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Fraunhofer Institute for Ceramic Technologies and Systems IKTS

Erzeugung von Prozesswärme durch direkte Verbrennung von Brennstoffen an Sauerstoff-liefernden Keramiken

4. Aachener Ofenbau- und Thermoprozess-Kolloquium,17. – 18. 10. 2023

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Outline
Fraunhofer

1. Introduction
2. Adsorbents for Oxygen: OSM
3. Membranes for Oxygen: MIEC
4. Direct Combustion at a Solid
5. R&D Projects for Heat and Power
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Fraunhofer Association: Applied research for the immediate benefit of the economy and society

> 30,000

3 billion €/a

€

76 institutes and research units

Fraunhofer Institute for Ceramic Technologies and Systems IKTS

> 750

75 million €/a

2 x Dresden
1 x Hermsdorf









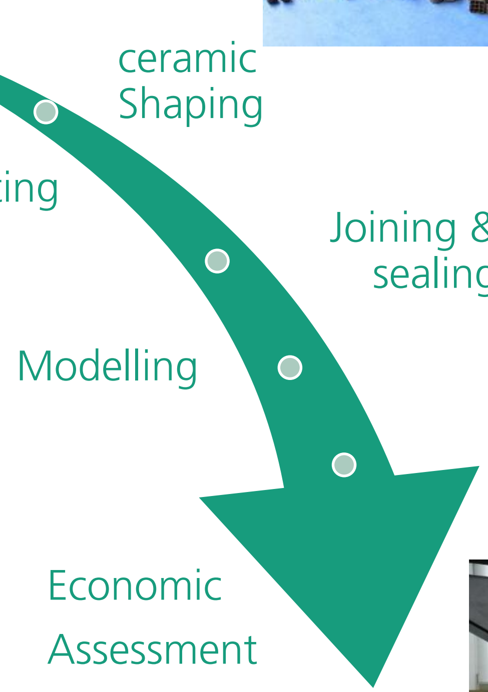

Introduction

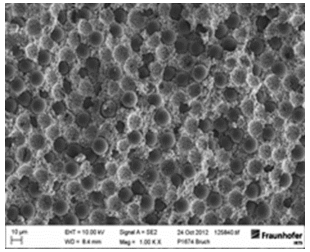
Department High Temperature Separation and Catalysis

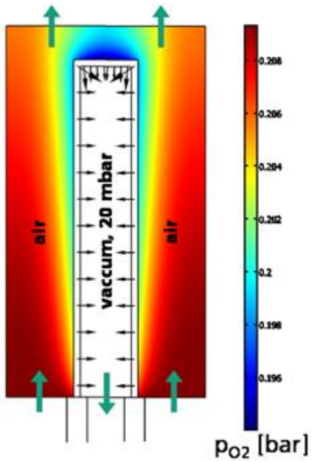
$La_{1-x}Sr_xMn_{1-y}Co_yO_3$ $(La,Sr)CoO_3$
$La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ $La_2Ni_{1-x}Cu_xO_4$
3YsZ/8YsZ/MC2 $MnCo_2O_4$
$BaZr_{0.8}Y_{0.2}O_{2.9}$ $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$
$Ce_{0.8}Gd_{0.2}O_{1.9}$ $Ca_{1-x}Sr_xMn_{1-y}Fe_yO_3$
$Ba_{1-x}Sr_xCo_{1-y-z}Fe_yB_zO_3$

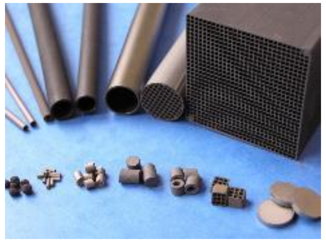
Materials – Mixed Oxides

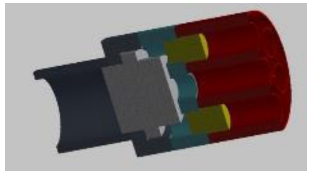
- **Structure**: Perovkites, Spinels, K_2NiF_4 type, Ruddlesden-Popper, Composites
- **alternative Catalysts** (no noble metals)
- **OSM** – Oxygen Storage Materials
- **MIEC** – Ionic Electronic Conductors (O_2, H_2-membranes)
- p-/n semiconductors, ion conductors, solid electrolytes

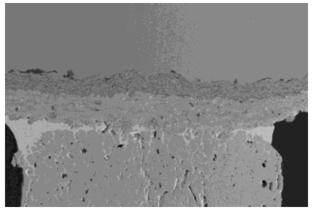








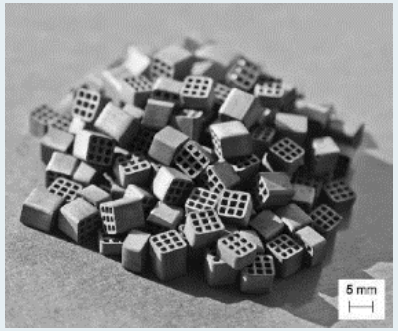




Introduction

Working Group: High Temperature Membranes and Storage Materials

Adsorbents

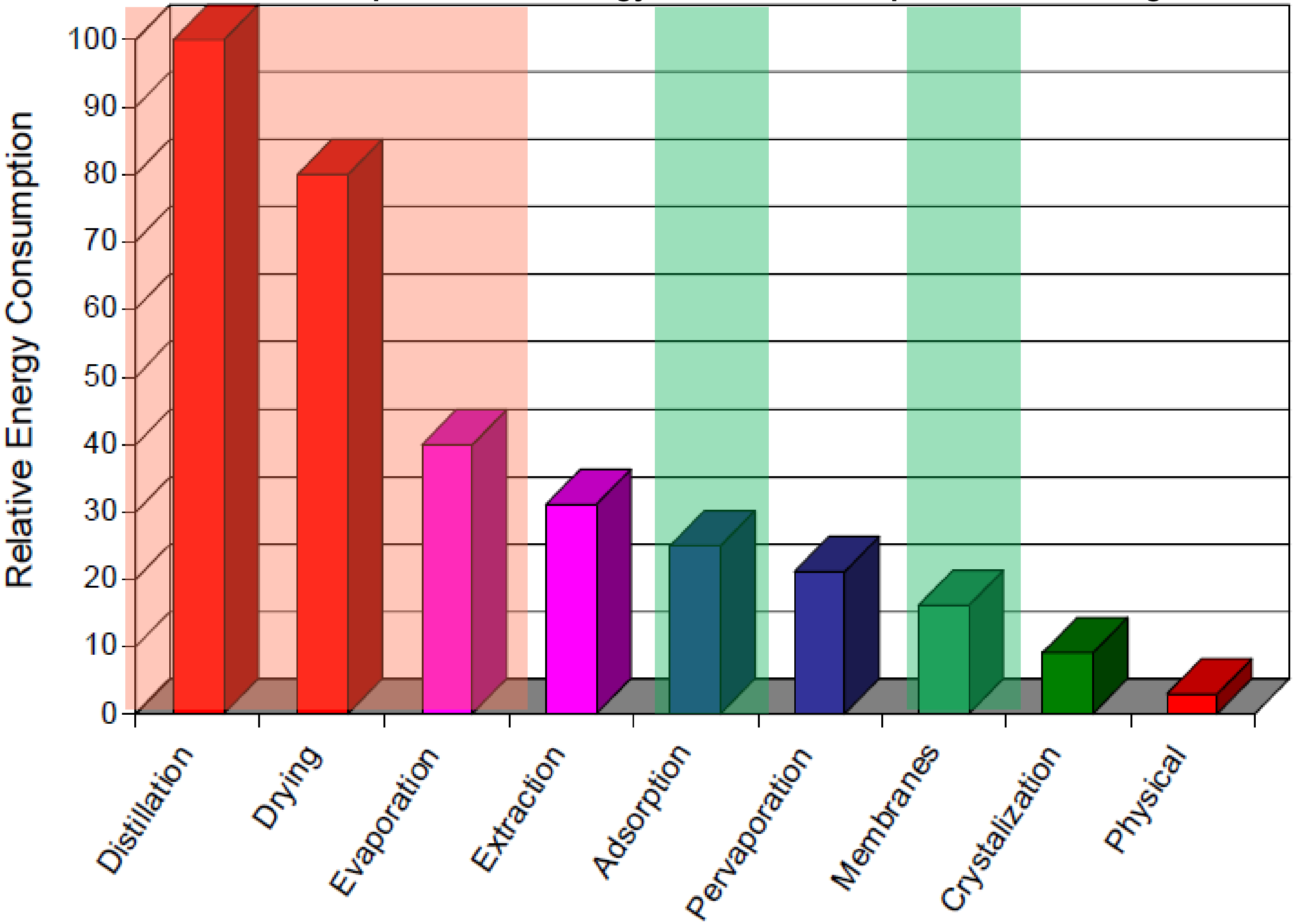


Membranes

Advantages

- low **energy demand** compared to **thermal separation processes**
- **ceramics** withstand:
  - agressive agents
  - high T, p
- special properties @high temperatures:
  - **O^{2-}/H^{+}** conductivity
  - **electrical** (n/p) conductivity
  - reversible **gas adsorption**

US Department of Energy, Materials for Separation Technologies, 2005



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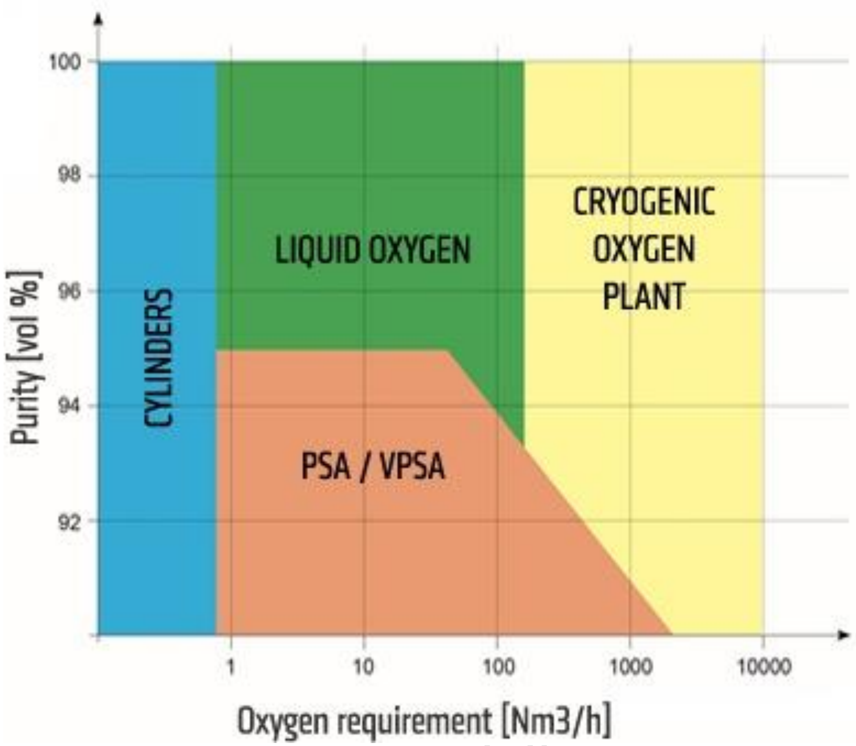
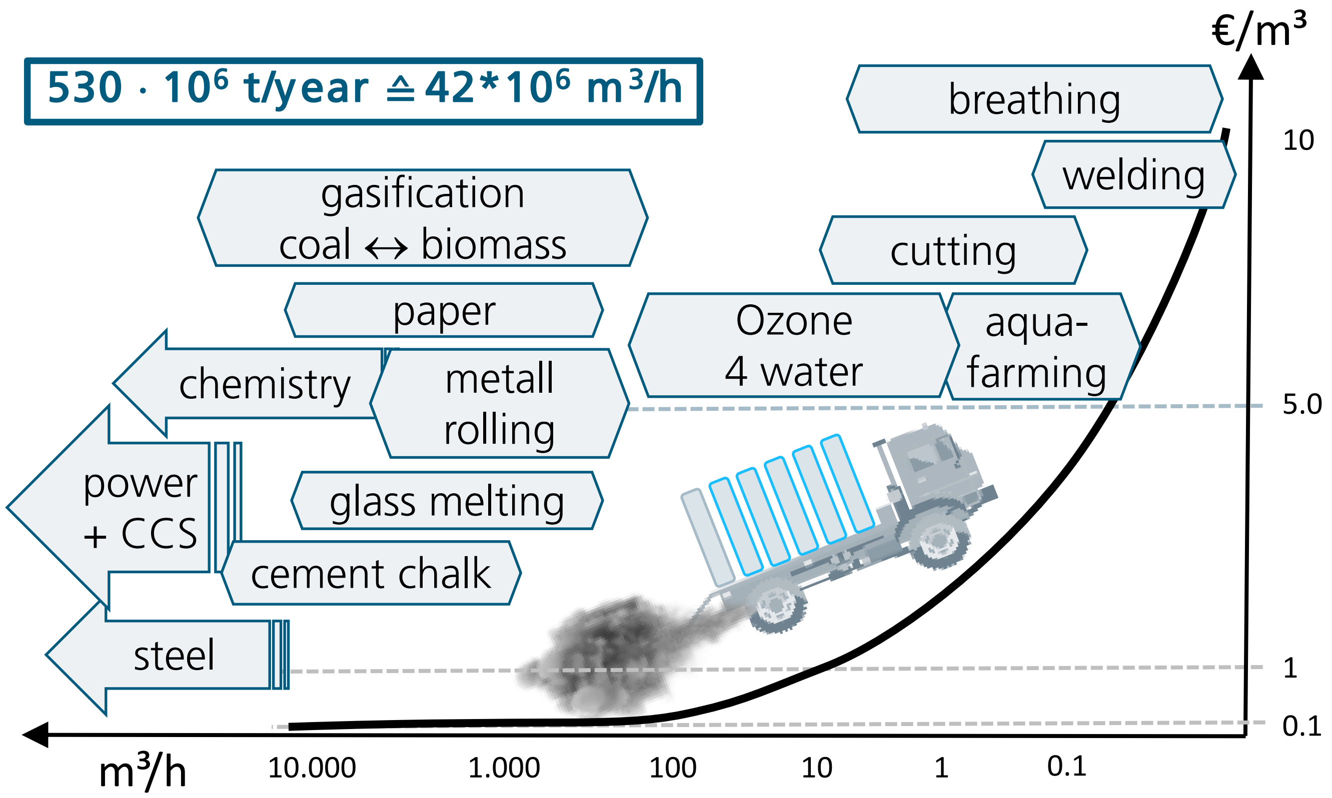
Introduction

Comparison of Oxygen Production Technologies, Market and Applications





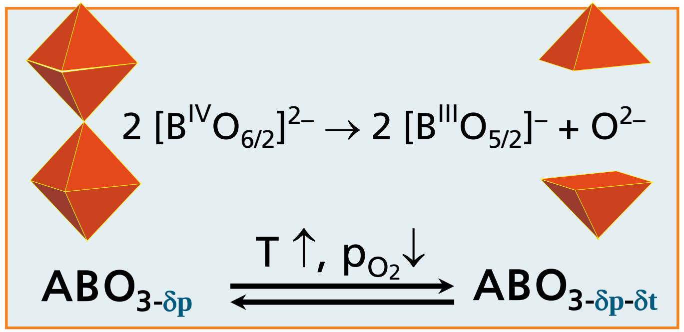
global market size: ~**34 billion €/year**

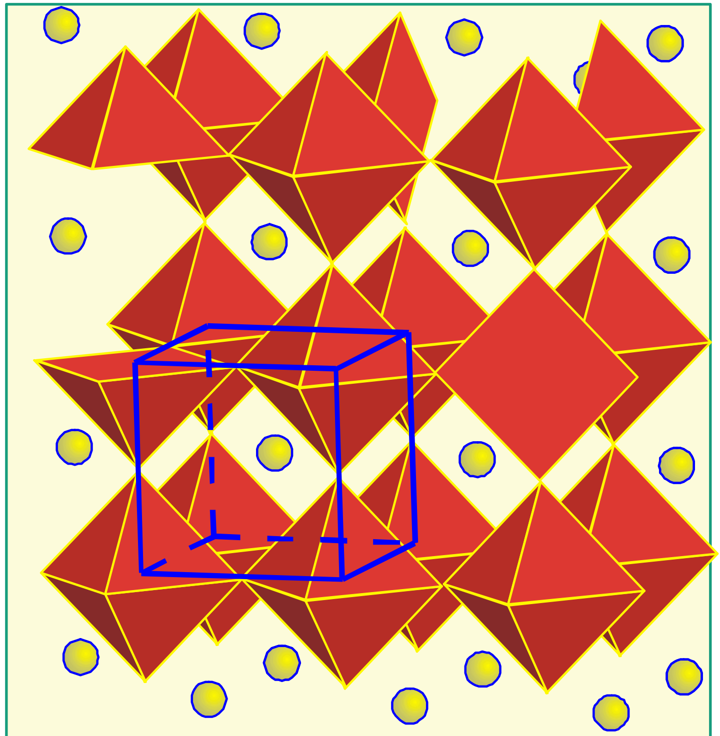
Adsorbents for Oxygen: OSM

OSM – Oxygen Storage Materials

Reversible O_2 Storage

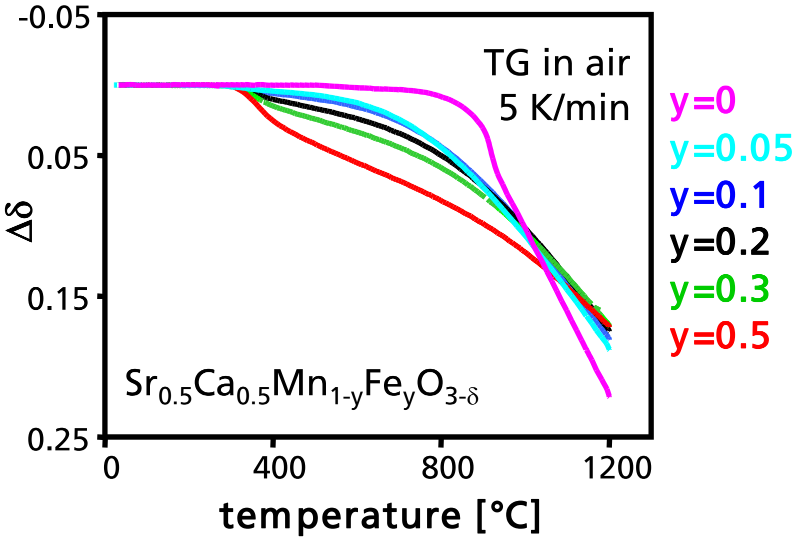
- Perovskite: crystal structure with permanent & temporary **O-Vacancies**
- **vacancy occupation** depending on **T, p_{O2}**, chemical **composition**
- **O_2 storage capacity:** themogravimetry (TG), TpD

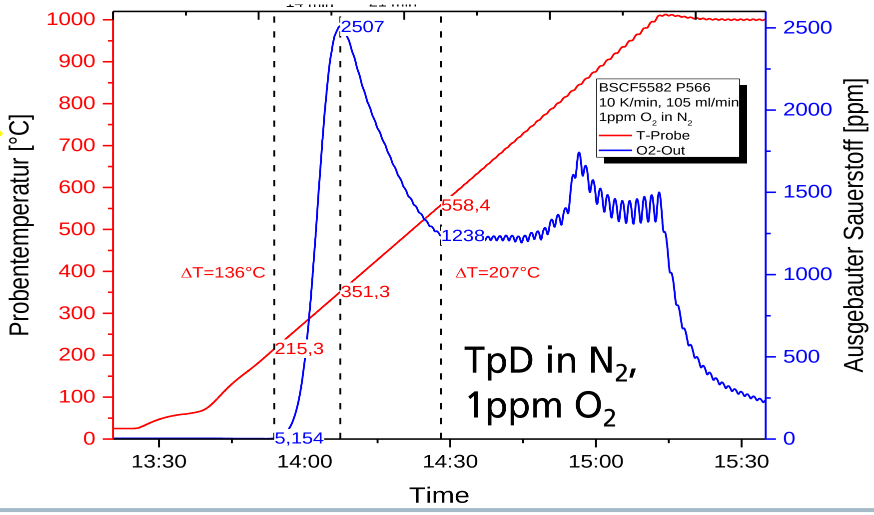




Structure of perovskite (unit cell) with arbitrary drawn oxygen vacancies

A ions BO6/2 octahedra





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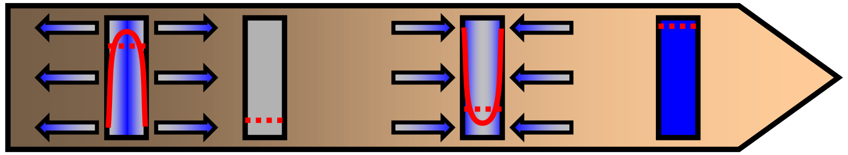
Adsorbents for Oxygen: OSM

OSM – Oxygen Transport by Bulk Diffusion, O_2 exchange, …

reduction: T_A, vacuum

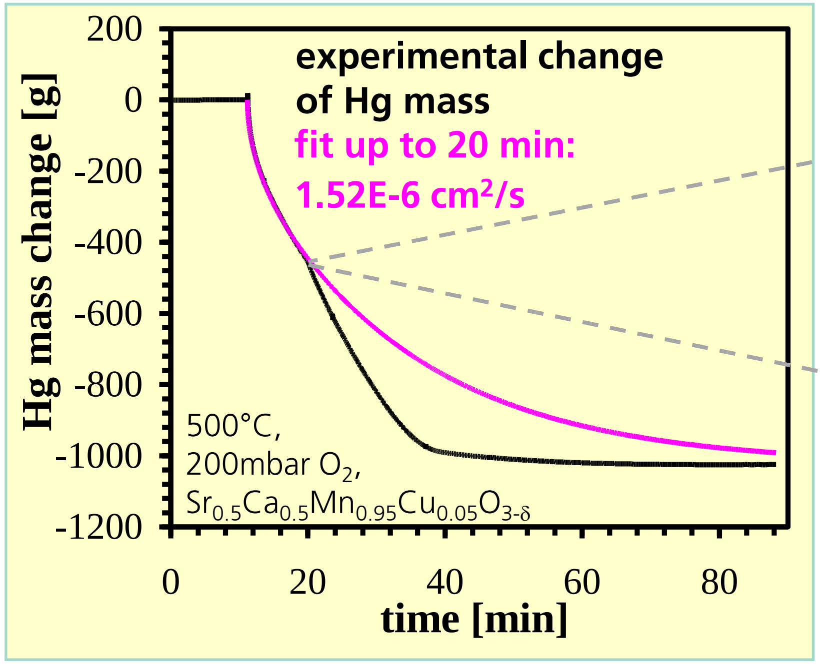
equilibration: T_E, vacuum

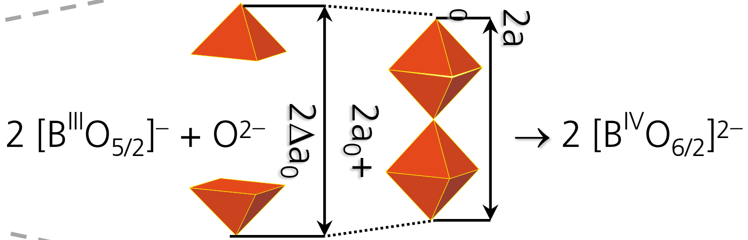
oxidative relaxation: $T_{E.}$, 200 mbar O_2

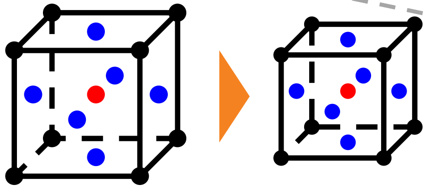


$\Delta m(O_2) = f(t)$

$\rightarrow$ **$D_{chem.}$**



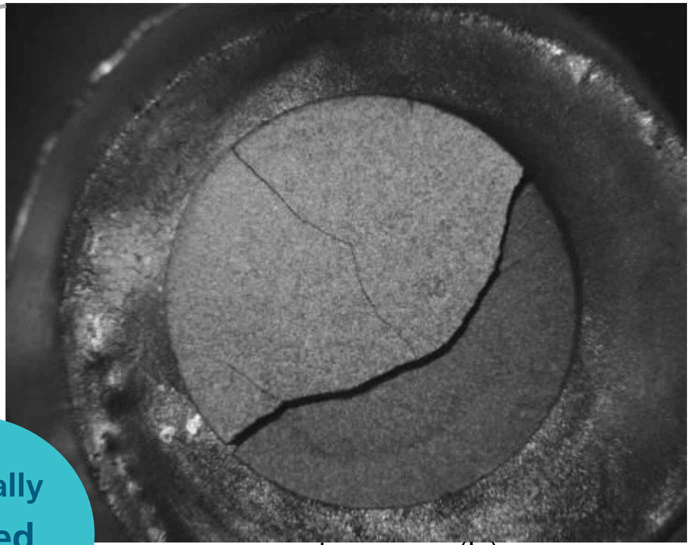




O_2 transport:

- O^{2-} **diffusion** within crystal lattice
- O^{2-}/O_2 exchange at OSM surface
- O_2 transport in open/closed pores
- mixing/reaction of O_2 with sweep gas

like salt ions in water



chemically induced expansion

tension, $p_{O_2}(h)$

compression, $p_{O_2}(l)$

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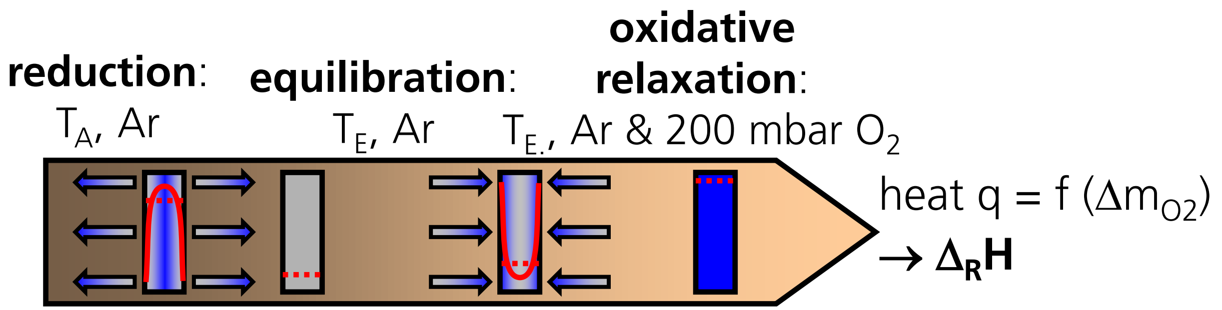
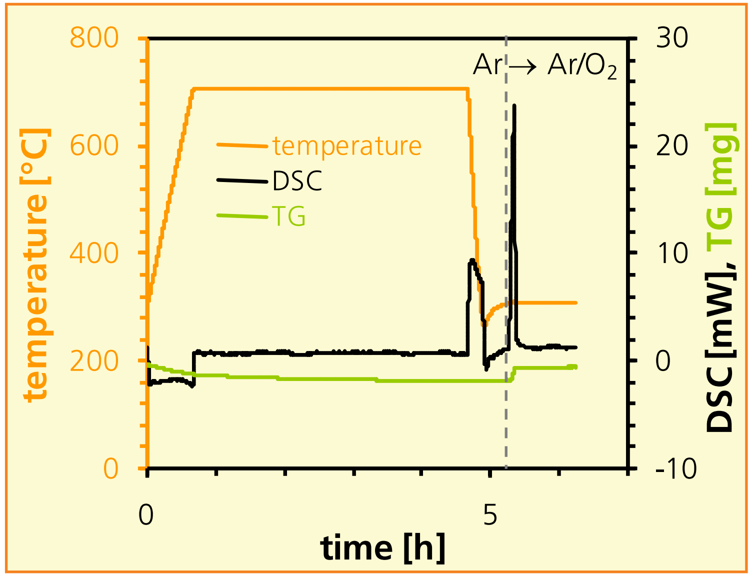
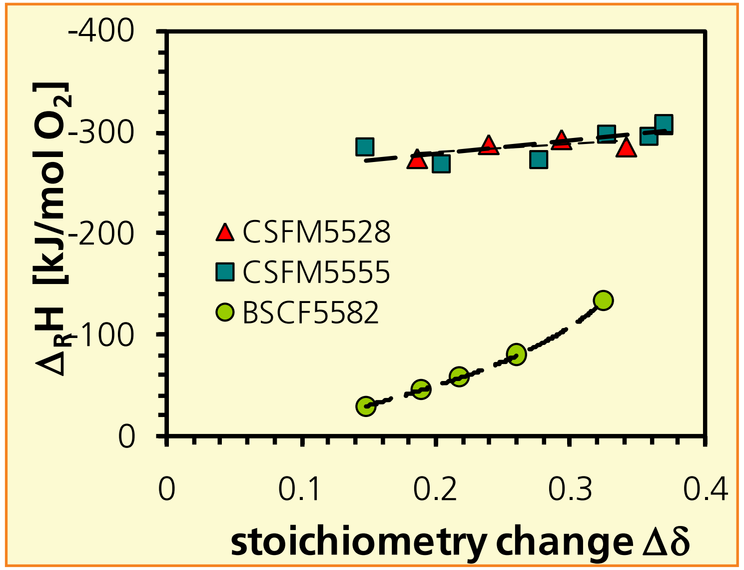
Adsorbents for Oxygen: OSM

Heat of Reaction for O_2 Incorporation (OSM oxidation) and O_2 Release (OSM reduction)







Reaction Enthalpy

- 20 - 350 kJ/mol O_2
- depends on:
  - stoichiometry change
  - reducable metal ions/ composition
- **O_2 exchange rate ~ $1/\Delta_R H$**

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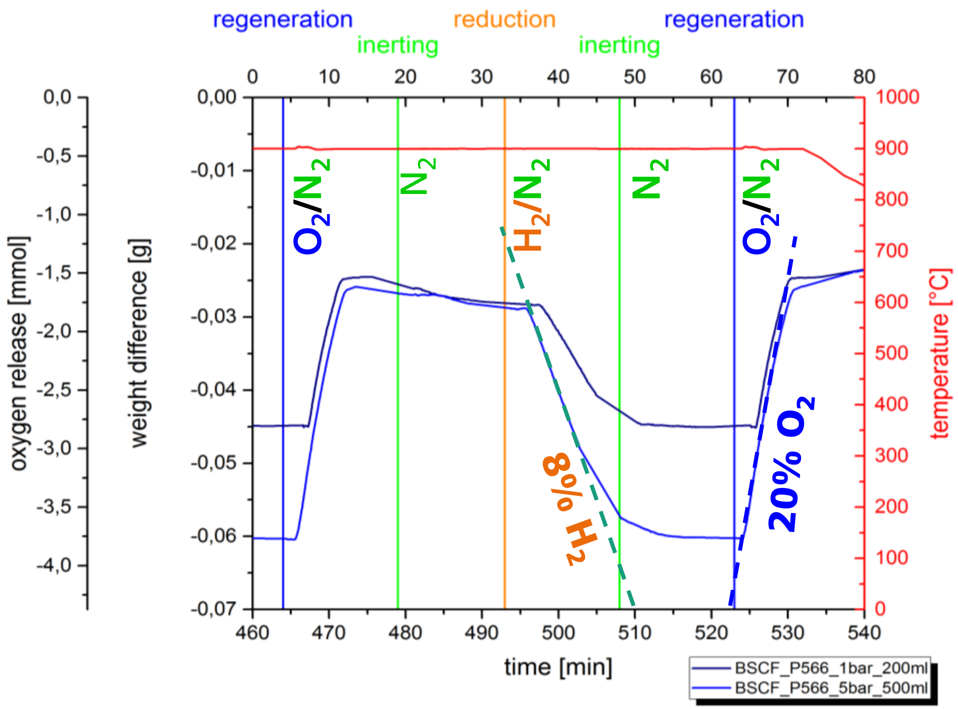
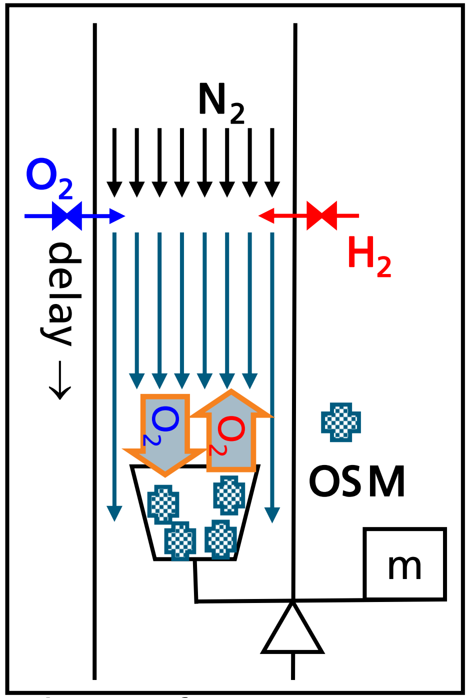
Adsorbents for Oxygen: OSM

Hydrogen Combustion @OSM – experimental Proof

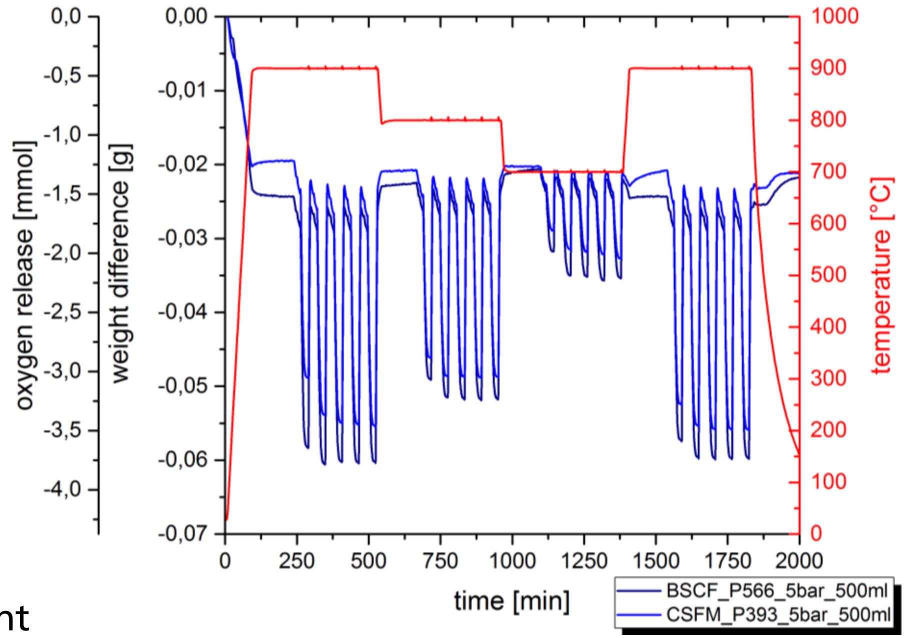
Combustion of H_2 on solid OSM (BSCF5582, CSFM5555, 1 and 5 bar, TG, $\Delta m = m(O_2)$)

- thermogravimetric measurement of O_2 release and uptake caused by H_2 dosage and combustion





Scheme of TG measurement



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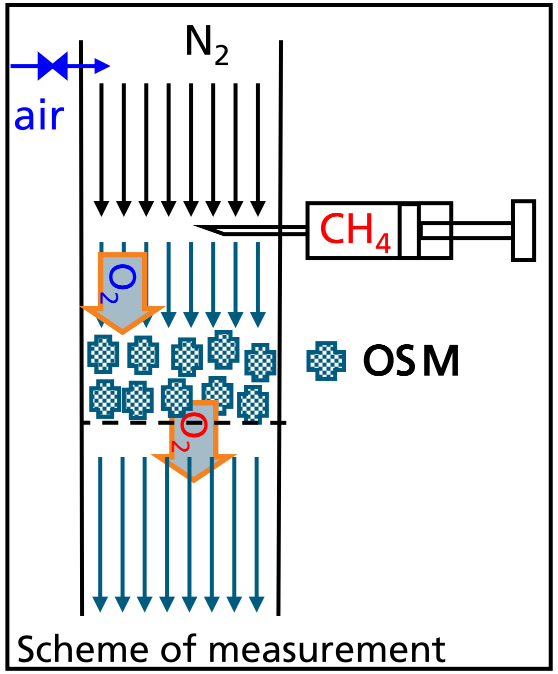
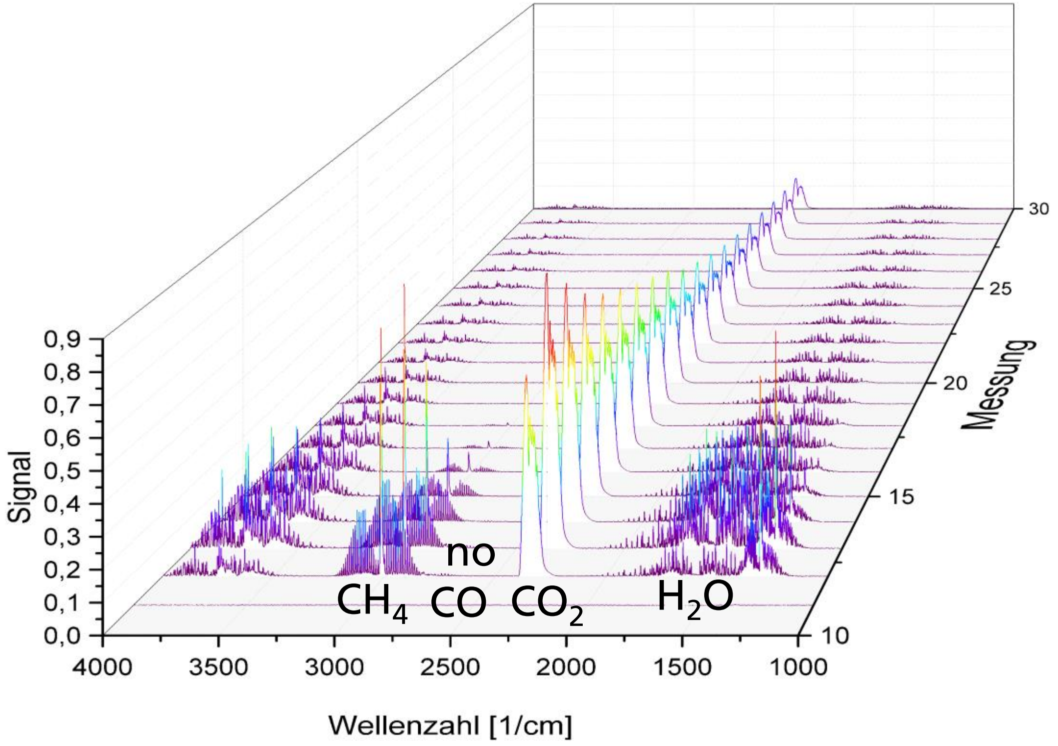
Adsorbents for Oxygen: OSM

Methane Combustion @OSM – experimental Proof

Combustion of CH_4 on solid OSM (BSCF5582, 1 bar, Infrared Spectrocopy, gas cuvette)

- CH_4 dosage by gas syringe,
- unburned fuel, but no CO
- total oxidation of a part of CH_4
- regeneration by air
- repeated combustion on a regenerated OSM sample
- reproducible process





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Adsorbents for Oxygen: Reactor

OSM – Routes for Realization (SoA for Power Plants)

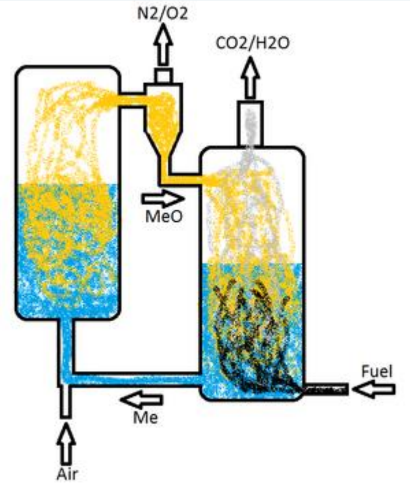
CLC: Chemical Looping Combustion

- for Power plants with **CO_2 capture**:
- cycling of OSM in **2 fluidized bed reactors**
- O_2 carrier: NiO, FeO, CuO, $FeTiO_3$ …

➢ **slow** O_2 release @low p_{O2}

➢ slow oxidation at the solid

➢ unburned fuel in flue gas



CLOU: CLC with O_2 Uncoupling

- OSM: mixed oxides based on **Perovskites**

➢ **fast** O_2 release @ambient p_{O2}, faster combustion, less material, no unburned fuel

CAR (BOC, UK) – Chemical Adsorption Reaction

- gas flow switching of non-reactive sweep gases to **2 packed bed reactors**!

➢ O_2 enrichment and production

GSC - Gas Switching Combustion

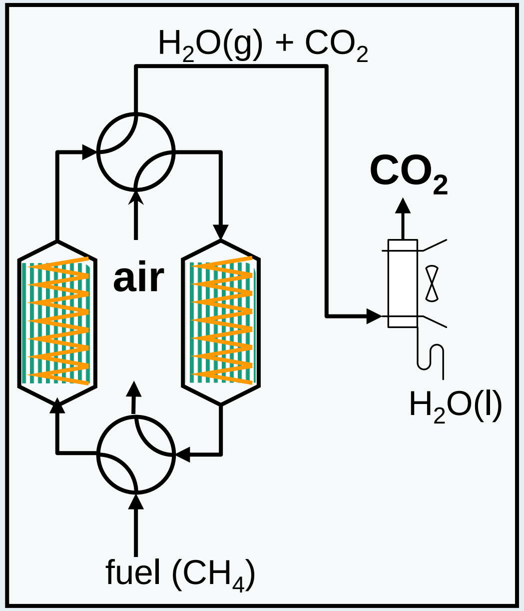
- **CLOU + CAR:** gas flow switching of reactive sweep gas (fuel) to **2 packed bed reactors**!

➢ **no fluidization**

➢ gas speed↓

➢ **small plants** possible

➢ applicable for **production** of **heat** with **CO_2 capture**



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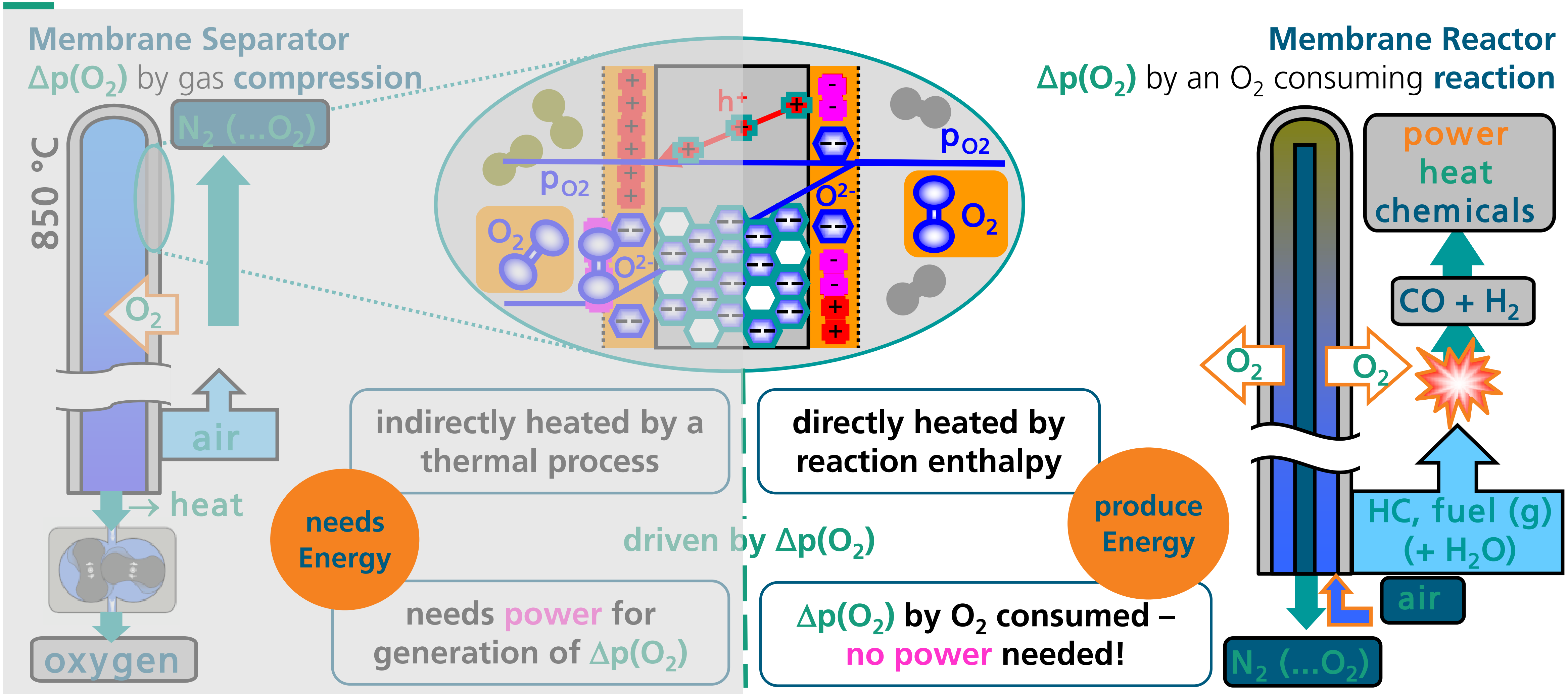
Membranes for Oxygen: MIEC

Mixed Electronic Ionic Conductor Membrane – OSM shaped as a Membrane



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Membranes for Oxygen: MIEC

CH_4 partial Oxidation in MBR – Syngas for Chemistry

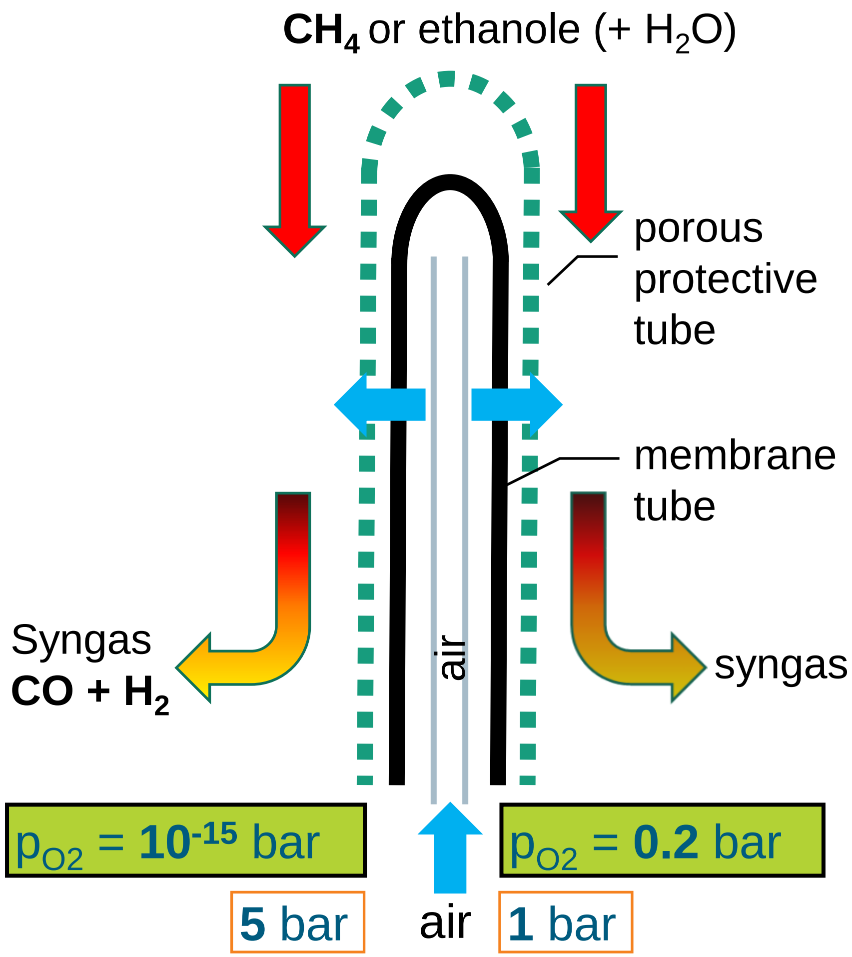
Syngas production in MBR

- O_2 delivered by MIEC membrane
- porous ceramic as diffusion barrier, enhanced stability
- syngas free of N_2 for synfuels (FT synthesis, CH_3OH …)

O_2 comes out of a solid

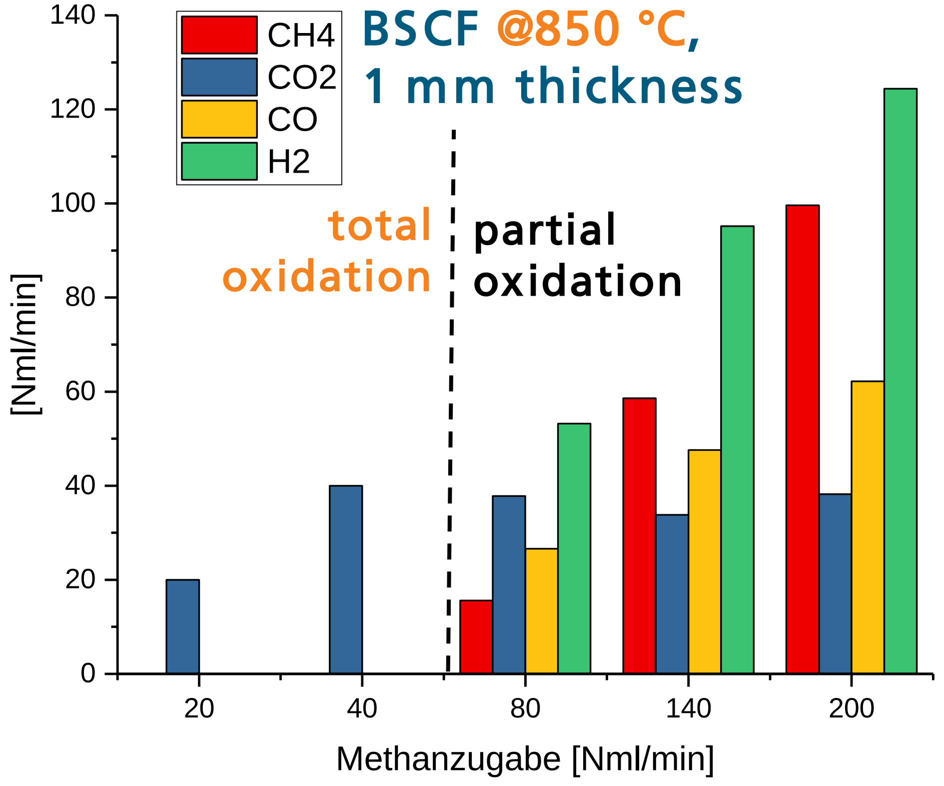
Total Oxidation = Combustion

- **heat** production with **CO_2 capture**
- without **auxiliary energy**

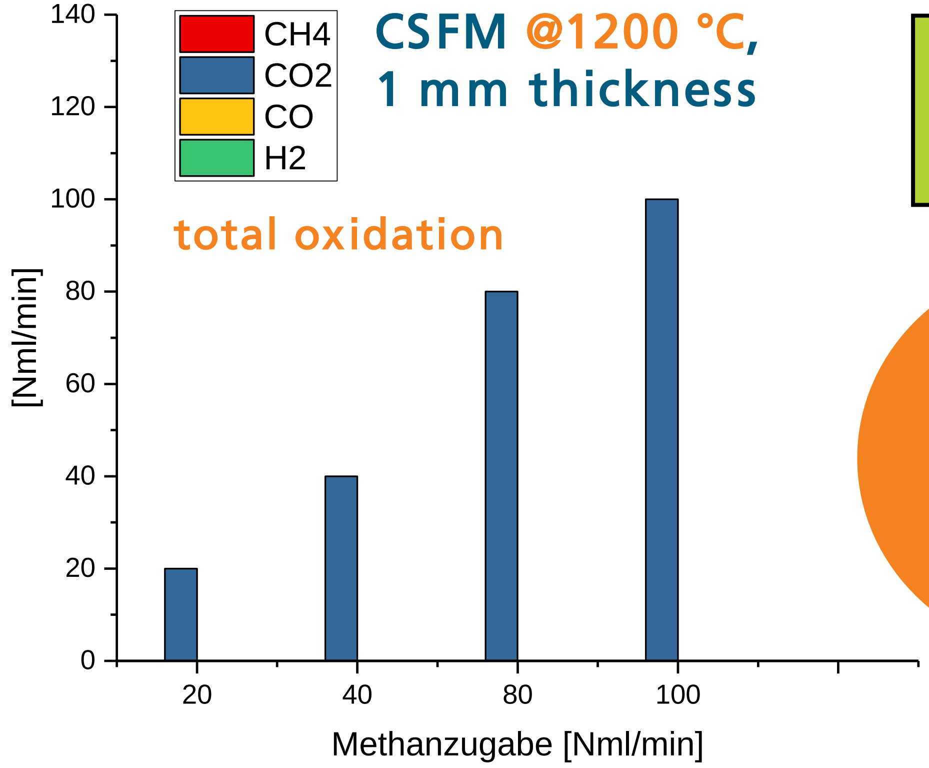


Membranes for Oxygen: MIEC

Methane partial Oxidation – CH_4 partial vs. total Oxidation (Combustion)



Reaction product compoition depends on ratio $CH_4 : O_2$

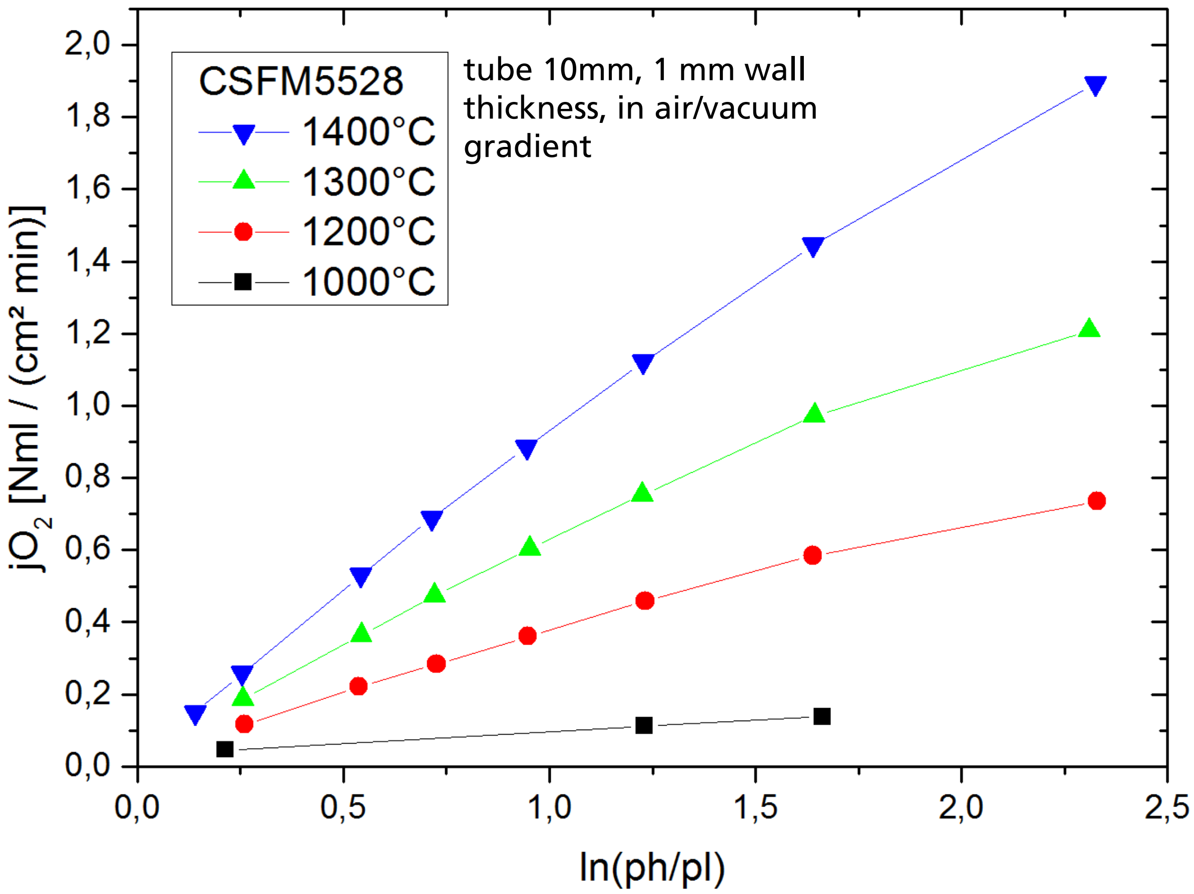


Why no partial oxidation?

CSFM @high temperature: **high O_2 throughput!**

Membranes for Oxygen: MIEC

MIEC for total Oxidation = CH_4 Combustion with integrated CO_2 Capture



$Ca_{0.5}Sr_{0.5}Fe_{0.2}Mn_{0.8}O_{3-\delta}$ developed 1998[1]

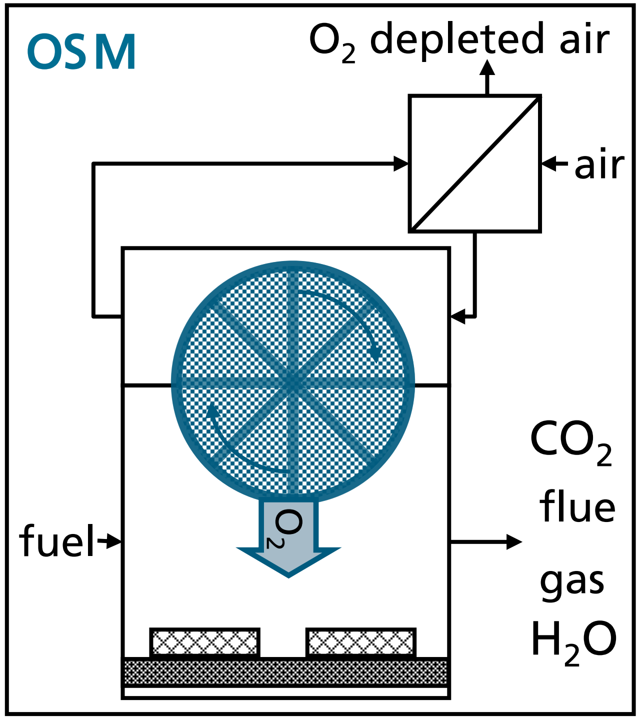
- low chemical expansion, stable in CO_2
- O_2 flux below 1000 °C is low
- asymmetric membranes with **improved O_2 flux** available
- **O_2 flux** increases steadily with **temperature**
- comparable to high-flux MIEC at low T
- **stable up to 1400 °C!**

well suited for fuel combustion in MR
(high and varying temperatures)

[1] Groschwitz, R., Kaps, Ch., Kriegel, R., Pippardt, U., Sommer, E., Voigt, I.: EP 1 110 594 B1, priority 10. 12. 1999

Direct Combustion at a Solid

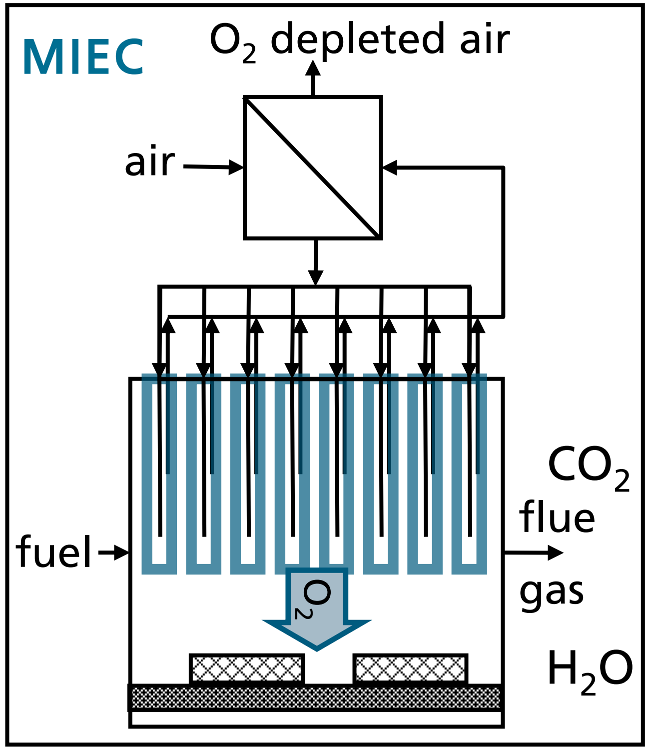
Direct Combustion of fuels at a solid Ceramic (OSM, MIEC)



- quasi continuous
- robust (mechanical, cracks)

Pros

- conversion corresponding to **Oxyfuel:**
  - **combustion efficiency** comparable **high**
  - lower **NO_x** emissions
  - **conc. CO_2** as flue gas (after steam cond.)
- **no energy** for **CO_2 capture** or **O_2 production**
- applicable for **different fuels/fuel amounts**:
  - air excess! → O_2 consumed corresponds to total oxidation only → no **lambda sensor**
- **risk minimization:**
  - explosions, defraglations (flameless conversion)
  - no pure O_2 – less oxidative properties



- continuous
- sensitive (mechanical, cracks)

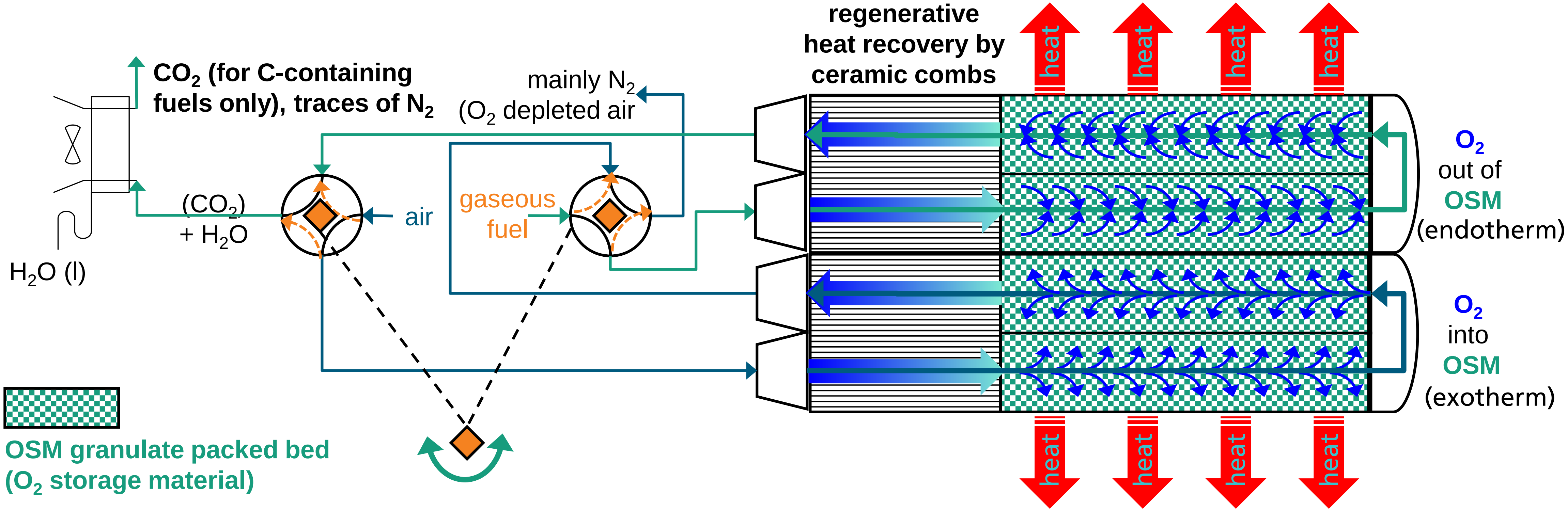
R&D Projects for Heat & Power:

OSM-Brenner: Erprobung von OSM für die Wärmeproduktion aus gasförmigen Brennstoffen[1]

Heat production with integrated CO_2 capture

- Tube burner with 2 twofold reaction chambers equipped with OSM packed bed.
- ➢ Kinetics, optimized OSM granulates, models & simulation, burner test rig

Universität der Bundeswehr München



[1] Erprobung von Sauerstoffspeichermaterialien (OSM) für die Wärmeproduktion aus gasförmigen Brennstoffen, AiF-IGF: 22675 BG /2 , 01/23 - 06/25

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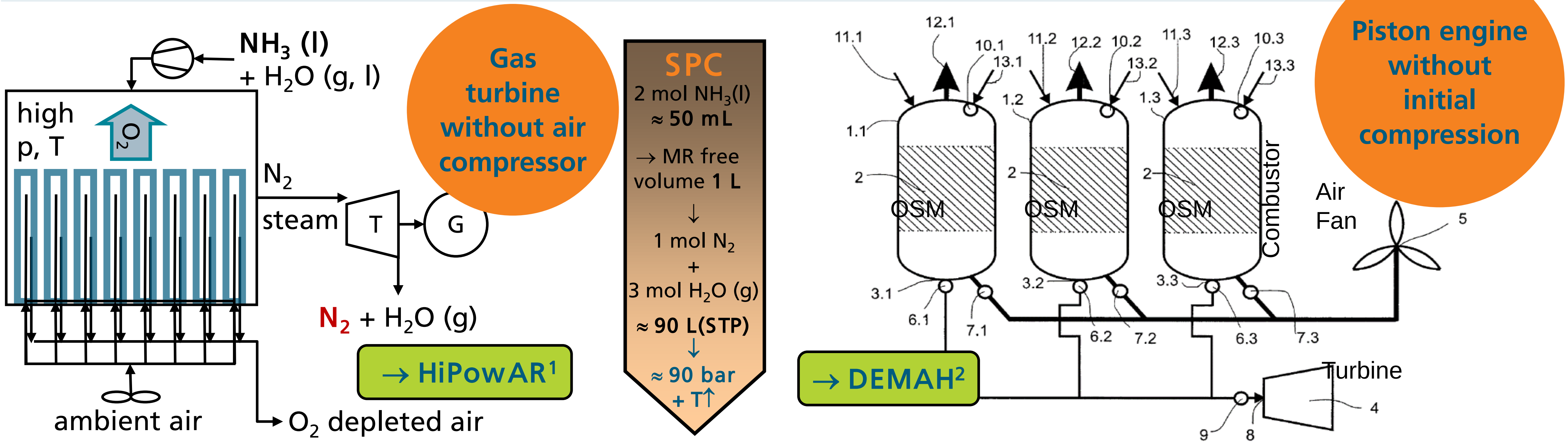
R&D Projects for Heat & Power:

Power Production by self-pressurizing Combustion: HiPowAR[1], DEMAH[2]

Power & Heat production with integrated CO_2 capture

- **ICE (I**nternal **C**ombustion **E**ngine**)** with **solid O_2 supply (MIEC, OSM)** with **self-acting pressure increase**
- no energy demand for air compression! no for compression → higher **efficiency** & **concentrated CO_2**
- Combustion: HiPowAR: isobar - **Ammonia** in MBR, DEMAH: isochor - **Hydrogen** in packed bed Reactor



[1] Highly efficient Power Production by green Ammonia total Oxidation in a Membrane Reactor. grant agreement no. 951880; [2] Demonstration der direkten Erzeugung mechanischer Antriebsenergie aus H_2., BMBF FKZ 03SF0644A

Summary

Direct Combustion at solid Ceramics

- compared to **Oxyfuel**:
  - similar efficiency, fuel conversion, NO_x emissions, CO_2 concentration
  - no costs or energy demand for Oxygen supply
  - lower risks or endangements, no oxidizing potential like for pure O_2
- easy adjustment of **fuel to air** ratio:
  - **air excess** related to solid ceramic (OSM, MIEC) necessary!
  - combustion consumes only the O_2 amount needed for total oxidation
  - no Lambda sensor necessary

➢ **safe conversion** of **different fuels** and **fuel amounts** without air adjustment

➢ promising process for:

  ➢ **CO_2 capture**

  ➢ **energy (cost) saving**

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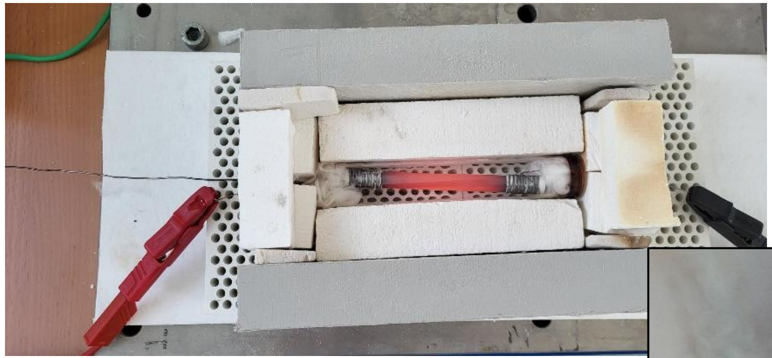
Outlook

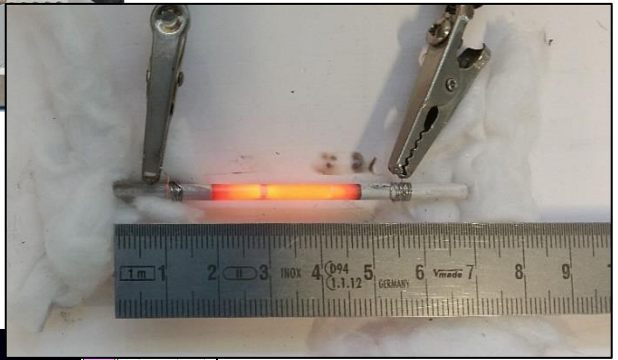
Start up direct Combustion at solid O_2 supply?

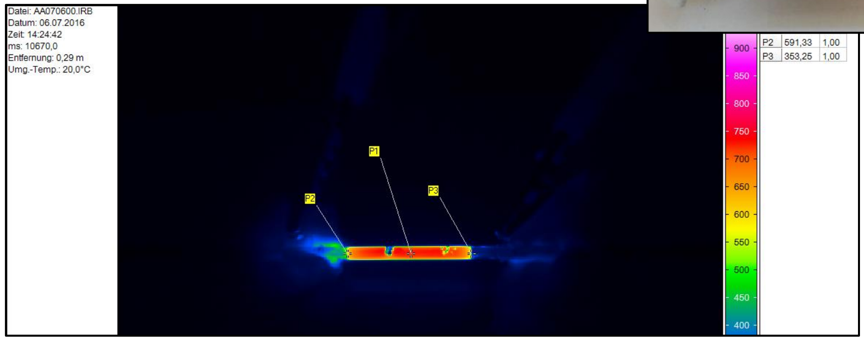
Direct Combustion needs 400 - 700°C @solid!

- **external heating** by conventional combustion?
  - additional costs for **initial gas burner**
  - Is the heat transfer fast enough?
- **external electrical** ignition heater? – as before
- **catalytic coating** for distinct fuels – **ignition at room temperature** (e.g. H_2)
- **microwave** excitation of **OSM/MIEC**
- **internal electrical heating** of **OSM/MIEC**!
  - very fast (: **<10 s,** up to **950 °C**

➢ **optimization of components:**
  - restriction of **resistivity variation** (with T) → chemical composition
  - **thermal shock resistivity** → geometry, porosity







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Vielen Dank für Ihre Aufmerksamkeit

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