Mitglied der Helmholtz-Gemeinschaft

Materials Science for Energy Systems

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Mission and Objectives

- Research and Development for sustainable, i.e. efficient, environmentally compliant and safe systems solutions for the demanding societal challenge „Energy“
- Identification and realisation of solutions from fundamentals to application
- Opening up new energy resources, explore new conversion methods and improve existing technologies

Outline

- Overview Energy Research in Jülich

- Slected Topics as Examples

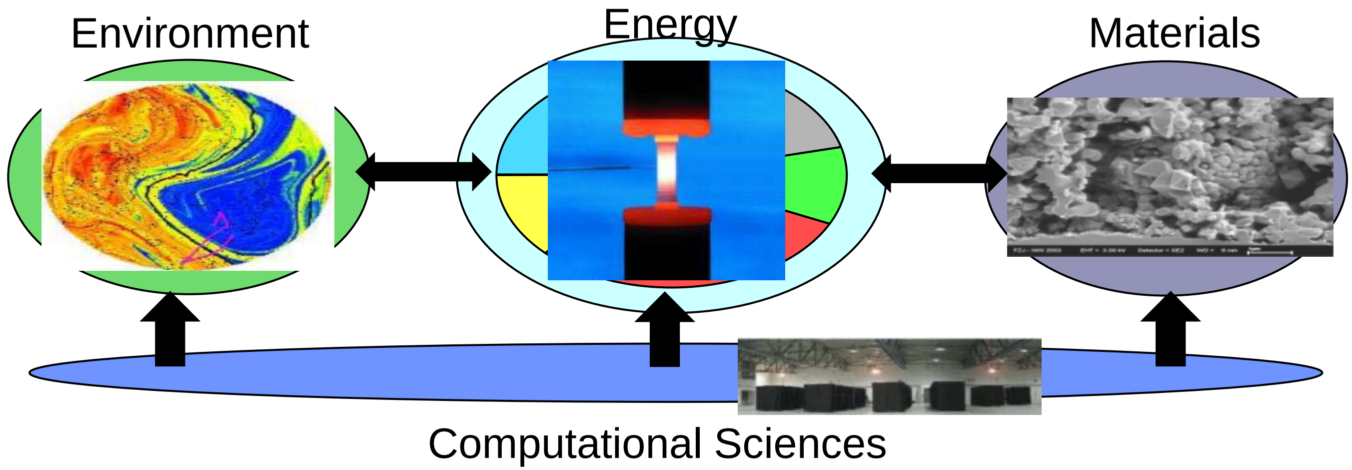
  - Investigation Method

    Knudsen Effusion Mass Spectrometry (KEMS)

  - Application

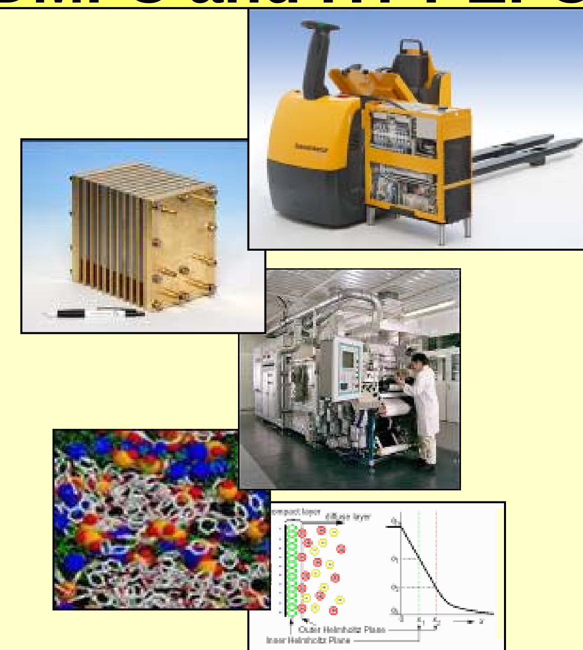
    CO_2 Reduction Technology

Research Field „Energy“



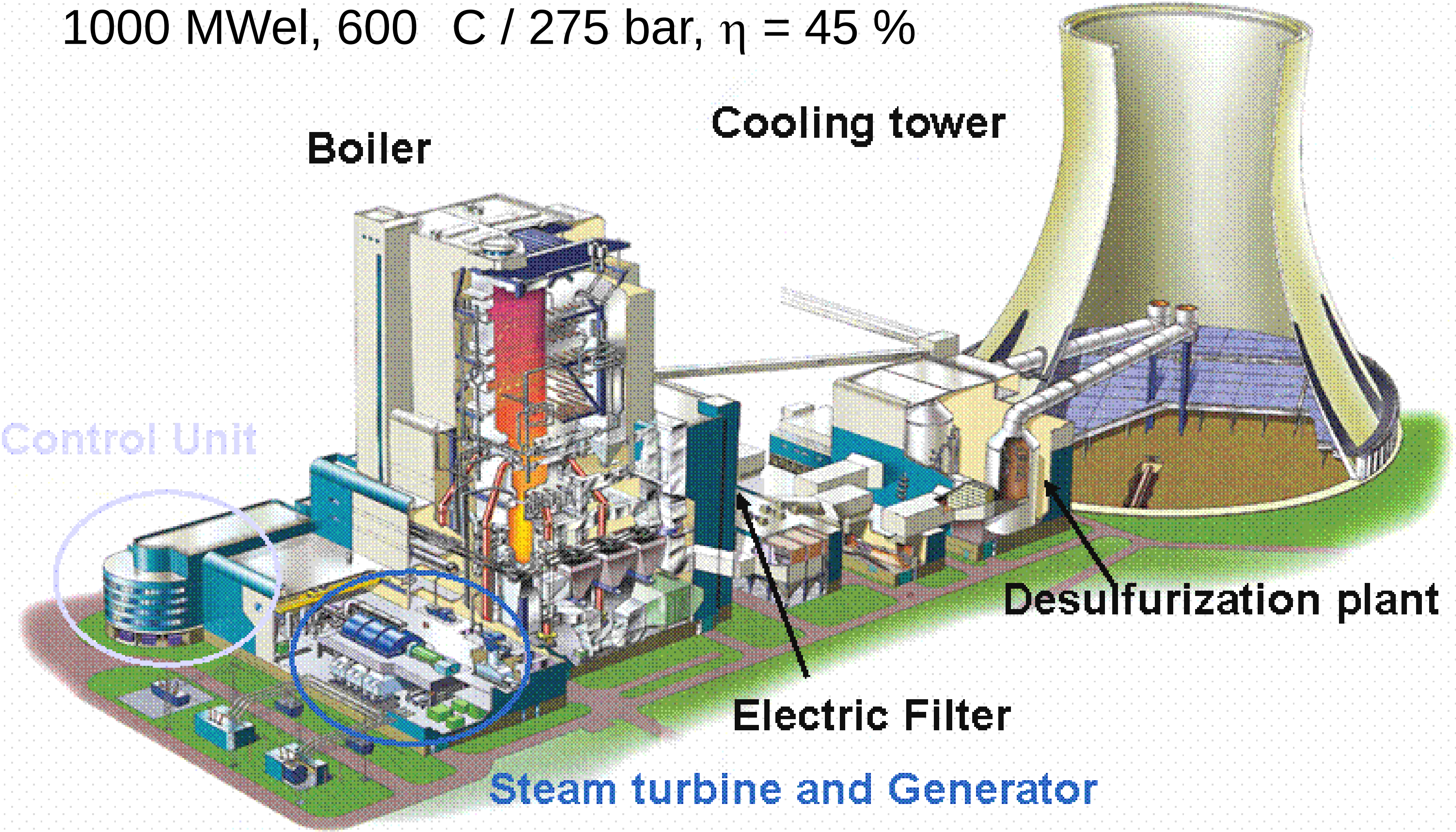
Institute of Energy Research	IEF
Materials Synthesis and Processing	IEF-1
Microstructure and Properties of Materials	IEF-2
Fuel Cells	IEF-3
Plasma Physics	IEF-4
Photovoltaics	IEF-5
Safety Research and Reactor Technology	IEF-6
Systems Analysis and Technology Evaluation	IEF-STE
Fuel Cell Project	IEF-PBZ
Nuclear Fusion Project	IEF-KFS

R&D Emphasis for Fuel Cells

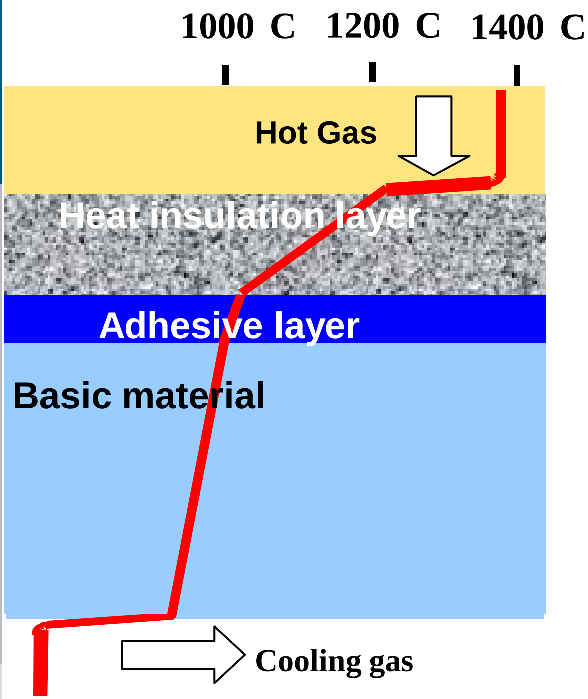
High-temperature Fuel Cell SOFC	Fuel Processing Systems	Polymer Fuel Cells DMFC and HT-PEFC
		
SOFC systems for efficient power generation (CHP) and on-board supply (APU)	H_2 from diesel or kerosene for on-board supply (APU) with fuel cells	DMFC systems for light traction HT-PEFCsystems for reformate utilization

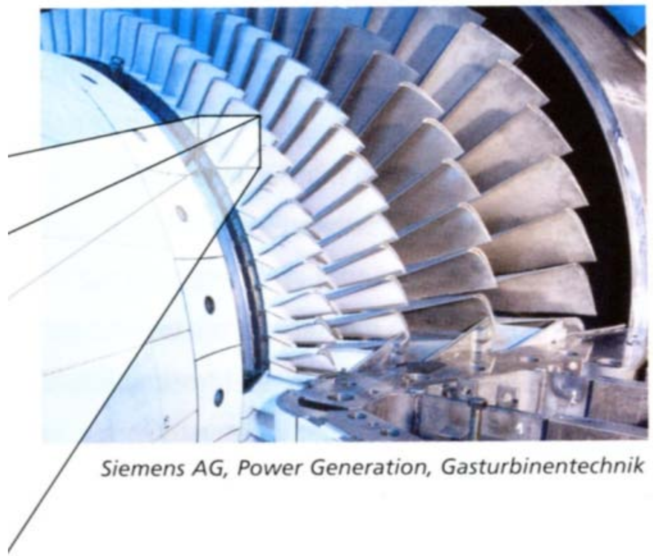
High efficient Power Plant BoA

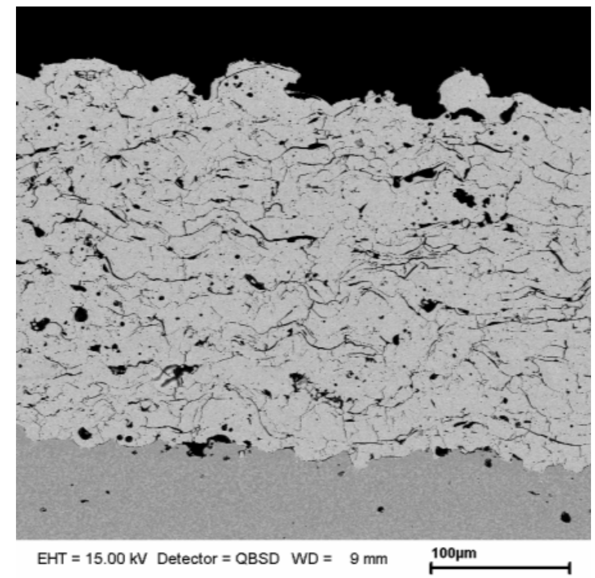
1000 MWel, 600 C / 275 bar, η = 45 %



Power Plant Technology:
High Efficiency by High Temperature Materials







- **Gas turbines:** High-temperature resistance through **ceramic heat protection**
- Advanced **alloys** for **boiler and steam turbine** applications

Photovoltaics:

Direct Conversion of Sunlight into Electric Energy

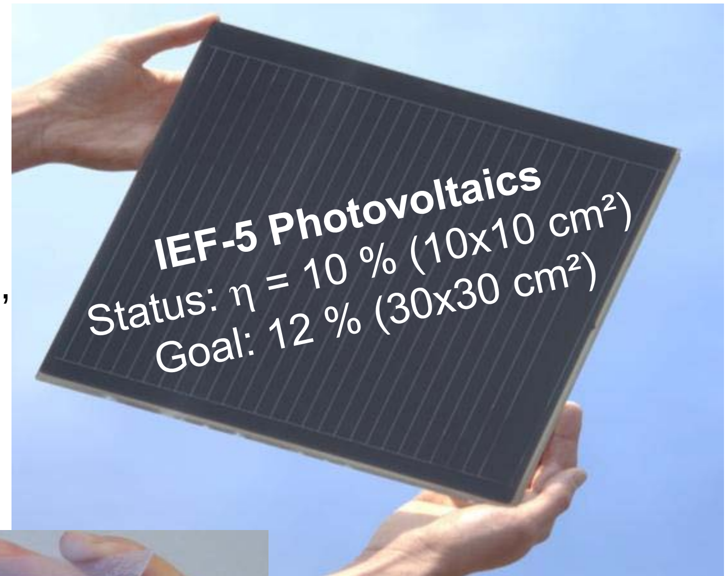
Silicon thin film:

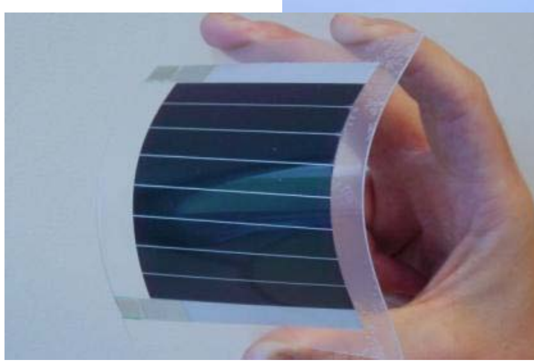
Thickness: < 2 µm

Processing at 200 C

Large areas (m²) on glass, foil,

a-Si module: 6-7 % (1 m²)



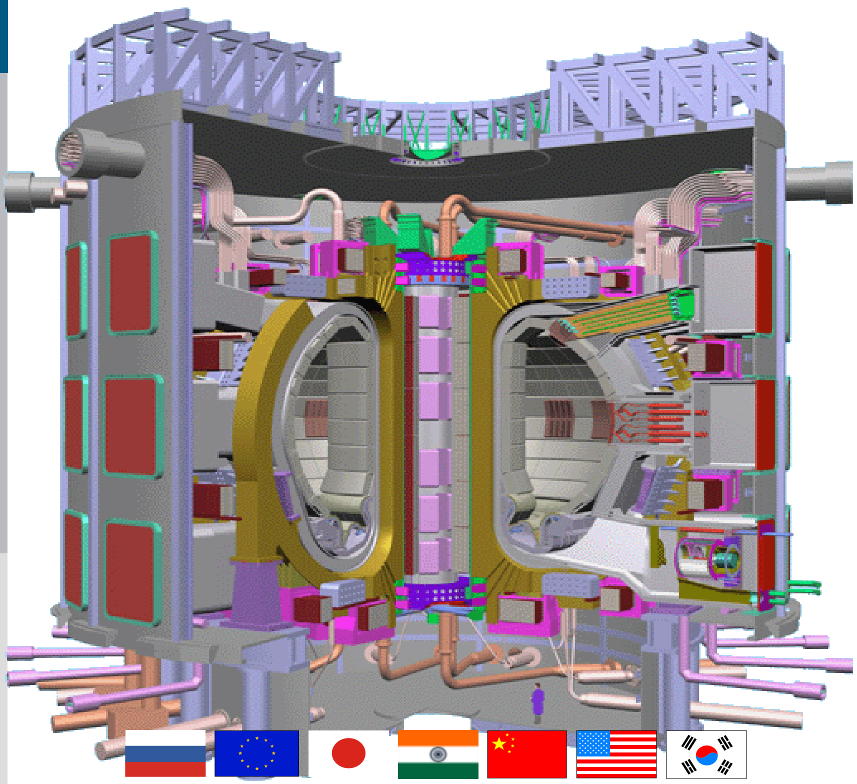


RTD objectives:

- Materials development
- Stack solar cells
- Photon management
- Production processes
- Increase efficiency & reduce costs
- Technology transfer

Fusion Research in Jülich

Objective: Realisation of a fusion power plant by 2035



Experimental platforms:

- Participation at JET, ITER and Wendelstein 7-X
- TEXTOR and JUDITH as development environment

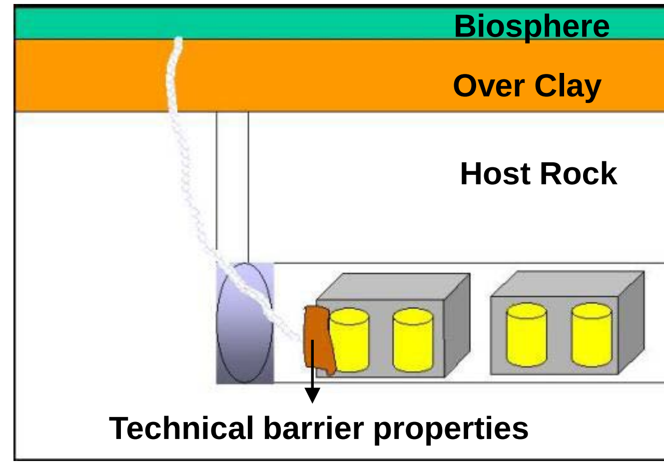
Programme topics:

- Plasma-wall interaction
- Materials for the plasma containing vessel
- Development of diagnostics
- Plasma physics, theory and modelling
- Training of scientists and engineers (in cooperation with universities)

Networks:

- EURATOM association and EFDA member (EU)
- Trilateral Euregio Cluster (B und NL)
- HGF Programme "Nuclear Fusion" in research field energy (D)
- IEA Implementing Agreement (USA, Japan, Kanada)

Nuclear Safety:
Nuclear Waste Disposal

Characterisation	Conditioning	Disposal
		
Identification and categorisation of radio nuclides	Reduction and sealing of waste	Quantification of mobilisation Specification of secondary phases

Systems Analysis:
Methods and Results

Methodological approach

Selection of sets of sustainable development indicators

Development and application of energy models focusing on technical, economic and societal structures

Scenario-based formulation of sustainable energy systems.

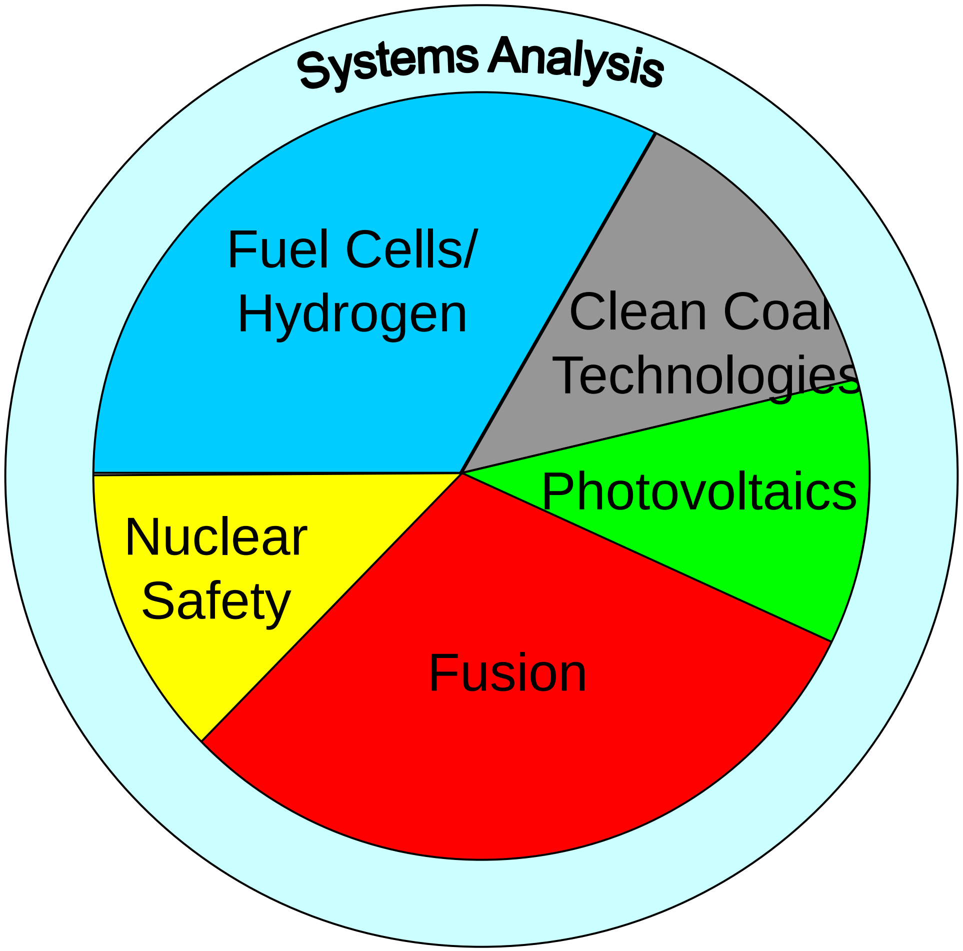
Results

Identification of societal and economic framework conditions for use and development of energy technology

Analysis of repercussions of technology innovations on society and economy

Sustainability-oriented assessment of technologies and corresponding innovation and investment strategies.

Jülich Energy Research: **Synopsis**



Materials Chemistry Group

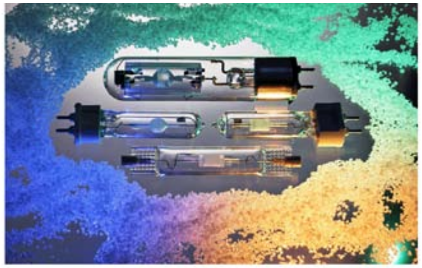
<u>Currently Running Projects and Applications</u>

- Thermodynamic Data for *Lighting Applications*

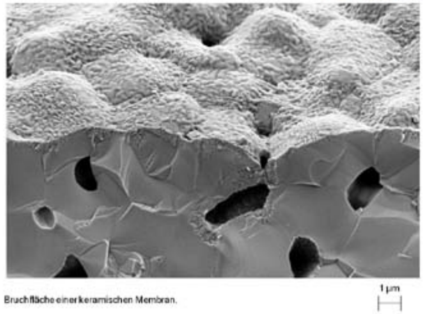
- Thermodynamic Data for *Intermetallic Phases*

- *Cr- vaporization from interconnector materials of SOFC*

- *CO_2 Reduction Technology and Reduction with Membranes*

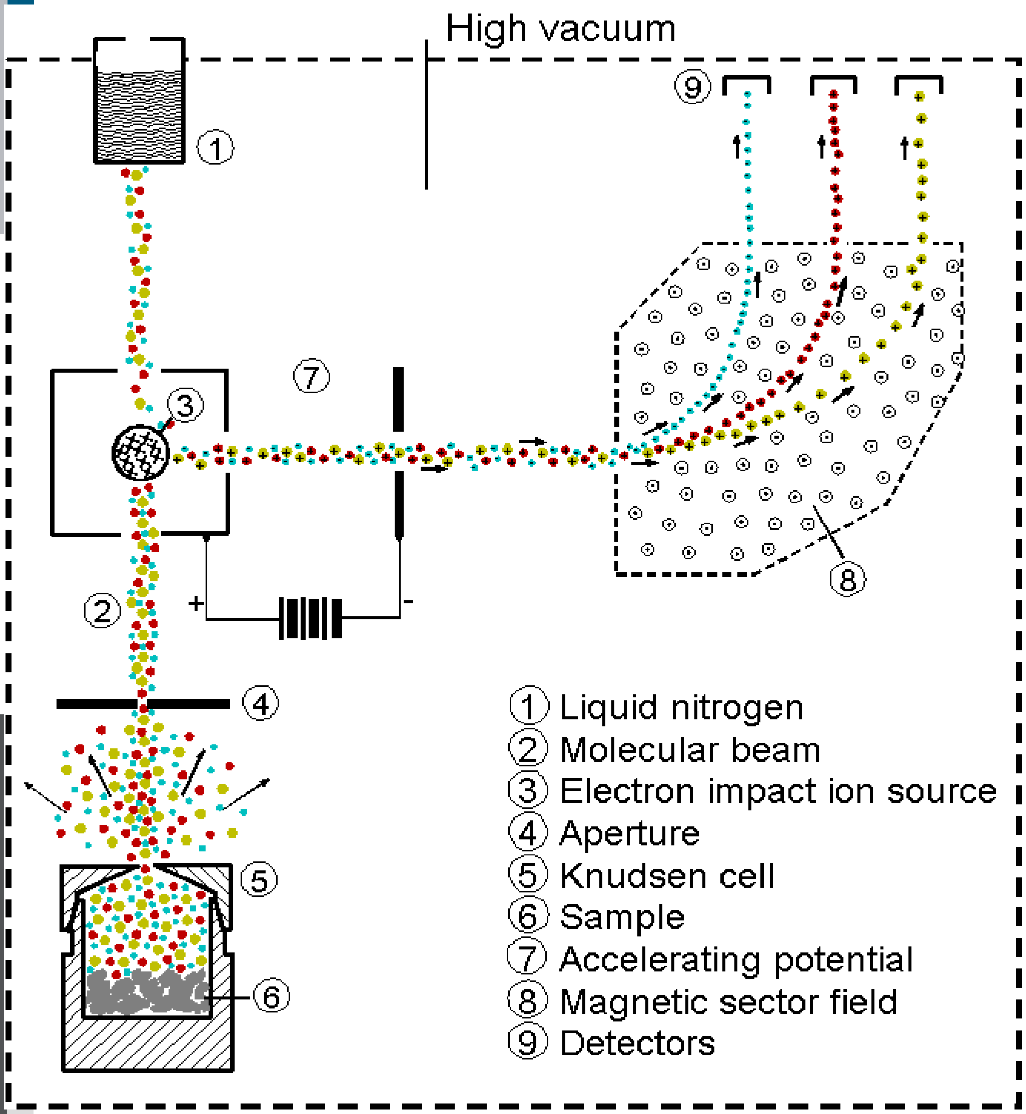


Hochenergieentladungslampen.



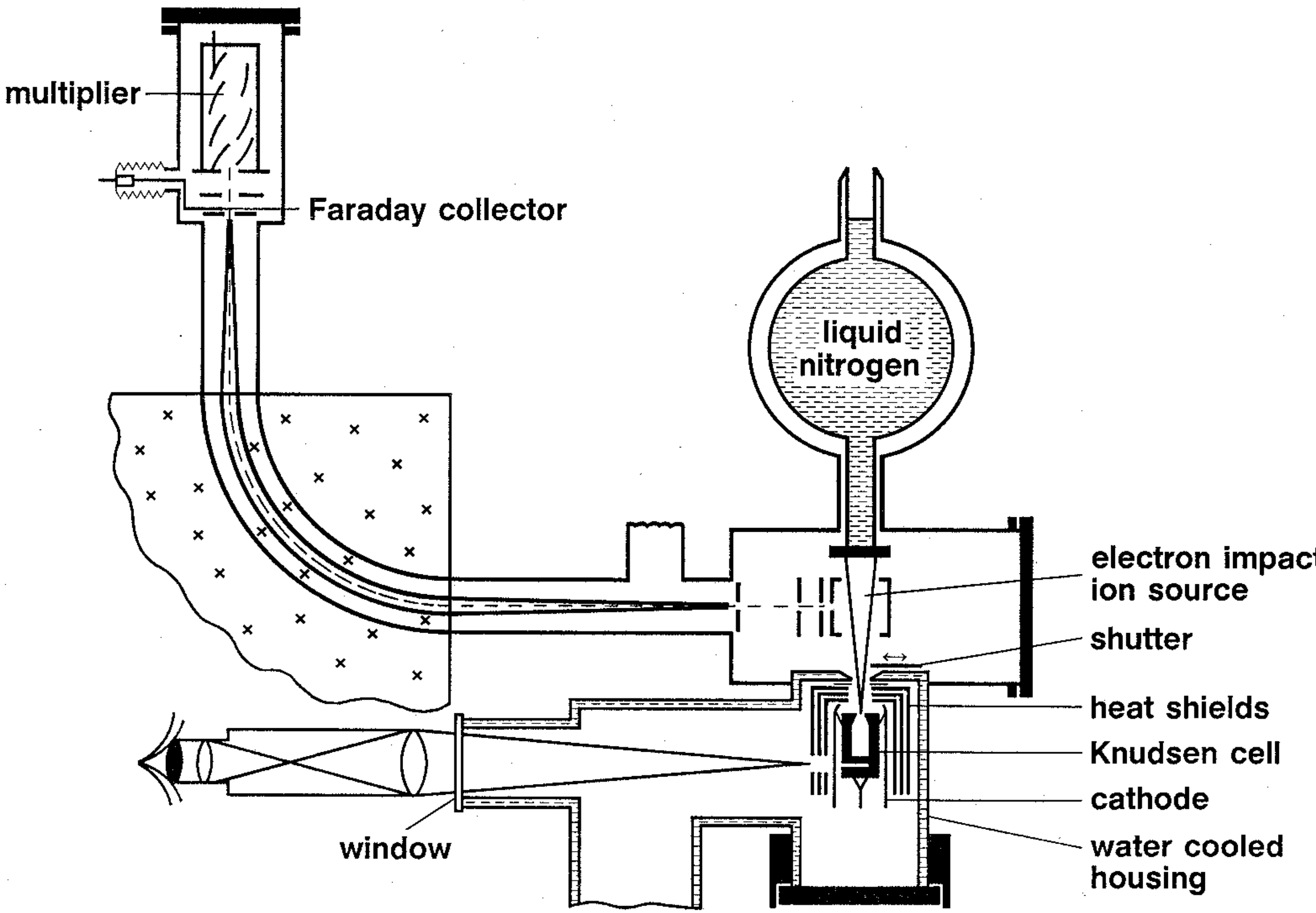
Bruchfläche einer keramischen Membran.

Principle of Knudsen Effusion Mass Spectrometry (KEMS)

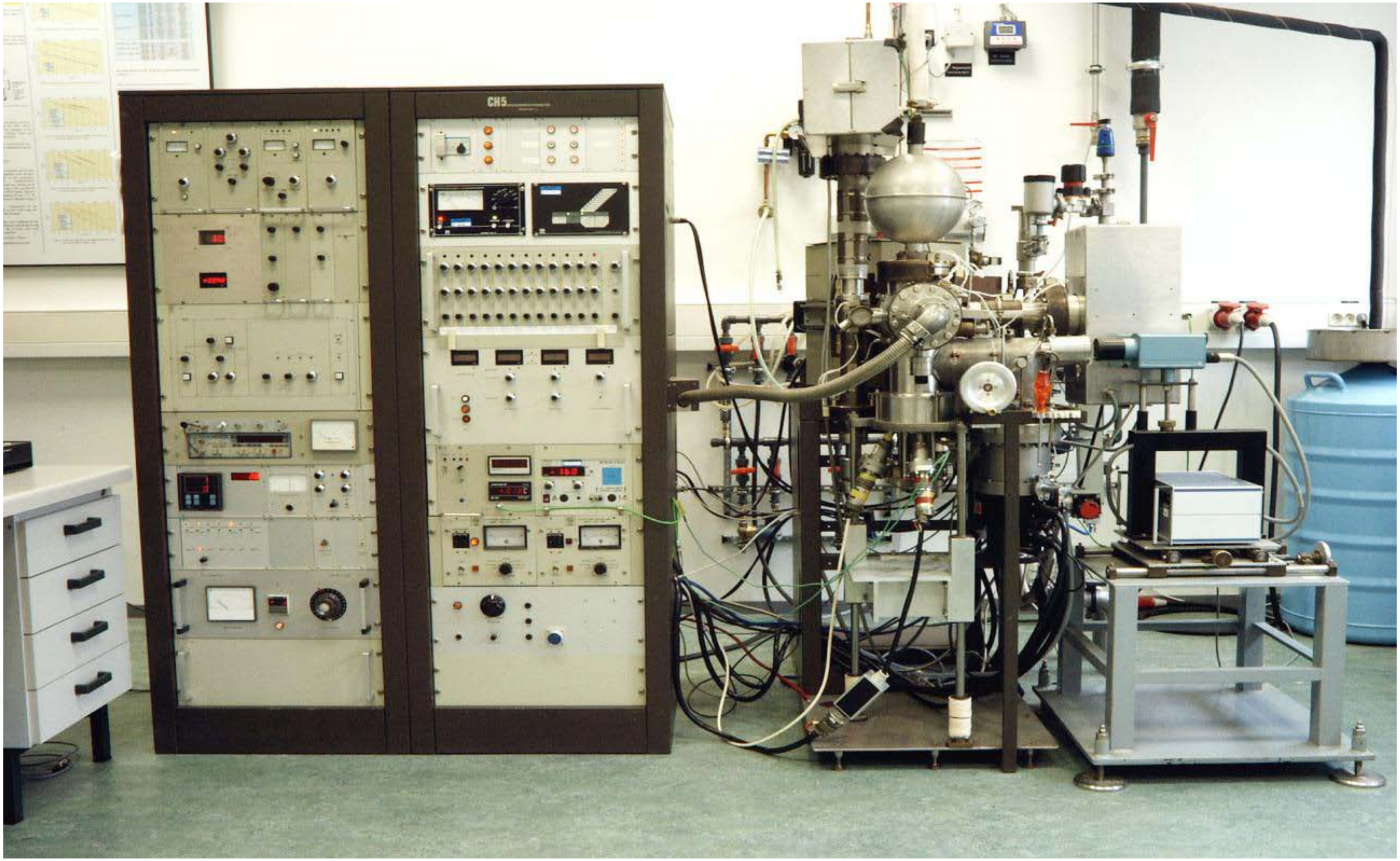


- **Vaporisation studies up to 2800 K**
- **Identification of gaseous species**
- **Determination of partial pressures (10^{-8} ... 10 Pa)**
- **Evaluation of thermodynamic data of**
  - **gaseous species**
  - **condensed phases**
- **Elucidation of corrosion processes**

Schematic Representation of a Knudsen cell magnetic field mass spectrometer system



Mass Spectrometer Knudsen Cell System (CH 5)



Experimental Determination of Partial Pressures p_i of Neutral Species i

$$p_i = k \frac{1}{\sigma_i} T \sum_j \frac{100}{\gamma_{i,j} A_{i,j}} I^+_{i,j} \quad = k \frac{1}{\sigma_i} \frac{I_i^+ T}{\gamma_i A_i}$$

T	**temperature**
$I^+_{i,j}$	**intensities of to the neutral species i related ions j**
$A_{i,j}$	**isotopic abundance**
$\gamma_{i,j}$	**multiplier gains**
σ_i	**ionisation cross section of the neutral species i**
k	**pressure calibration constant**

Determination of Thermodynamic Properties

$$\Delta_r G_T^0 = \Delta_r H_T^0 - T\Delta_r S_T^0$$

Gibbs free reaction energy **reaction enthalpy** **reaction entropy**

2nd law

$$\Delta_r G_T^0 = -RT \ln K_p^0$$

$$K_p^0 = \prod_j \left(\frac{p_j}{p^0} \right)^{\nu_j}$$ **from meas.**

$$\ln K_p^0 = -\frac{\Delta_r H_T^0}{RT} + \frac{\Delta_r S_T^0}{R}$$

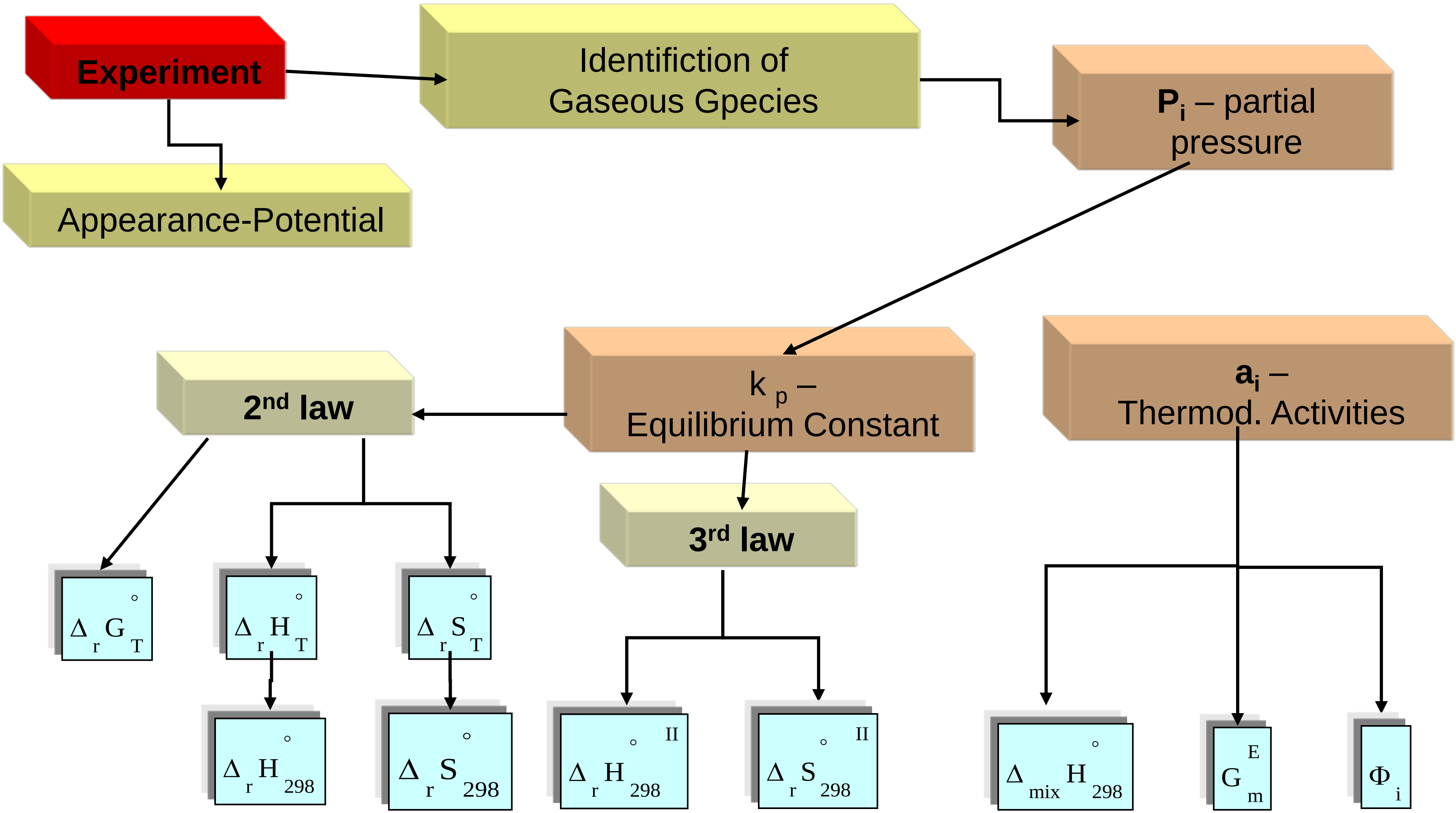
3rd law

$$\Delta_r H_T^0 = -T\left(R \cdot \ln K_p^0 - \Delta_r S_T^0\right)$$

$$\Delta_r S_T^0 = -\frac{\left(\Delta_r G_T^0 - \Delta_r H_T^0\right)}{T}$$

$$\Delta_r H_{298}^0 = -T\left[R \cdot \ln K_p^0 + \Delta_r \left(\frac{G_T^0 - H_{298}^0}{T} \right)\right]$$

Potential of Knudsen Effusion Mass Spectrometry



Mechanism of chromium poisoning

Gas Chanel:

Cr_2O_3 (s) + 1.5 O_2 (g) + 2 H_2O (g) → 2 $CrO_2(OH)_2$ (g)

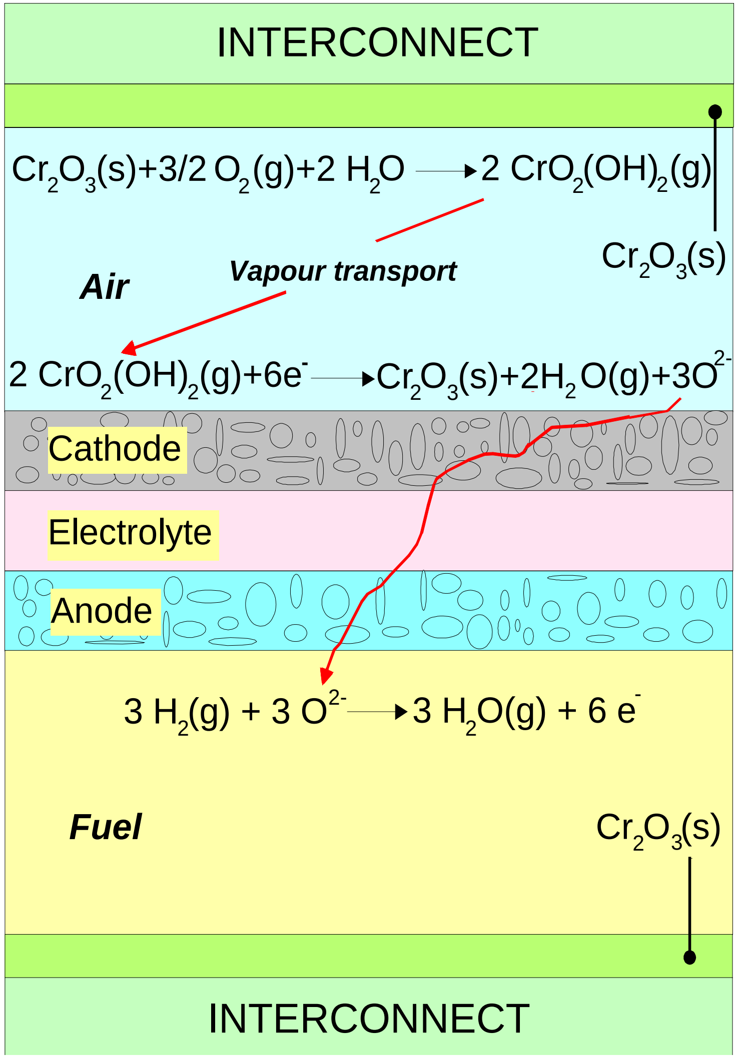
2 CrO_3(g) + 6 e^- → Cr_2O_3(s) +3 O^{2-}

Cathode:

$CrO_2(OH)_2$ (g) + 6 e^- → Cr_2O_3 (s) + 2 H_2O (g) + 3 O^{2-} (g)

$CrO_2(OH)_2$ (g) + MnO → MnCr2O4 (s) + 2 H_2O(g) + 1/2 O_2 (g)

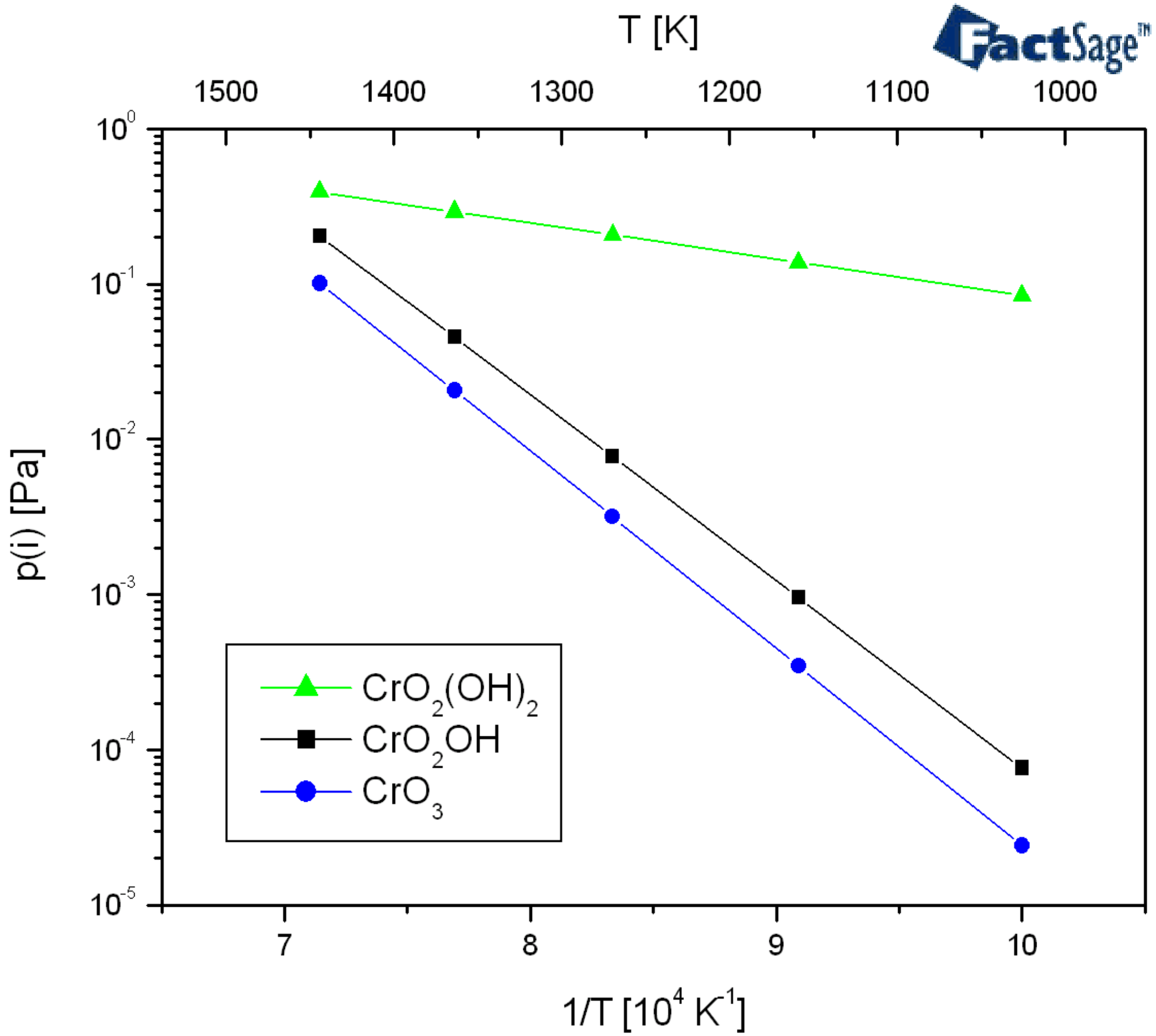
3 $CrO_2(OH)_2$ (g) + ABO_3 → ACrO4 (s) + BCr_2O_4 (s) + 3 H_2O (g) + 3 O_2 (g)



ref: K. Hilpert, D. Das, M. Miller, D.H. Peck, and R. Weiss, *J. Electrochem. Soc.* **143**, 3642 (1996)

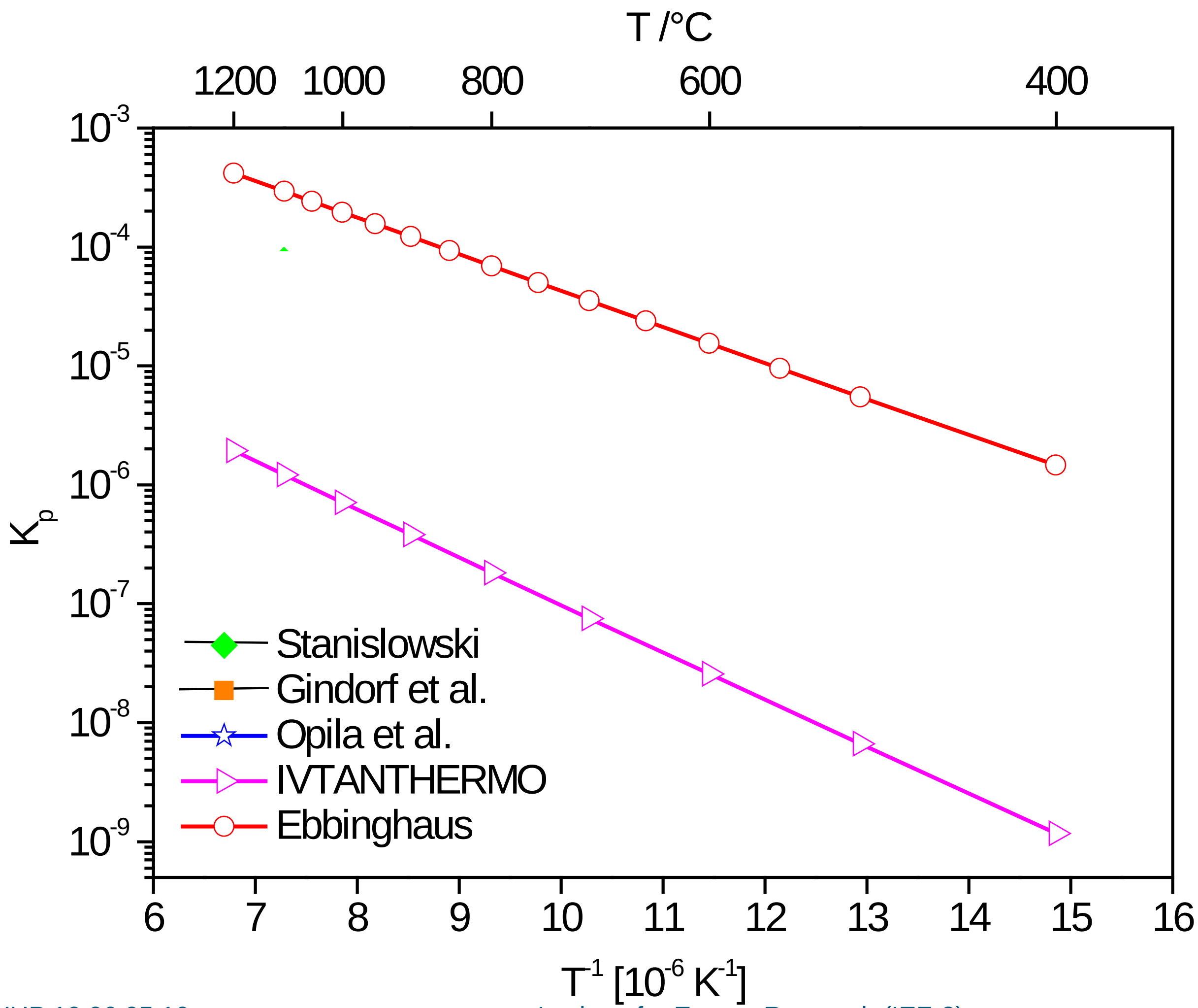
Vapor Species over Cr_2O_3(g) in humid air

(p_{H2O}= $2\cdot10^3$Pa, p_{O2}=$2,13\cdot10^4$Pa)

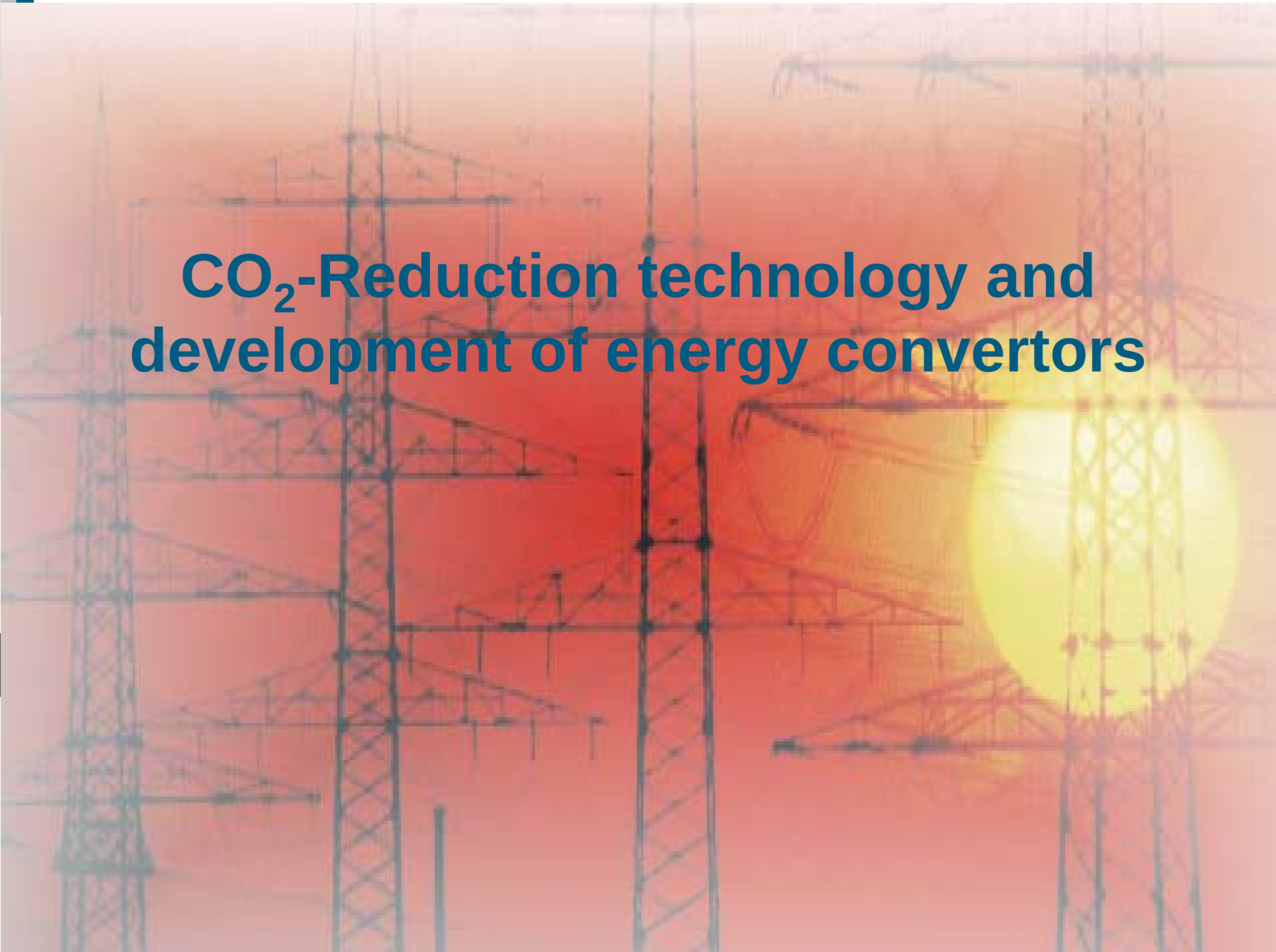


Temperature dependence of equation

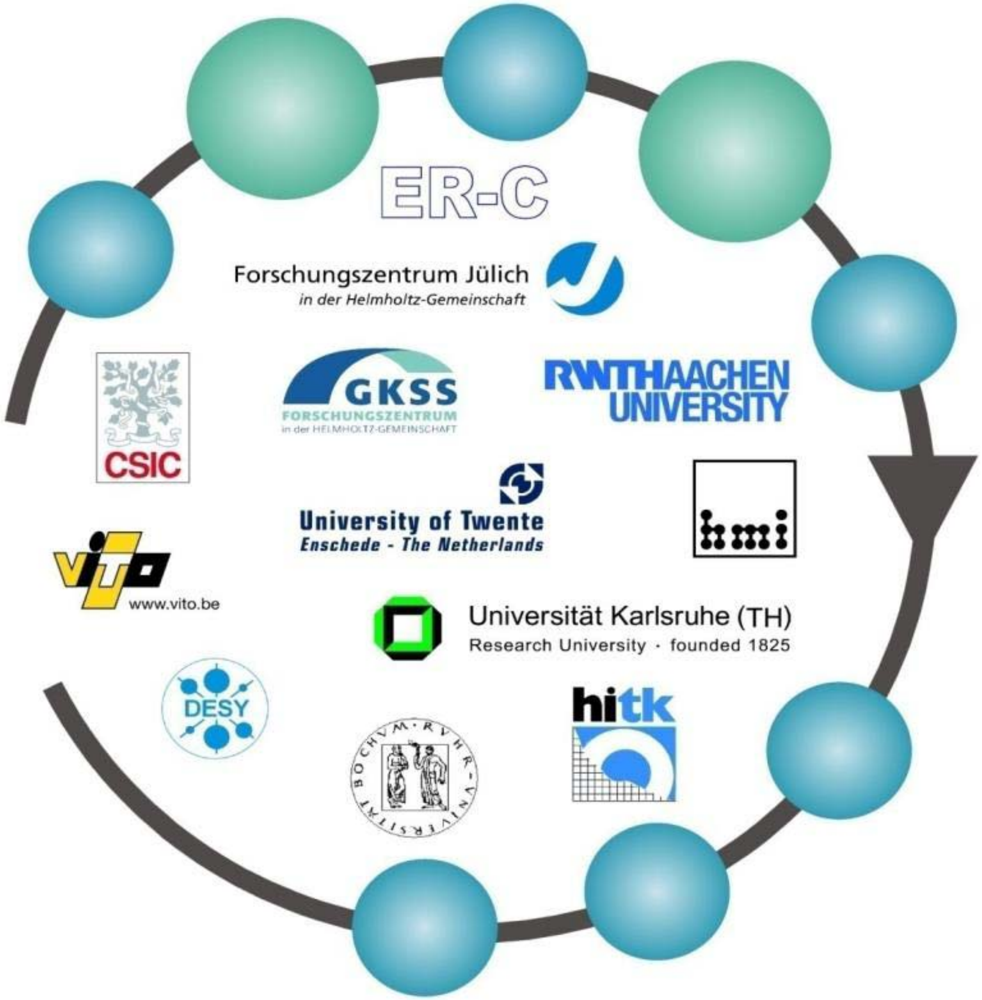
$$Cr_2O_3(s) + \tfrac{3}{2}O_2(g) + 2\,H_2O(g) \leftrightarrow 2\,CrO_2(OH)_2(g)$$



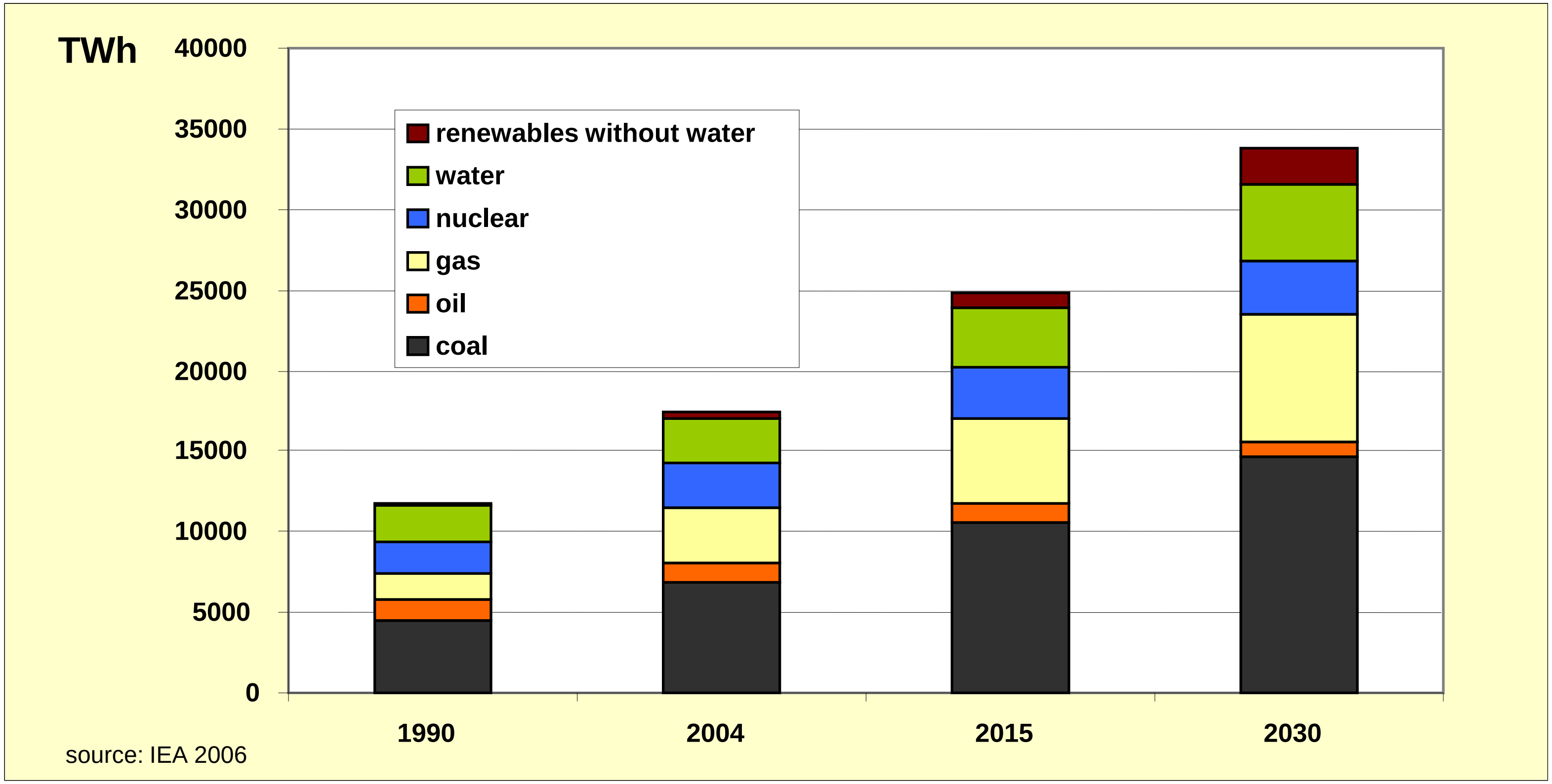
CO_2-Reduction technology and development of energy convertors



HGF Alliance MEM- BRAIN Partners



Global electricity generation



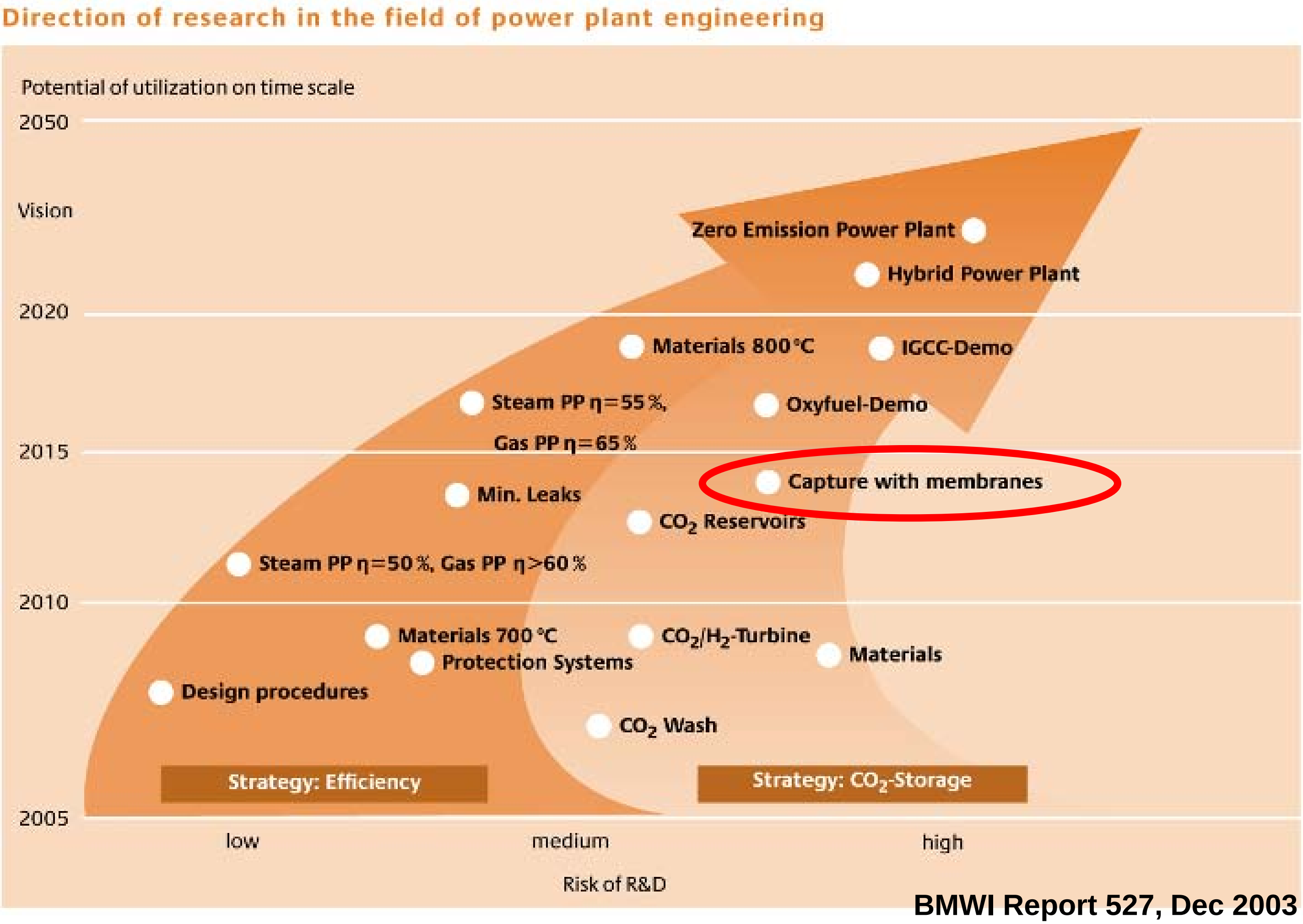
reference scenario World Energy Outlook 2006, IEA

Gas 2004 - 2030: + 128%

Coal 2004 -2030: + 112%

Long-term energy mix with CO_2- emissions

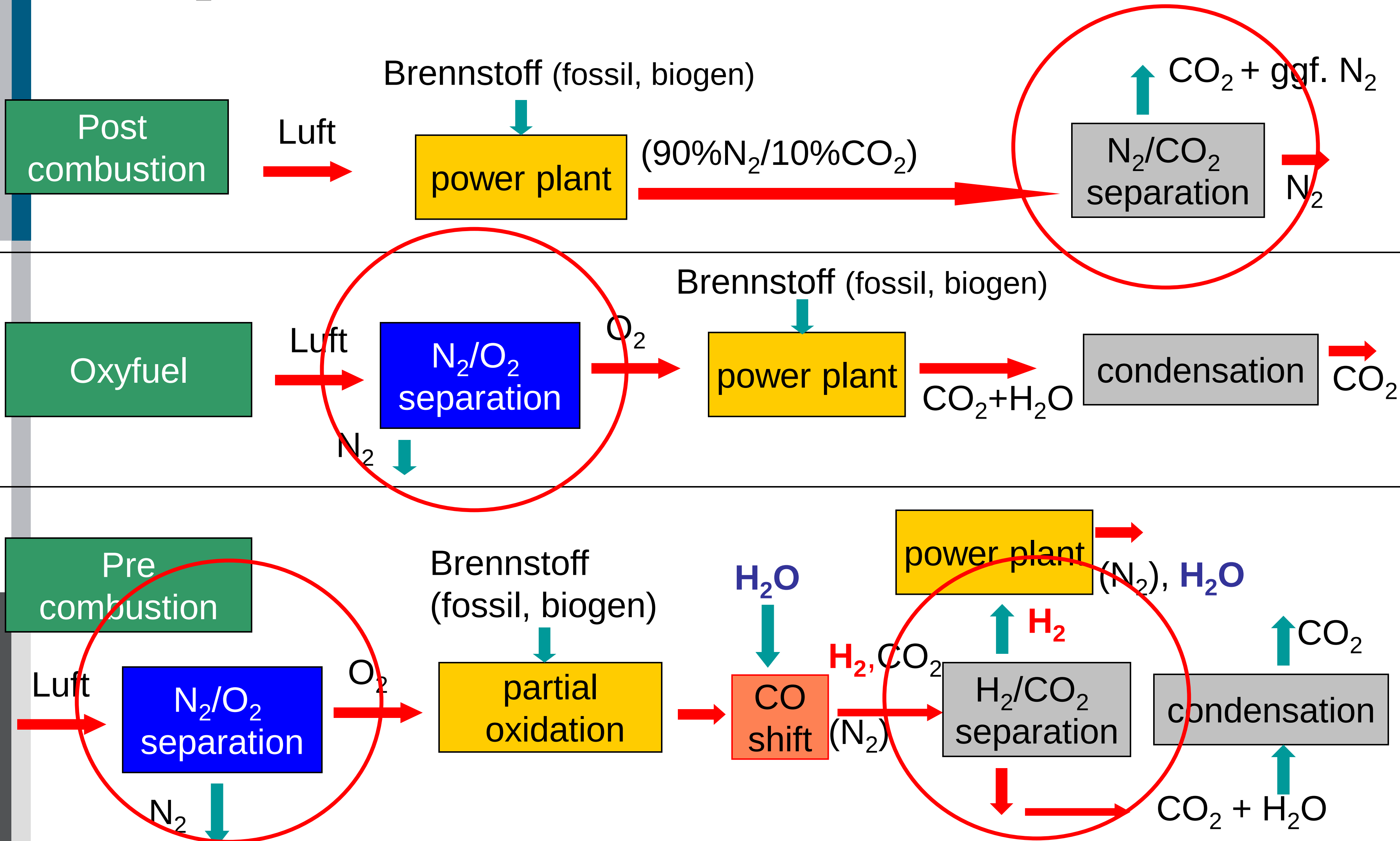
German CO_2- reduction strategy (COORETEC)



BMWI Report 527, Dec 2003

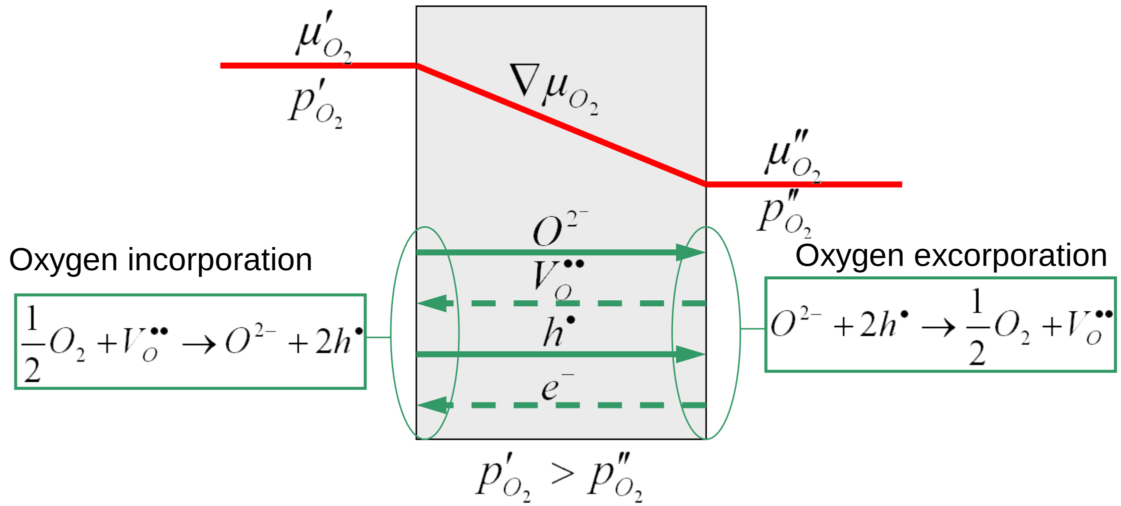
Similar strategies: UK, USA, Canada, Australia

CO_2- separation technologies



Introduction
Oxygen transport membrane

$$O_2(g) + e^- \leftrightarrow O_2^-$$
$$O_2^- + e^- \leftrightarrow O_2^{2-}$$
$$O_2^{2-} \leftrightarrow 2O^-$$
$$O^- + V_O^{\bullet\bullet} + e^- \leftrightarrow O_O^x$$



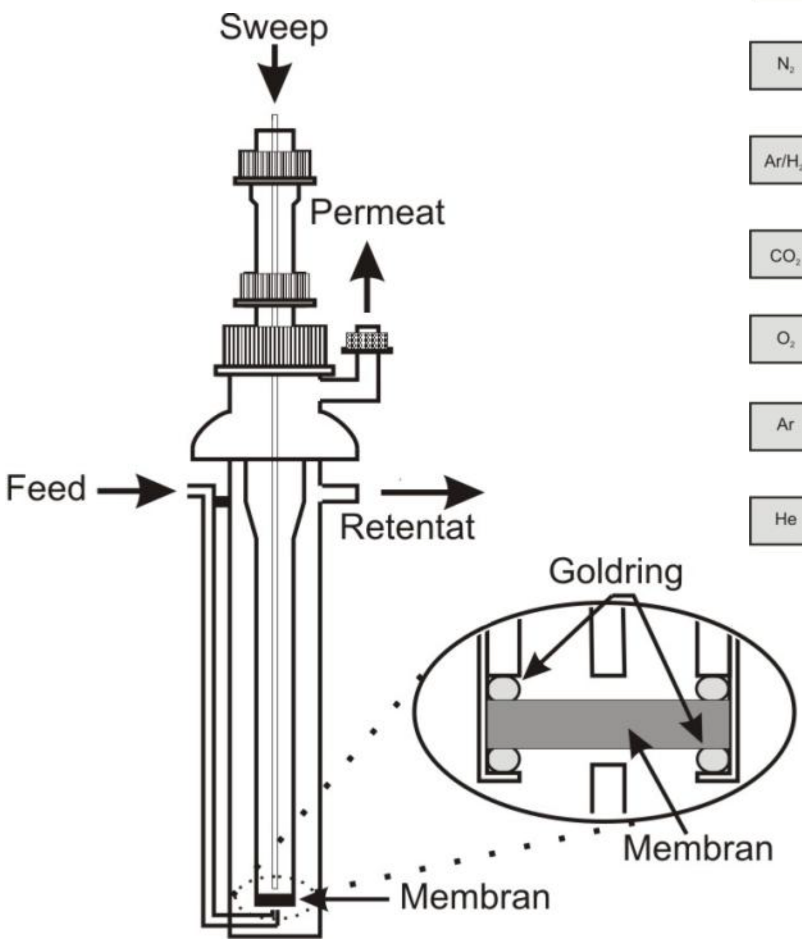
Solid state diffusion → simplified Wagner - equation

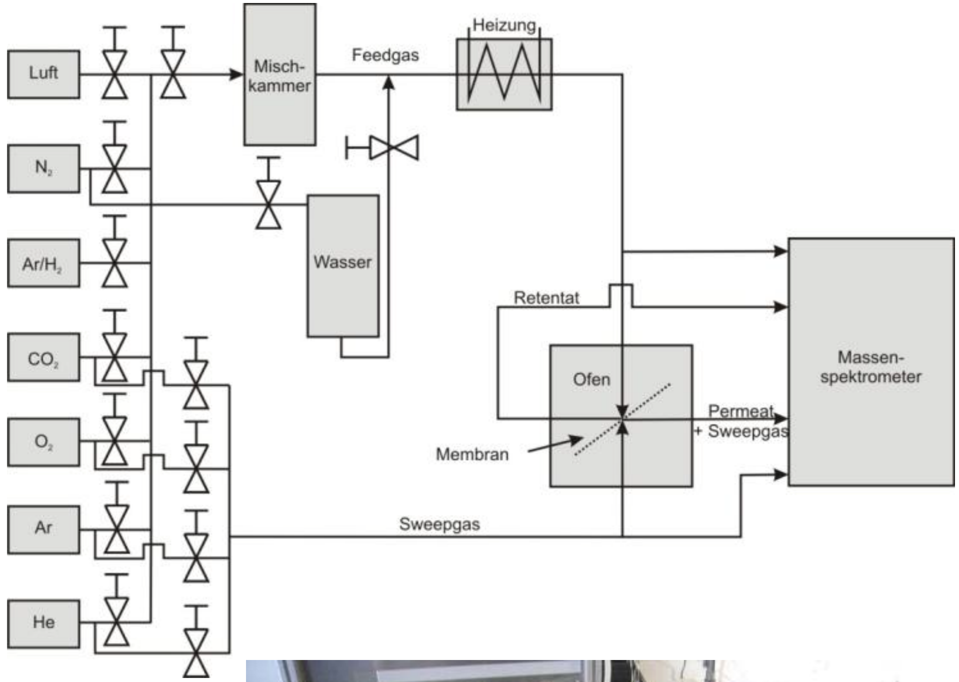
$$j_{O_2} = \frac{RT}{(4 \cdot F)^2} \cdot \frac{1}{L} \cdot \frac{\sigma_i \cdot \sigma_e}{\sigma_i + \sigma_e} \cdot \ln \frac{p'_{O_2}}{p''_{O_2}}$$

Preconditions for high permeation rates

- ambipolar conductivity
- high temperature
- p_{O2} gradient
- low membrane thickness

Measurement of Permeation





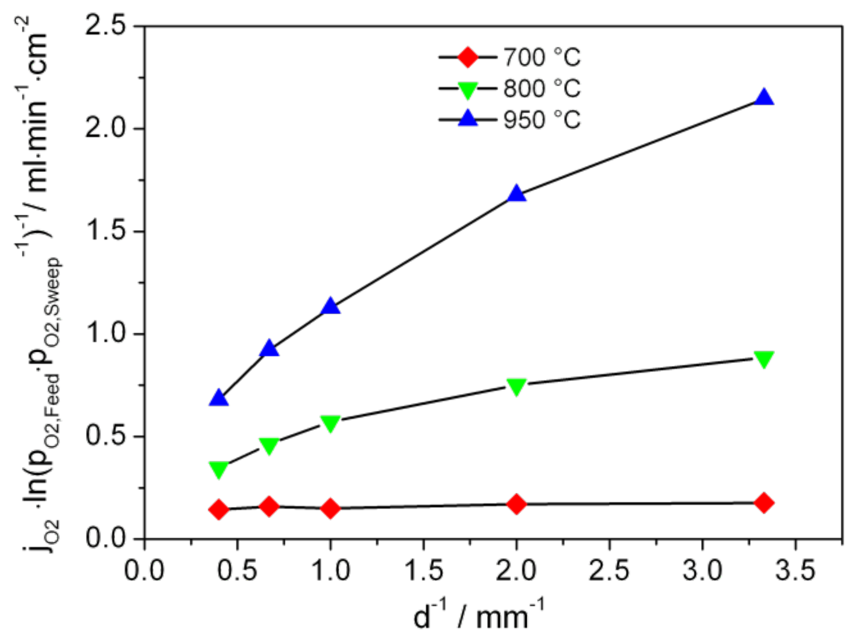
Permeation behaviour of planar membranes
Influence of membrane thickness

Permeation increases with reducing membrane thickness

- Temperature dependency
- Increase in permeation smaller than theoretical expectations due to surface limitations
  → No linear dependency on reciprocal thickness
- Surface limitations seem to be stronger at lower temperatures

Rate-determining step

- < 700 C: surface limitations
- > 700 C: bulk diffusion



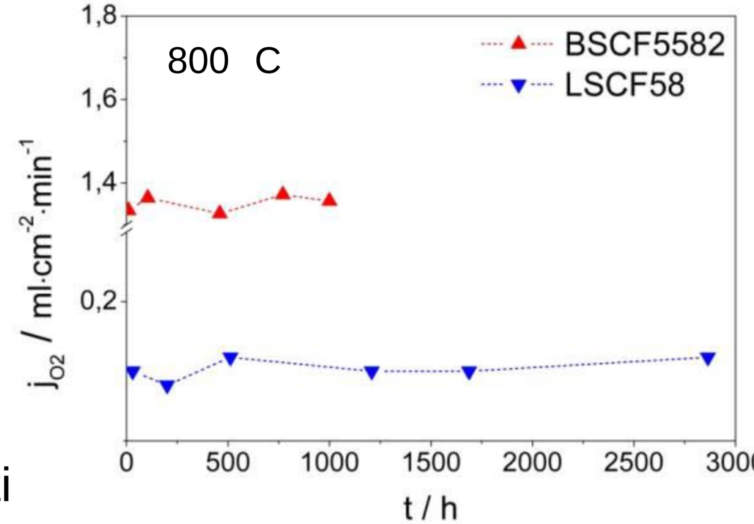
Permeation behaviour of planar membranes
Long-term stability

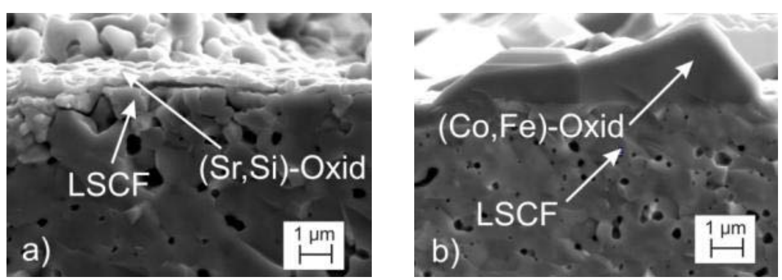
BSCF5582

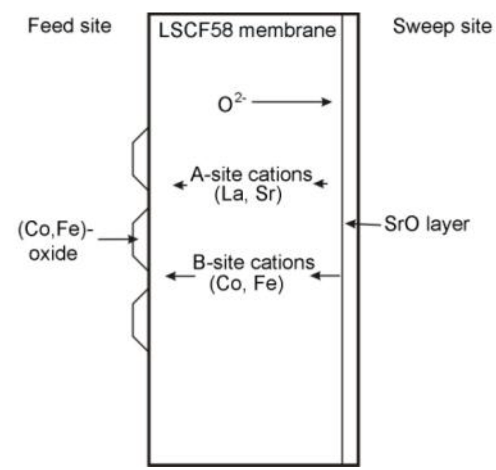
- Good long-term stability in CO_2-free atmosphere over 1000 hours
- Experiment still running

LSCF58

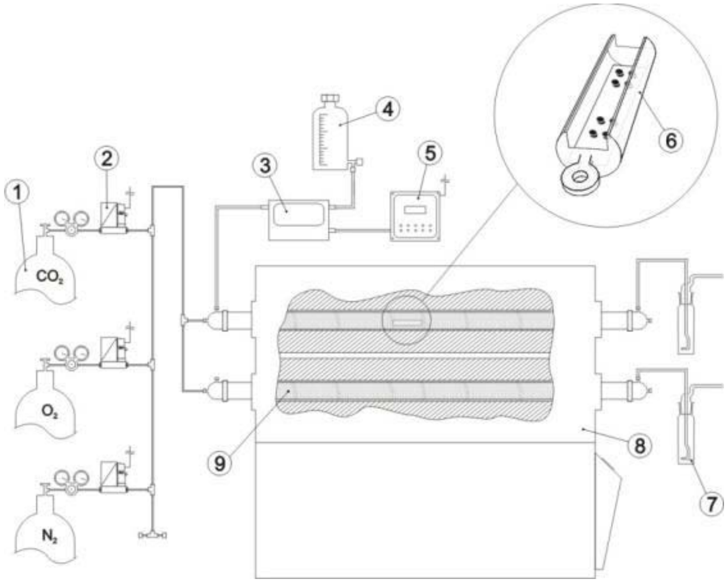
- Good long-term stability in CO_2-free atmosphere over 3000 hours
- Gradient in $p(O_2)$ leads to gradient in cati opposite direction
  → Kinetic demixing
  → Mobility of A-site and B-site cations different

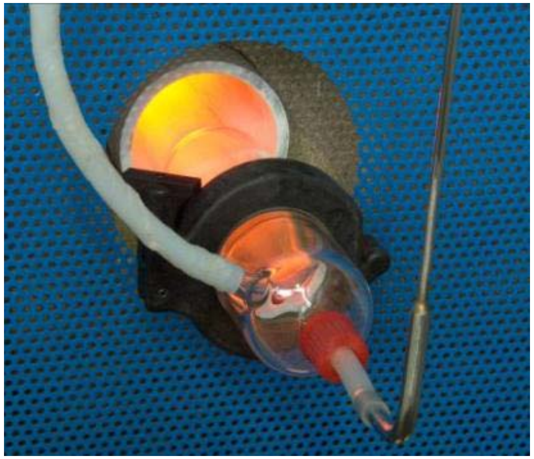






Stability Investigations





Annealing

- Investigation of Thermochemical Stability in Dependence of Temperature and Gascomposition

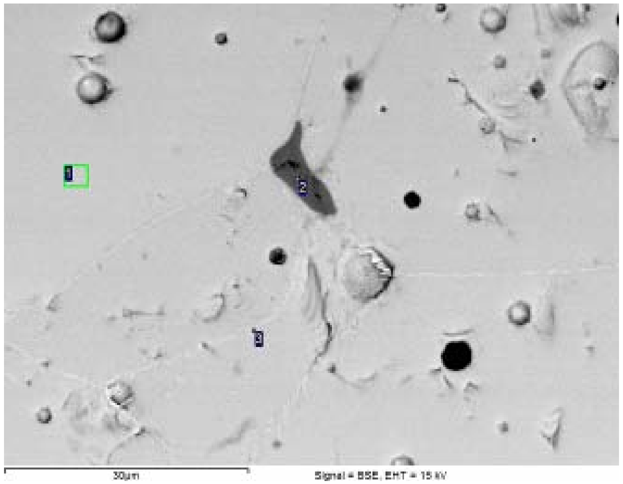
- Sample: pill, powder
- Gases: O_2, N_2, CO_2, Ar, H_2O_D
- Temperature: ≤ 1000 °C
- Pressure: 1 bar

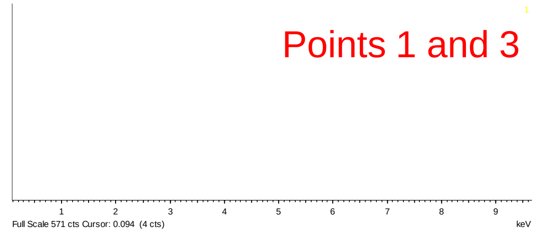
Characterization Methods

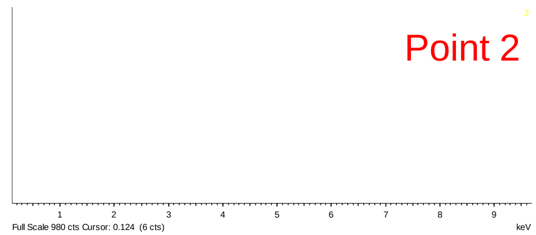
- SEM (EDX / WDX)
- XRD
- Chemical Analysis

Stability Investigations on BSCF

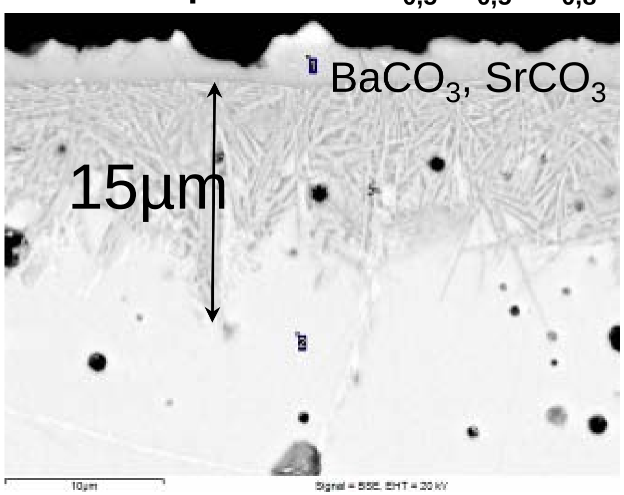
SEM picture and EDX spectra of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ annealed at 800 C in air for 200h

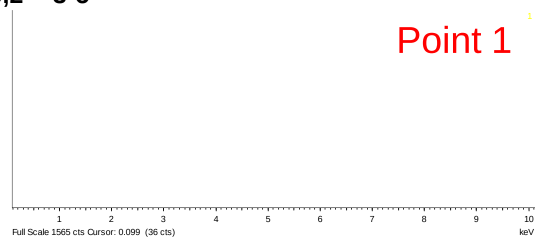


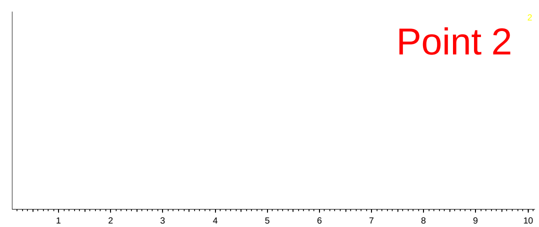




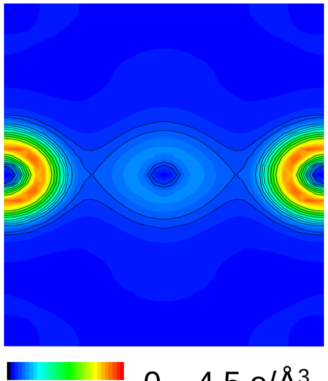
SEM picture and EDX spectra of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ annealed at 800 C in air+10% CO_2 for 200h



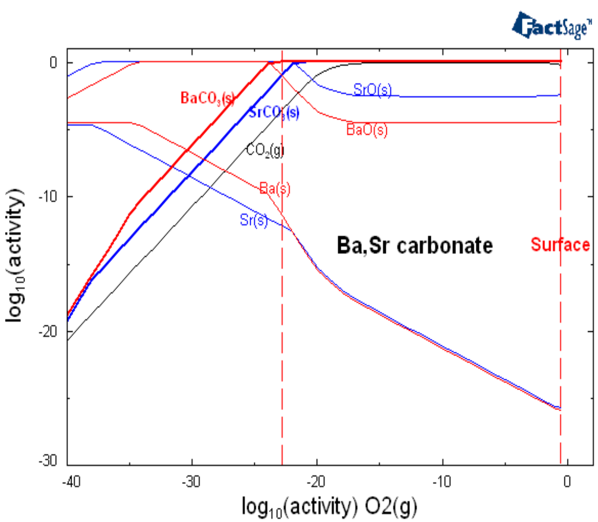




Computer Based Model calculations



Electron density distributions



Calculate the thermodynamic stabilities and Thermomechanical properties of LSCF and BSCF based on *ab initio* calculations

Perform Model Calculations: Predict Phase Formations and Phase Changes under Operation Relevant Atmospheres (Long Term Stability)

Compare Calculations with Experimental Results (Thin Film Synthesis and Applications)

Understand and Predict the Role of Composition Changes of the Material (Losses due to Vaporization, Impurities, Dopants, Vacancies,…)

Model Representation for Microstructure Dependence of Mechanical and Thermochemical Material Properties

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    CO_2 Reduction Technology

Thank you for your attention!