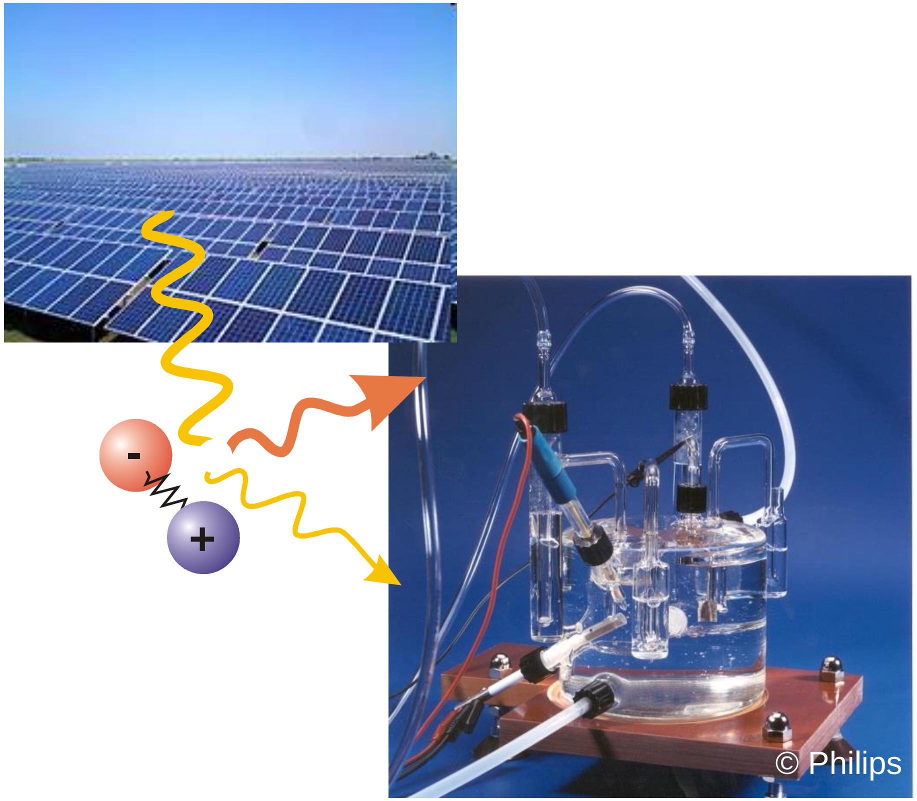
Expertengespräche
„Applied Power-to-Gas“

Dienstag, 13. Mai 2014, 13.30 – 18.30 Uhr

HSR Hochschule für Technik Rapperswil
Oberseestrasse 10
CH-8640 Rapperswil



Aktueller Stand
Power-to-Gas
in der
Schweizer Forschung

Andreas Borgschulte

Andreas.borgschulte@empa.ch

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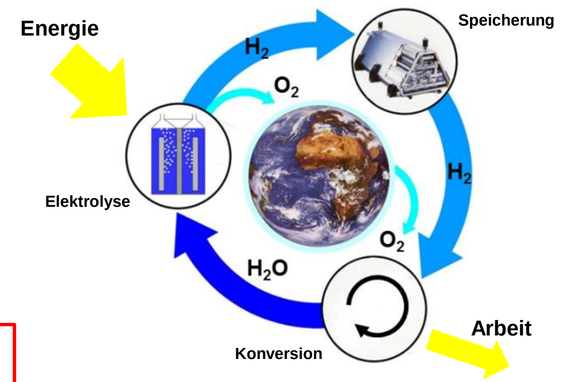
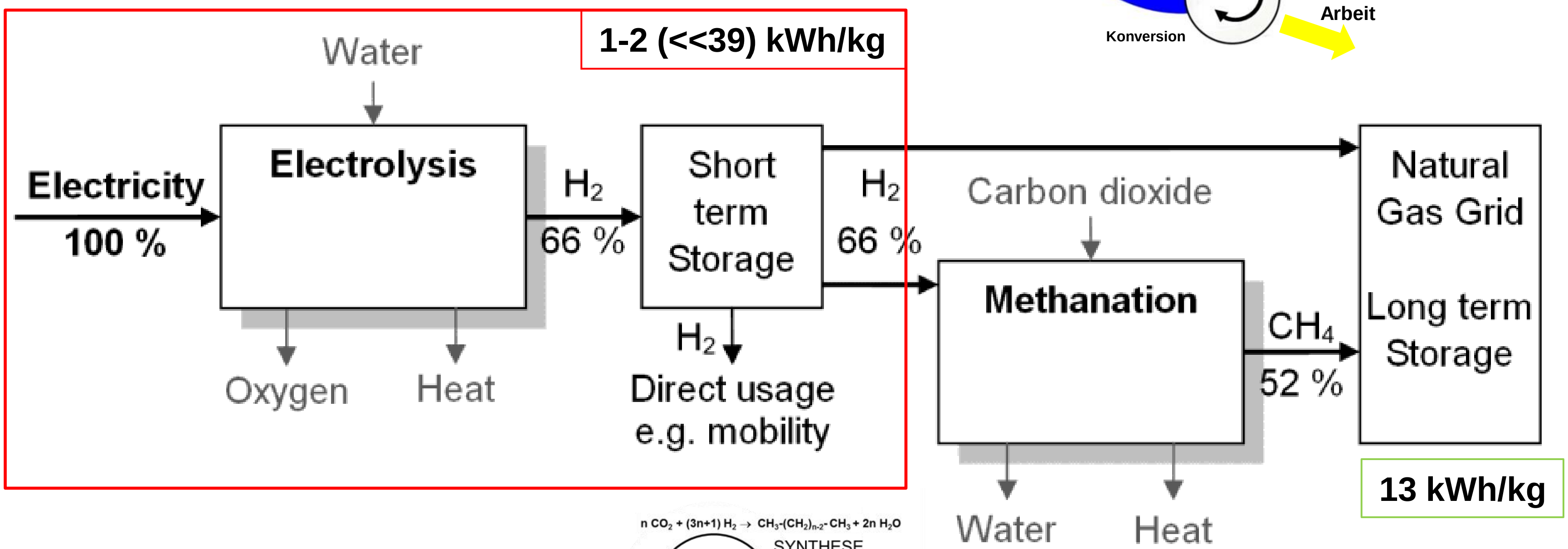
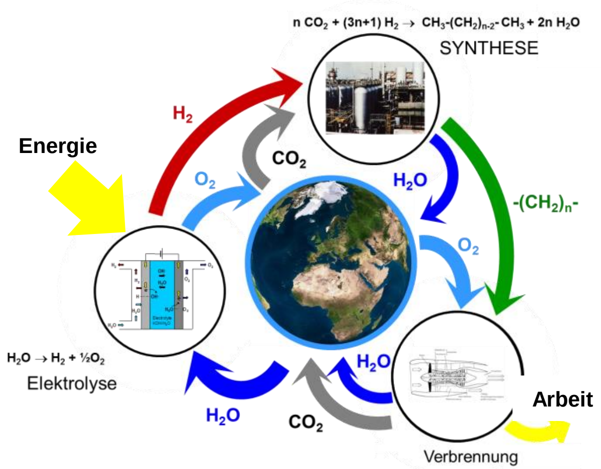
Materials Science & Technology

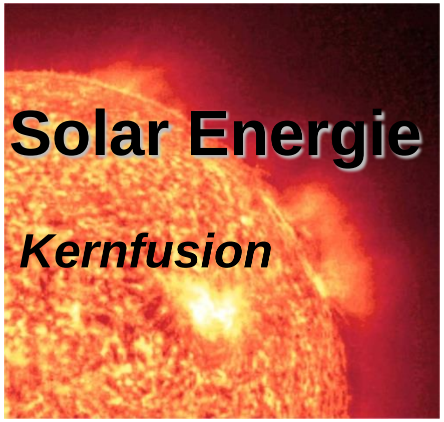
Was ist “Power-to-gas”?







Energie"quellen"



fossile biogene → Kohle, Erdöl, Erdgas

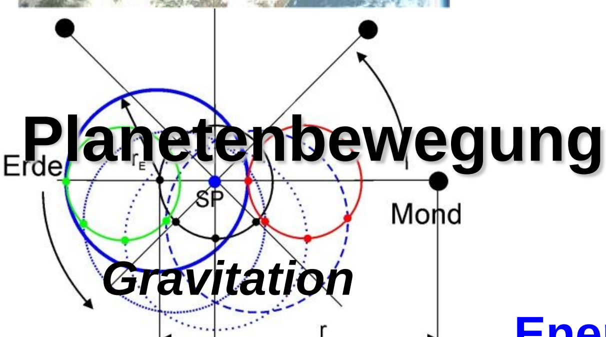
biogene → Biomasse

Photosynthese

→ Wärme, Wind, Wellen, Niederschlag, Strömungen

fossile Minerale → Uran, Thorium

→ Geothermie

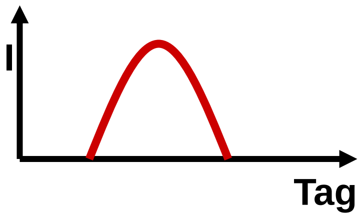


→ Gezeiten

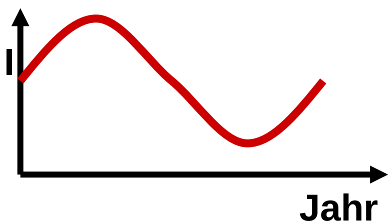
Energieträger and Energieflüsse

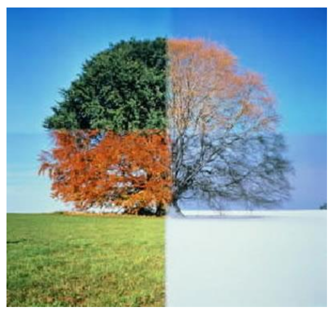
Erneuerbare Energie

Tag-Nacht-Zyklus

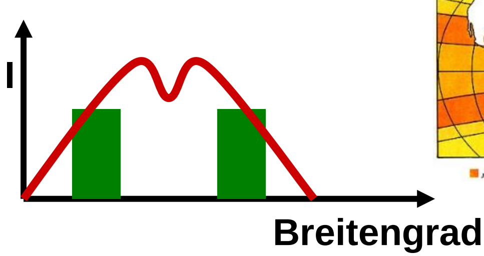


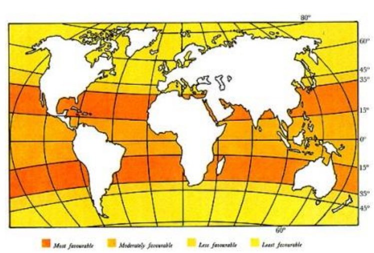
Saisonaler Zyklus





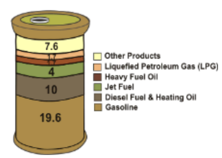
Örtliche Verteilung



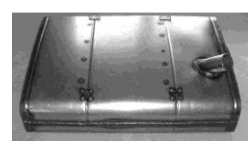


Wandlung

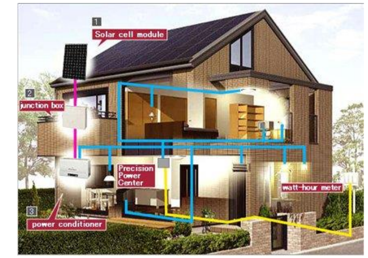
Speicherung



Transport

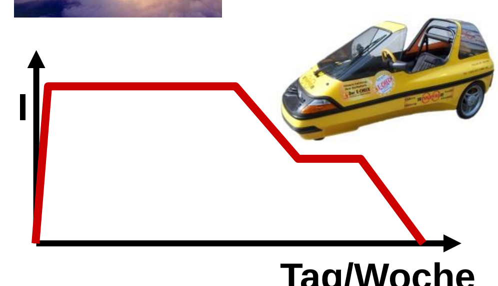


Häuser
Wärme



Industrie
Wärme & Arbeit

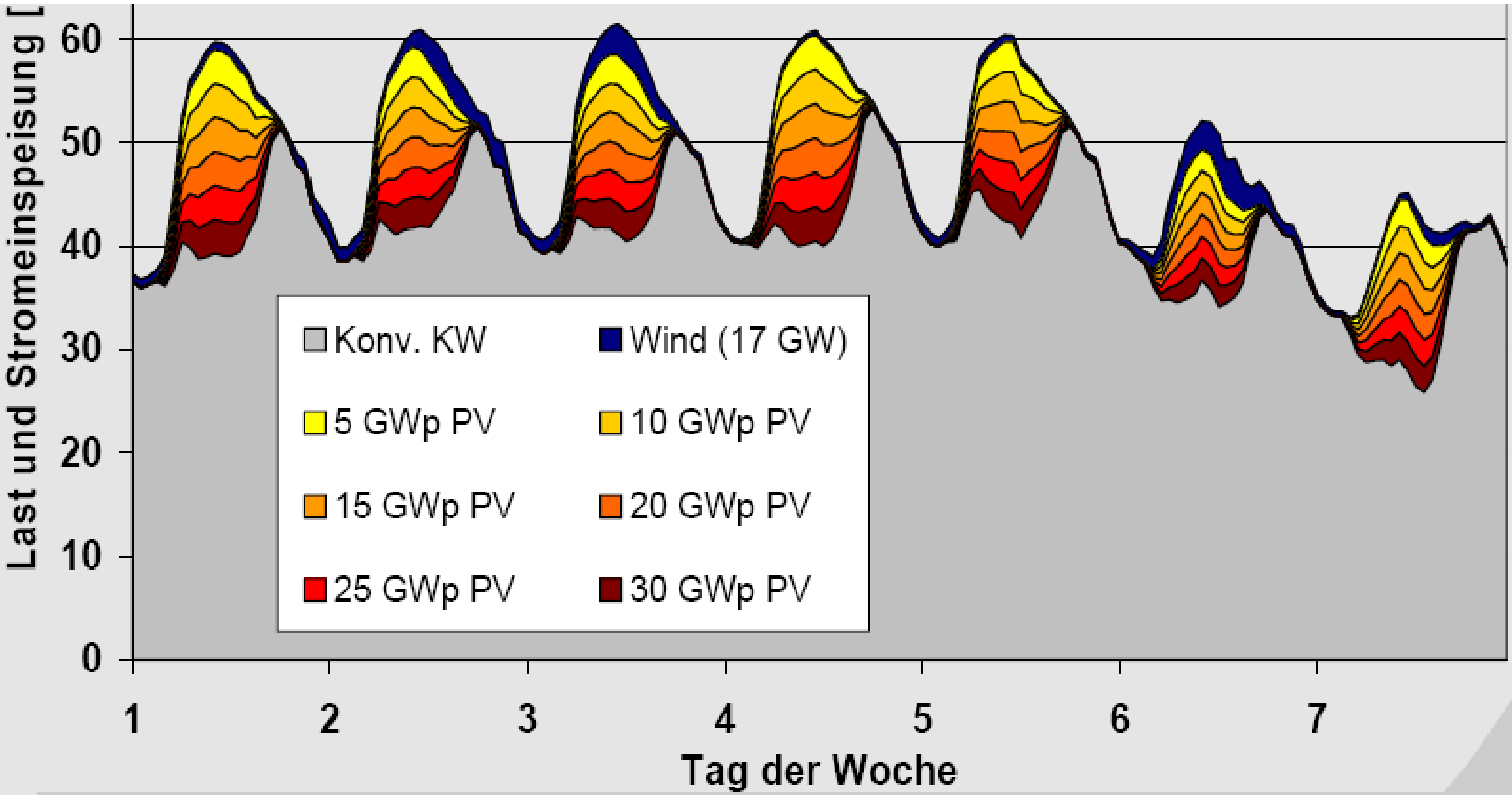
Mobilität
Arbeit



Korrelation Nachfrage und Energieproduktion

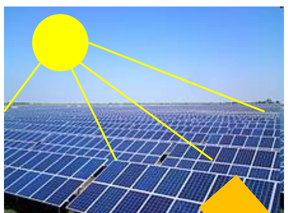
ON JUNE 16th 2013 something very peculiar happened in Germany's electricity market. The wholesale price of electricity fell to minus €100 per megawatt hour (MWh). That is, generating companies were having to pay the managers of the grid to take their electricity. It was a bright, breezy Sunday. Demand was low. Between 2pm and 3pm, solar and wind generators produced 28.9 gigawatts (GW) of power, more than half the total. The grid at that time could not cope with more than 45GW without becoming unstable.

The Economist Oct 12th 2013

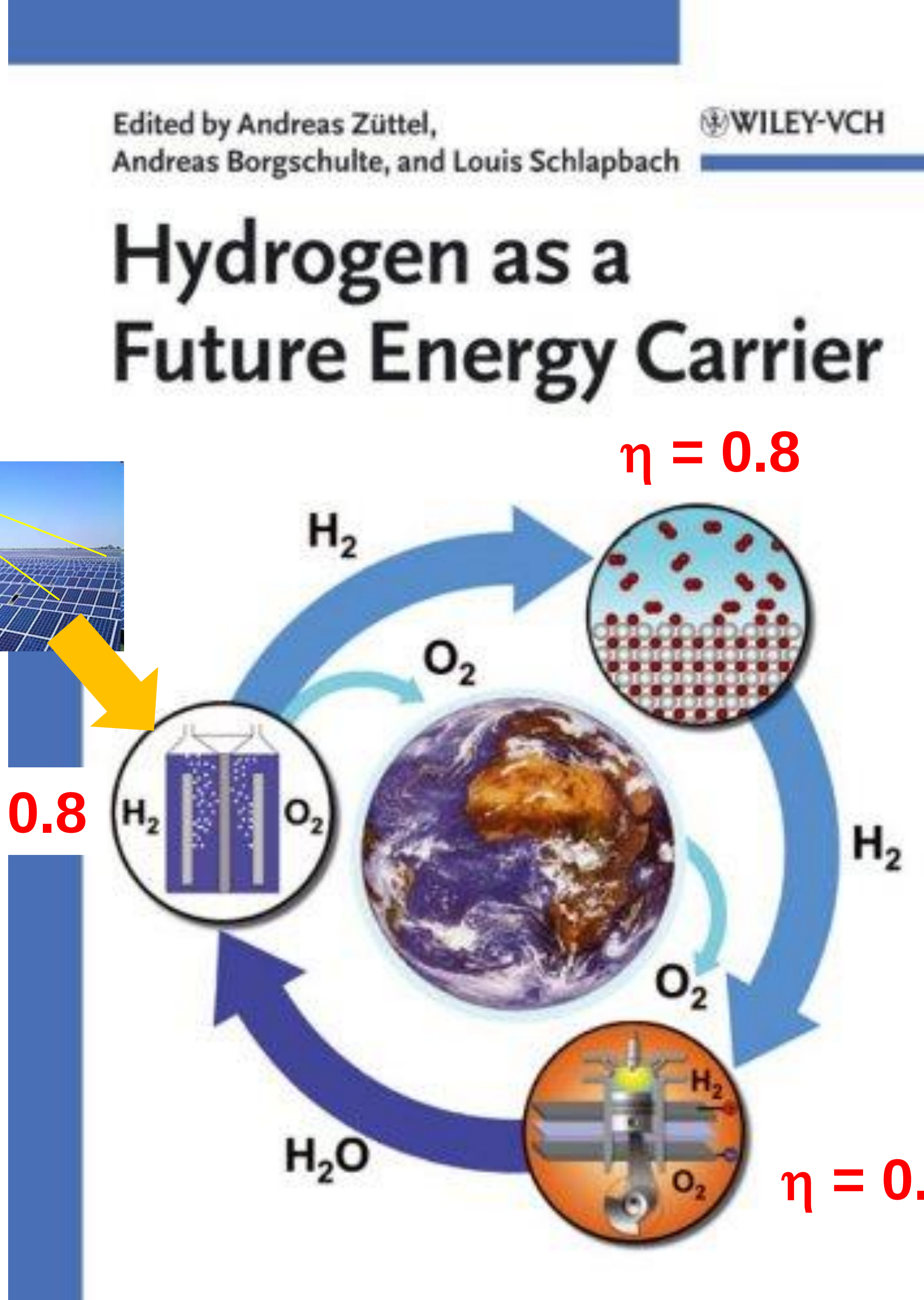


Institut für Solare Energieversorgungstechnik
Verein an der Universität Kassel

Ref.: Winfried Hoffmann, 2007



$\eta = 0.1$



$\eta = 0.8$

$\eta = 0.8$

$\eta = 0.05$

$\eta = 0.6$

HYDROGEN ENERGY

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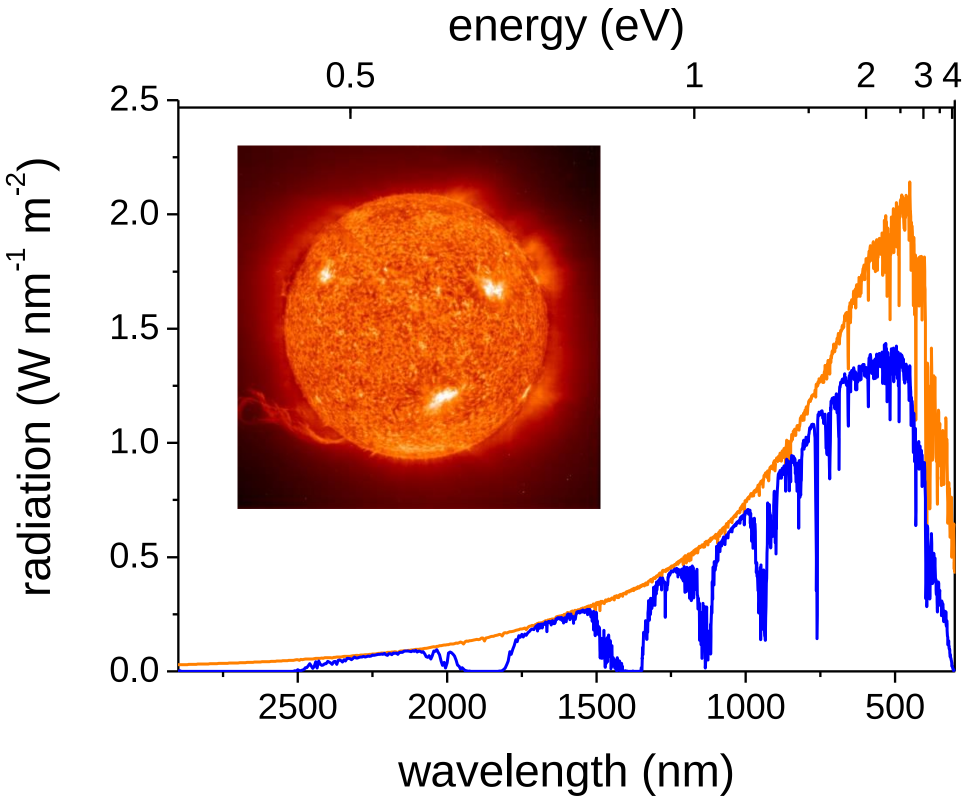
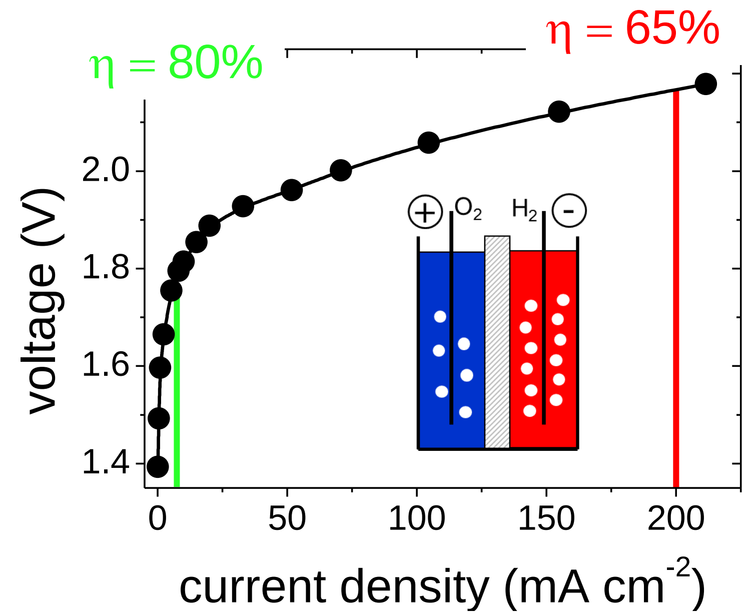
Solare Energie





Alkali-Elektrolyseur
~200 mA/cm²

Solarkonstant:e P = 1000 W/m²

$U \sim 2$ V

$$j_{Ph} = \eta \cdot \frac{P}{U} \cdot \frac{1}{A} = 50 \frac{\mathrm{A}}{\mathrm{m}^2} = 5 \frac{\mathrm{mA}}{\mathrm{cm}^2}$$

5 mA/cm²
= Solar water
splitting device

M. H. Miles et al., J. Electrochem. Soc., 123, 332 (1976).

“Light-to gas”

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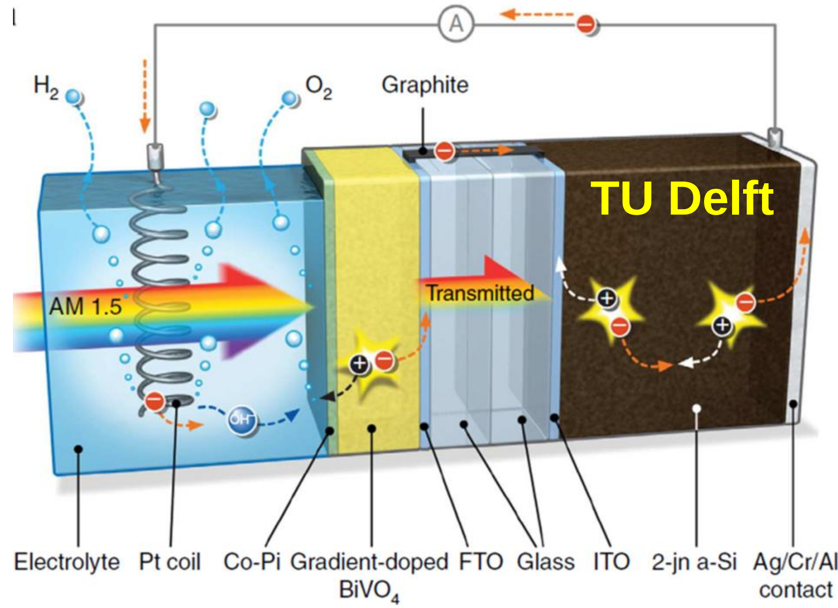
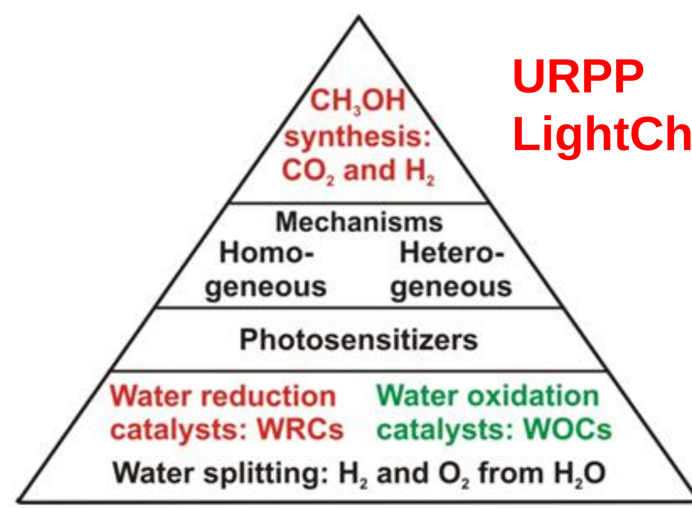
- **Uni Zürich: URPP LightChEC**, http://www.lightchec.uzh.ch The main objectives of the URPP Solar Light to Chemical Energy Conversion are to discover and develop new molecules, materials and processes for the *direct storage of solar light energy in chemical bonds* **(Artificial photosynthesis)**



Abdi, F. F. et al. Nat. Commun. 4, 2195 (2013).

- **EPFL**: The **PECHouse** Initiative has allowed to create a competence center for *hydrogen production by direct photo-electrolysis* (PEC)



URPP LightChEC

M. Grätzel

Brute force approach: Solarenergie bei 1500°C

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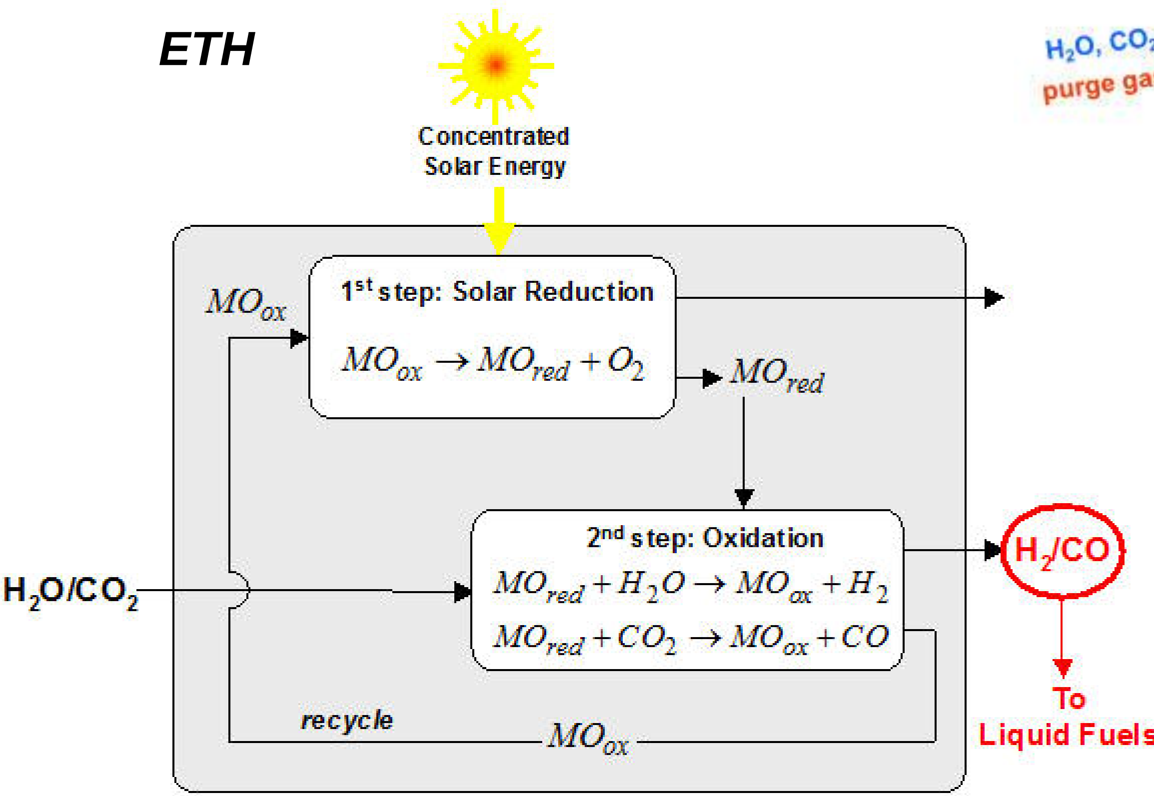
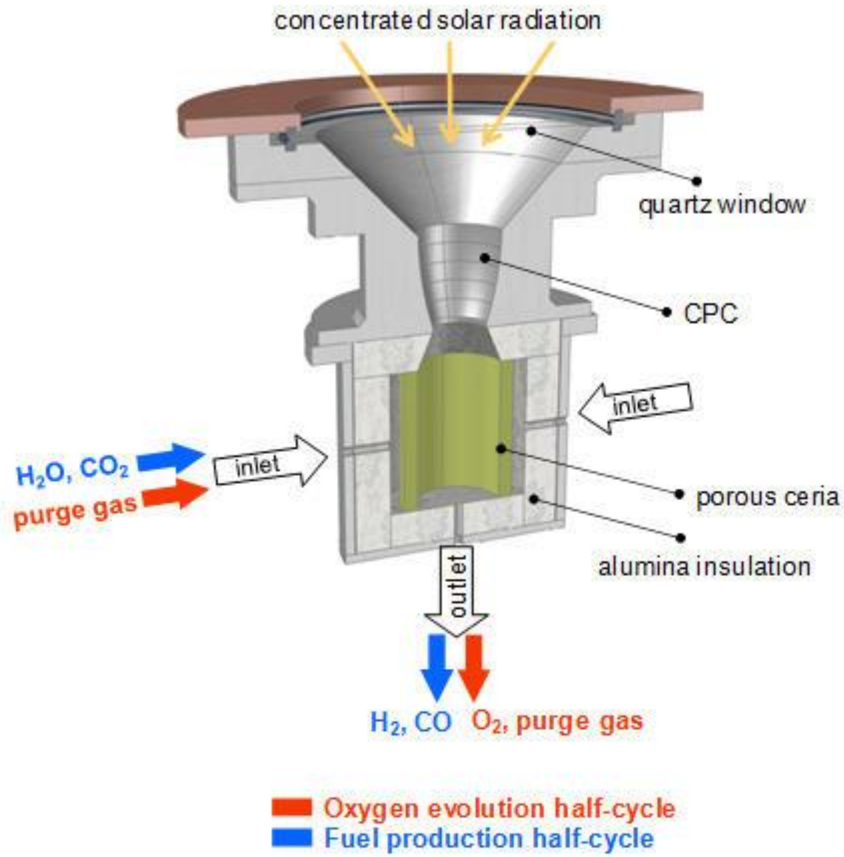
ETH





Chueh W.C., Falter C., Abbott M,,
Scipio D., Furler P., Haile S.M.,
Steinfeld A. Science, Vol. 330,
pp. 1797-1801, 2010.

EU-Horizon 2020 - *WORK PROGRAMME 2014-2015*

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LCE 9 – 2015: Large scale energy storage

Specific challenge: The high penetration rates of variable renewable energ the need for large scale energy storage to balance the production and co quantities of electricity and during longer time periods. Demonstration acti will aim to progress large scale energy storage and reduce the barriers as storage concepts. An important market uptake challenge is to red (technological, economic, regulatory, environmental, social and other associated with the deployment of existing or new storage concepts.

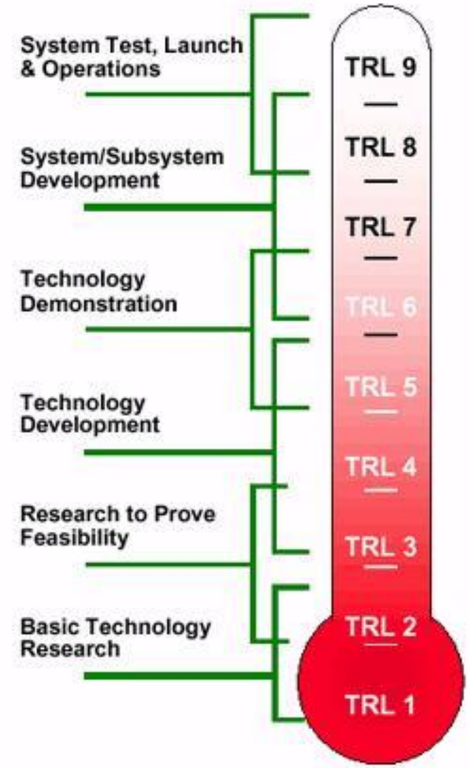
Scope: Activi t reached already TRL to TRL 6-7 (es). This would inclu on to the e ergy storage

Technology Readiness Level

Marktreife ab TRL1: 8-15 Jahre, BfE 2030
Perspektive: 33% erneuerbare Energieträger

Activities should pursue direct electricity or indirect storage (electricity vectors). interfaces for integrating management. where appropriate, synergies between electricity grid, ot storage and final energy use must be taken into account.

Starting energy: electricity



Integrated Power to Gas concepts allowing electricity storage through the production of synthetic gas to be stored in the gas grid in the form of synthetic/green methane are eligible.

Electrolysis proposals and proposals with pure hydrogen injection in the natural gas grid are not in the scope of this activity; they should be submitted to the Hydrogen/fuel cells joint undertaking.

Power-to gas

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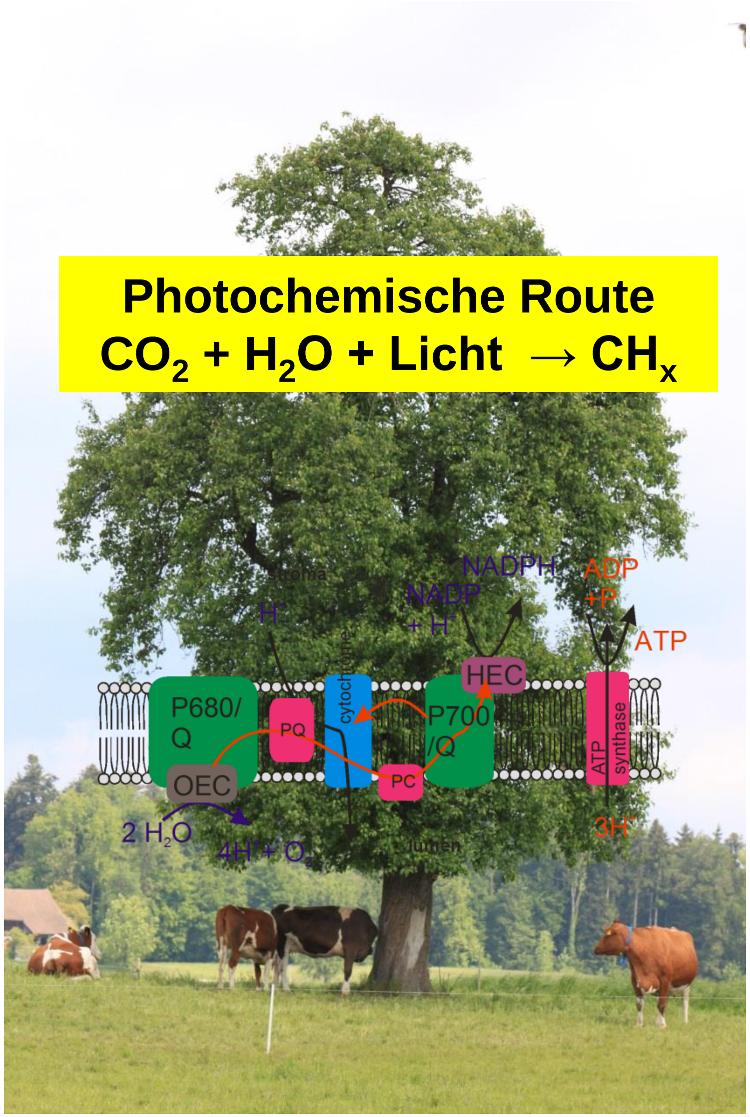
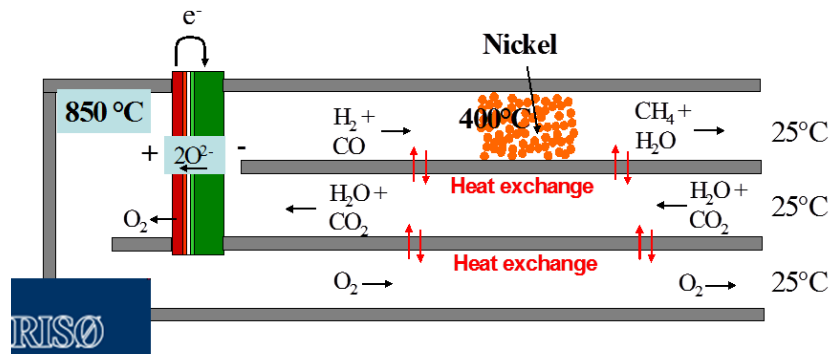
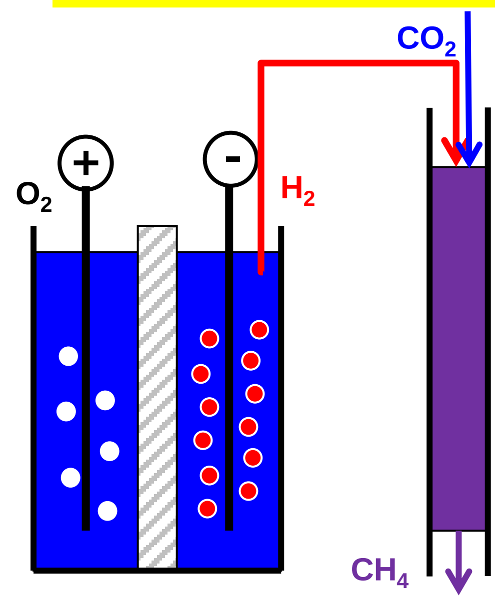


Photochemische Route
$CO_2 + H_2O + \text{Licht} \rightarrow CH_x$

Elektrochemische Route
$CO_2 + H_2O + \text{Elektrizität} \rightarrow CH_x$

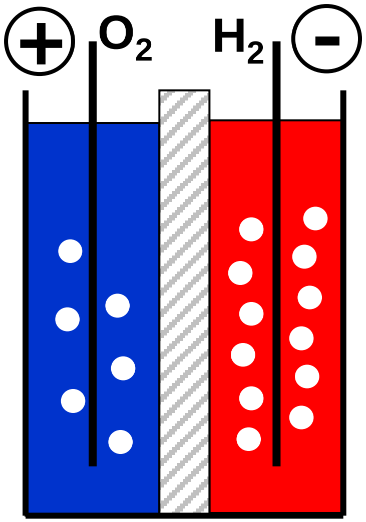


Chemische Route
$CO_2 + H_2 \rightarrow CH_x$



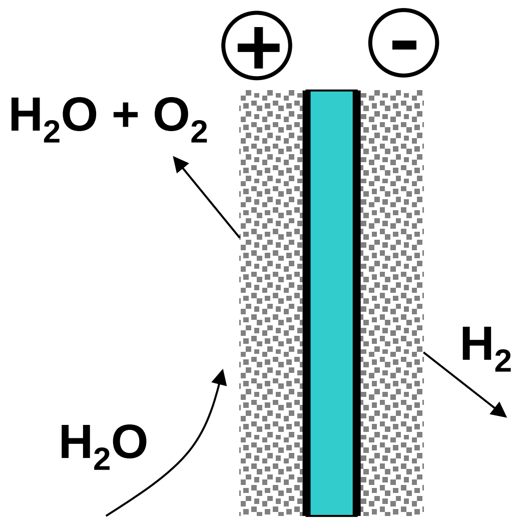
Prinzip Wasserelektrolyse

Diffusion Membrane Electrolyser



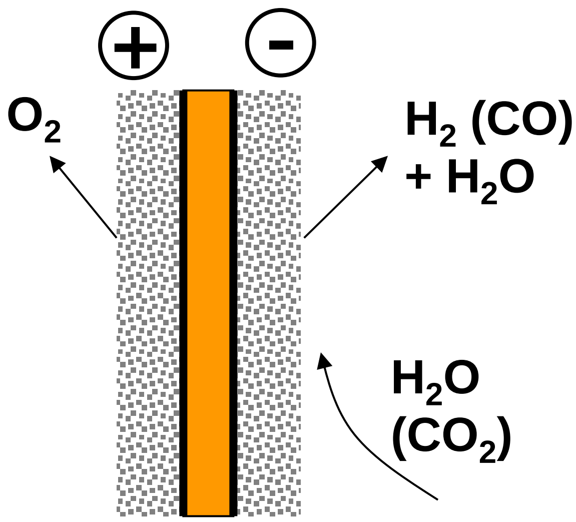
Membran
30% KOH, 80°C

Polymer-Electrolyte (PEM) Electrolyser



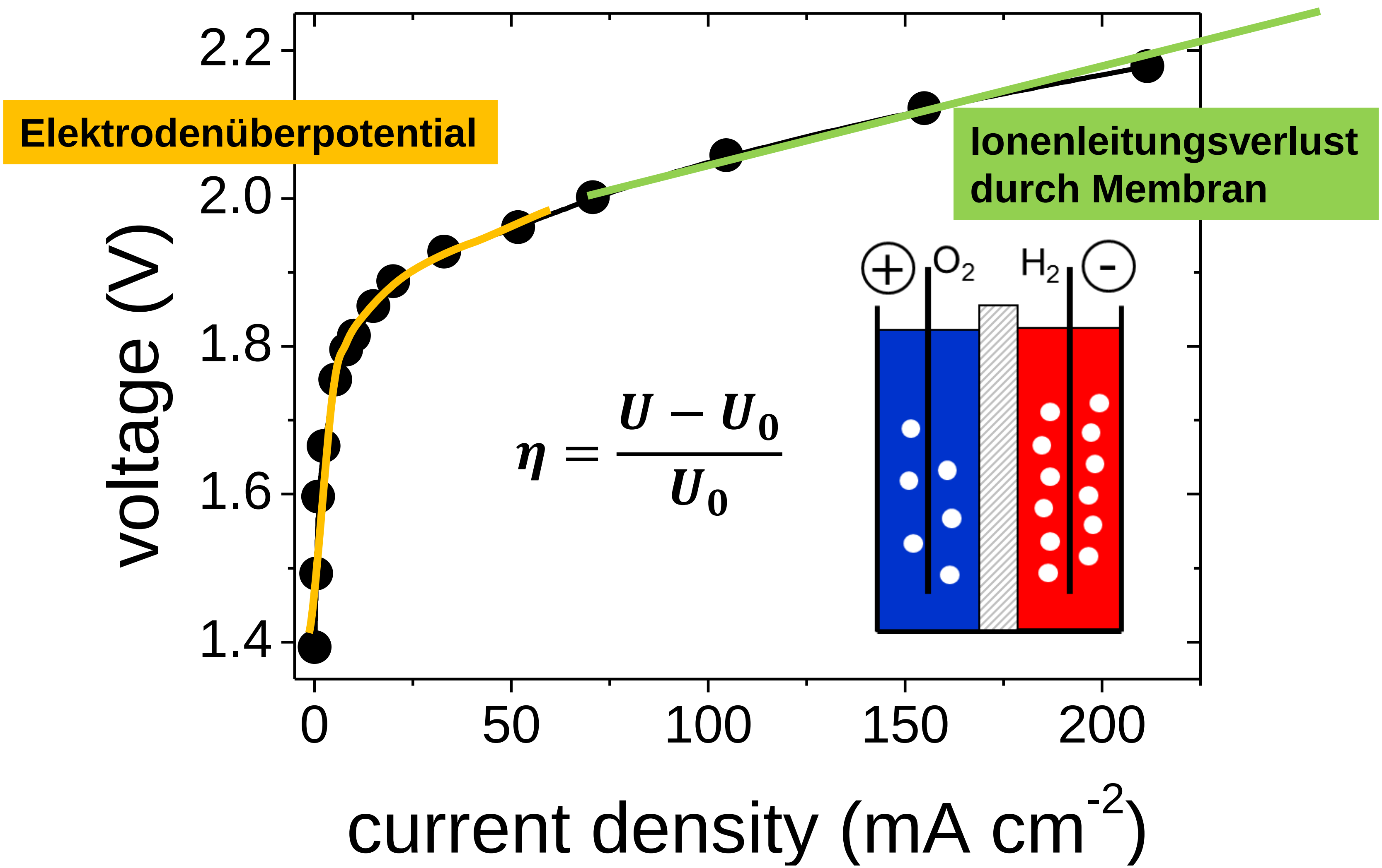
Nafion® (H^+)
reines H_2O, 100°C

Solid oxide Electrolyte (SOE) Electrolyser



ZrO_2 (O^{2-})
H_2O Dampf bei 800°C

Elektrolyse



M. H. Miles et al., J. Electrochem. Soc., 123, 332 (1976)

Forschungsaktivitäten zu Elektrolyse-bauteilen

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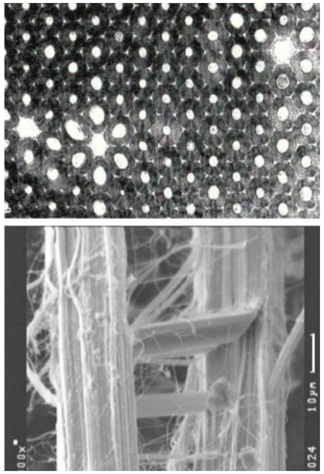
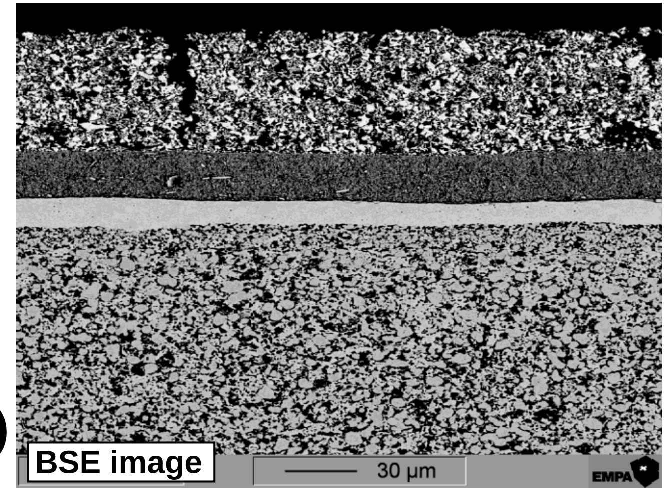


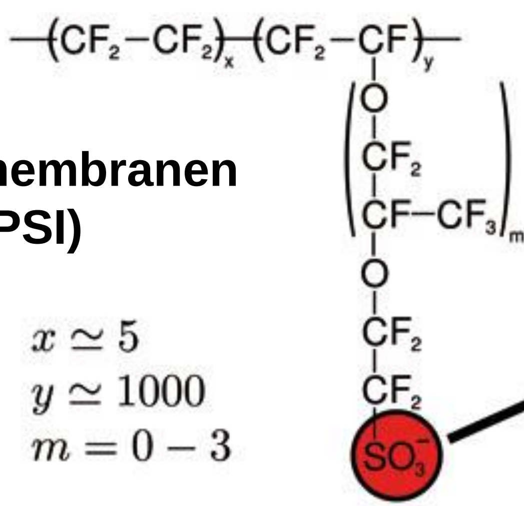
**Asbest-Membranen
(Empa, IHT)**

**HT-Membranen/
Elektroden
(Empa, PSI, EPFL, ZHAW)**

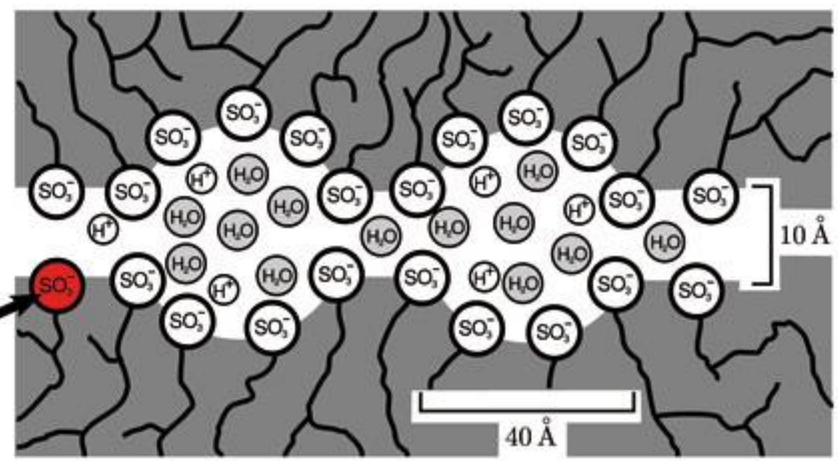


neue Materialien…

**Nafionmembranen
(PSI)**



$x \simeq 5$
$y \simeq 1000$
$m = 0 - 3$



Elektrolyse-Systeme

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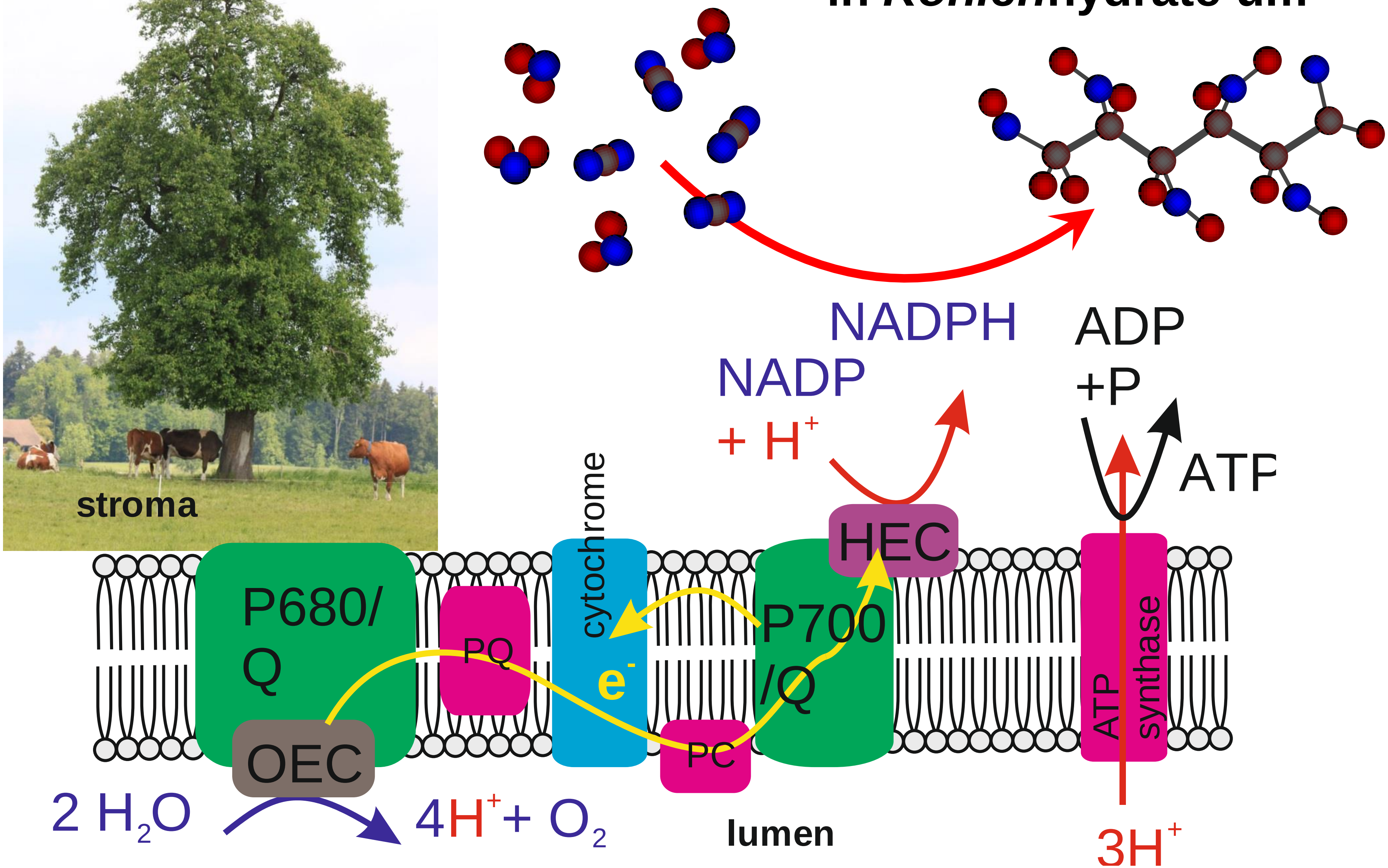
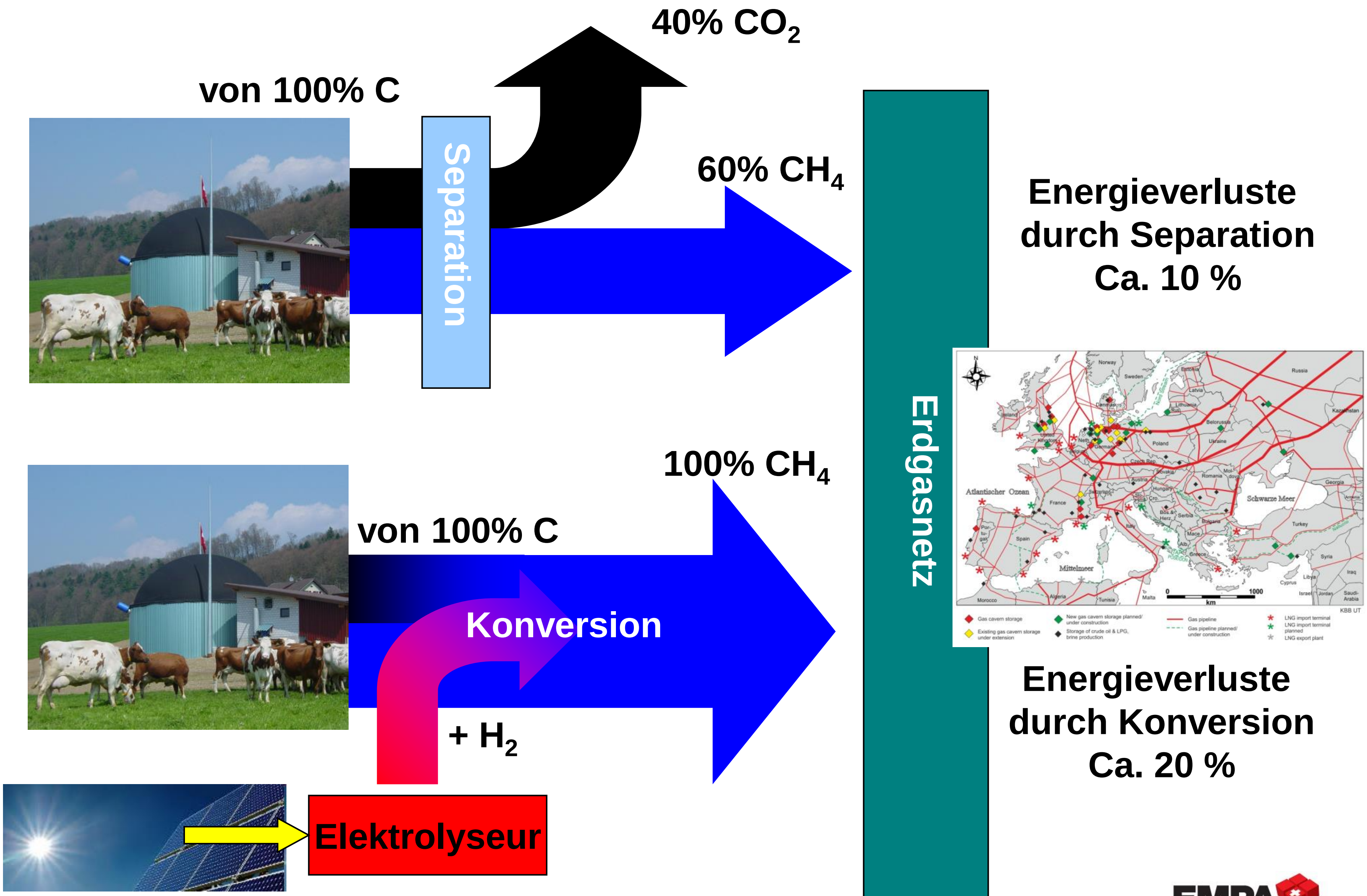
Ref.: T.Smolinka, Fraunhofer ISE

Pflanzen wandeln H_2O and CO_2 in *Kohlen*hydrate um



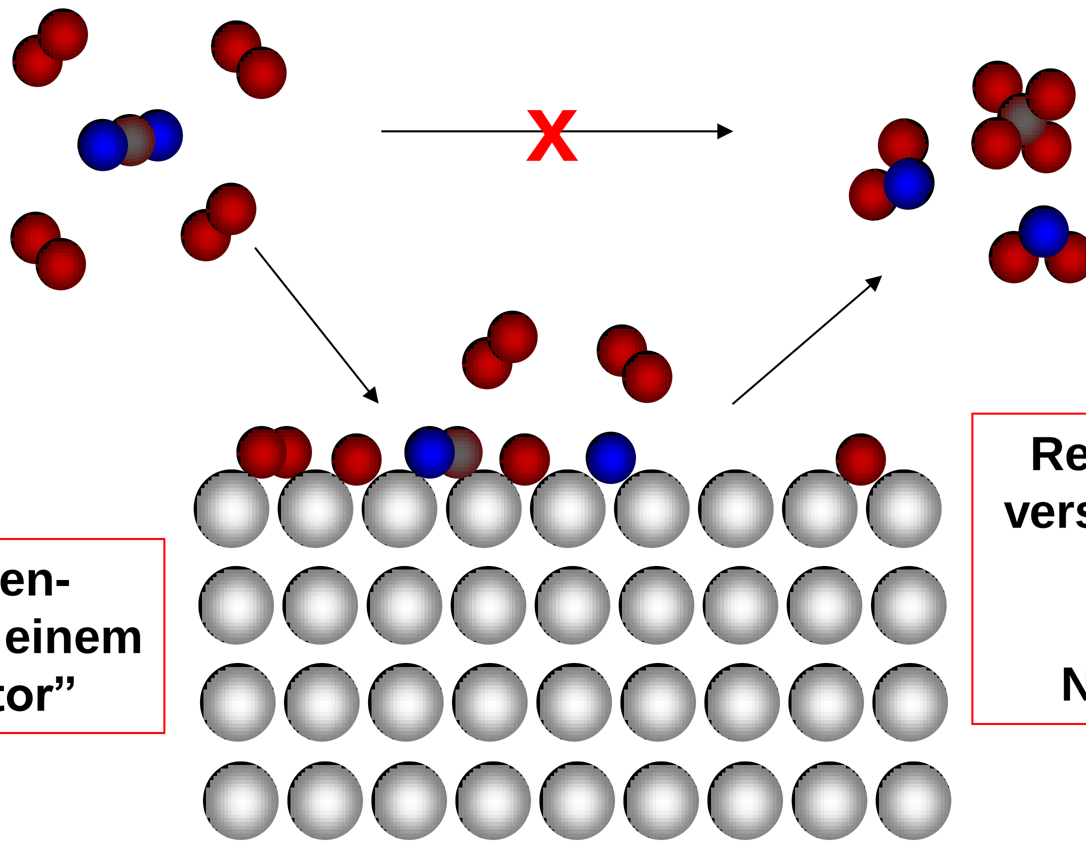
Biogas nach “Zero-emission Biogas”



M. SPECHT, et al., ERDÖL ERDGAS KOHLE 126 (2010) 342; KBB Underground Technologies GmbH | Baumschulenallee 16 | D-30625 Hannover

Sabatier Reaktion

$$4\ H_2 + CO_2 \qquad CH_4 + 2\ H_2O$$

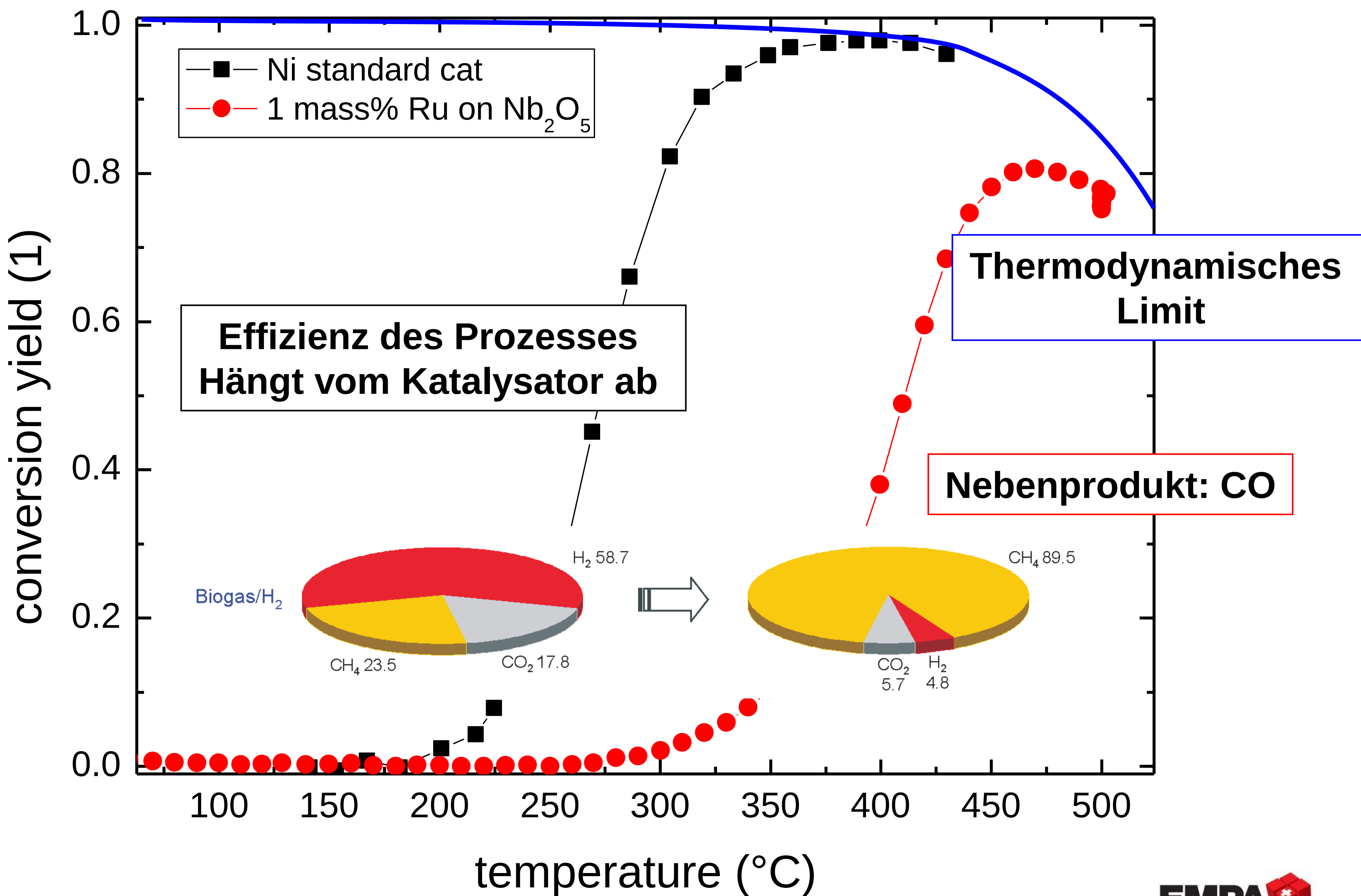


Oberflächen-Reaktion auf einem "Katalysator"

Reaktion durchläuft versch. Teilreaktionen

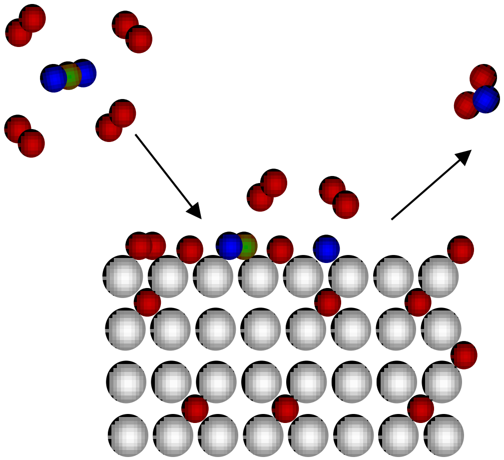
Ungewollte Nebenreaktionen

Reduktion von CO_2 auf Katalysatoren

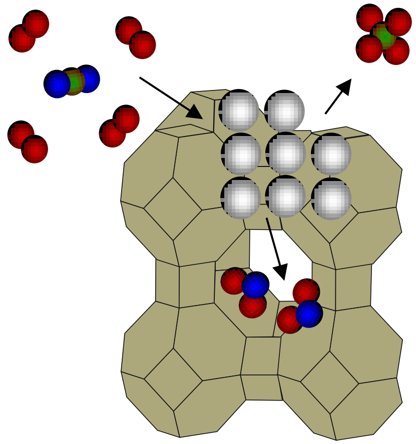


Idea from M. SPECHT, et al., ERDÖL ERDGAS KOHLE 126. (2010)342.

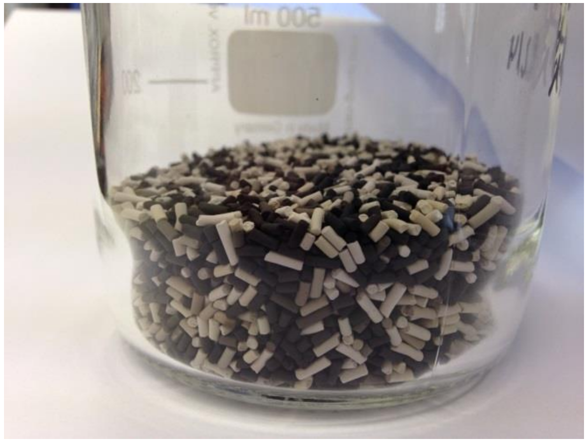
Wasserabsorption stimulierte Methanation



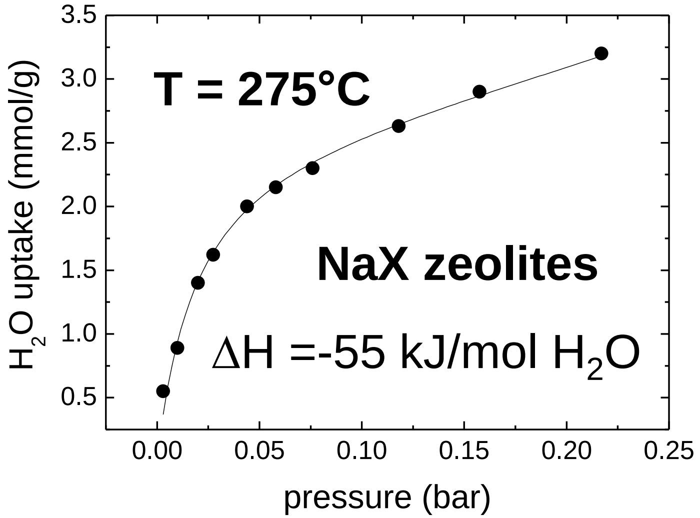
Schema Normaler Kat



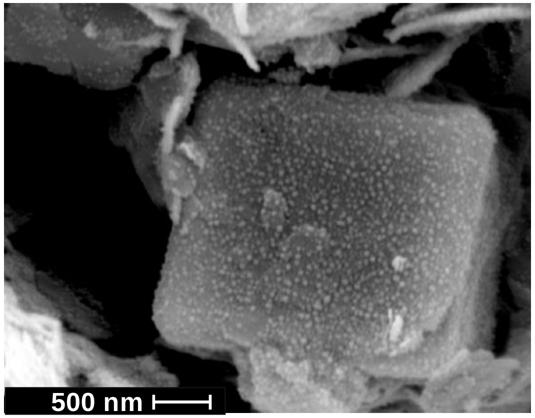
Schema Sorptions-Kat

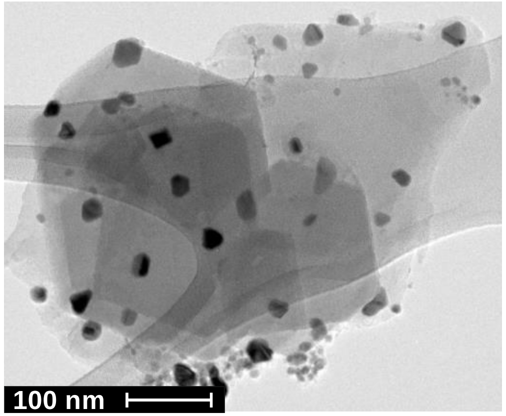


Realisierung



B. T. Carvill, et al., AIChE J. 1996, 42, 2765.





SorptionsKat: SEM/TEM

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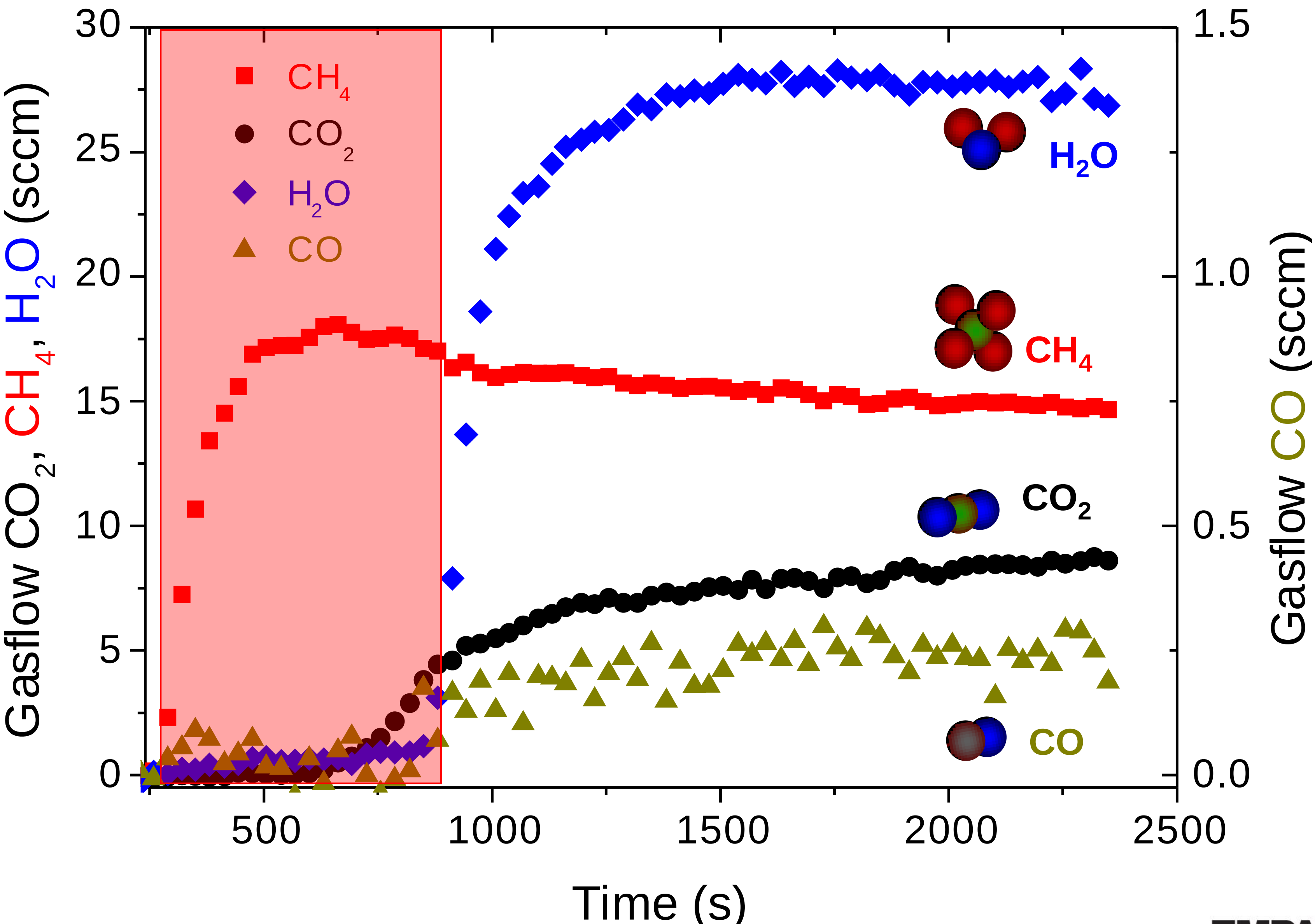
Ein chemischer Reaktor mit 100% Umsatz



Borgschulte, et al. Phys. Chem. Chem. Phys., 15, 9620 (2013).

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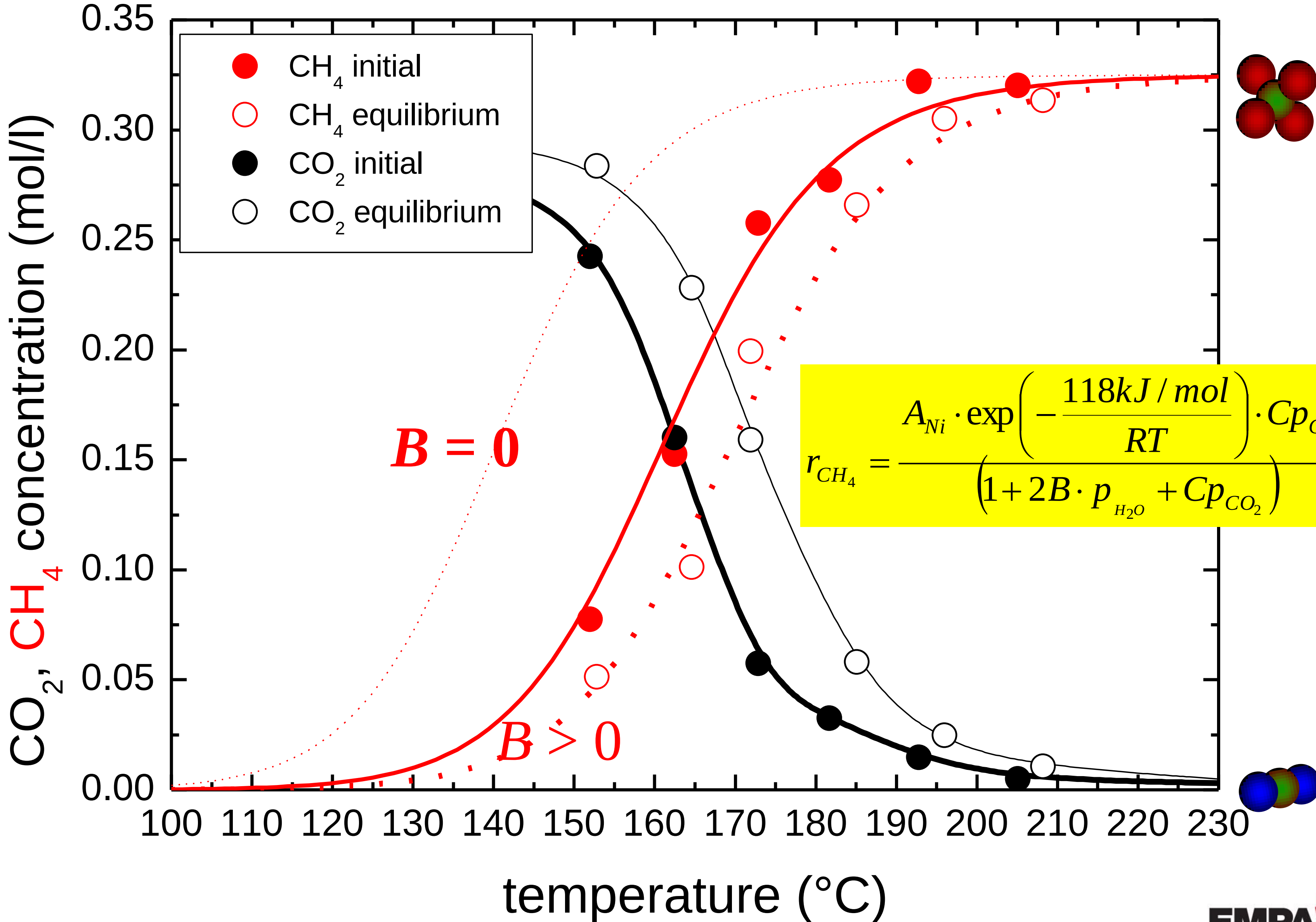
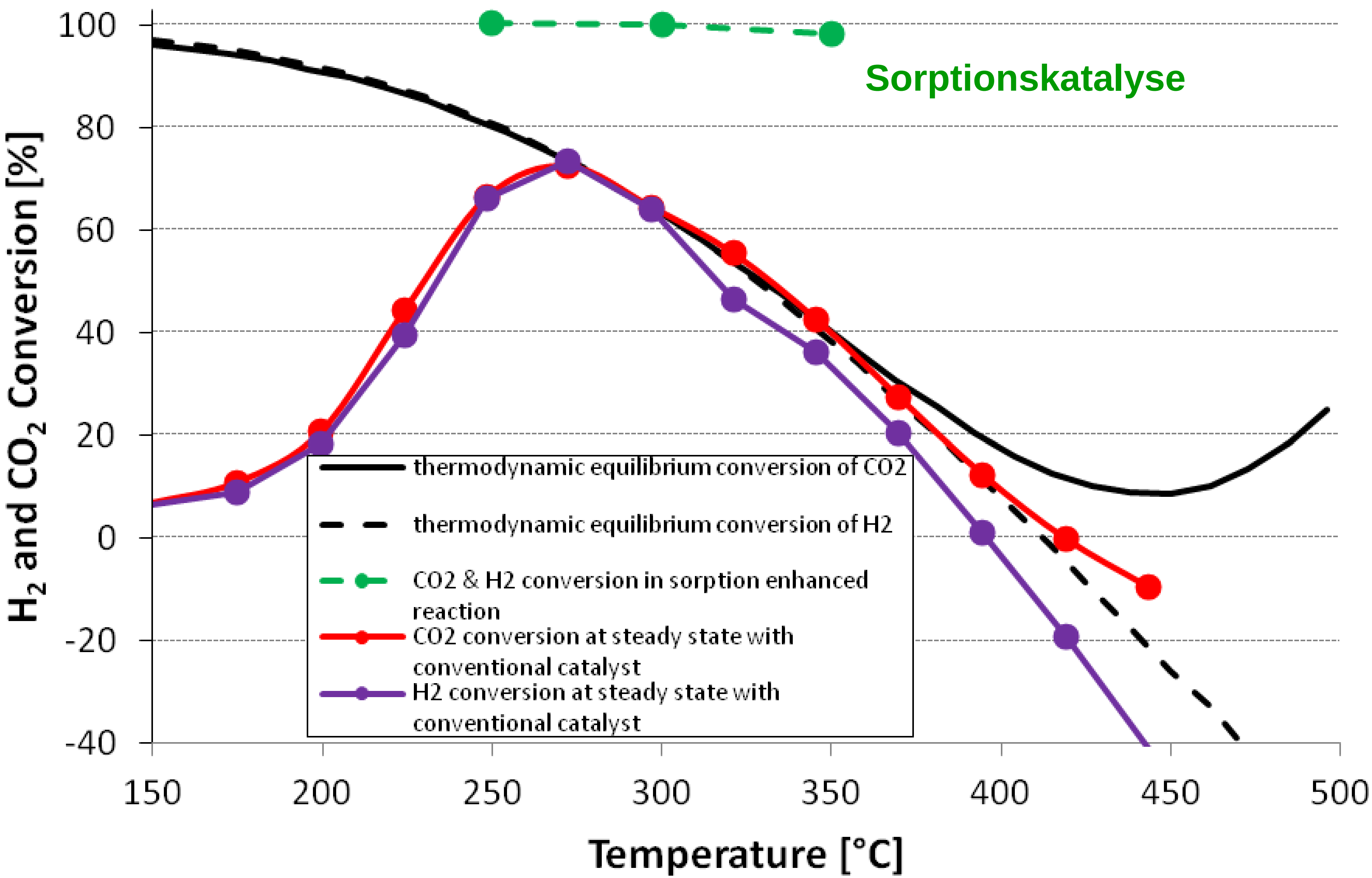
Temperaturabhängigkeit der Sorptionsreaktion (Ni @ 5A)



$$r_{CH_4} = \frac{A_{Ni} \cdot \exp\left(-\frac{118 kJ/mol}{RT}\right) \cdot C p_{CO_2}}{\left(1 + 2B \cdot p_{H_2O} + C p_{CO_2}\right)}$$

T. Van Herwijnen et al. J. Catal. 28, 391 (1973), Borgschulte, et al. Phys. Chem. Chem. Phys., 15, 9620 (2013).

Eindrucksvolle Wirksamkeit der Sorptionskatalyse



S. Walspurger, G. D. Elzinga, J. W. Dijkstra, M.Sarić and W. G. Haije, Chemical Engineering Journal, 2014, 242, 379

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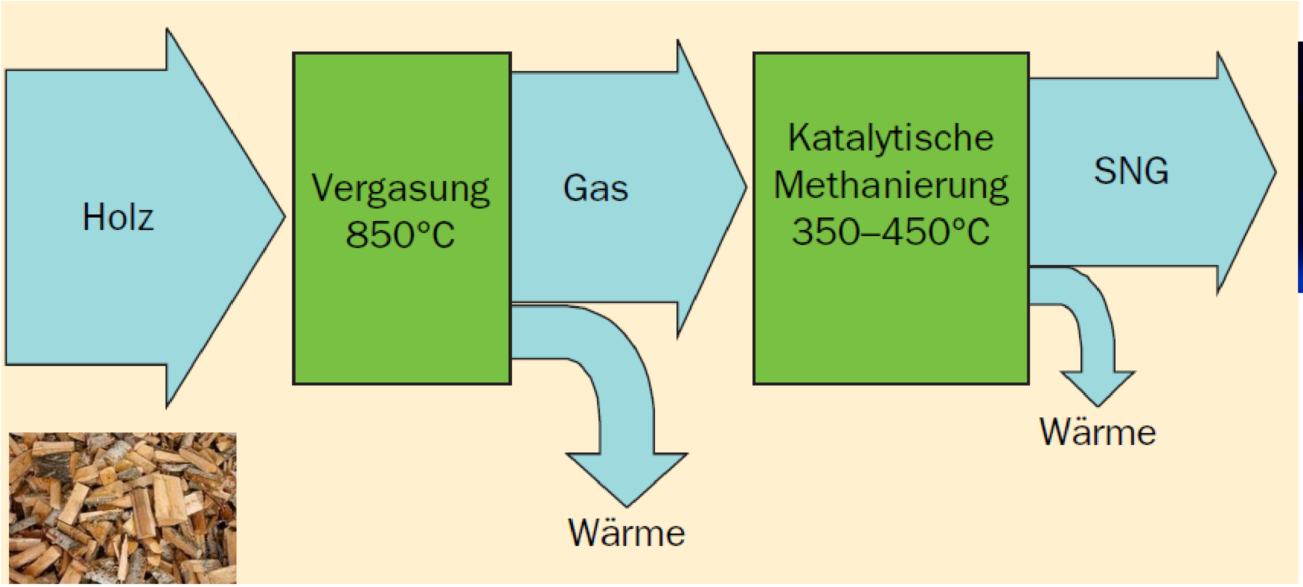
Synthetisches Erdgas aus Biomasse: Holz

- PSI:

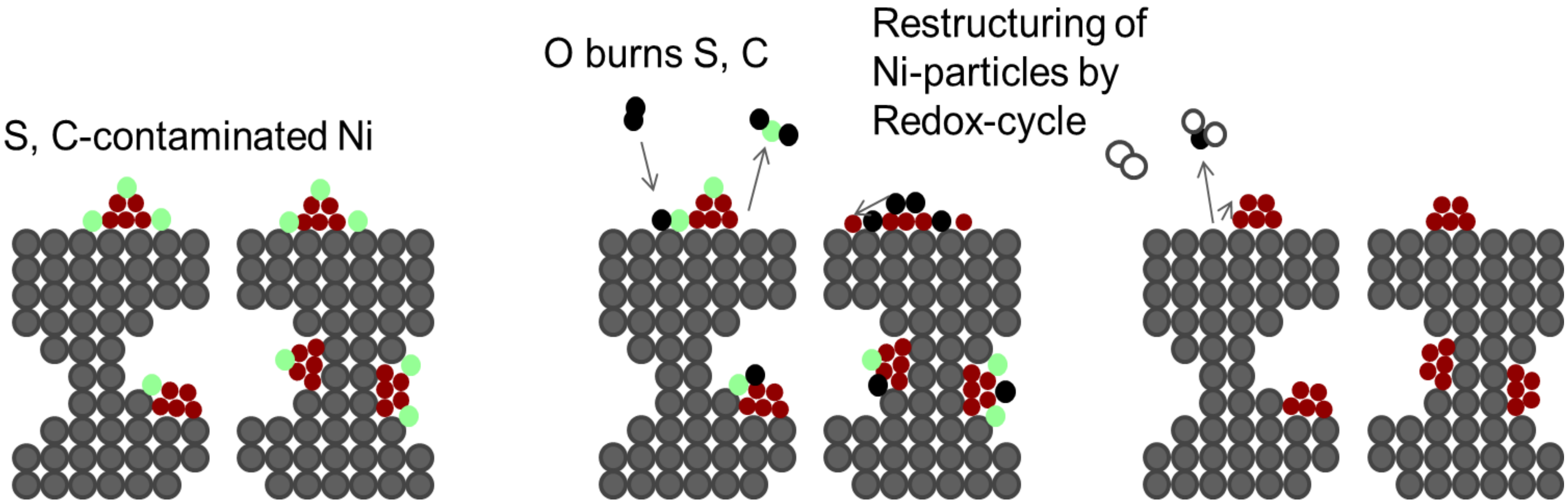


- Herausforderung: Methanisierung von stark (S) verunreinigtem Holzgas (~ $CO + H_2 + X$)

- S ist starkes Katalysatorgift

Biollaz et al., Applied Catalysis A: General 313 (1), 14 – 21 (2006).

Lösung durch SmartCats: Gemeinsames Projekt ZHAW/Empa



- Sorptionskatalyse braucht regelmässige Trocknungszyklen (Pressure swing desorption)
- Trocknung wird kombiniert mit Redox-Zyklen

CO_2 kann mehr

A. Züttel EPFL Valais / Wallis in Sion VS

Air $\rightarrow$ 100% CO_2

air: (80% N_2, 20% O_2, 0.038% CO_2)

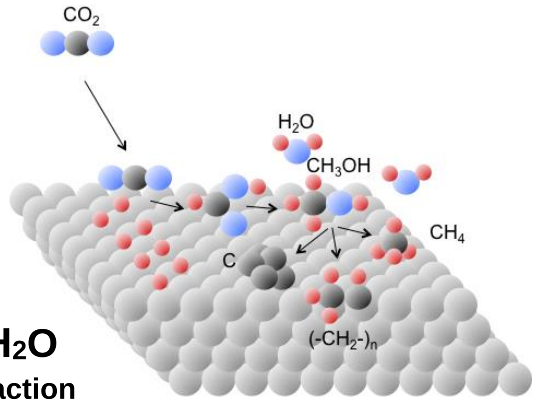
$M + H_2O \rightarrow H_2$

$M + CO_2 \rightarrow CO + MO$

Chem. Reduction

$H_2O \rightarrow H_2 + O_2$

Electrolysis



$CO_2 + H_2 \rightarrow CO + H_2O$

Rev. Water gas shift reaction

$nCO + (2n+1)H_2 \rightarrow [-CH_2-]_nH_2 + (n-1)H_2O$

Fischer-Tropsch synthesis

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Sabatier reaction

$nCH_4 \rightarrow [-CH_2-]_nH_2 + (n-1)H_2$

Methan activation

$M + \frac{1}{2}H_2 \rightarrow MH$

Hydride formation

$nCO_2 + (6n+2)MH \rightarrow [-CH_2-]_nH_2 + 2nH_2O$

MH synthesis

$nCO_2 + (n+1)H_2O \rightarrow [-CH_2-]_nH_2 + (n+1)/2O_2$

Co-electrolysis

$nCO_2 + nH_2O \rightarrow [-CHOH-]_n + nO_2$

Photosynthesis

$[-CHOH-]_n + H_2 \rightarrow [-CH_2-]_nH_2 + n/2O_2$

carbonhydrate $\rightarrow$ hydrocarbon

$CaCO_3 \rightarrow CO_2 + CaO$

$CaO + H_2O \rightarrow Ca(OH)_2$

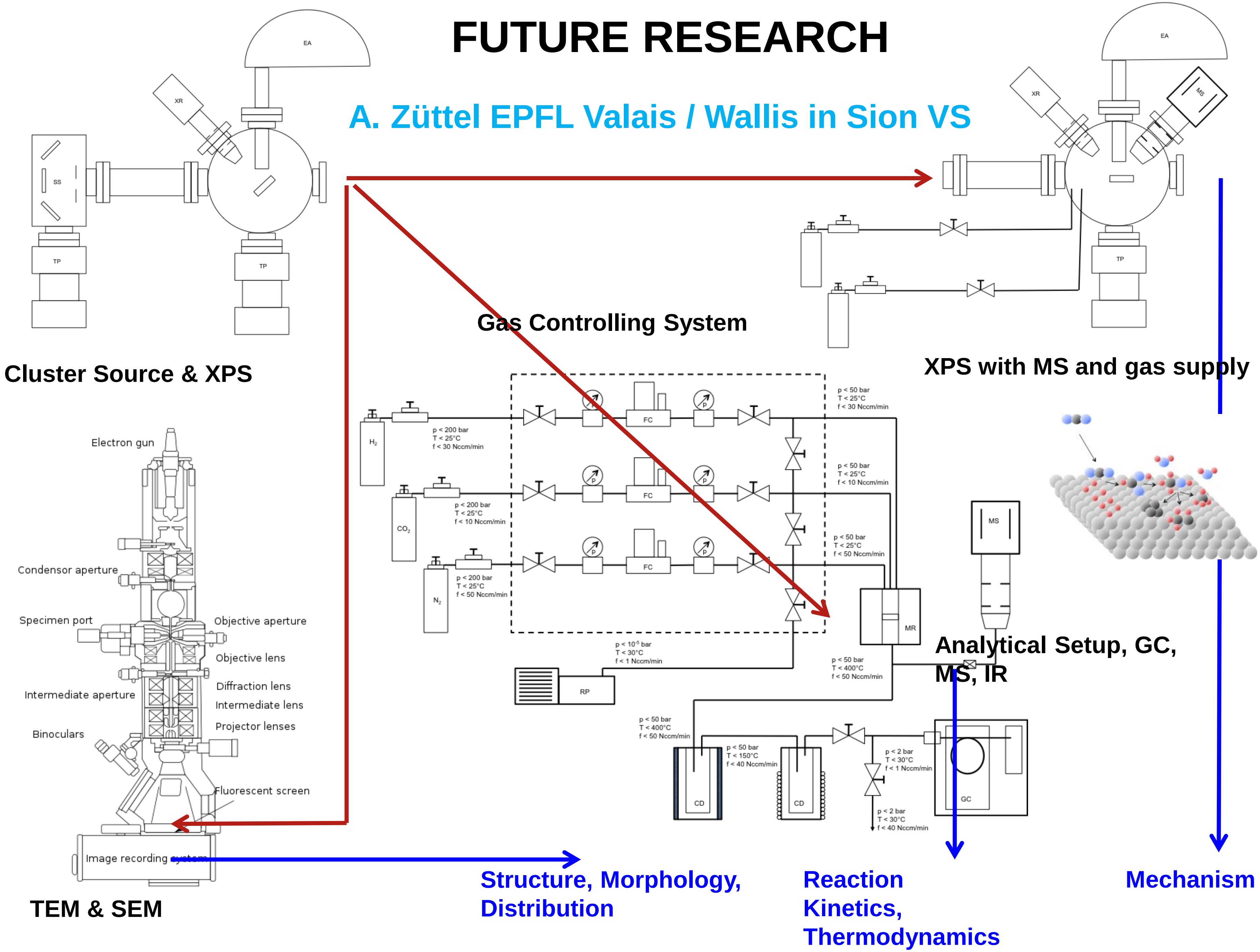
$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$

Sequestration

EMPA Materials Science & Technology

FUTURE RESEARCH

A. Züttel EPFL Valais / Wallis in Sion VS



"Power-to-gas" in der Schweiz