DIFFER
Dutch Institute for
Fundamental Energy Research

University of Stuttgart
Germany

CO_2-Neutral Fuels

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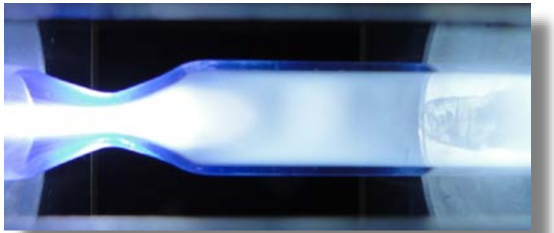
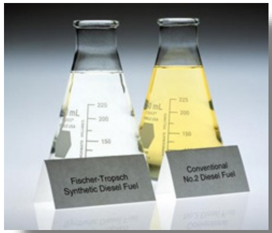
Smart CO_2 Transformation

EERA
European Energy Research Alliance



DPG AK Energie, Bad Honnef, 20-21 October 2016, Germany

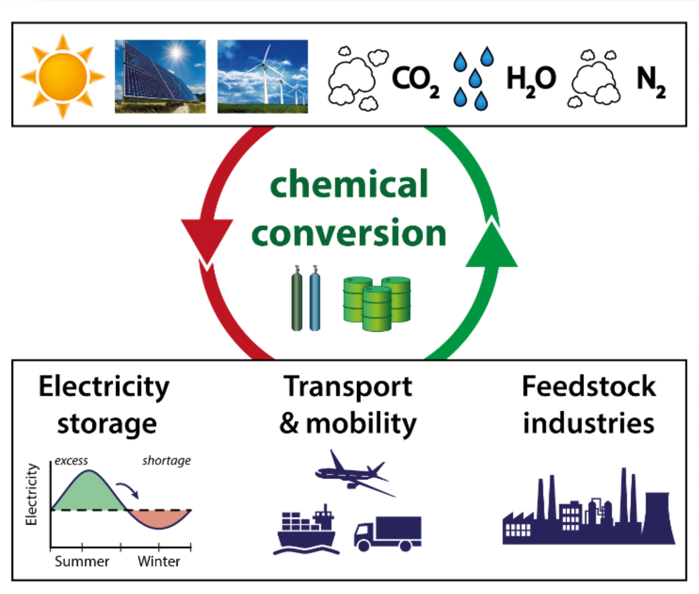
DIFFER is part of FOM and NWO

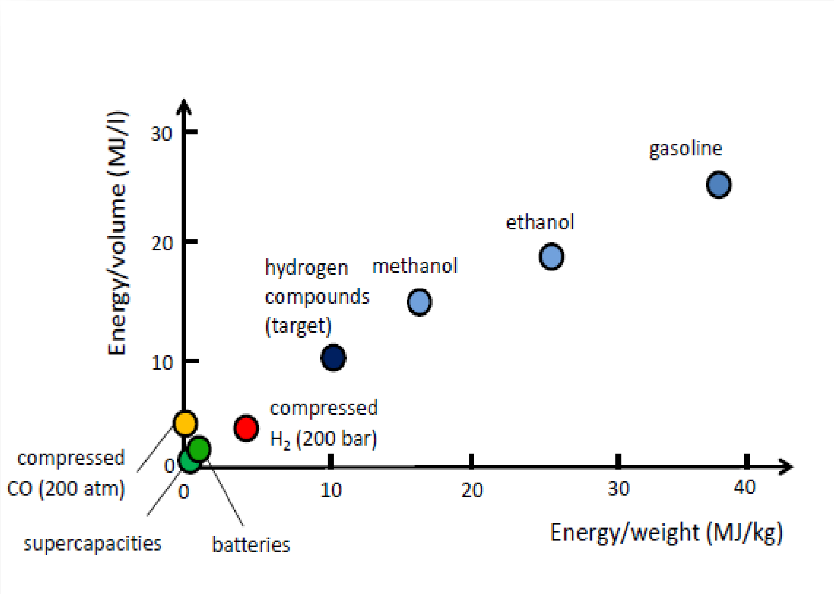
CO_2 Neutral fuels: What are they?

Hydrocarbons synthesised from water and air

- powered by Renewable Electricity
- CO_2 recirculated after use

Characterised by high energy density and existing infrastructure





Why CO_2 Neutral Fuels?

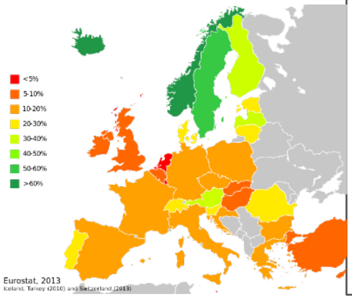
- UNFCCC Paris 2015: CO_2 emission curbed by 80%-95% in 2050 vs. 1990
- Transport target EU-RED 2050:
  - 60% CO_2 emission reduction
  - Aviation 40% RE by 2050 (~2% of global CO_2 emission)
- Transport makes up ~25% EU primary energy consumption

→ Batteries and Hydrogen emission free, but

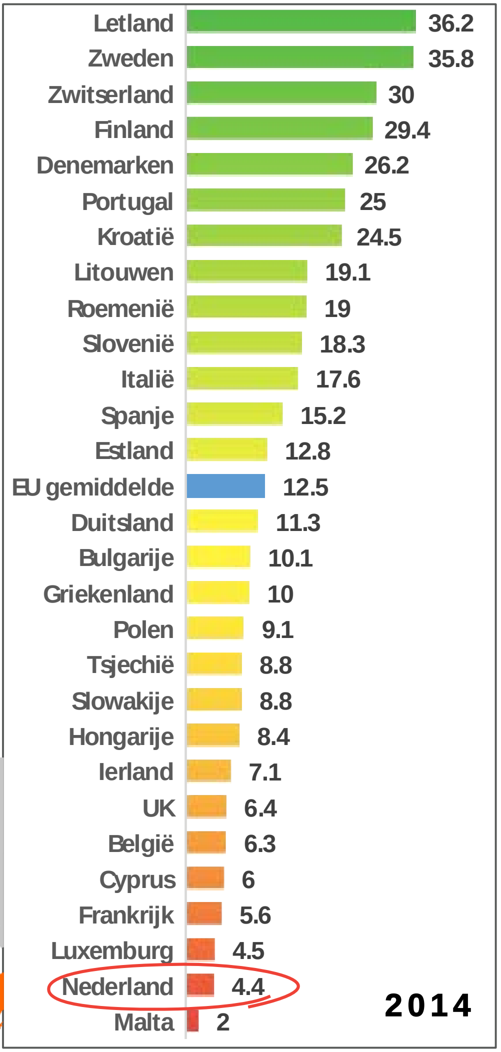
  → low volumetric energy density (hence mobility range limit)

→ Bio Fuels

  → limited by Fuel vs. Food/Flora trilemma (jet fuel alone 5M barrels/day kerosene)



% renewables EU



Energiewende

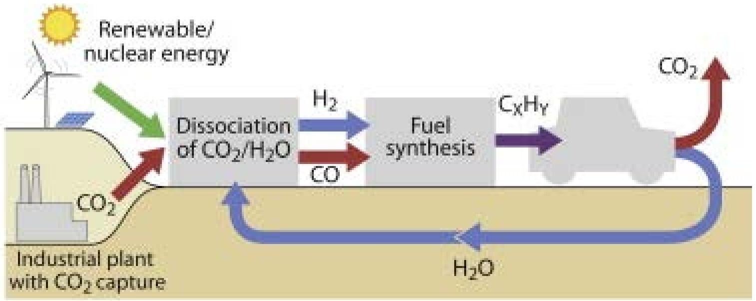
Aimed at phasing out Fossil and Nuclear and replace by Renewables

- Goal 80% electricity from Renewables in 2050
- Presently: 30% RE, 45GW installed wind power
- 30% RE on average: sunny and windy day 90% RE (8 May 2016). Cloudy and Calm: fossil coal, lignite and gas scrambled to cover demand
- Result: Dynamic grid control problem and CO_2 emissions up
- Objectives: clean, affordable, reliable energy supply not met
- Subsidised through guaranteed 20 yr electricity price (20B€/yr)
- Reform now drafted: Auction on generating capacity
- Needed: System Approach of generation, transmission, distribution to customers consistently managed
- Includes Energy Storage: BMBF Kopernikus Programme P2X

Carbon neutral fuel cycle: P2X – CCU

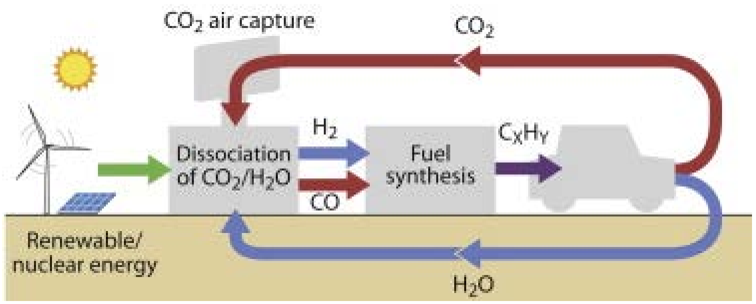
Graves et al., Ren. Sustain. Energy Rev. **15**, 1, (2011)

Point source capture of fossil CO_2
→ not climate neutral, emission delayed



Power-to-X
X = gas or liquid fuel or chemicals

Direct air capture of CO_2
→ climate neutral fuel cycle



P2X + CCU
CCU: carbon capture and utilisation

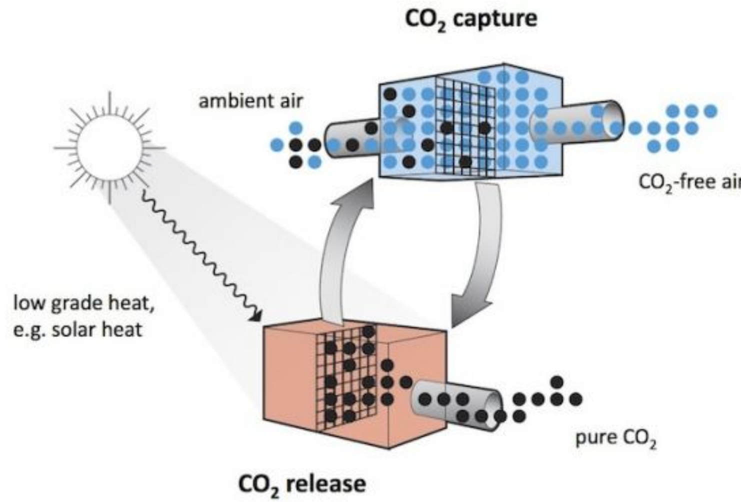
P2X is most critical part both technically and economically

Technology benchmark: costs of H_2
- Electrolysis >6 €/kg H_2 (fossil fuel <1 €/kg H_2)
- CO_2 capture: point source 40 €/tonne, direct air 400 €/tonne

Direct air capture of CO_2

Klaus Lackner Tree captures 1 tonnes CO_2/day. Wet-dry cycle epoxy.

To supply wind farm with CO_2 to be split by P2X, an approximately equally sized Lackner wood is needed.



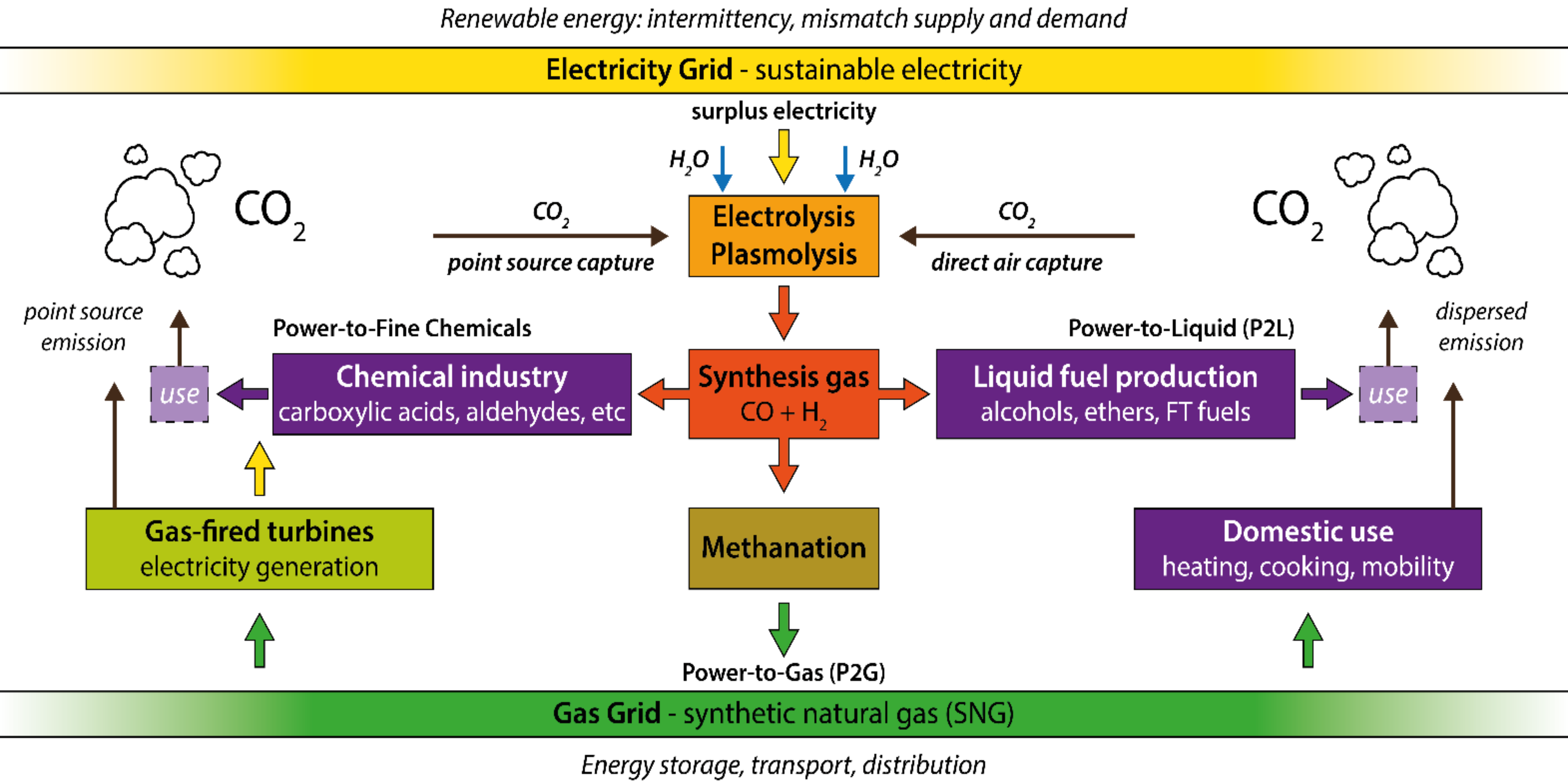
First commercial CO_2 air capturing plant, Hinwil (CH), capacity 900 ton CO_2 /yr, swept area 6x12m^2 amine granules

Coupling Electricity, Gas and Oil infrastructure

Surplus renewable electricity expected 2050:

Germany 110-148 TWh, France 44-91 TWh, The Netherlands 30-55 TWh

Energy Storage capacity NL gas net 552TWh

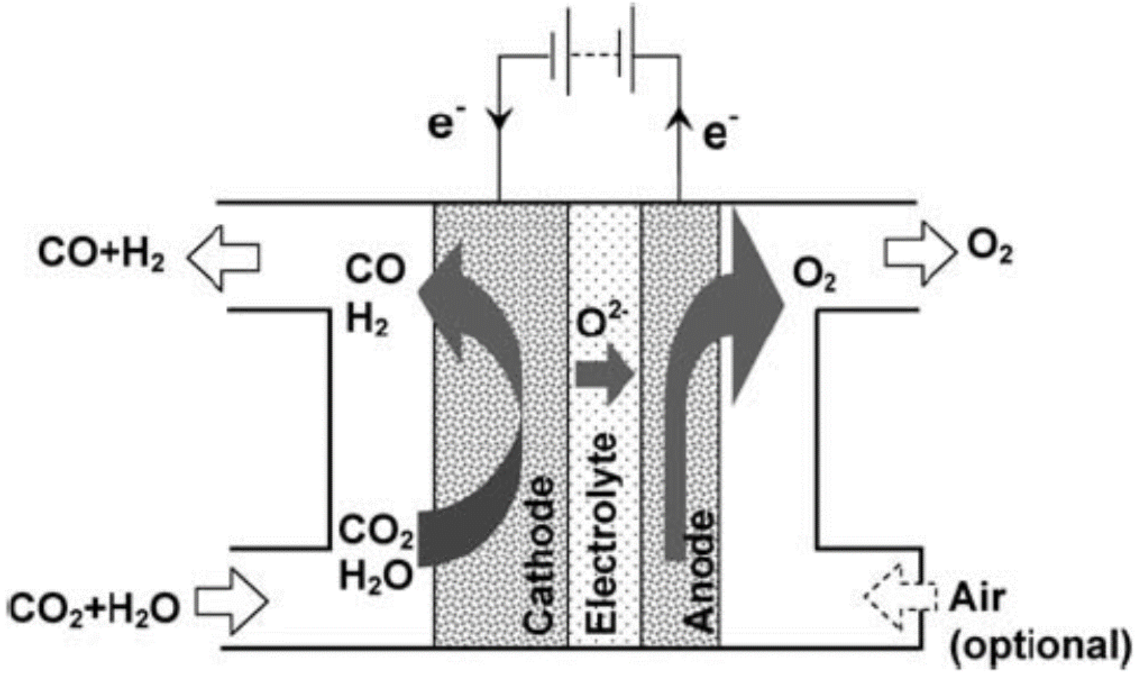


Splitting H_2O and / or CO_2 by electrolysis

- **Alkaline** electrolyte (100 yrs large scale, mature technology)
  - Power density low (< 0.5W/cm^2)
  - Hydrogen output pressure low (< 30bar)
  - Safety (caustic electrolyte)
- **PEM** (polymer electrolyte membrane), pre-commercial
  - Power density ~1W/cm^2
  - Rapid dynamic response
  - Degradation membrane
  - Catalyst material Pt, Ir (Scarce)
  - MW unit (Siemens)
- **SOEC** (solid-oxide electrolyser cell)
  - High power density, energy efficiency, output pressure
  - High Temperature operation (800°C, pressure 50-100 bar)
  - Co-electrolysis H_2O and CO_2
  - Degradation under high current density operation
  - Upscaling from kW range hampered

SOEC Co-Electrolysis at DTU

- External DC voltage pumps O^{2-} ions from porous **cathode** (Ni/YSZ)
- through dense solid **electrolyte** (YSZ = Yttrium Stabilised Zirconia)
- to porous **anode** ($La_{1-x}Sr_xMnO_3$/YSZ) at high temperature (800 °C)



DTU Technical University of Denmark

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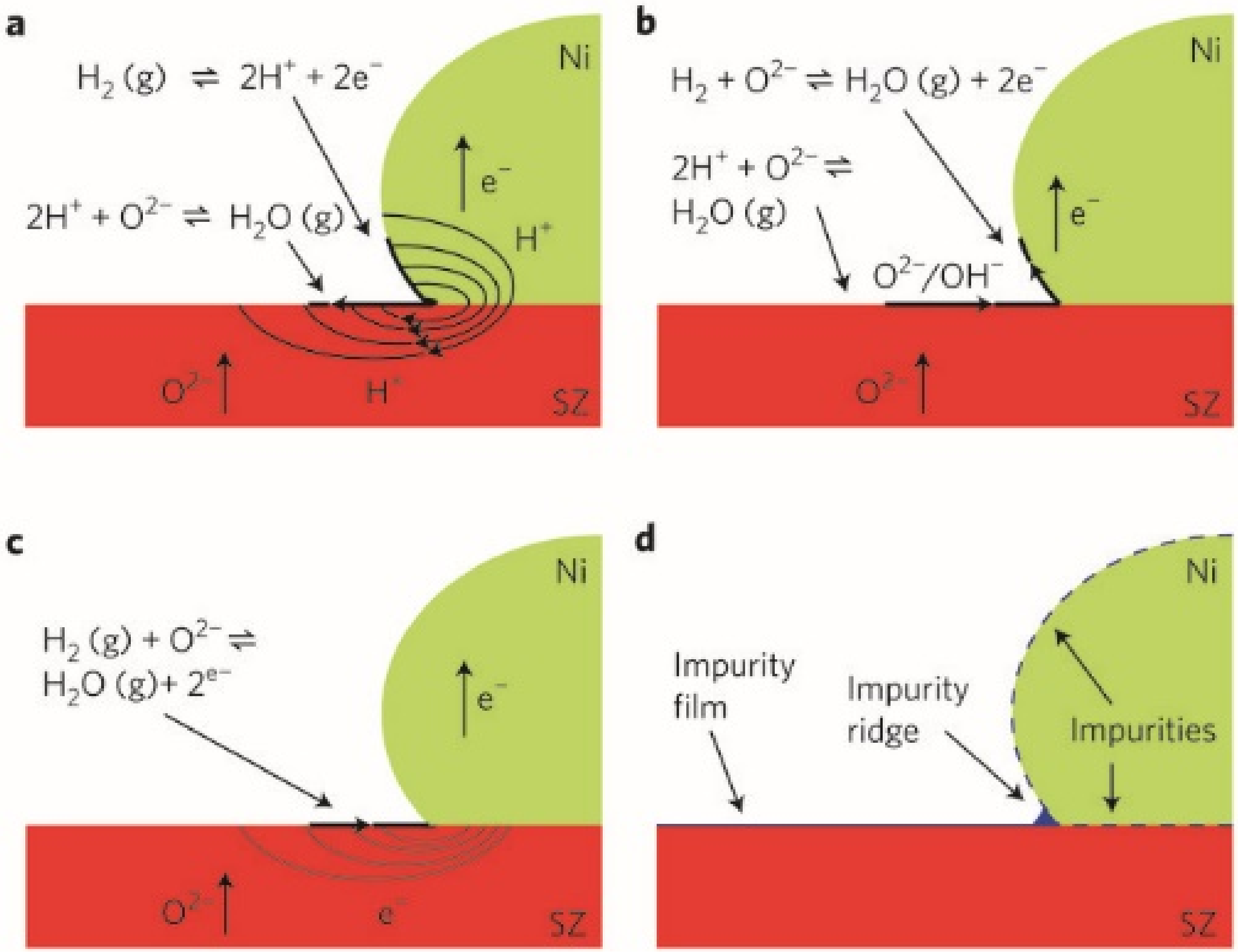
Electrolysis is a surface process happening at the nm interface between electrode, electrolyte and catalyst a 3-phase boundary phenomenon not understood

John Irvine et. al. Nature Energy 1, p.1-23 (2016)



Fuel Cell mode

a. H_2 absorption and dissociation on Ni surface to form H^+ migrating to site for water formation

b. Migration of O^{2-} or OH^- along electrolyte and Ni surface to form water

c. Water formation at electrolyte surface and electron transport through the electrolyte

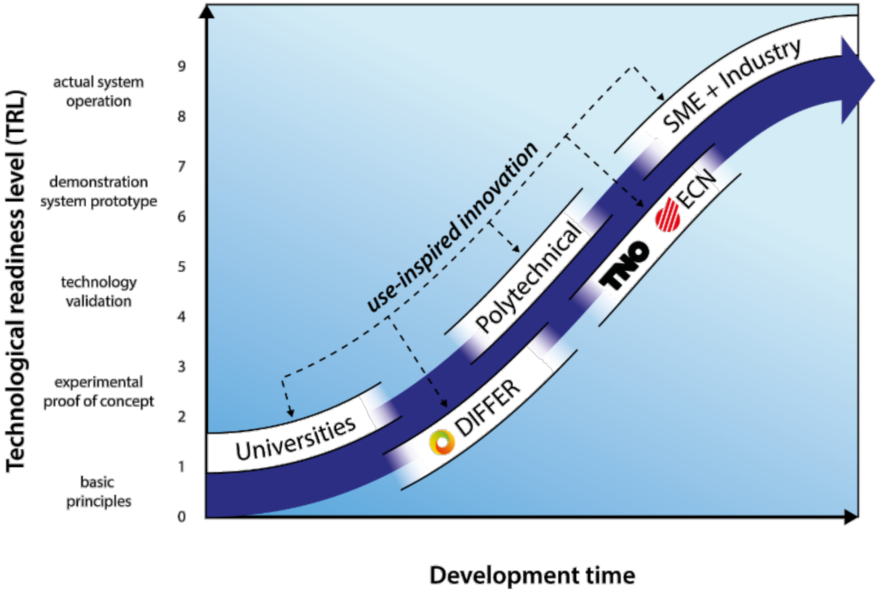
d. Role of impurities (glassy Silicate) at the 3PB to block the water formation reaction

The DIFFER Institute, Eindhoven, NL

Science for Future Energy

Mission: Basic **scientific research** into
Fusion Energy and **Solar Fuels**,
Based on in house **high-quality technical infrastructure**,
collaboration with Academia, National Research Organisations and Industry,
building a **national community** in **energy research**.

Relocated mid 2015
University Campus Eindhoven



Why plasma for CO_2 conversion?

Characteristics of CO_2 plasmolysis

Ease conditions for CO_2 splitting by channelling energy in molecular vibration to break chemical bond, not to heat the gas (non-equilibrium)

- Energy efficiency comparable to Electrolysis (~60% demonstrated)
- High gas flow and power flow density (45W/cm^2)
- Fast dynamic response (intermittent power supply)
- No scarce materials employed (Pt catalyst in PEM)

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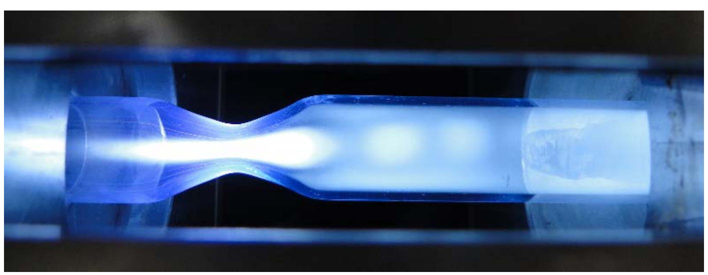
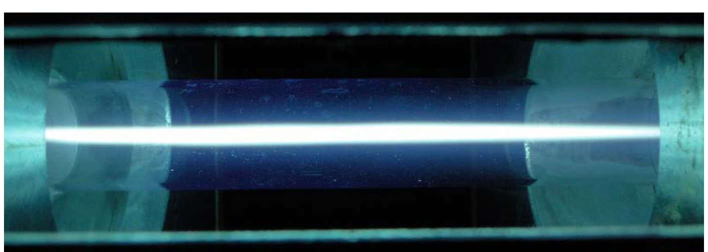
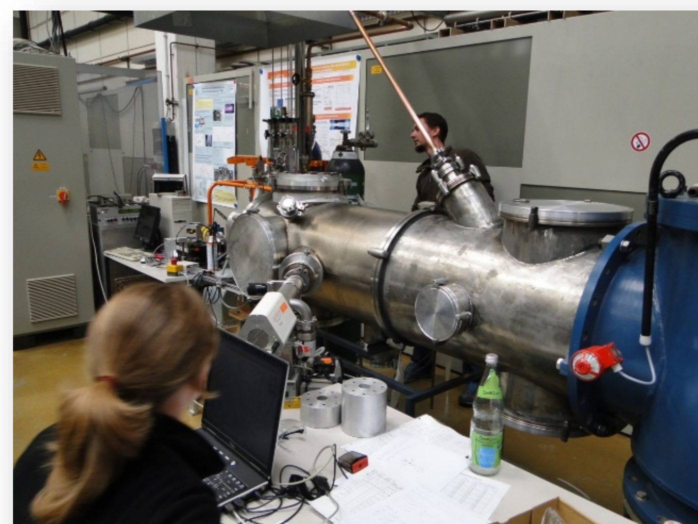
IGVP: 30 kW @ 915 MHz







Out of equilibrium $T_{vib} > T_0$ chemistry

Chemical reaction scheme

$CO_2 \rightarrow CO + O$ (ΔH=5.5 eV)

followed by reuse energetic **O** radical

$CO_2 + O \rightarrow CO + O_2$ (ΔH=0.3 eV)

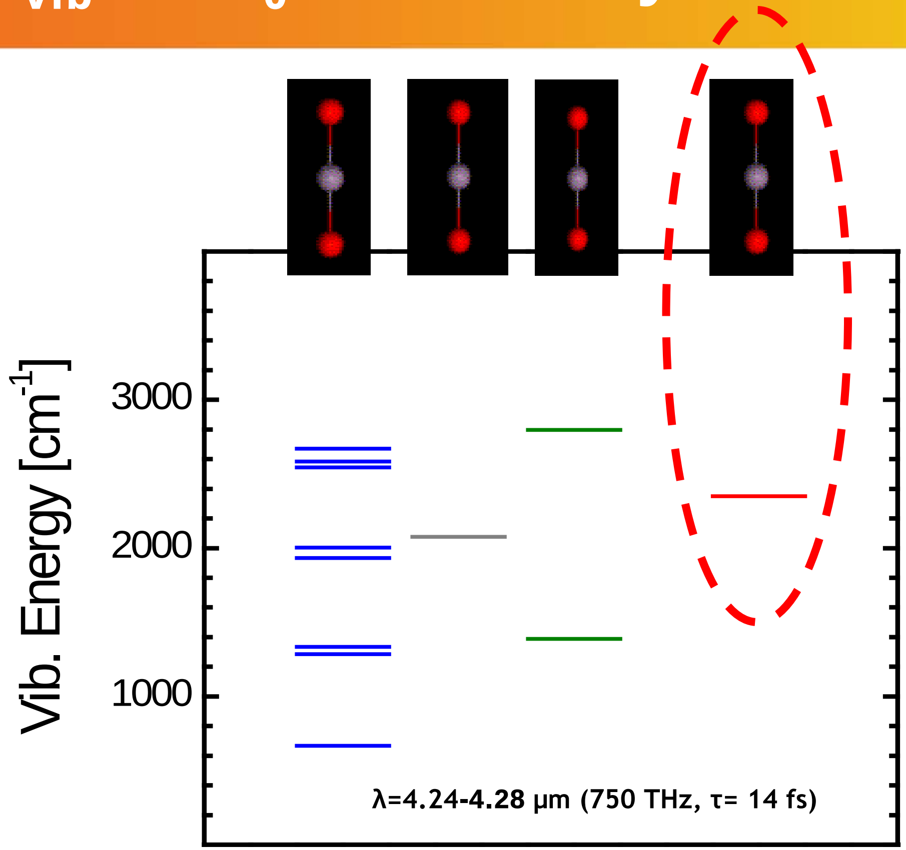
Net

$CO_2 \rightarrow CO + ½\ O_2$ (ΔH=2.9 eV)

Efficiency to be increased by

Concentration of electron energy on vibrational excitation of CO_2 in asymmetric stretch mode

$$\eta = CF/W = \alpha\ H/E_v$$

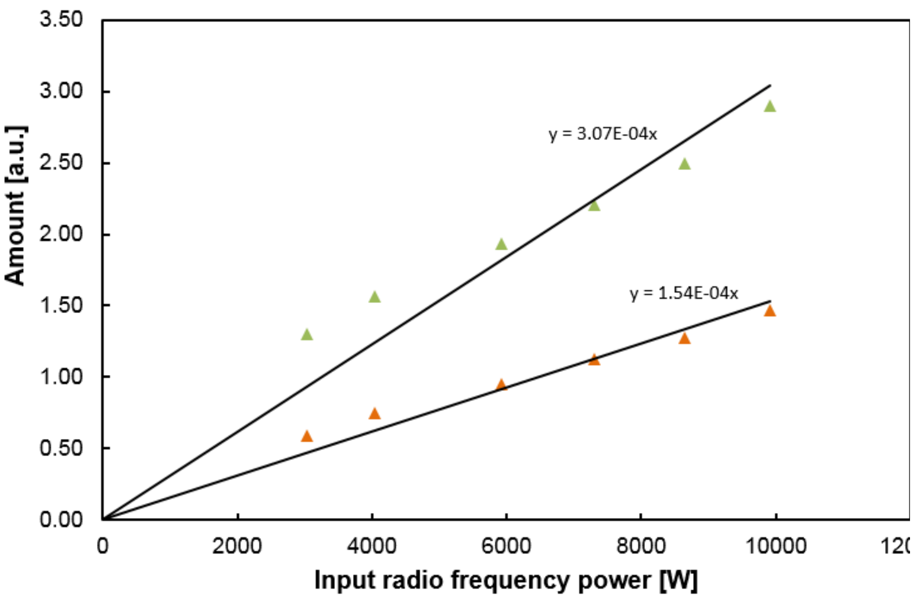


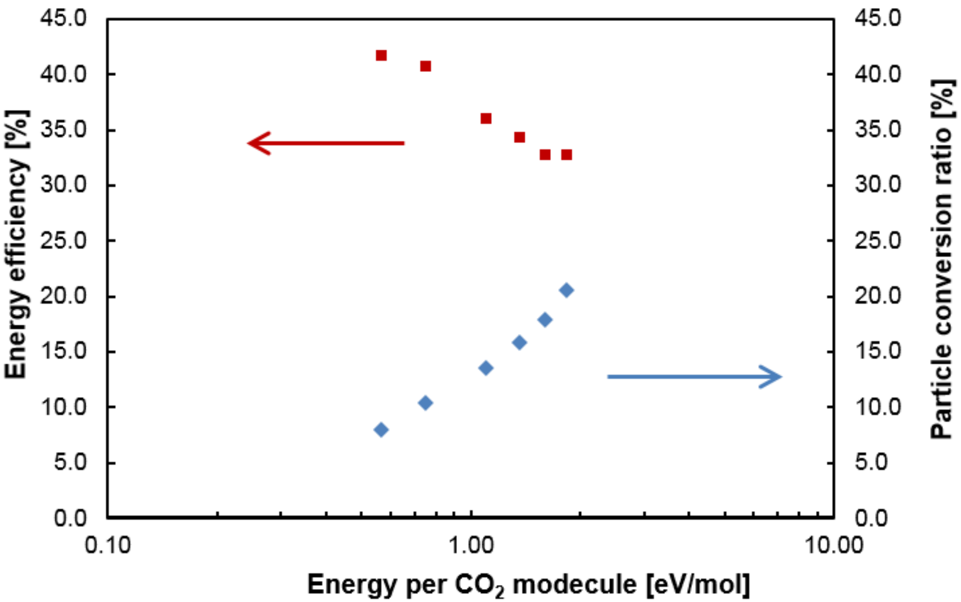
Arrhenius/Fridman:
Activation energy reduced by vibration energy

$$k = A \exp (\alpha E_v - E_a)/kT$$

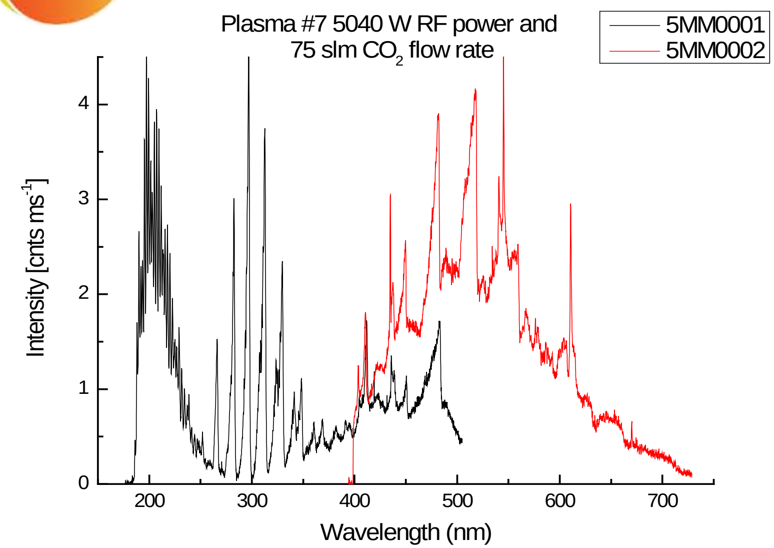
Experimental Results: Mass Spectroscopy

- CO and O_2 production as function **RF Power**

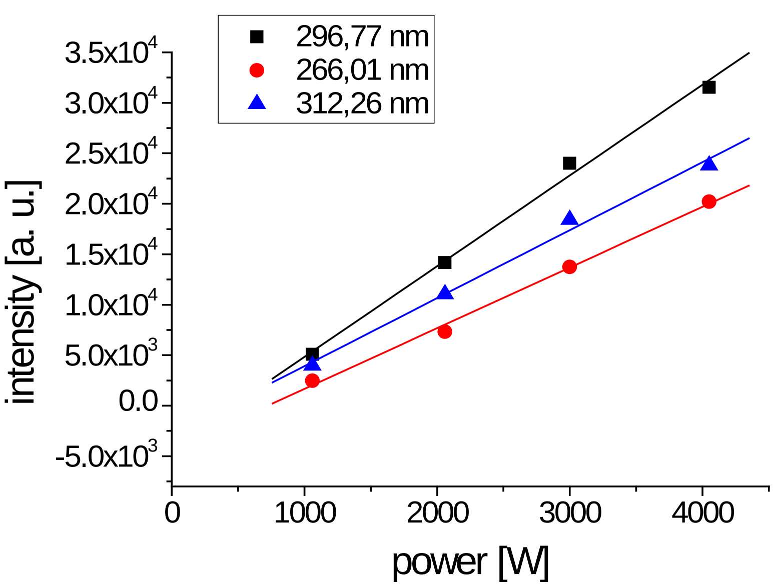


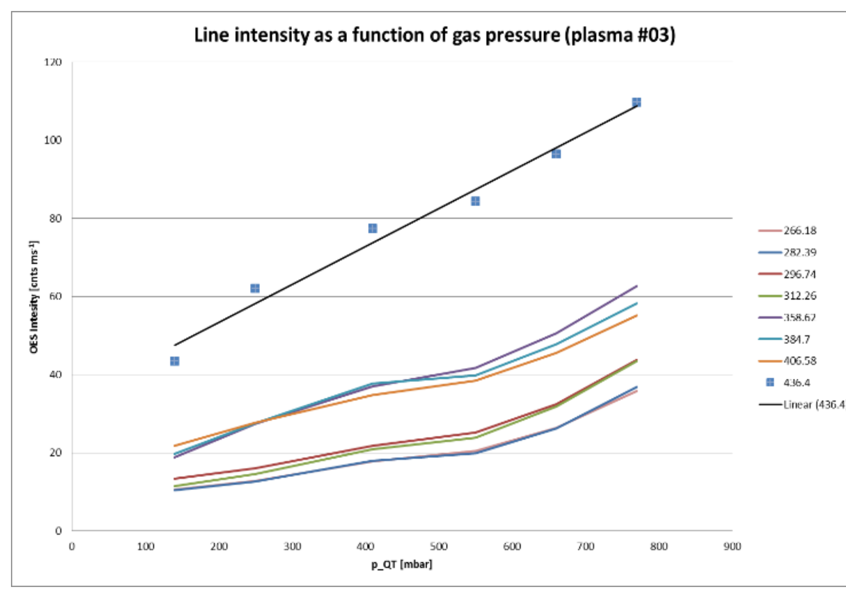


Optical Spectroscopy



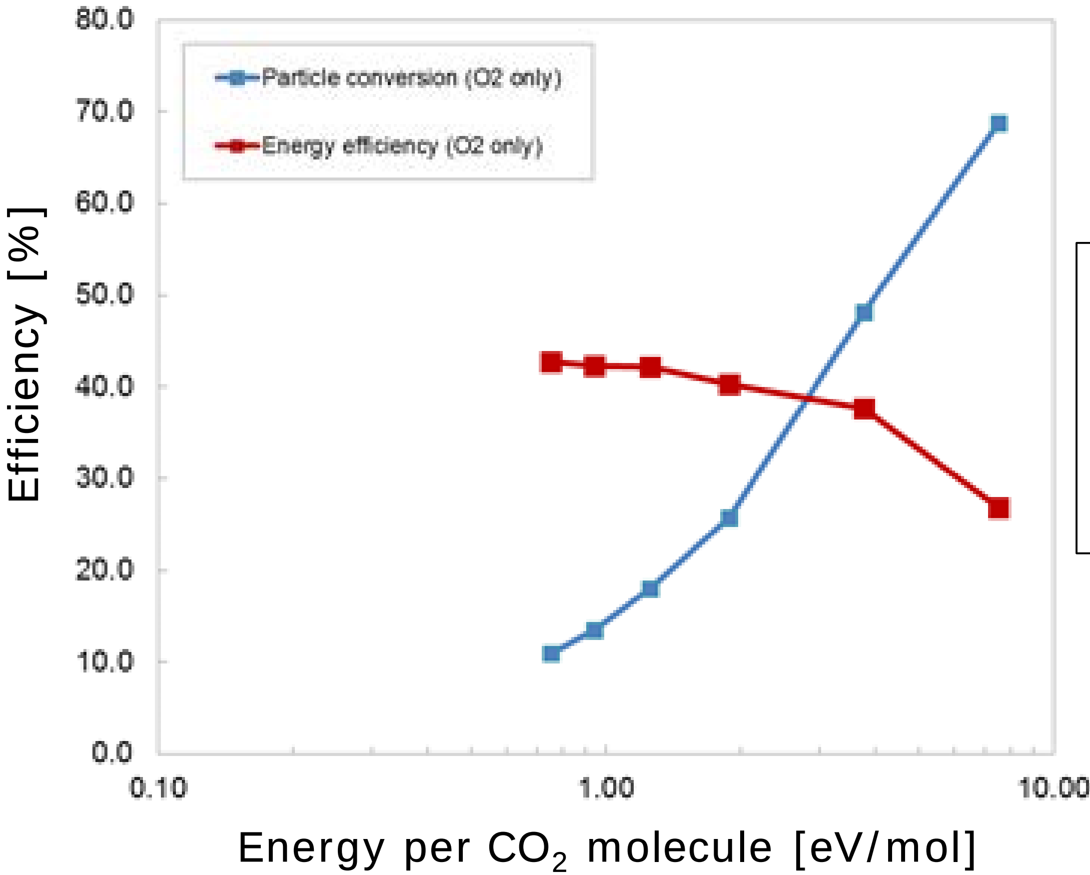
- CO third positives, fourth positives, Angstrom and Triplet identified.
- CO line intensity increases linear with RF power and gas pressure





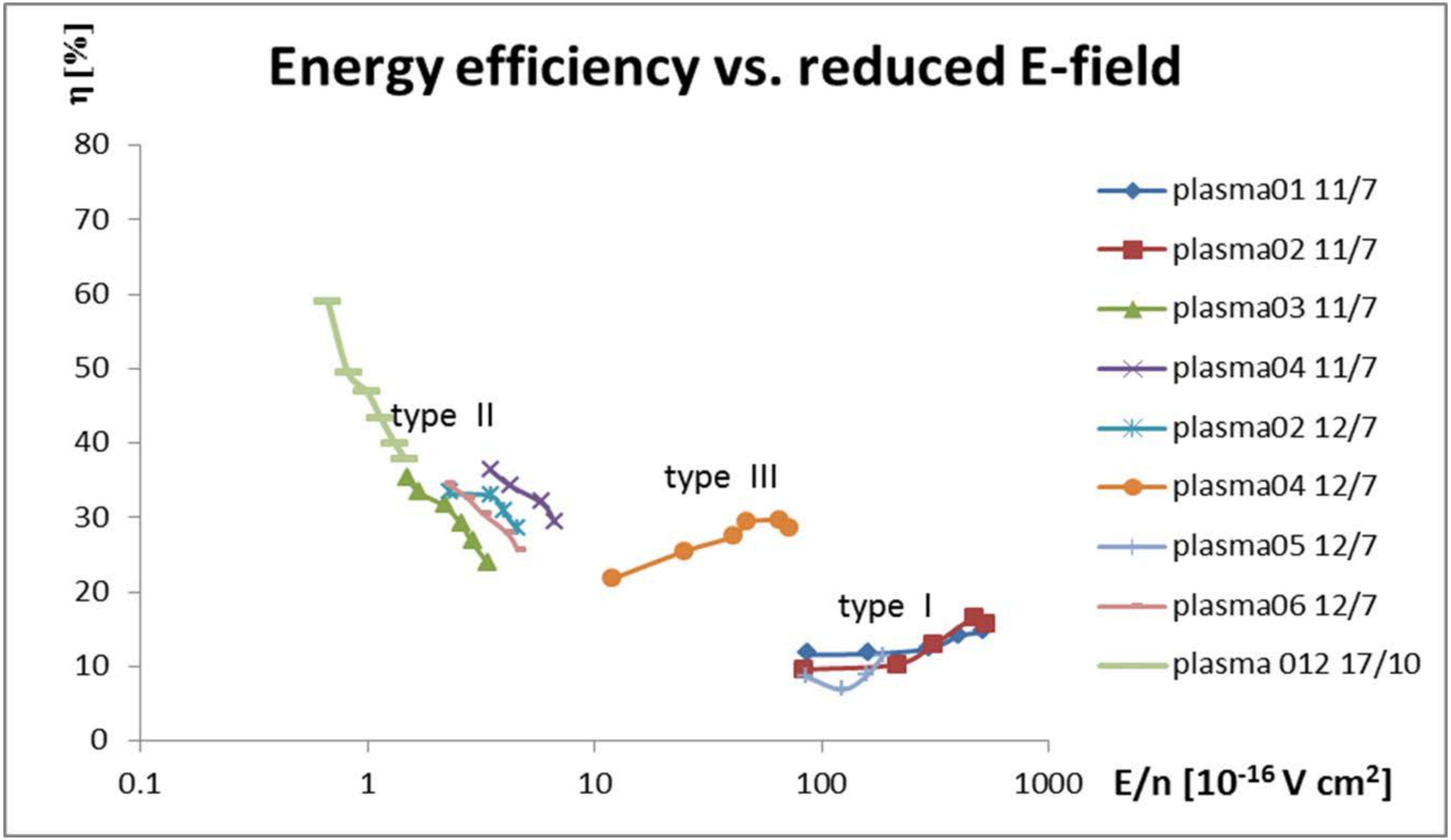
Experimental Results

- CO production as function **Gas flow**

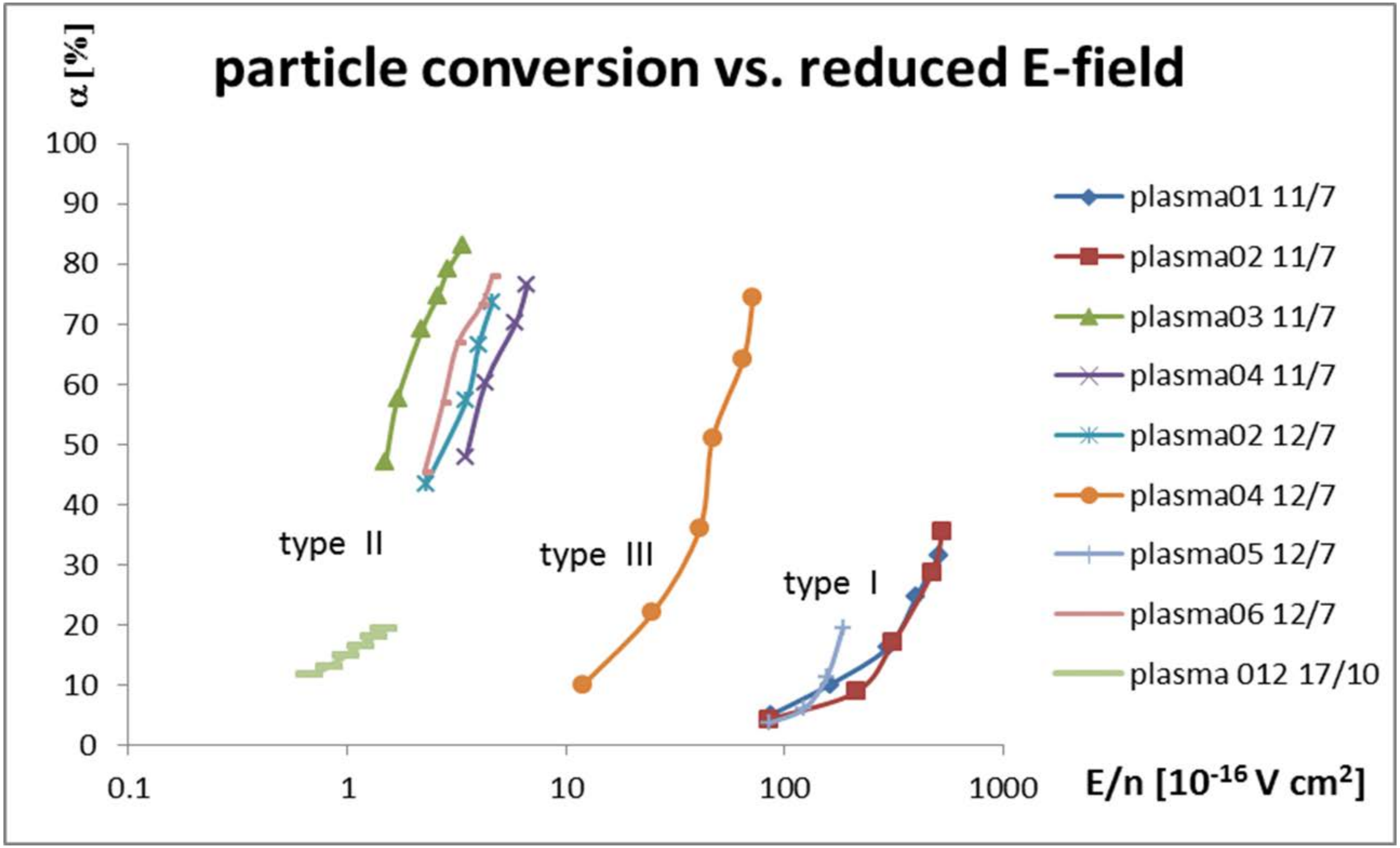


10 kW RF absorbed
75 slm CO2, conversion 10% CO
(non optimised for safety risk)
Pressure 500 mbar,
Energy Efficiency 30%

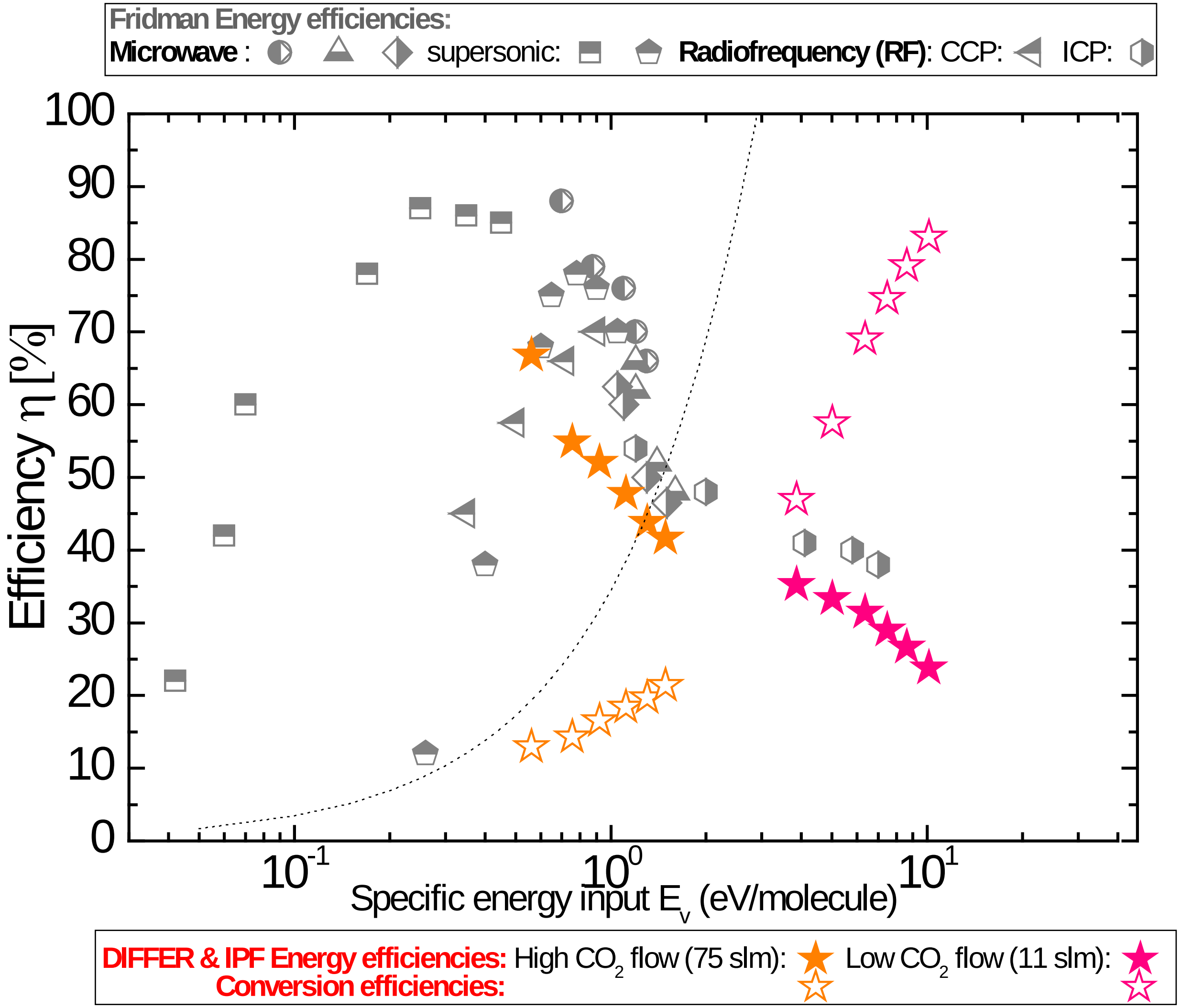
Experimental Results



Experimental Results

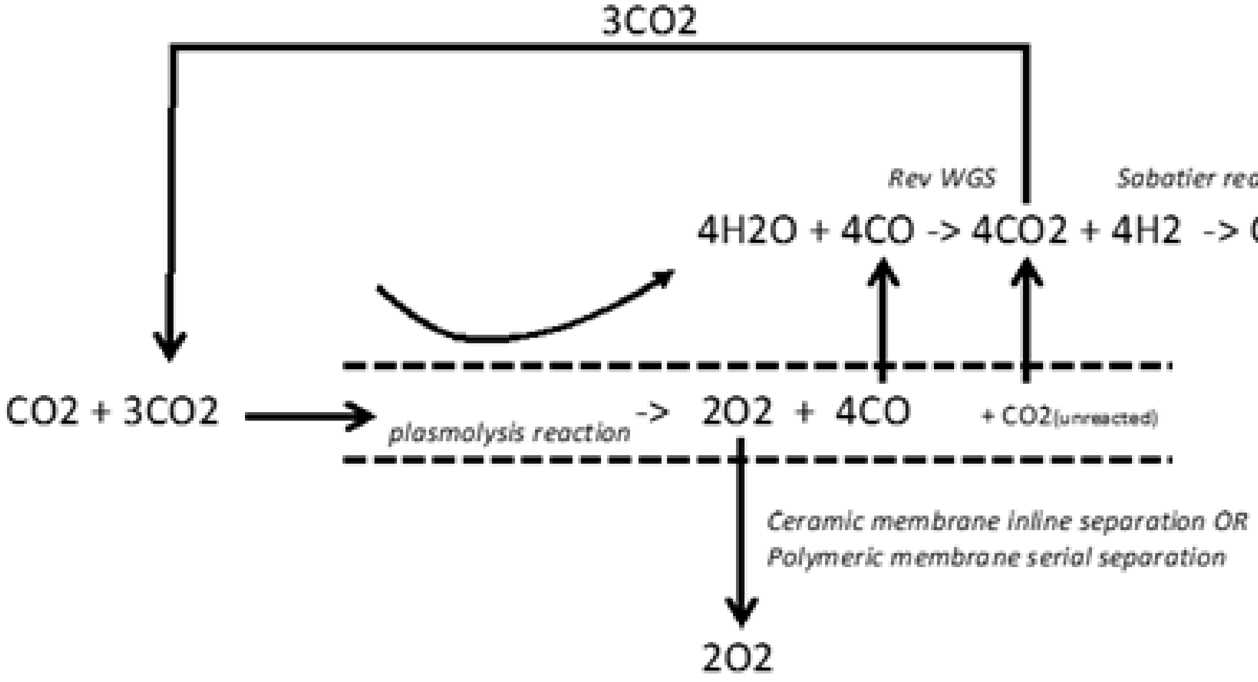


Energy efficiency of CO_2 plasma conversion



O_2 separation from CO (similar sized)

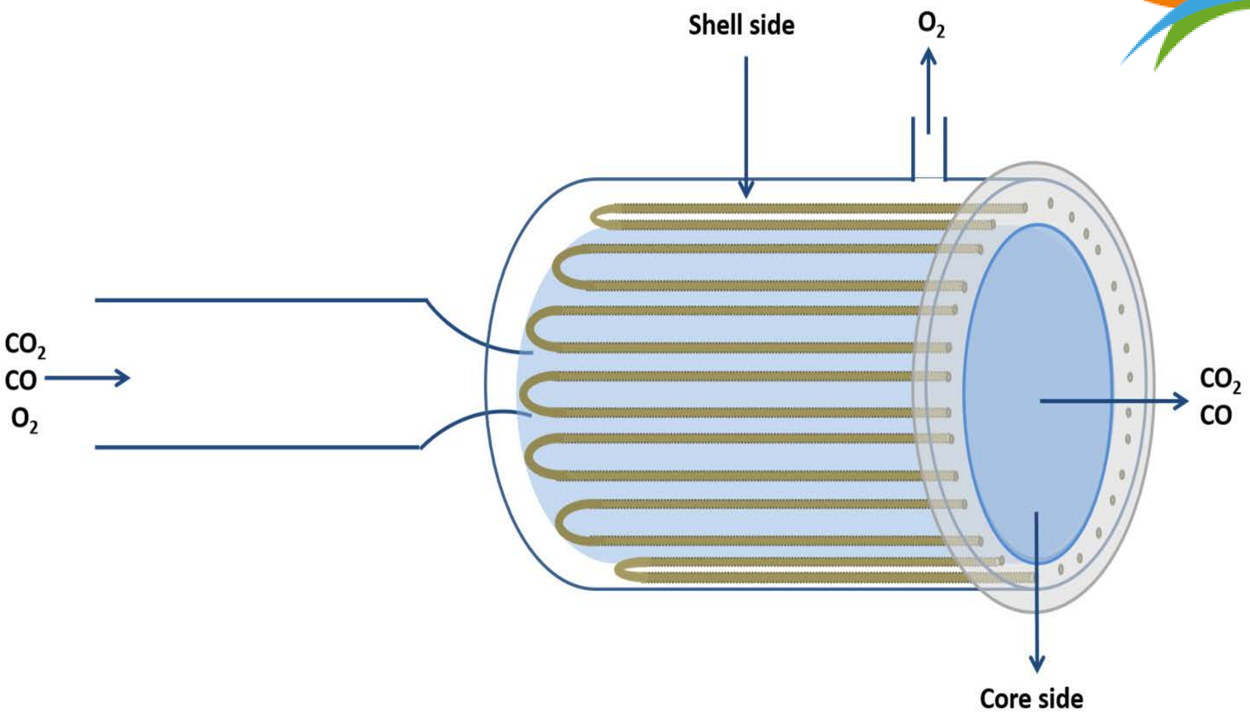
- MIEC mixed ion electron conductive membrane (pressure driven) BSCF ($Ba_{0.5}\ Sr_{0.5}\ Co_{0.8}\ Fe_{0.2}\ O_{3-d}$) has been shown to produce an O_2 flux of 60-80 ml/cm^{2}per min.
- Electro chemical Oxygen pump (Voltage driven) YSZ (Yttrium stabilized Zirconia).



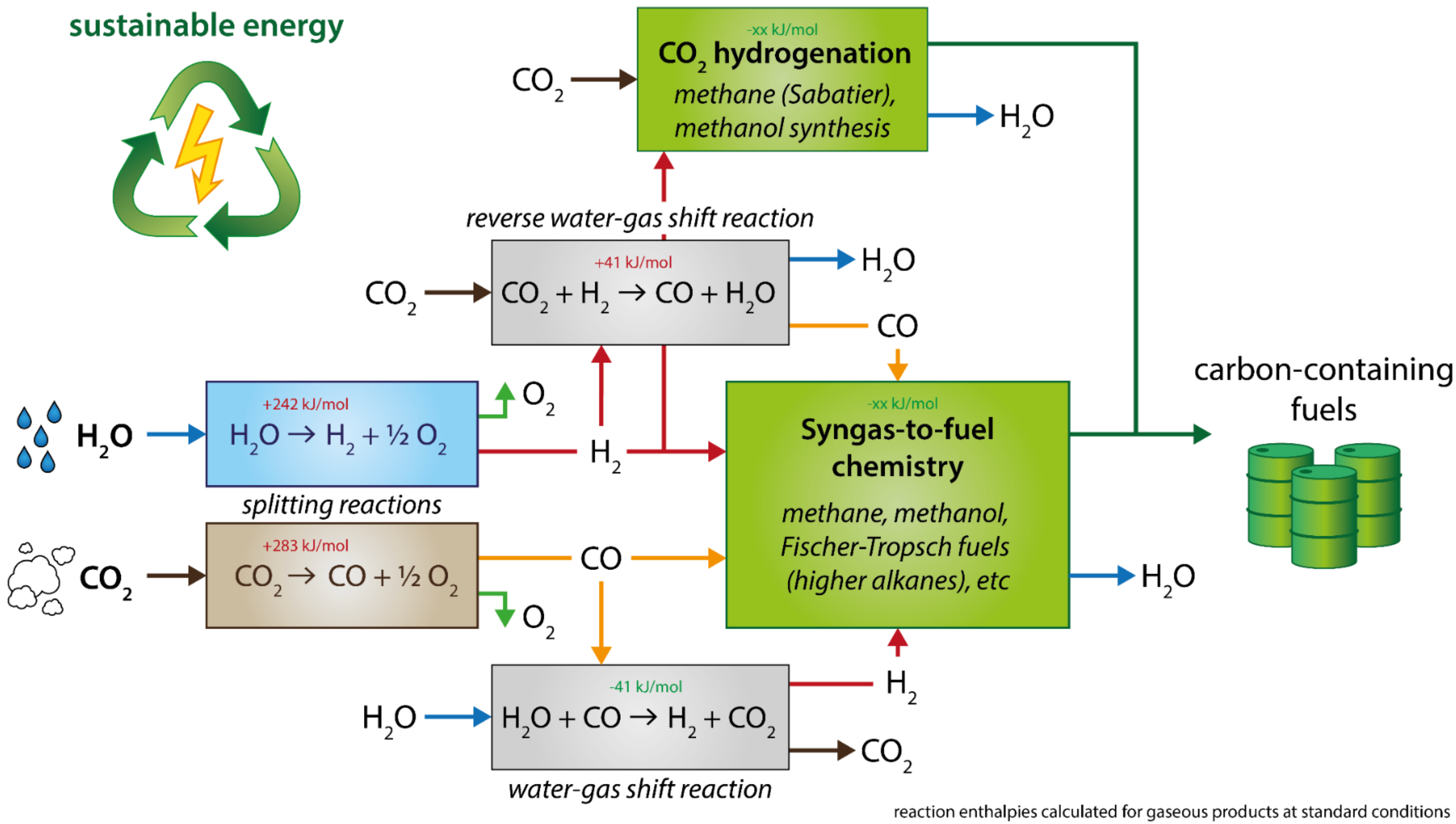
Separation of CO, O_2, CO_2 mixture

YSZ Oxygen selective membrane to separate O_2 from CO, CO_2 mixture

Hairpin shaped membranes fitted into SS assembly



From H_2O and CO_2 to sustainable hydrocarbons



10 year Kopernikus Program Power-to-X

Objectives high CO_2 reduction with max CO_2 valorisation, decentralisation, upscaling, public acceptance and export

Yr 1 to 3

- 6 Research Clusters; FZ Jülich, RWTH Aachen, Dechema together with Associated Partners (KIT Energy Lab 2.0)
- Electrolysis, Catalysis, Material and Process design to produce Hydrogen and Syngas
- P2X Road mapping together with Socio-Economic groups and SME

Yr 4 to 7

- 4 Technology Clusters for validation, integration and Pilot projects

Yr 8 to 10

- 3 System Demonstration and Application (Industry lead)

Conclusions

- P2X provides vast seasonal energy storage capacity and provides flexibility in the energy supply from Renewables
- P2X-CCU enables a CO_2 neutral fuel cycle based on hydro-carbons and existing infrastructure
- Technical challenge: innovation in CO_2 splitting and CO-O_2 separation
- Economic challenge: cost reduction, government regulation, business case expected to emerge around 2030, cost of CO_2 to reach € 200/tonne
- In 10 yrs time, cost Wind and Solar tumble, whilst cost of decommissioning, waste disposal and climate change factored into cost of nuclear and fossil power.
- System approach is essential in future energy system, incl. waste disposal, storage and customer acceptance