation of CO_2. The development of solid oxide cells (SOC) for oxygen separation is therefore a key objective. The electrodes of SOC must be electrically conductive, active for oxygen absorption and transport, and inactive for the back reaction of CO with O_2. Metal oxides, with a perovskite structure and a common formula of ABO_3, are versatile compounds whose electronic properties are tuned by cation substitutions on A and/or B sites. Hence, perovskites are good candidates for SOC electrodes. The performance of perovskites for O_2 transport and CO_2 reduction is found to be related with the formation energy of oxygen vacancies in their bulk structures. Using basic chemical descriptors, such as ionic radiuses, coordination numbers, and oxidation states, as well as the newly developed tolerance factor equations, we generated virtual libraries of perovskites with different chemical formulas of ABO_3, $A^{I}_{0.5}A^{II}_{0.5}BO_3$,$AB^{I}_{0.5}B^{II}_{0.5}O_3$, and $A^{I}_{0.5}A^{II}_{0.5}B^{I}_{0.5}B^{II0.5}O_3$. Next, we performed high-throughput density functional theory calculations on the screened, potentially interesting candidate perovskites, and calculated their oxygen vacancy formation energies. To predict the electronic conductivity of the computationally identified stable perovskites, we performed density of states calculations. Our preliminary results show that out of 470 cubic ABO_3 and $A^{I}_{0.5}A^{II}_{0.5}BO_3$type perovskites, $11ABO_3$ and $39A^{I}_{0.5}A^{II}_{0.5}BO_3$ type perovskites are suitable candidates for CO_2 reduction, whereas 7 ABO_3 and $33A^{I}_{0.5}A^{II}_{0.5}BO_3$ type perovskites are good candidates for the SOC design of the KEROGREEN project.

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Self-consistent Fokker-Planck approach to vibrational kinetics of CO_2 plasma

Authors: P. Viegas, M. C. M. van de Sanden, S. Longo and P. Diomede

In recent years, much attention has been dedicated to low-temperature plasmas to efficiently convert greenhouse CO_2 into new carbon-neutral fuels or useful chemicals. To further understand the underlying mechanisms of CO_2 dissociation in low-temperature plasmas, including the role of vibrational kinetics, numerical modelling is essential. Most of the present literature on the subject is based on the State-to-State approach (STS), which is convenient but time consuming and jeopardizes the computational efficiency of multidimensional models. The authors have developed a new method which is based on describing the vibrational distribution function (VDF) of the asymmetric stretching mode of CO_2 as the numerical solution of a Fokker-Planck (FP) equation.
In this work, the FP approach is self-consistently coupled to a global model describing a CO_2 plasma. Results obtained with the FP model are validated through comparison with STS results and the FP approach is shown to be much more computationally efficient. Moreover, insight into the influence of each kinetic process on the VDF is provided.

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In-situ measurements of temperatures and species densities in contracted CO_2 microwave plasma for solar fuel production

Authors: A.W. van de Steeg, G.J. van Rooij

Microwave plasma is studied in the context of CO_2 dissociation for (solar) fuel production and thereby closing the carbon cycle and addressing intermittency of sustainable energy sources. CO_2 microwave plasma has been observed to exhibit different regimes of operation in terms of plasma shape, which are set by the operating pressure. Understanding of the shape characteristics and the inherent changes in species densities as well as gas temperature and their relation to system performance is lacking and it is the subject of this contribution. Special attention is given to the role of oxygen atoms in the quenching trajectory as a potential pathway to improving performance.

In this work, rotational Raman spectroscopy is applied to measure in-situ the density of all relevant species, namely CO_2, CO, O_2 and O. This is thereby, to our knowledge, the first diagnostics that can give in reactive conditions of up to 6000K the densities of all relevant species in one single spectrum. It is observed that, in the final stage of plasma contraction, the filamentary core of the plasma consists of only CO and oxygen atoms. In the more diffuse plasma regime that is favorable for performance, non-thermal-equilibrium compositions are observed. In particular, CO_2 and O_2 densities are higher than expected for a thermal composition at the measured temperatures. Finally, flow speed is recognized as an important parameter, albeit not in the core of the plasma. It determines the quenching rate and therewith the species distribution in the reactor effluent. In conclusion, in-situ rotational Raman measurements in CO_2 microwave plasma are demonstrated to provide new insight into plasma contraction as well as into the important role of oxygen atoms and quenching for the reactor performance.

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Automated screening of single atom catalysts for solar fuel conversion

Authors: Narasimhan Viswanathan, Ilker Tezsevin, Süleyman Er

Single atom catalysts (SACs) require smaller amount of active materials than conventional catalytic surfaces and nanomaterials. We generate virtual libraries of SACs both in gas phase and immobilized on a 2D host material. Next, using high-throughput density functional theory calculations, we study the fundamental interactions between the newly generated SAC candidates and special, descriptor chemical species of H and N, for the reduction reactions of H_2O and N_2, respectively. We predict the catalytic performance of SACs in gas and condensed phases by comparing the interaction of descriptors with SACs to that of the well-known metal surfaces (Pt and Ru) used in experiments for these reactions. Amongst the SACs that have been immobilized on substrates, we identified 9 candidates for the reduction of H_2O and production of H_2, and 3 candidates for the reduction of N_2 and production of NH_3.

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A multi-scale computational framework for electroactive materials discovery for redox flow batteries

Authors: Qi Zhang, Abhishek Khetan, Süleyman Er

Given the enormous scale, complexity and variety in chemical space of organic molecules, computational high-throughput screening is an essential approach that enables a rational and time efficient discovery process for estimating the relevant key properties of new electroactive materials. In this work, we systematically investigate quantitative structure-property relationships between first-principles calculated reaction energies and experimentally measured redox potentials of small redox active molecules from seven different sources. To accelerate the discovery of new electroactive materials for aqueous redox flow batteries, we developed a multi-scale approach, which involves eleven different electronic structure (ES) and nine different semi-empirical (SE) quantum chemistry methods as well as different implicit solvation environments, to quickly predict the properties of candidate materials. We show that optimizing structures in the gas phase using SE methods followed by computation of single point energies using ES methods in the Poisson-Boltzmann implicit solvation model, offers the same predictive accuracy as high-level ES methods but at a significantly lower computational cost. We also show that single linear correlations across all data points from different experimental sources are able to predict the redox potentials with coefficients of determination R2>0.97. These results show promise for a robust and fast prediction of materials properties on a large number of candidate battery materials.

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A multi-scale computational framework for organic electrode materials discovery for Li batteries

Authors: Xuan Zhou, Abhishek Khetan, Süleyman Er

Organic electrode materials are interesting candidates for the development of high-performance batteries that are scalable, sustainable, and cost-efficient. The chemical space of candidate electrodes from organic materials is too vast to be explored by experiments. The exploration of this space can benefit enormously from robust *ab initio* computational modelling and accelerated high-throughput search. Modelling of organic electrode materials faces unique methodological issues owing to a wide variety in redox mechanisms, presence of both amorphous aggregate and crystal phases, as well as the complex effects of electrolytes on stability and conductivity. To efficiently navigate through the chemical space, good materials property descriptors are required that are accurate and fast to compute. In this work, we chose the redox potential as a prime property, and show that the first-principles reaction energy of reduction in an implicit solvation environment is a simple and yet an effective descriptor for it. We collected experimentally measured redox potentials from eight different sources on N-type organic electrodes, which were then used as calibration targets for a large variety of electronic structure (ES), semi-empirical (SE) methods, and a combination of the two. We found that a multi-scale approach involving a combination of structural optimizations using SE methods and solution phase energy predictions using ES calculations offers the fastest results with best accuracy.

Committee:

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PROJECT INFORMATION

The KEROGREEN project runs from **1 April 2018 to 31 March 2022**. The main milestones are:

Year 1: definition of the O_2 gas separator, the CO purifier and the Water Gas Shift (WGS), Fischer-Tropsch (F-T) and Hydrocracking (HC) units.

Year 2: subsystems validated including the plasma oxygen separator, CO purifier, WGS, F-T and HC sub systems.

Year 3: integration of sub-systems, notably the oxygen separator and plasmolysis reactor and the WGS, F-T en HC units.

Year 4: integration of the entire system at KIT with a critical review for system readiness planned at M42, concluded by integrated system tests.

The project runs in synergy with nationally funded projects, whilst the European Energy Research Association (EERA) links to the European Joint Programme on Energy Storage. The project is carried out by the following partners:

DIFFER is responsible for development of the microwave plasma reactor to split CO_2, plasma modelling and perovskite plasma membrane interaction experiments and modelling and tests of the integrated CO_2 plasmolysis - O_2 seperator assembly.

VITO develops the Oxygen separator with tests and characterisation of a lab scale single membrane and of a full scale multi membrane assembly for integration with the plasmolysis reactor at DIFFER.

Cerpotech develops advanced ceramic powders for catalytic Oxygen separation membranes, including characterisation of morphology, particle size and purity.

HYGEAR engineers and builds the Oxygen separator for integration with the plasmolysis reactor and develops the CO purification unit for integration with the Oxygen gas separation unit.

KIT-IMVT develops the Water Gas Shift and the Hydrocracking units and is responsible for process simulation and the data base. It will provide the site installation of the fully integrated KEROGREEN system.

KIT-ITAS carries out sustainability analysis.

INERATEC develops the Fischer-Tropsch synthesis unit and carries out the system engineering and system integration into a container sized module. INERATEC is winner of the German Entrepreneur Award 2018 Category Sart-Up,
and the Cleantech Open Global Ideas Challenge 2018.

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Cerpotech

vito

KIT Karlsruher Institut für Technologie

HYGEAR

INERATEC