Towards electrification of the chemical industry: Synergistic integration of plasmolysis and electrolysis

Waldo Bongers, Paola Diomede, Juehan Gao, Michail Tsampas, Floran Peeters, Dirk van den Bekerom, Tom Butterworth, Adelbert Goede, Pieter Willem Groen, Teofil Minea, Qin Ong, Tim Righart, Gerard van Rooij
Tiny Verreycken, Stefan Welzel, Bram Wolf, and Richard van der Sanden

UT /MESA+, ECRG: Henny Bouwmeester

TU/e /MMP: Zandrie Borneman, Cees Weijers

OPEN TECHNOLOGY PROGRAMME connecting innovators

NWO Applied and Engineering Sciences

DIFFER is part of NWO

Solar Fuels program

Program lines:

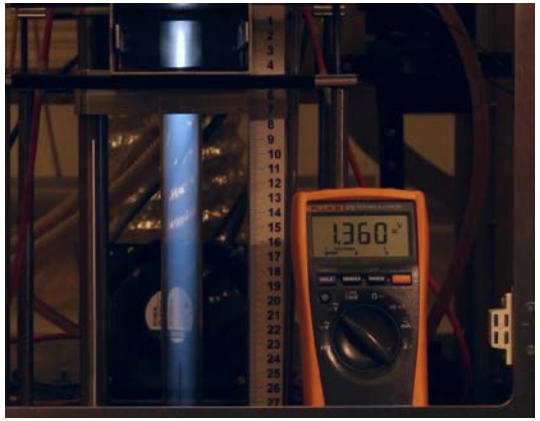
I. Non-thermal chemical processes

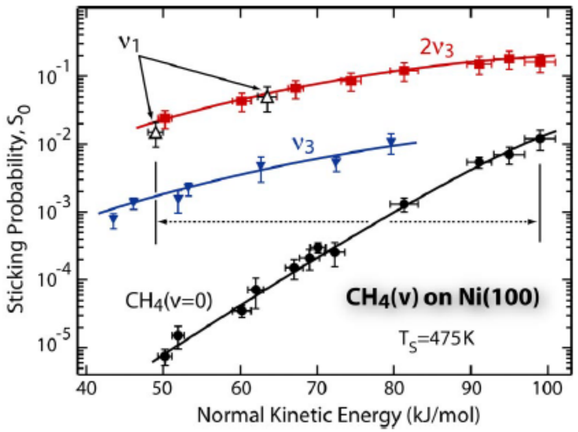
II. Functional materials and interfaces

III. Light-matter interaction

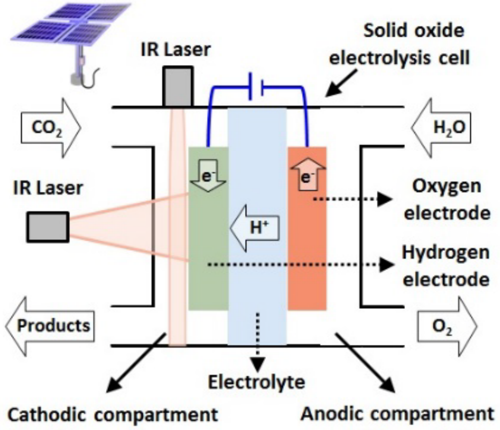
Novel non-thermal routes to **improve kinetics** and **selectivity** of **key catalytic processes**

Nonequilibrium plasma reduction, plasma assisted electrochemistry & mode selective (surface) chemistry





Photon assisted electrochemistry



G.J. van Rooij et al., Faraday Discuss. **183**, 233 (2015)

S. Yan *et al.* Science **316**, 1723 (2007)

Solar Fuels program






Program lines:

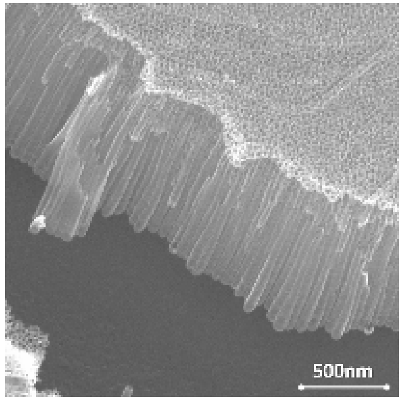
I. Non-thermal chemical processes

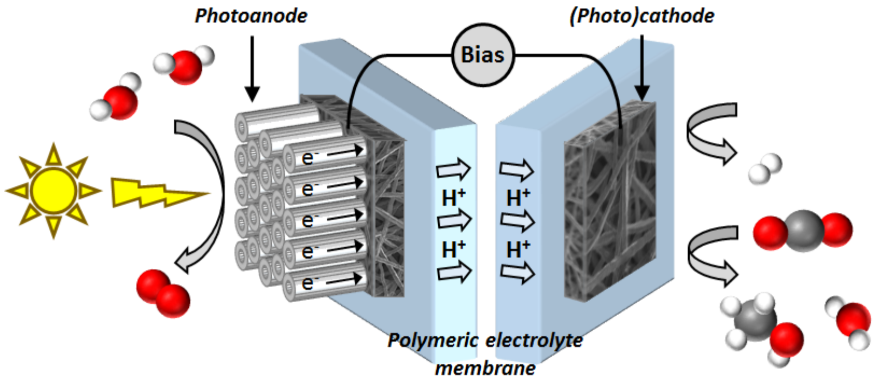
II. Functional materials and interfaces

III. Light-matter interaction

Understanding the **structure-property** relations of **functional materials** and the **processes** occuring at the **electrode-electrolyte interface**

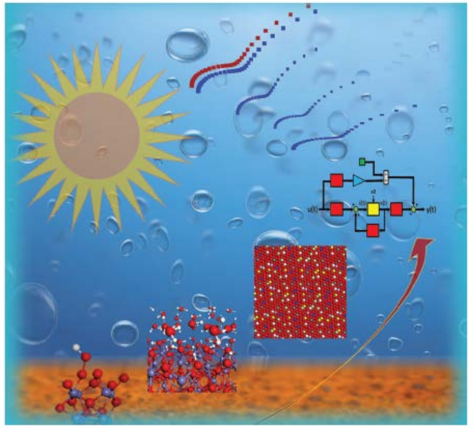
Nanostructuring of Ti felt used as photo-anode in a photo-electrochemical cell (PEC)





T. Stoll et al., Int. J. Hydrogen Energy **41**, 17807 (2016)

Multi-scale modeling of interface electrode-electrolyte (DFT, ..)



X.Q. Zhang et al., Chem. Sus. Chem. **9**, 1223 (2016)

Solar Fuels program

Program lines:

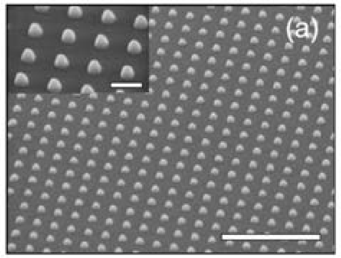
I. Non-thermal chemical processes

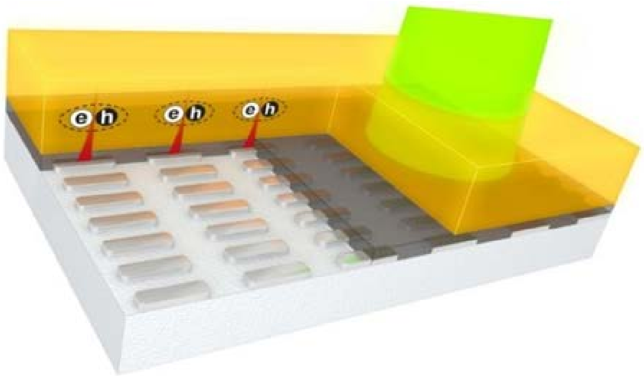
II. Functional materials and interfaces

III. Light-matter interaction

Improve chemical processes by exploring **nanostructured functional materials** to enhance **light capture and absorption** and **charge transport**

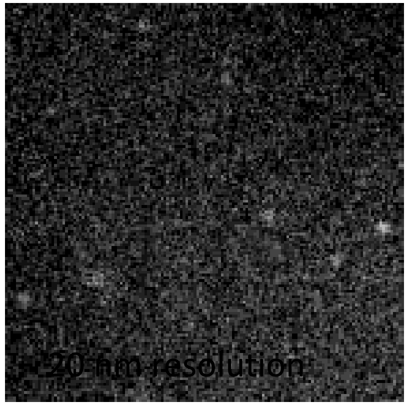
Resonant open cavity structures combined with catalysis to modify the chemical selectivity or to enhance transport and charge recombination

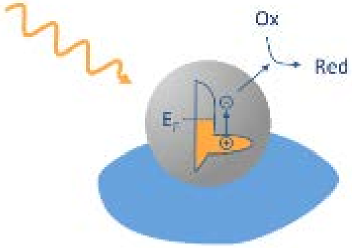




M. Ramezani et al., Optica **4**, 31 (2017)

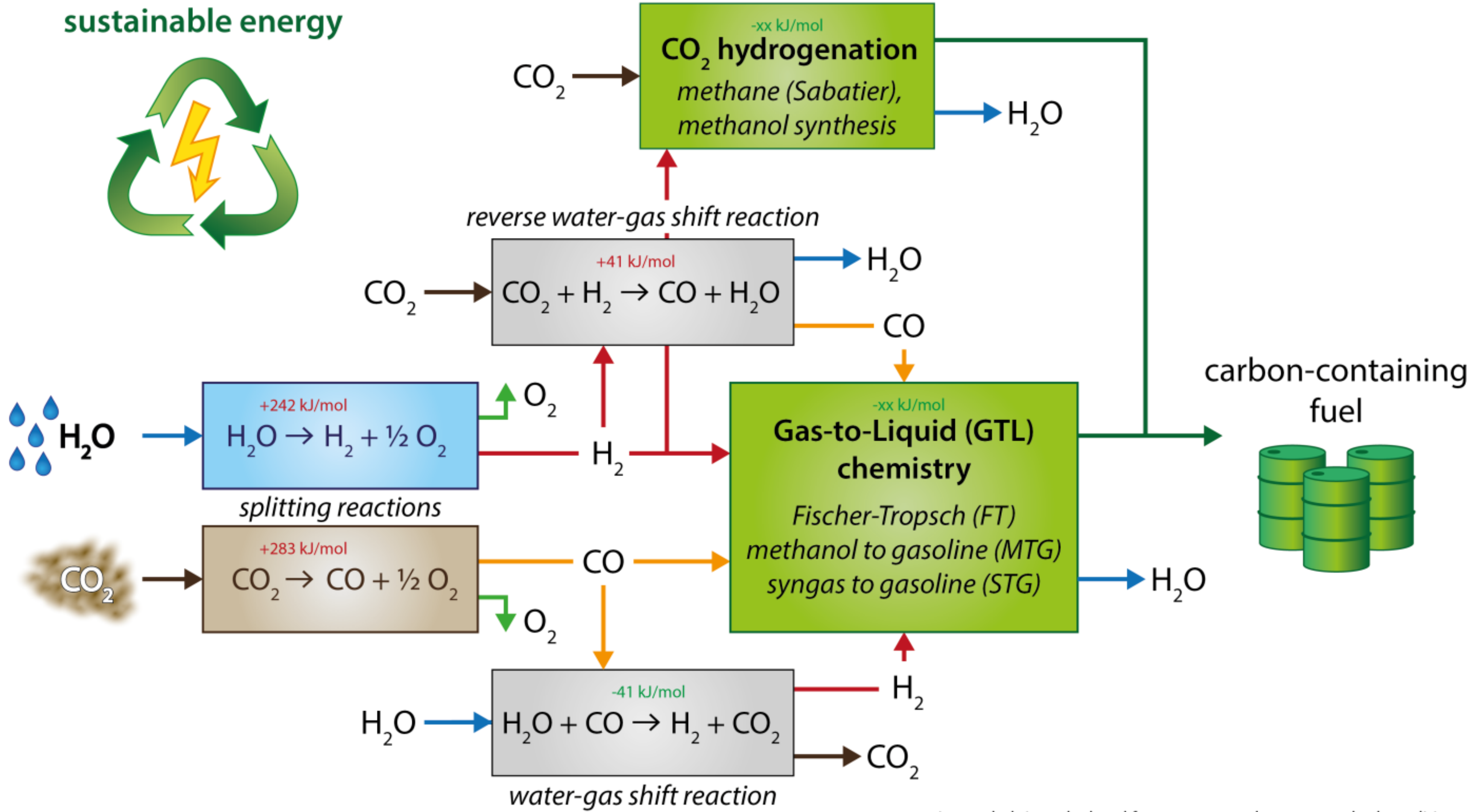
Plasmon enhanced catalysis on metal nanoparticles





A. Baldi et al., to be published (2017)

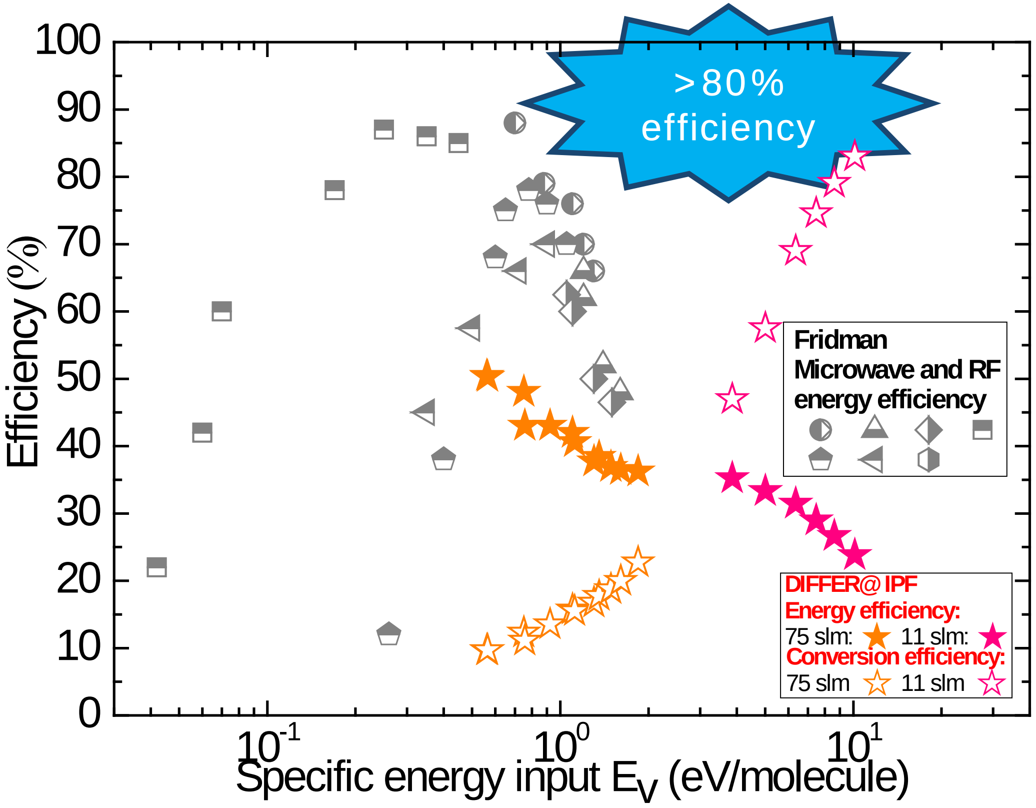
Solar fuel plant: chemical routes



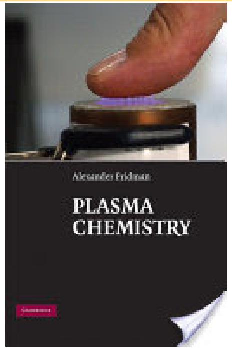
reaction enthalpies calculated for gaseous products at standard conditions

Microwave plasma discharge for CO_2 dissociation

$CO_2 \rightarrow CO + \frac{1}{2} O_2 \quad \Delta H = 2.9\,eV$



Alexander Fridman., Plasma Chemistry
Cambridge University Press, 5 May 2008
- Technology & Engineering



Advantages:

- High energy efficiency in the non-thermal regime by non-equilibrium microwave plasma
- Fast on-and-off switching
- No rare materials needed
- High power density, up scalable technology

Challenges:

- creating cool non-equilibrium plasma
- High energy efficiency at high conversion
- Efficient gas separation

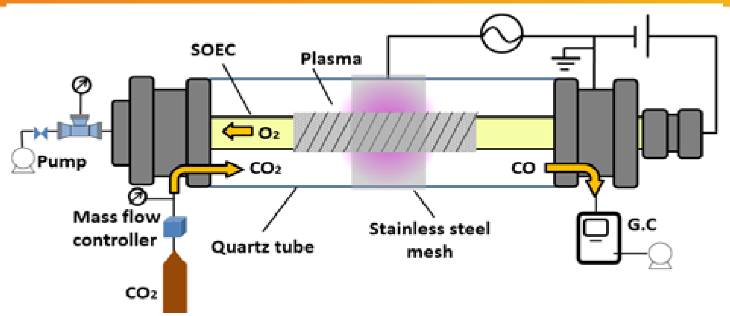
Legasov, Fridman et al., Sov. Phys. Dokl. Akad. Nauk vol. 238, p. 66-69 (1978) Am. inst. phys p. 44 (1978)
Asisov, Fridman et al., 5th International Symposium on Plasma Chemistry, Edinburgh, vol. 2, p. 774 (1981)
Asisov, Fridman et al., Sov. Phys., Dokl. Akad. Nauk , vol. 271, p. 94-98 (1983) Am. inst. phys p. 567 (1984)

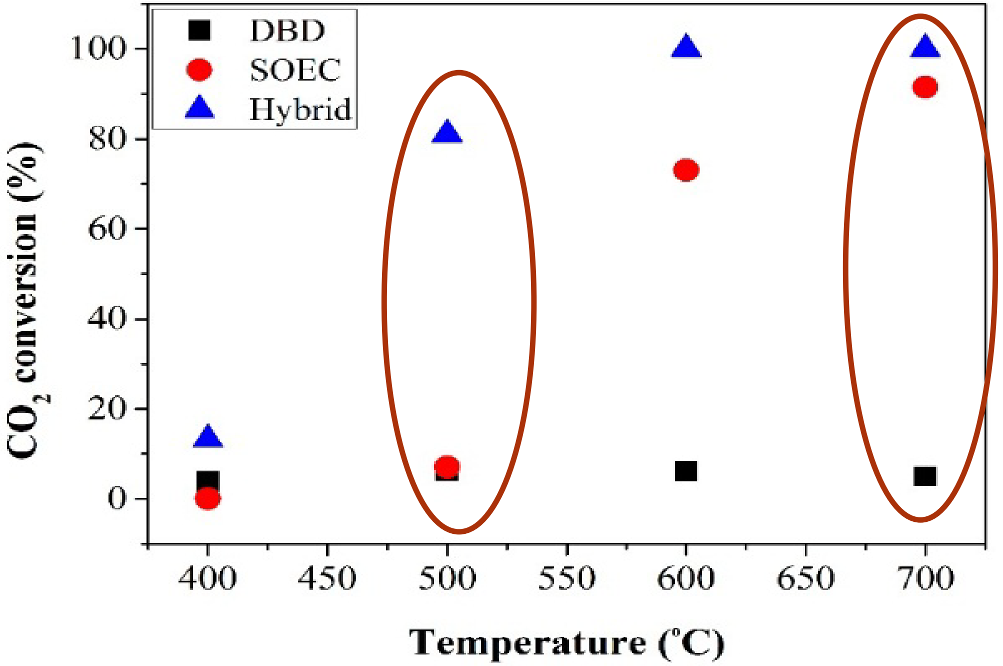
Waldo Bongers, Henny Bouwmeester et al., Plasma Processes and Polymers 2016
http://dx.doi.org/10.1002/ppap.201600126

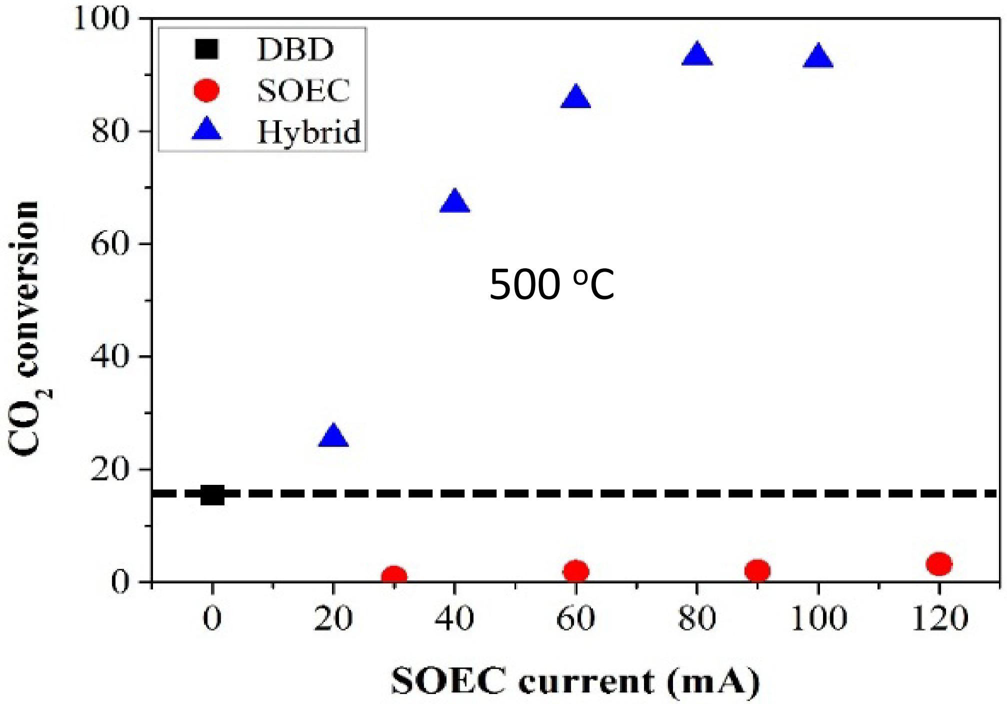
Integration of plasmolysis and electrolysis in a Nutshell

Integration of Dielectric barrier discharge (DBD) plasma reactor and Solid oxide electrolyser cell (SOEC)

Y. Tagawa et al., Kagaku Kogak Ronbunshu 37 (2011) 114.
L.L. Tun, N. Matsuura, S. Mori, 22nd International Symposium on Plasma Chemistry, O-15-3 (2015).







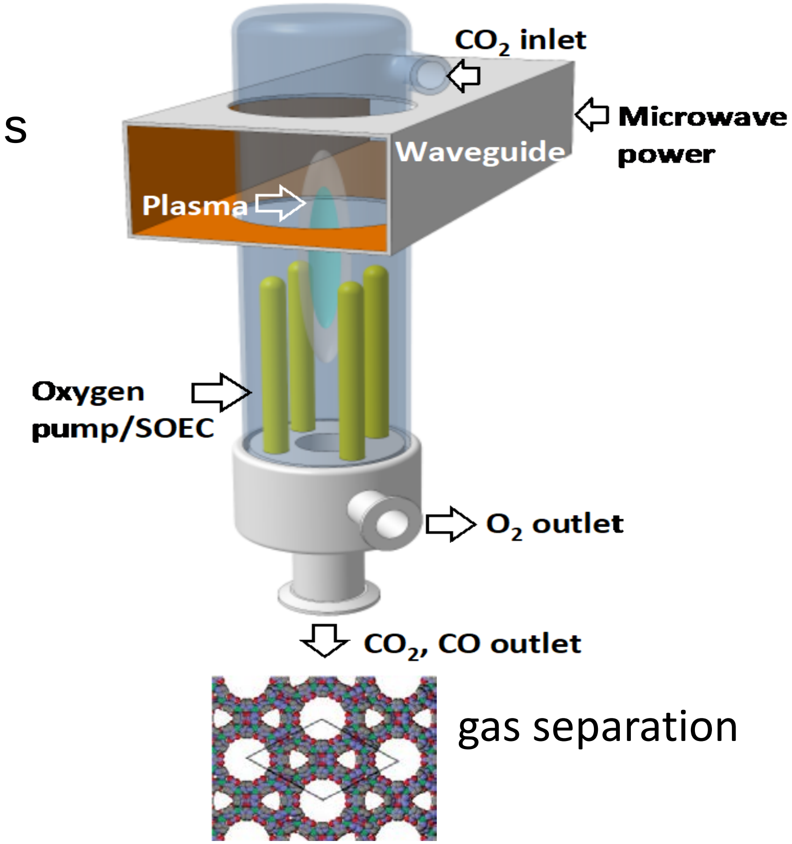
Integrated (hybrid) system improves conversion efficiency and/or lowers operating temperature of SOEC

Integration of plasmolysis and electrolysis in a Nutshell

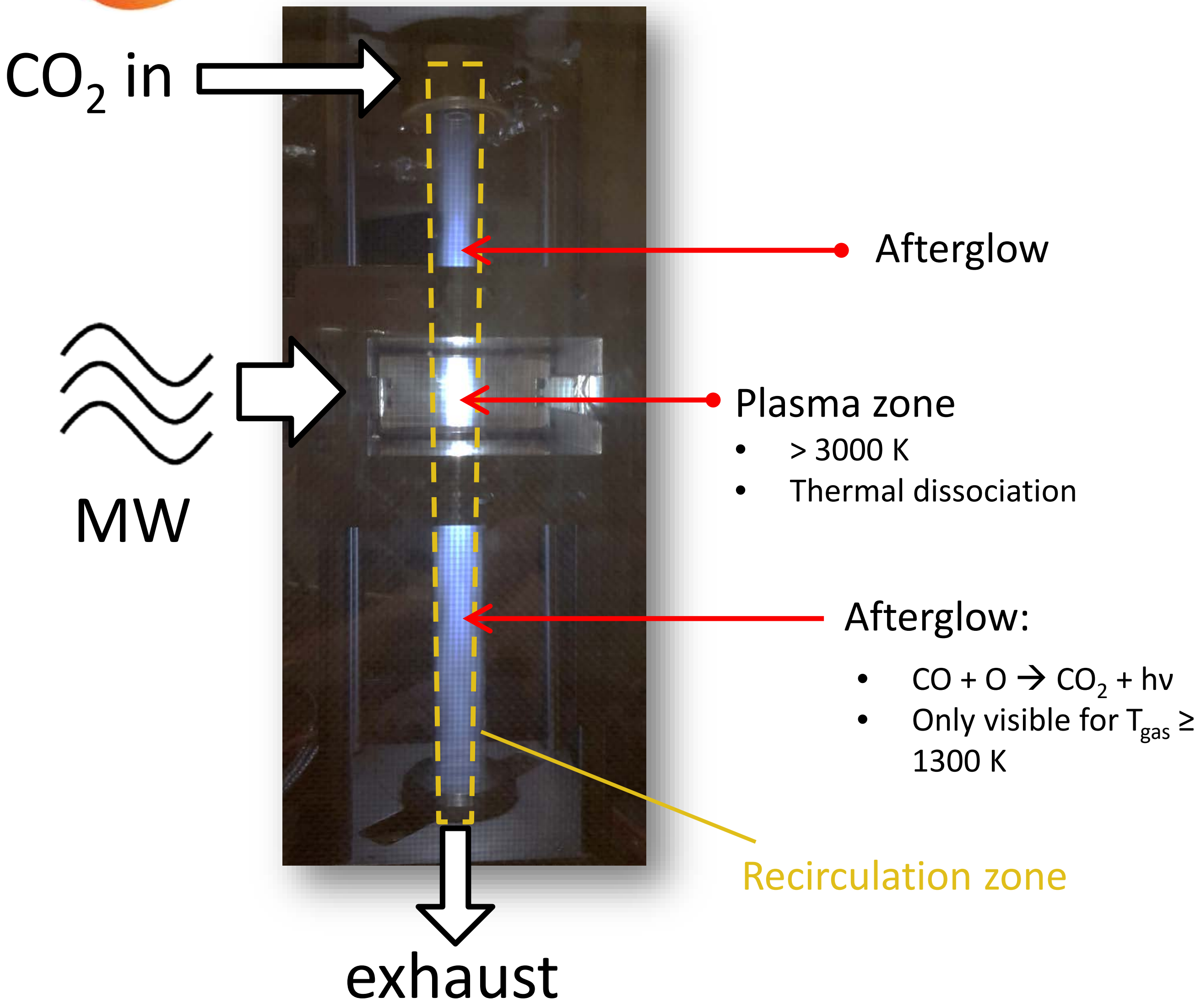
Aim: *enhancing the conversion and energy-efficiency of CO_2 dissociation by synergistic integration of plasmolysis, electrolysis and membrane gas separation*

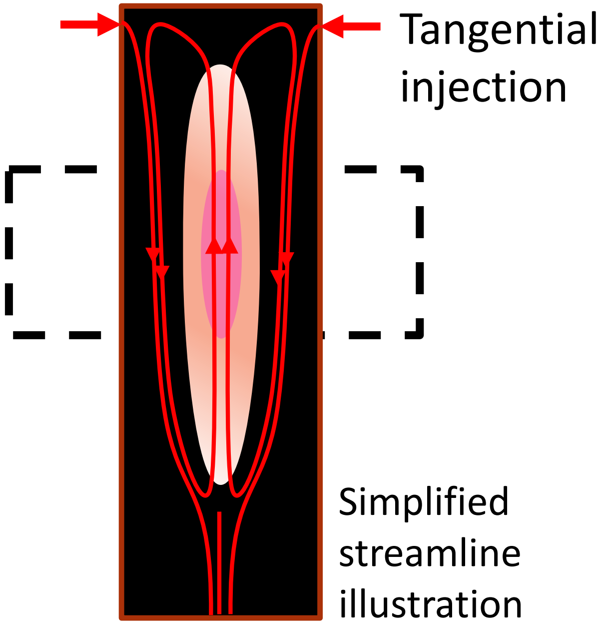
Research objectives

- Optimization and evaluation of candidate SOEC cathode materials
- Modelling of plasma chemistry under different stoichiometric conditions
- Boost energy efficiency of plasma conversion by controlling non equilibrium conditions, e.g., by power pulsing (Ampleon semiconductor source)
- Integration of SOEC in CO_2 plasma reactor; integration of membranes
- Study of synergistic effects achieved by integration
- Development of membranes for selective CO_2 separation



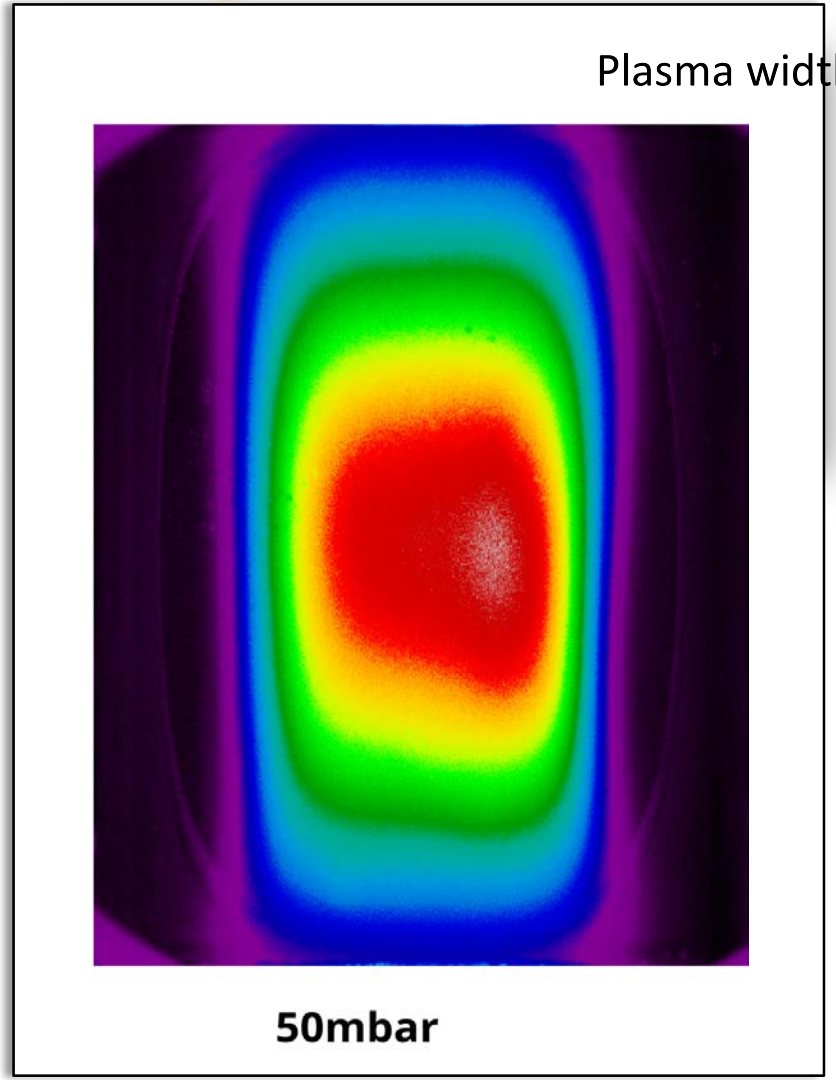
The Forward vortex CO_2 plasma reactor

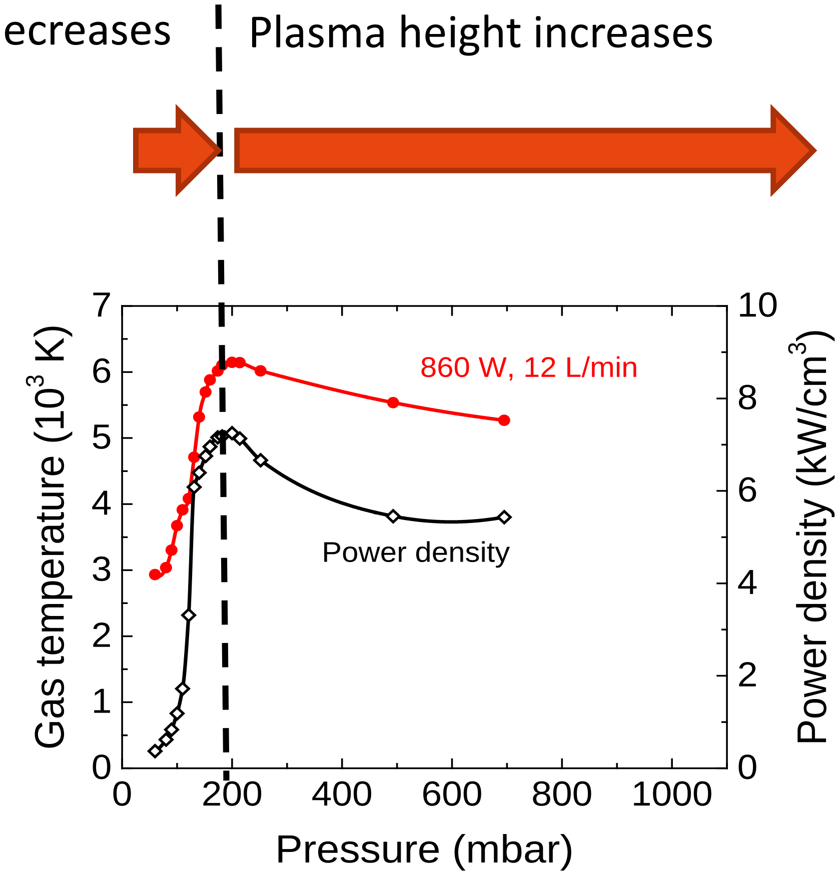


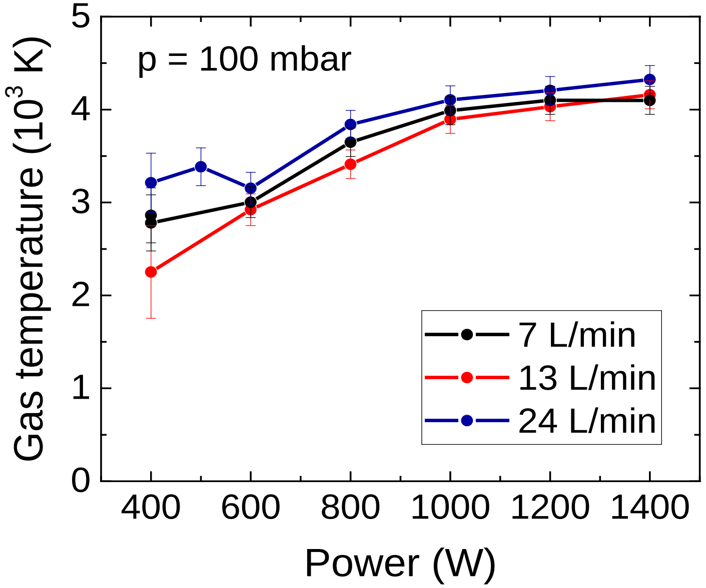


- For (high power) plasma reactors, understanding species transport and temperature is key for optimizing efficiencies and position of the SOEC

The Forward vortex CO_2 plasma reactor





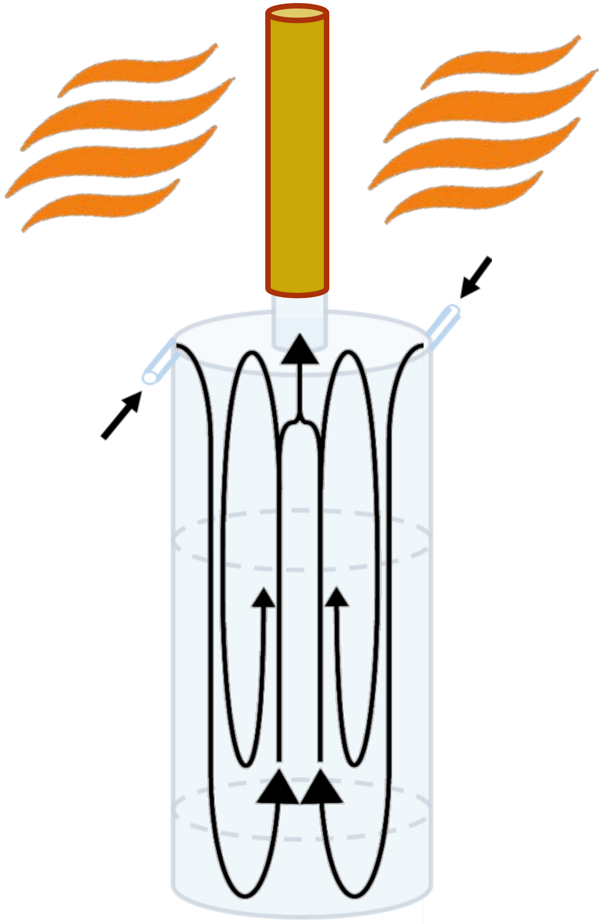


T_{gas} > 3000 K

- ➢ High E/n_0 (>> 200 Td est.)
- ➢ Significant VT relaxation
- ➢ Thermal plasma core

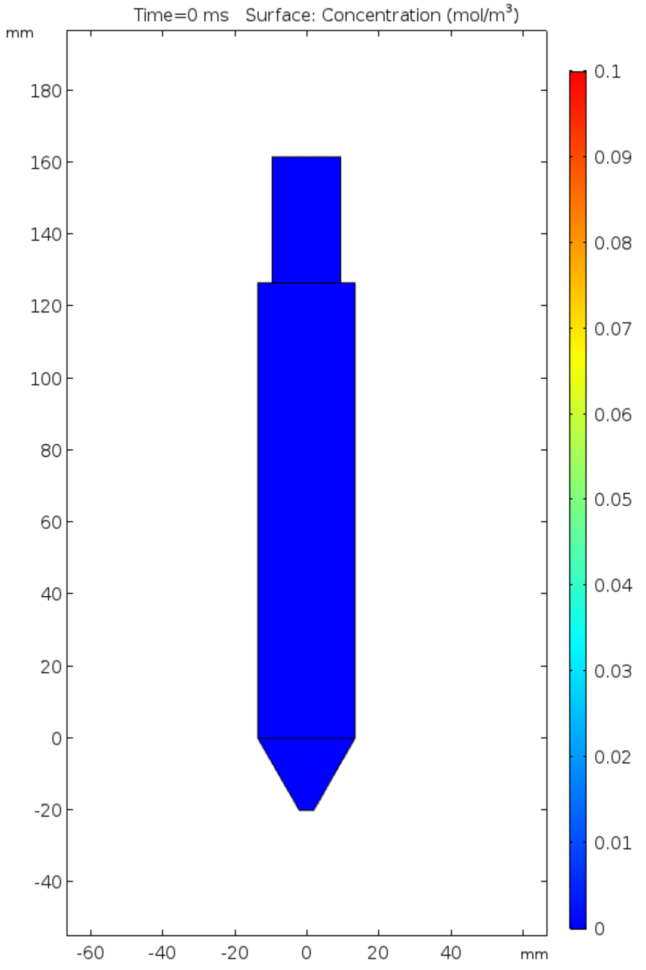
No dependence on flow

The Reverse vortex CO_2 plasma reactor



With current reactor design:

- Advective (bulk flow) extraction of CO, and fast thermal quenching in metal exhaust
- But still significant recirculation:
  - ➢ creates ‘heat reservoir’ leading to plasma temperatures > 4500 K
- Reverse vortex reactor modelling is being performed to optimize design
- Reactor with variable exhaust width currently under construction
- Plasma residence time and plasma gas temperature measurements with new design scheduled for next 6 months



physixfactor R & D SOLUTIONS

last DIFFER Plasmolysis results

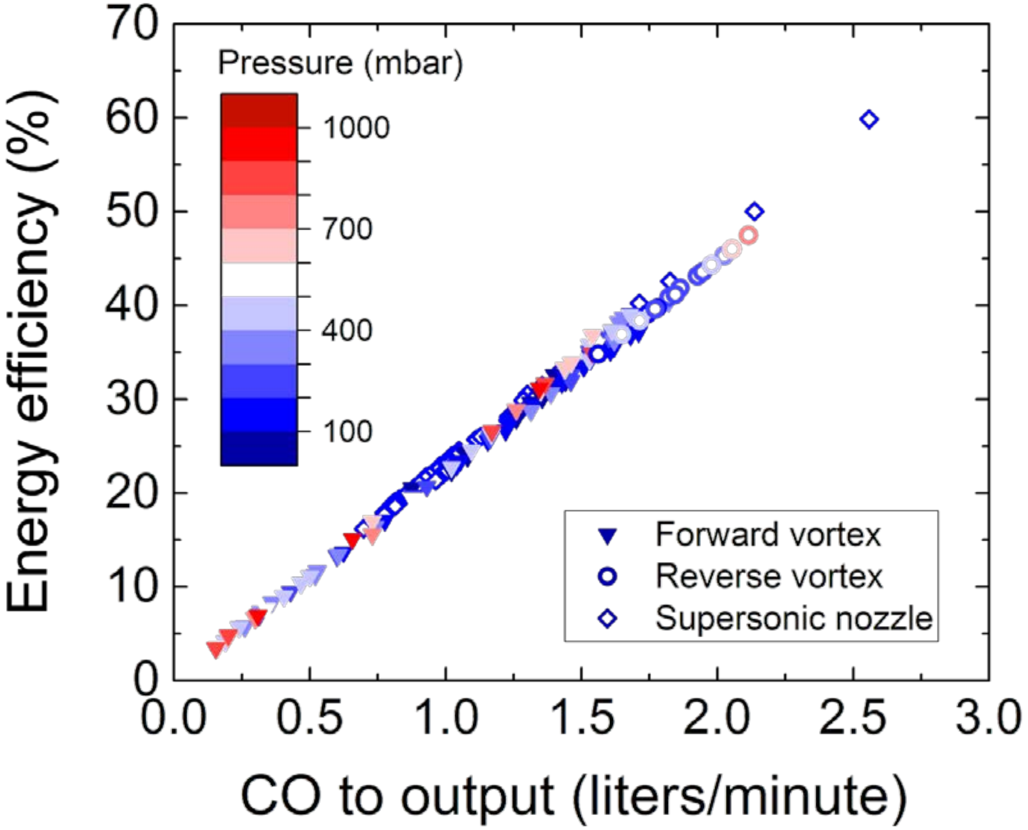
Plasma reactor

(a)

(b)

(c)

(d)



(a) Forward vortex (FV), (b) Reverse vortex, (c) Supersonic nozzle, (d) efficiency versus CO produced at 1 kW input power

Project Summary

SOEC development (MESA+ /ECRG UT, PHSF, DIFFER)

- Optimization and evaluation of candidate electrode materials
- SOEC fabrication and performance testing

Reactor design & integration/modeling (PSFD, DIFFER)

- Plasma modelling -> optimal parameters non-equilibrium
- Reactor specs/design and diagnostics for non-equilibrium control
- Reactor manufacturing, diagnostics and commissioning
- SOEC and membrane reactor integration; overall performance testing
- Field tests

Development CO_2 separation membranes (MMP, TU/e)

- Membrane support development
- Composite and internally skimmed asymmetric membranes
- Tuning/enhancing/evaluation performance by embedding particles

Cooperating in Research at Solar Fuels groups

Richard van de Sanden

- Photo-Electrochemical Materials & Interfaces
  Anja Bieberle
- Atmosperic Plasma proc. of Functional Films
  Hindrik de Vries
- Nonequilibrium Fuel Conversion
  Gerard van Rooij
- Nanomaterials for Energy Appications
  Andrea Baldi
- Materials and Surface Science
  Michael Gleeson
- Plasma Solar Fuels Devices
  Waldo Bongers
- Photoelectrocatalysis for Solar fuels
  Michail Tsampas
- Computational Plasma Physics & Chemistry
  Poala Diomede
- TU/e Group Molecular Solar Energy
  Rene Janssen

Solar Fuels Facility & Instrumentation
Stefan Welzel

“Light” “Materials” “Plasma”

CEPEA group

Group name: Catalytic and electrochemical processes for energy applications

Group leader: Mihalis Tsampas

Expertise: Electrochemistry, Catalysis, Reactor engineering

Our goal: Combine solid state electrochemistry with additional activation knobs for:

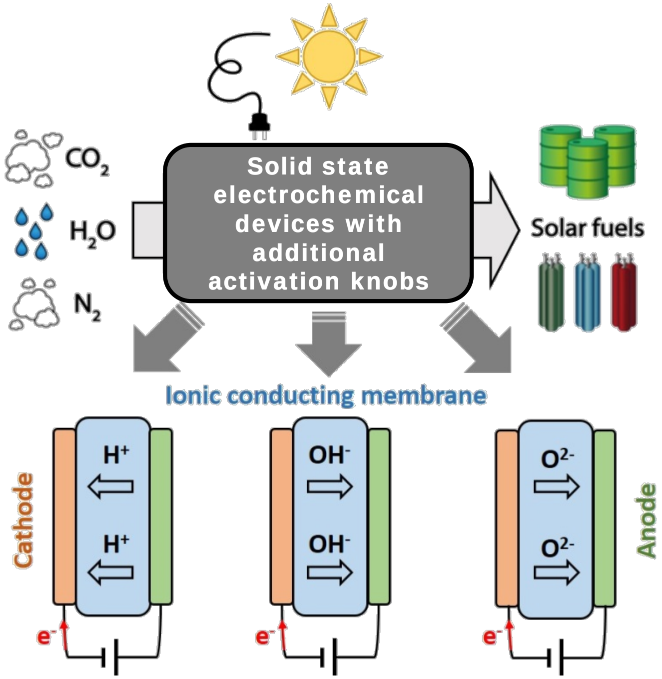
- developing novel routes for renewable energy storage,
- boosting activity and steering the selectivity of CO_2 or N_2 fixation by H_2O.

Unique approach: Novel electrochemical device architectures aiming for synergy with:

- Material research
- Light or vibrational excitation

Our devices offer:

- Adaptability with external stimulation: light, plasma, laser
- Flexibility (various ionic agents, operating at wide T window)



Plasma chemistry modelling

Group name: Computational plasma physics and chemistry

Group leader: Paola Diomede

Expertise: Modelling, Computational techniques, Simulation of non-equilibrium molecular plasmas

Plasma Chemistry Modelling

Task objectives

- Implementation and testing of simulations for advanced pilot hybrid plasmolysis reactor specification and design
- Evaluation and optimization of the reactor performance in synergy with the experiments

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Challenges

- Very complex plasma chemistry → large number of chemical reactions and species
- Description of plasma/surface interactions
- Complex gas flow

NFC Group

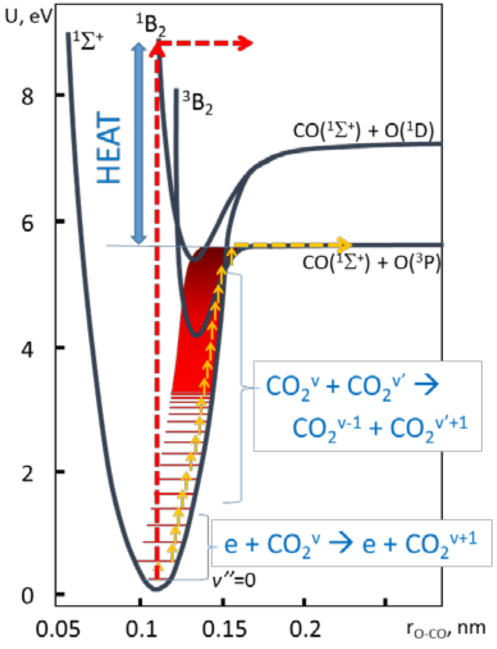
Group name: Non-equilibrium Fuel Conversion

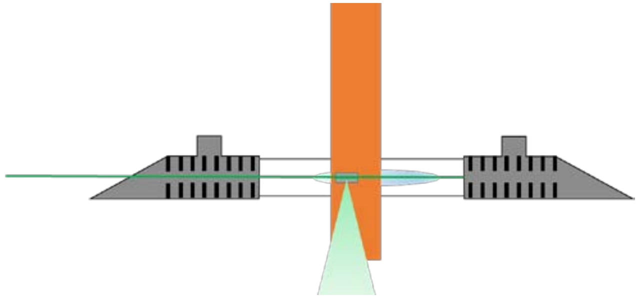
Group leader: Gerard van Rooij

Expertise: Physics and chemistry

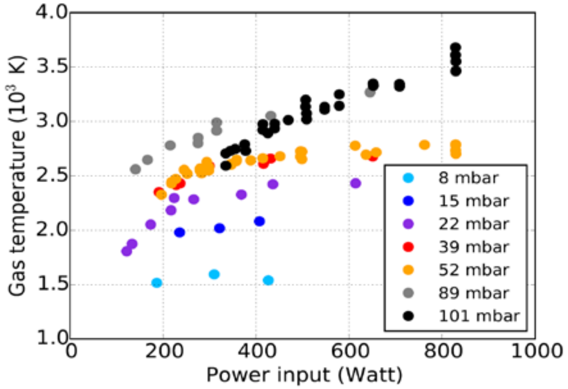
Vibrational excitation: Achieving and exploiting strong non-equilibrium (high vibrational excitation at low gas temperature)

1. Understanding vibrational excitation dynamics and underlying molecular physics;
2. Understanding chemistry of excited species, homogeneous and with heterogeneous catalyst;
3. Focus on CO_2 and N_2 fixation, CH_4 chemistry

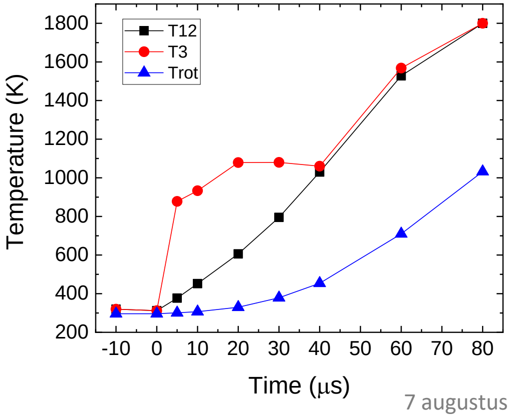




Gas temperature @13 slm



Vibrational excitation dynamics



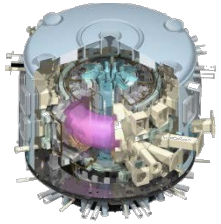
Thank you for your attention, Questions?

Spare slides: Why electrification of chemical industry: the TeraWatt Challenge[1]

Energy mix required to meet rising global energy demand

Sustainable energy production to replace fossil fuels (CO_2 neutral !)

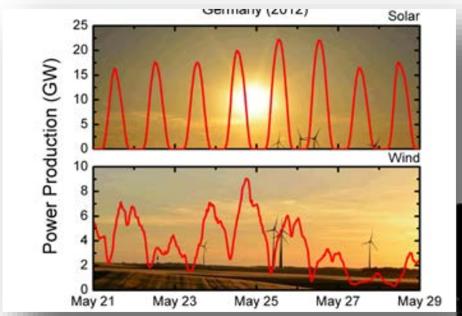
- **Solar panels**
- **Wind turbines**
- **Bio-based processes and chemicals**
- **(Geo)thermal processes**
- **Hydro-energy**
- **…**
- **Nuclear fusion**

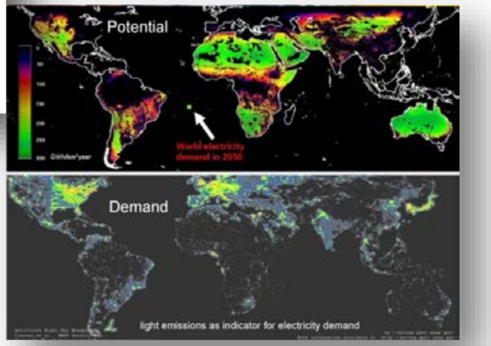


Match supply and demand

Inhomogeneous and intermittent character of sustainable sources

- **Smart grids**
- **Electrical energy storage**
- **Geothermal / geostatic storage**
- **Chemical products / fuels (CO_2-neutral!)**
- …

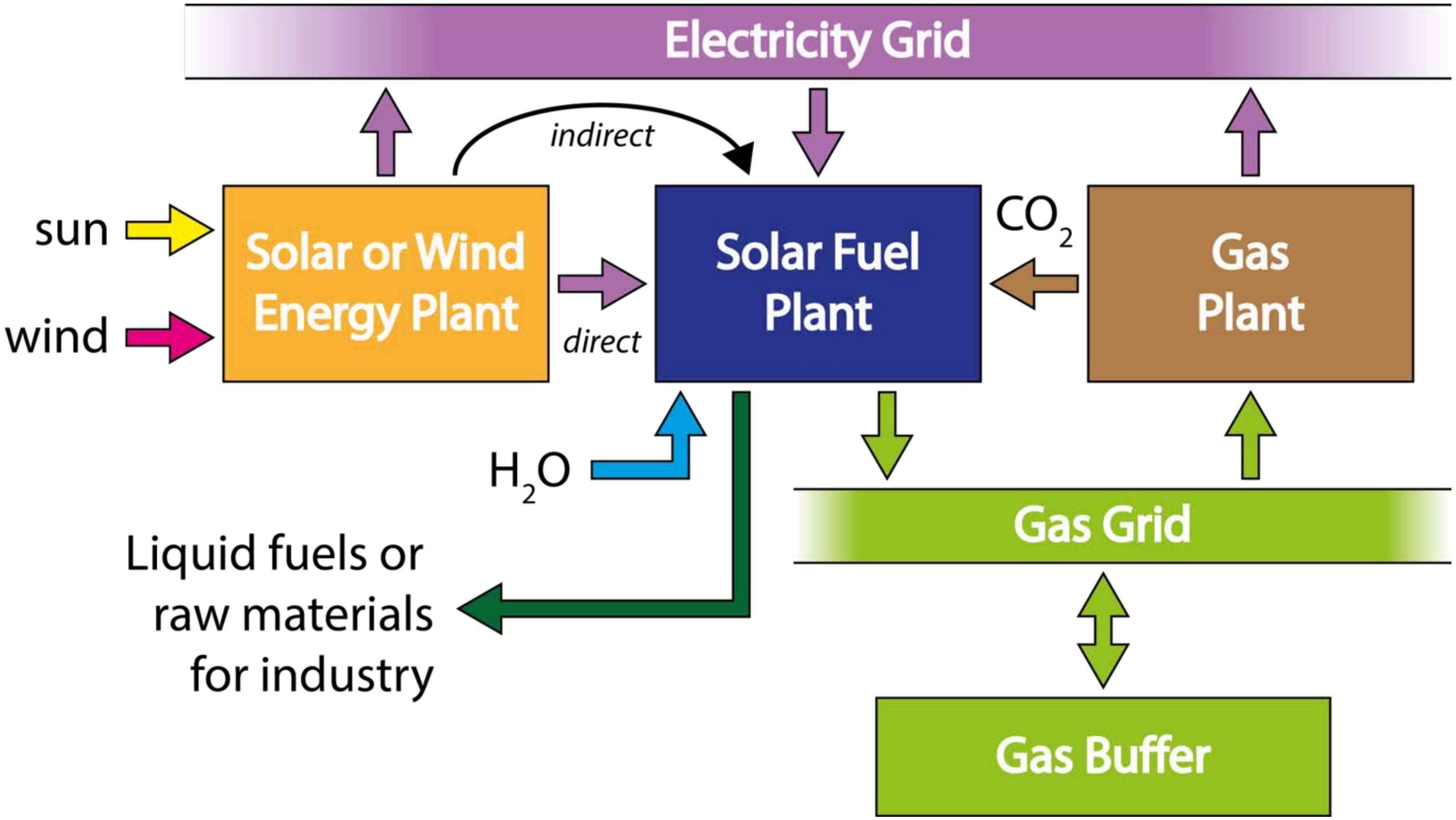




[1] *M.I. Hoffert et al. Nature* ***385,*** *881 (1998)*

P2G: CO_2 and H_2O as feedstock for fuel and products

Solar fuel = hydrocarbon fuel or product produced from CO_2, (water) and renewable energy



CO_2 dissociation: efficiency definition

Basic reaction	$CO_2 + M \rightarrow CO + O$	$\Delta H = 5.5$ eV
Use of O radical	$CO_2 + O \rightarrow CO + O_2$	$\Delta H = 0.3$ eV
Total	$\mathbf{CO_2 \rightarrow CO + \frac{1}{2} O_2}$	$\mathbf{\Delta H = 5.8/2\ eV = 2.9\ eV}$

- **Energy efficiency $\eta = \Delta H/E_{CO}$**

  E_{CO} = energy cost to produce one CO molecule

- **CO_2 conversion factor $\alpha = E_v/E_{CO}$**

  E_v = specific energy input

  $E_v = P/Q$ = Power / gas flow rate

$$\eta = \frac{\Delta H \cdot \alpha}{E_v} = \frac{\Delta H \cdot \alpha \cdot Q}{P}$$

α determined using FTIR spectroscopy / mass spectrometry (ex situ)