FH MÜNSTER
University of Applied Sciences

CIW FB Chemieingenieurwesen
Department of Chemical Engineering

United Nations Educational, Scientific and Cultural Organization

2019 IYPT International Year of the Periodic Table of Chemical Elements

The Elements: #1

Hydrogen

„Fuel of the Universe“

$^{2}H + {}^{3}H \rightarrow {}^{4}He + n + 17.59$ MeV

Latin: Hydrogenium

Greek: υδρογόνο

Living Document of the H_2-Cluster
FH Münster
University of Applied Sciences
Prof. Dr. Thomas Jüstel, Dpt. CE

Occurences

Universe	approx. 90% of all atoms, 9% He, 1% „metals“ approx. 75% of the total mass
Sun (spectral type G2V)	approx. 80% of all atoms approx. 50% of the total mass
Earth‘s surface	Oceans, earth‘s crust, atmosphere approx. 15% of all atoms approx. 0.9% of the total mass
Earth‘s body	almost exclusively in bound form water, hydrocarbons, biomass

Abundance of Hydrogen Isotopes

Planet Earth

^{1}H	light hydrogen	Protium	99.99 %
^{2}H (D)	heavy hydrogen	Deuterium	0.015 %
^{3}H (T)	superheavy hydrogen	Tritium (β-Emitter)	10^{-15} %

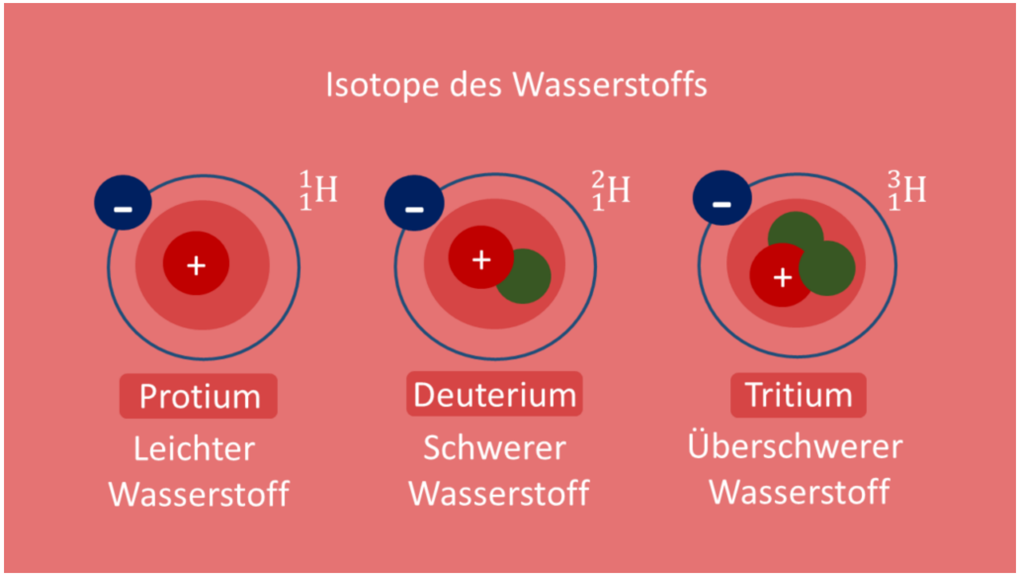
Formation of tritium in the higher atmosphere:

$$^{14}N + n \rightarrow {}^{3}H + {}^{12}C$$

$$^{3}H + OH\cdot \rightarrow {}^{1}H^{3}HO$$

Half-life:

$\tau_{1/2}(^{3}H)$ = 12.32 years



Production

a) In the lab $Zn + 2\,HCl \rightarrow ZnCl_2 + H_2$ $(2\,H^+ + 2\,e^- \rightarrow H_2)$
$CaH_2 + 2\,H_2O \rightarrow Ca(OH)_2 + 2\,H_2$ $(2\,H^- \rightarrow H_2 + 2\,e^-)$ comprop.

b) Technical $2\,H_2O \rightarrow 2\,H_2 + O_2$ (water electrolysis, SMR)
$CH_4 + H_2O \rightarrow 3\,H_2 + CO$ (steam reforming)
$C_{16}H_{34} + 8\,O_2 \rightarrow 16\,CO + 17\,H_2$ (partial oxidation, POX)
$C + H_2O \rightarrow H_2 + CO$ (coal gasification to water gas)
$C_nH_{2n+2} \rightarrow C_{n-1}H_{2n} + H_2 + C$ (thermal cracking of hydrocarbons)

Reactivity

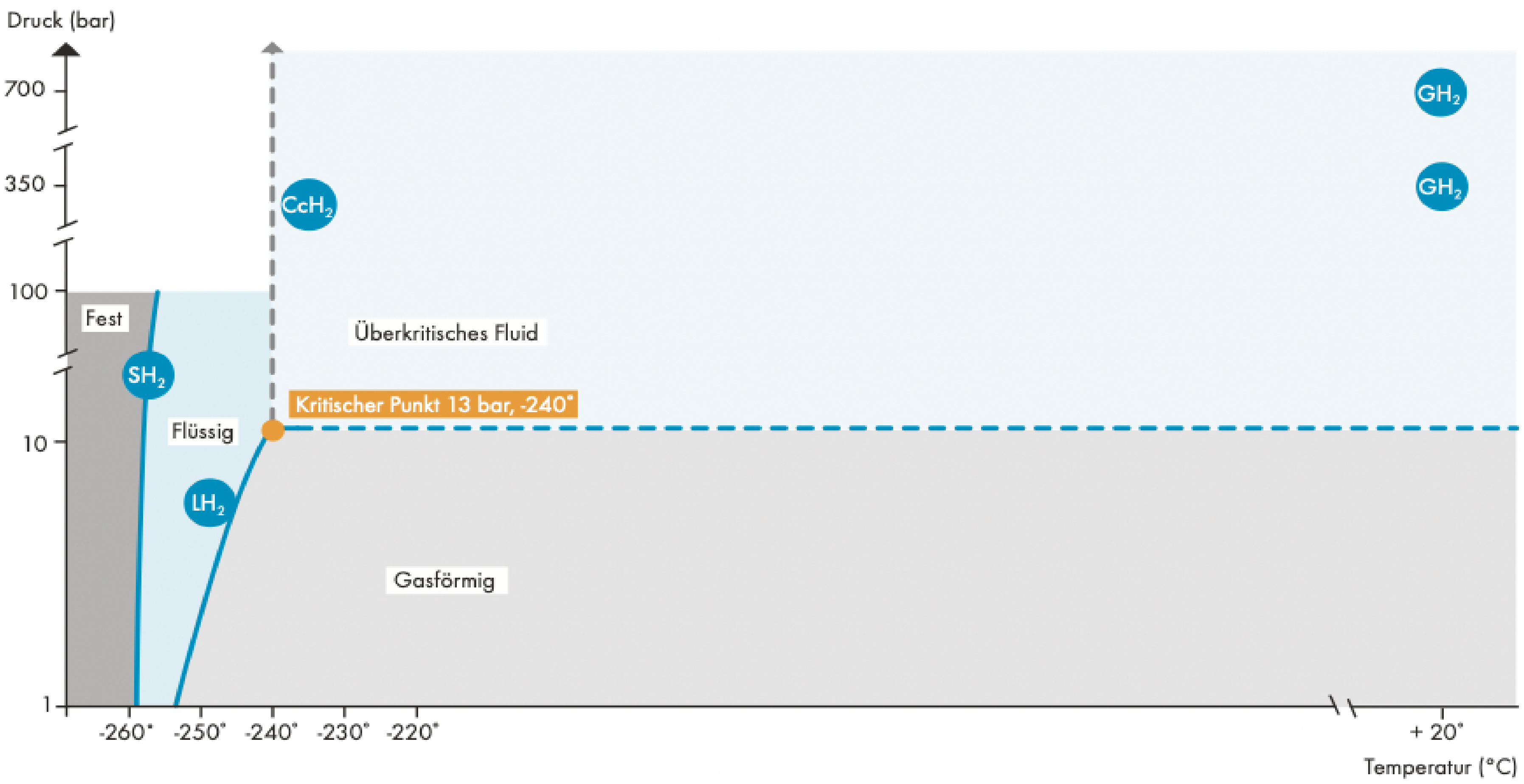
- Molecular hydrogen is inert at ambient temperature: $\Delta H_{diss.} = 436$ kJ/mol
- The strongly exothermic oyhydrogen reaction $H_2 + O_2 \rightarrow 2\,H_2O$ must be activated
  $\Rightarrow$ T > 400 °C, UV radiation, sparks, Pt catalysts, ...
- Atomic hydrogen is very reactive and reduces the oxides of „noble“ metals such as CuO, SnO_2, PbO and Bi_2O_3, to the metals
- Formation of H atoms: microwaves, electric arcs, about 8% dissociated at 3000 °C

Physical Properties

Relative atomic mass	1.0079 g/mol	
Atomic radius	52.7 pm („Bohr radius“)	
Electron configuration:	$1s^1$	
Electronegativity:	2.2 (Pauling)	
1st ionization energy	13.598 eV	
Oxidation states	+I, 0, -I (hydrides)	
Normal potential	0.0 V (zero point, as reference electrode)	
Melting point	-259.1 °C	
Boiling point	-252.0 °C	
Critical temperature	-234 °C	
Density at 273 K	0.0899 kg/m³	
Solubility in water	22 ml per liter of water at 0 °C, 1013 mbar	
Specific heat capacity	14304 J/kgK	
Thermal conductivity	0.1805 W/mK (highest of all gases)	
Isotopes	^1H (Protium)	stable
	^2H (Deuterium)	stable
	^3H (Tritium)	ß⁻-decay to ^3He

Physical Properties

T-p phase diagram of Hydrogen

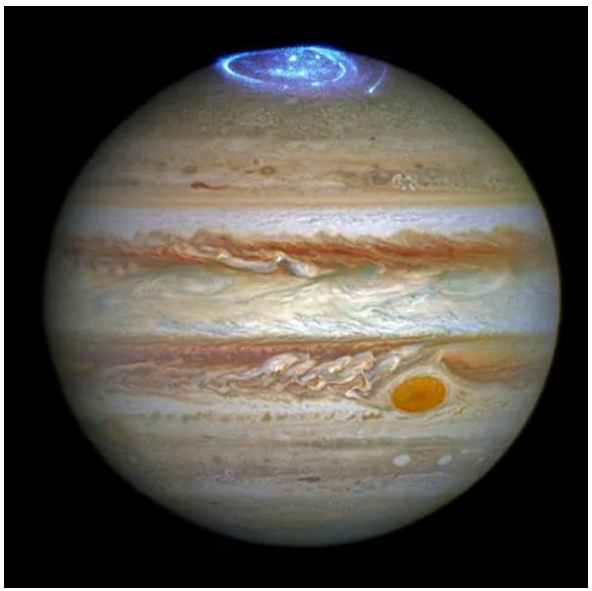


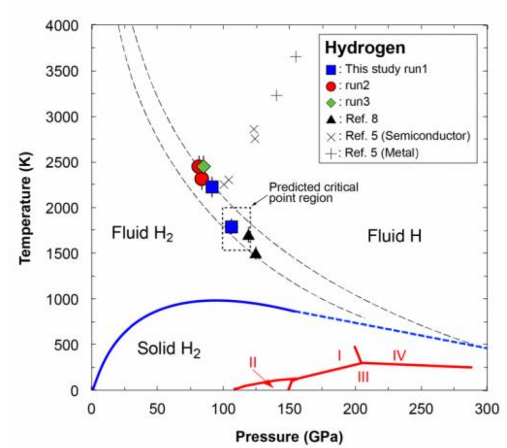
Physical Properties

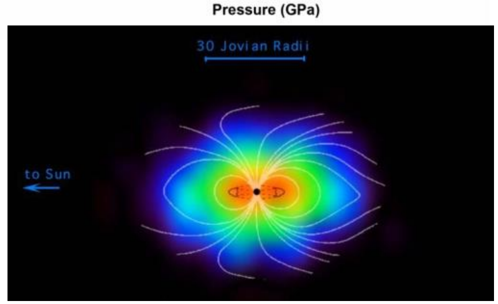
Solid Hydrogen

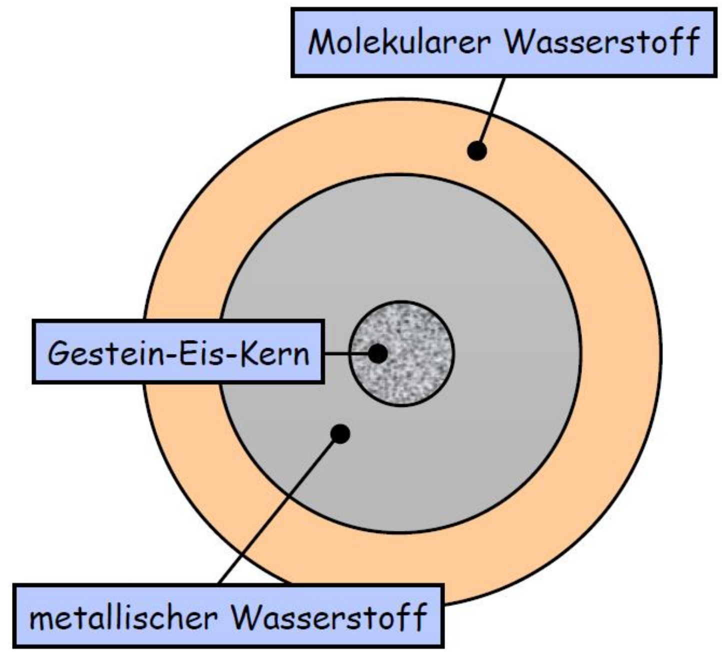
~ $1.1 \cdot 10^6$ bar ~ $1.5 \cdot 10^6$ bar

molecular (transparent, insulator) → molecular (electrically conductive) → atomic metal (superconductiong through metal hydrides: MeH_x?)









Jupiter
~ 318 Earth masses
~ 60 Jupiter radii magnetic field

Inner structure

Physical Properties

Thermal splitting of H_2 into radicals

Temperature [°C]	**1500**	**2000**	**3000**	**4000**	**5000**	**6000**
Fraction of neutral H	**10^{-3}%**	**0.08%**	**8%**	**62%**	**95%**	**99%**

„Colorimetry“

- **Green hydrogen** — **Through electrolysis with electricity from PV, wind and hydropower**
- **Gray hydrogen** — **Through steam reforming**
- **Blue hydrogen** — **Grey hydrogen, where the CO_2 is captured and stored stored**
- **Turquoise hydrogen** — **Through thermal decomposition of methanol**
- **Red hydrogen** — **Red hydrogen Through electrolysis with electricity from nuclear power plants**
- **White hydrogen** — **Through geochemical processes in reservoirs**

Physical Properties

Neutral Hydrogen H^0 (HI)

$1s^1 \rightarrow$ ground state: n = 1

Hyperfine structure transition at 21.11 cm (1.420 GHz) due to spin-spin-coupling

Predicted in 1944 by van de Hulst
Discovered in 1951 by Ewen & Purcell

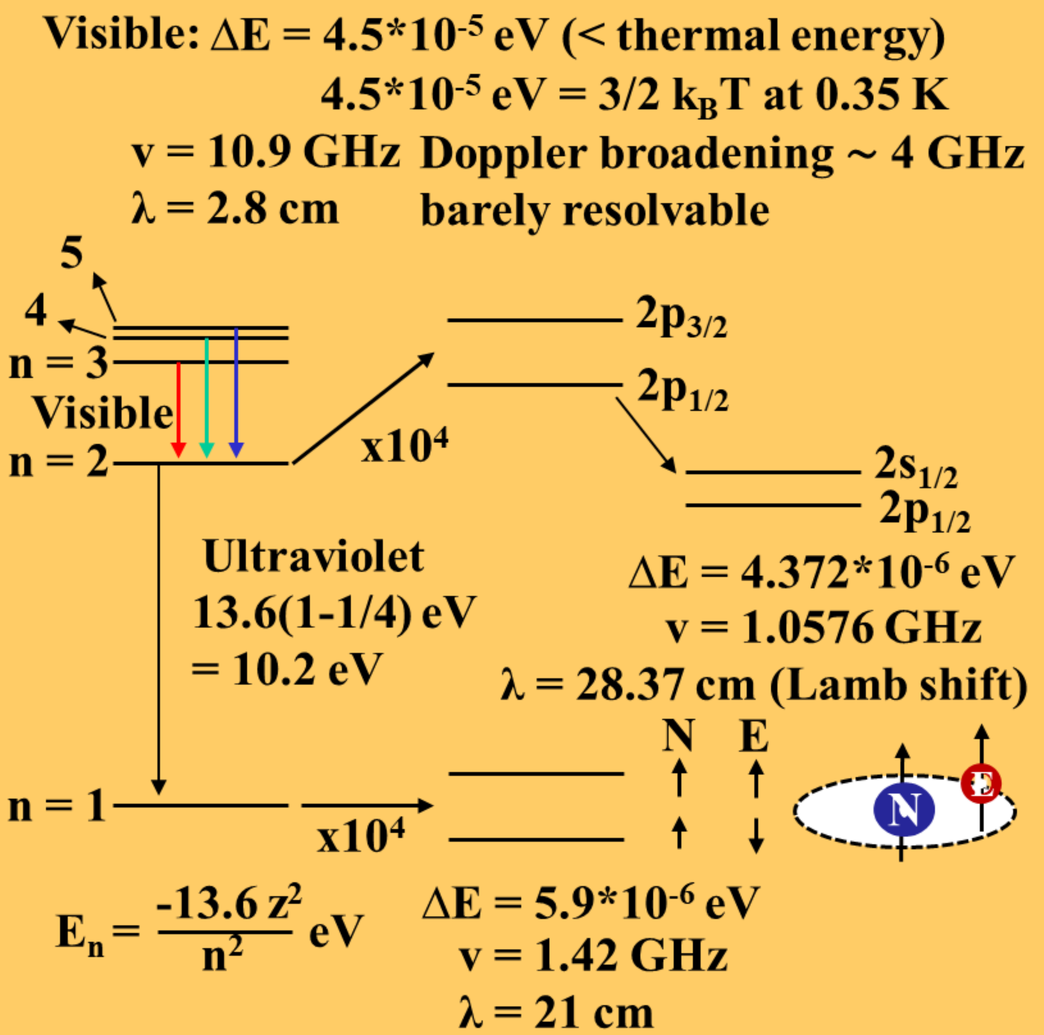
Used for distribution and kinematics of the neutral gas in the Milky Way

Fine structure transition (LS-splitting)
$^2p_{3/2} - {}^2p_{1/2}$ 28.37 cm (1.06 GHz)

Balmer series transitions in the VIS:

5-2	434.047 nm
4-2	486.133 nm
3-2	656.272 nm

Neutral Hydrogen (HI) energy levels



Physical Properties

Buoyancy due to the lowest density of all gases

$\rho(H_2)$ = 0.09 g/l = $M(H_2)/V_M$ compare to ρ(air) = 1.29 g/l

Buoyancy: ρ(air) - $\rho(H_2)$ = 1.2 g/l bzw. 1.2 kg/m^3

**→ First gas balloon by
Jacques Charles, December 01st, 1783 (Paris City Palace)**

Highest diffusivity v of all gases

$v \sim 1/(M)^{1/2}$

Effusion from containers and hydrogen diffuses relatively easily even through metals such as iron, platinum or palladium!

History

Discovery of Hydrogen — **Sir Henry Cavendish** — **1766**

- **Through the effect of sulphuric acid on metals**
- **Isolation of the gas and first description of its properties > "Flammable air"**
- **Reaction of hydrogen and oxygen produces water**

Naming — **Antoine Lavoisier** — **1783**

First electrolysis of water — **Paets van Troostwijk** — **1789**

Fuel cells — **Sir William Grove** — **1839**

„Galvanic gas battery"

Cold combustion of hydrogen and oxygen:

Anode: $2\,H_2 \rightarrow 4\,H^+ + 4\,e^-$

Cathode: $O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$

History

Solubility of Hydrogen in Pd	**Thomas Graham**	**1866**
Visionary prediction:	**Jules Verne**	**1870**

"Water is the coal of the future. The energy of tomorrow is water that has been decomposed by electric current. The elements of water broken down in this way, hydrogen and oxygen, will secure the earth's energy supply for the unforeseeable future.“

→ ***Photocatalytic water splitting is the primary energy process of the biosphere!***

Liquid Hydrogen	**James Dewar**	**1898**
Bohr's atomic model	**Nils Bohr**	**1913**
Atomic bond in the hydrogen molecule **1s - 1s σ bond**	**W. Heitler & F. London**	**1927**
Discovery of deuterium	**Harold Clayton Urey**	**1931**

History

Risks associated with the use of hydrogen: Flammable, explosive gas

Zeppelin LZ129 „Hindenburg“ explosion, Lakehurst, NJ		**May 6th, 1937**
Challenger explosion after take-off, Cape Canaveral, FL		**Jan 28th, 1986**
Installation of H_2 furnace „Hector“ FH Münster, Dpt. CE (T_{max} ~ 1850 °C: Accident free operation so far!)		**May 14th, 2008**
Superconductivity in LaH_{10} at 250 K	**M.I. Eremets**	**2019**
Superconductivity in C-S-H_2 at 288 K, 267 GPa	**R.P. Dias**	**2020**
Superconductivity in LuH_2:N at 294 K, 1 MPa	**R.P. Dias**	**2023**

Applications

Hydrogenations, reducing agents, fuel, ammonia synthesis & energy sources

1. Hydrogenation of C=C bonds ⇒ Hardening of vegetable oils (→ margarine), hydrotreating of crude oil: $R\text{-}CH{=}CH\text{-}R + H_2 \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}R$

2. Reducing agent ⇒ Metallurgy: Mo, W, Ge, Co, steel etc.
$WO_3 + 3\,H_2 \rightarrow W + 3\,H_2O$

3. Ammonia synthesis ⇒ Haber-Bosch process
$N_2 + 3\,H_2 \rightarrow 2\,NH_3$

4. Fuel for space probes and spacecrafts ⇒ Space Shuttle ⇒
liquid tank $2\,H_2 + O_2 \rightarrow 2\,H_2O$
solid rockets $8\,Al + 3\,NH_4ClO_4 \rightarrow 4\,Al_2O_3 + 3\,NH_3 + 3\,HCl$
steering rockets $2\,NO_2 + CH_3N_2H_3 \rightarrow 2\,N_2 + CO_2 + 2\,H_2O + H_2$

5. Energy source: precursor for synthetic fuels such as NH_3, N_2H_4, $CH_3N_2H_3$, methane, methanol, ethanol, triphenyltoluene (TPT), and so on

6. Methanol synthesis: $CO + 2\,H_2 \rightarrow CH_3OH$
$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O$

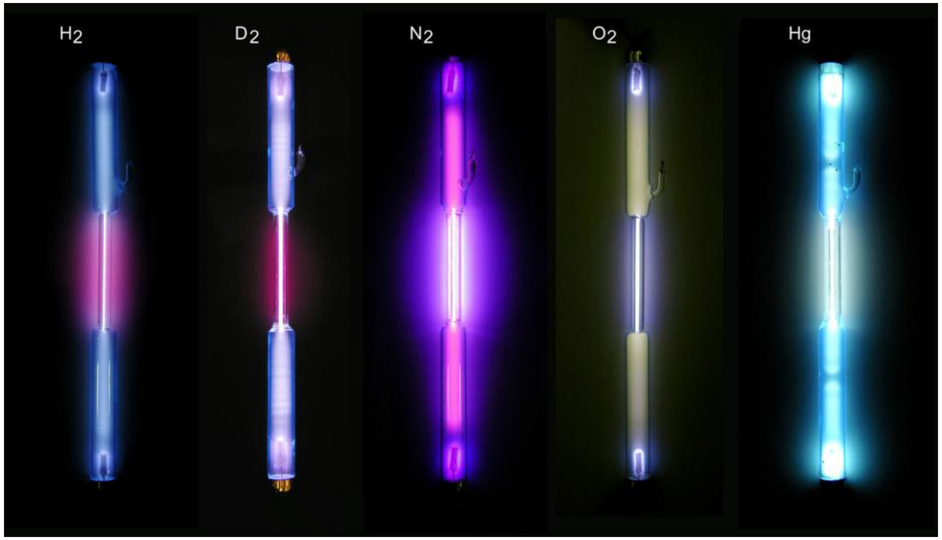
Applications

Energy source

• Autogenous welding	H_2/O_2	oxy-fuel gas blowers up to 3000 °C
• Fuel cells	H_2	60 MJ/kg at 50% efficiency
• Rocket engines	H_2	120 MJ/kg
• Aircraft turbines	Kerosene	43 MJ/kg
• Nuclear fusion (ITER)	D_2/T_2	72 TJ/kg (energy source of stars)

Light sources

- Hydrogen spectral lamp
- Deuterium lamps for VUV spectroscopy



Source: Wikipedia

Applications

Fuel cells

= galvanic cells that converts chemical reaction energy of a continuously supplied fuel and an oxidizing agent into electrical energy:

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$ + electrical energy

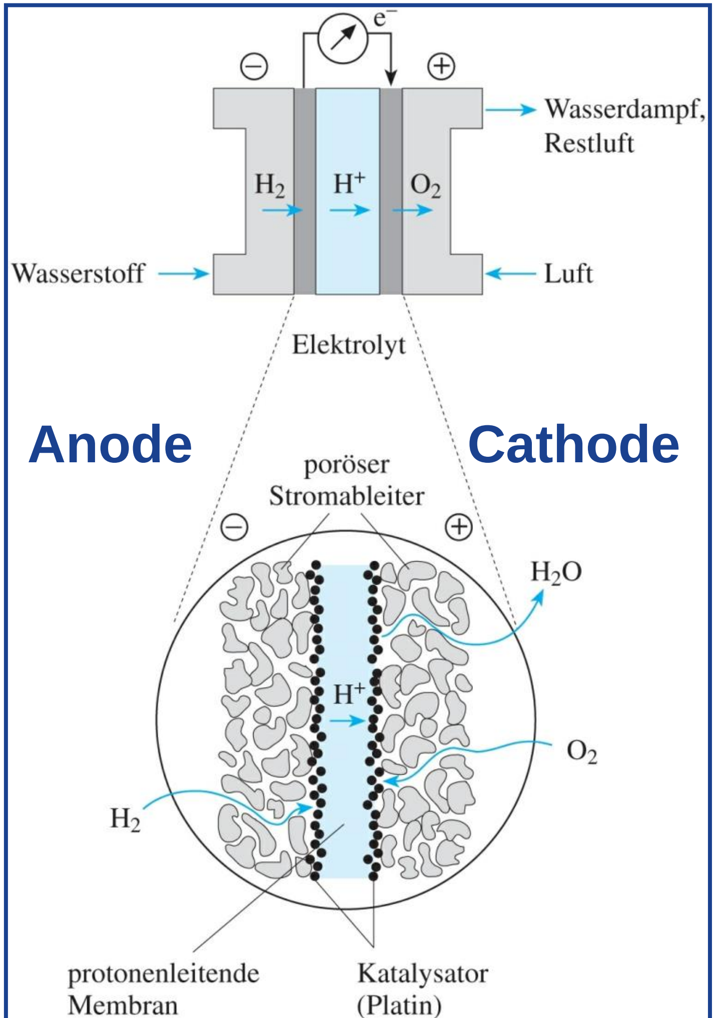
Anode: $H_2 + H_2O \rightarrow 2\ H_3O^+ + 2\ e^-$

Cathode: $1/2\ O_2 + 2\ H_3O^+ + 2\ e^- \rightarrow 3\ H_2O$

$\Delta_r H^0 = -572$ kJ/mol , U = 0.5 – 1.0 V

⇒ Decentralized energy generation + electric vehicles

Structure of a fuel cell



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung14-04.jpg

Hydrogen Storage as Hydrides

Motivation

- Safe storage
- Hydrogen densities as in the liquid or higher
- No loss during storage
- Storage is reversible

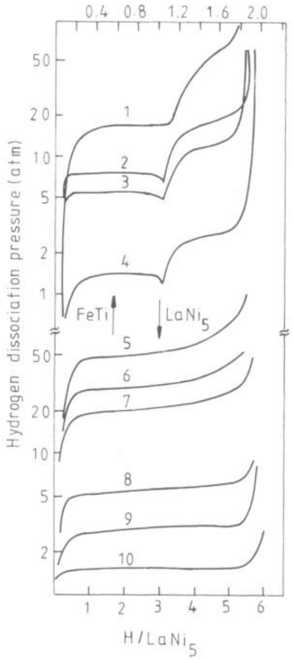
Requirements for hydride storage

- low mass
- fast kinetics for hydrogen absorption
- large reversible storage capacity
- exothermic hydrogenation reaction
- endothermic reverse reaction

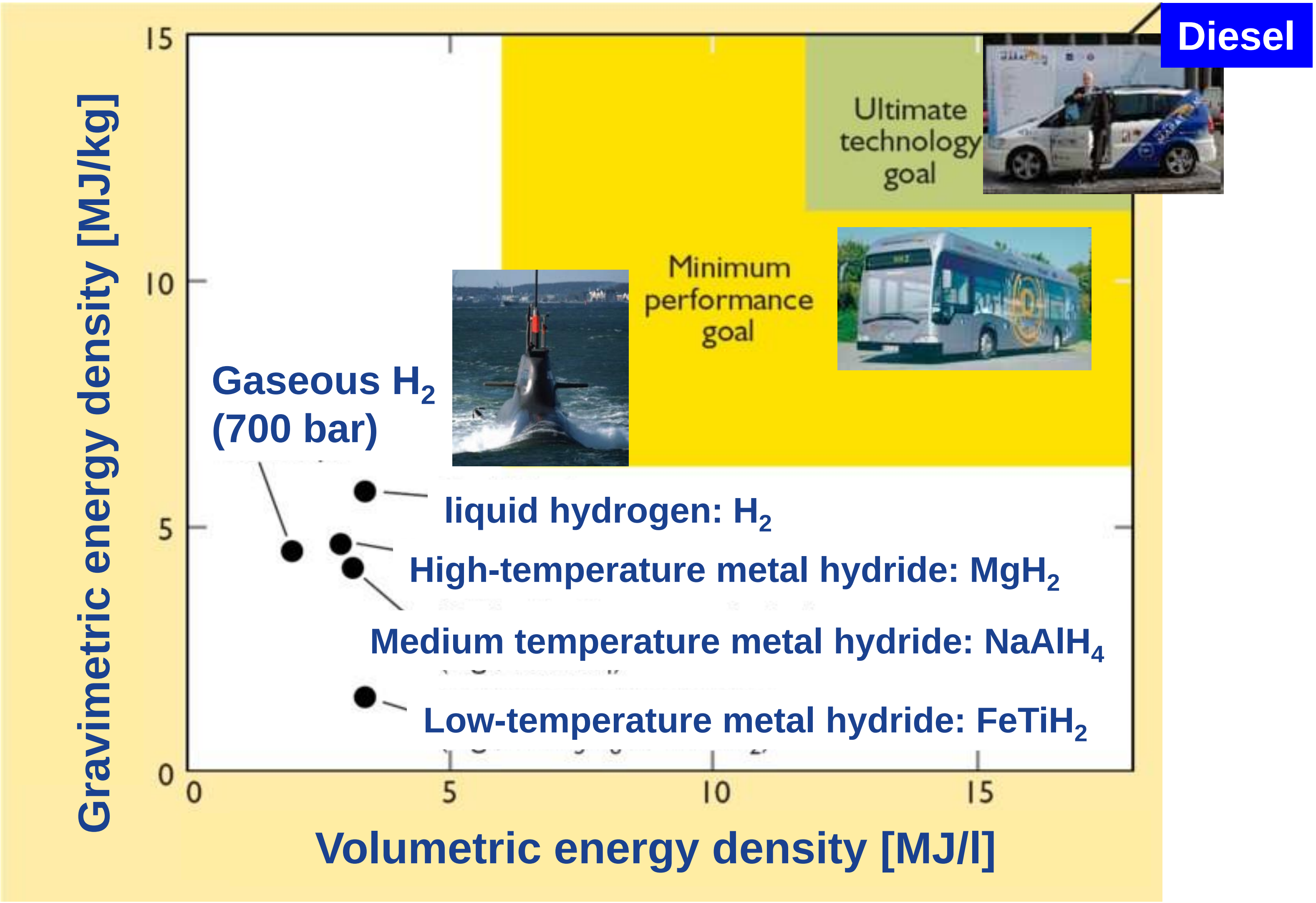
Examples

- Pd, V, Nb too low H_2 uptake
- Ti, Zr, SEE store large amounts of H_2, but almost irreversible reaction
- $LaNi_5$ ($CaCu_5$-type, P6/mmm) + 3 $H_2 \rightarrow$ $LaNi_5H_6$ (25% lattice expansion, P31m)
- FeTi (CsCl-type)

Figure 7.11. Pressure–composition isotherms of $LaNi_5$ hydride and FeTi hydride. 1, 343 K; 2, 313 K; 3, 303 K; 4, 273 K; 5, 413 K; 6, 393 K; 7, 373 K; 8, 333 K; 9, 313 K; 10, 293 K. (After Cohen & Wernick, 1981.)



Hydrogen Storage Status



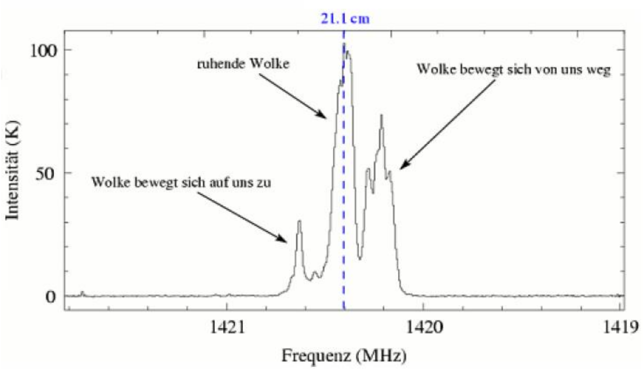
Analytics

› **Astronomy**

21.11 cm hydrogen line (1420.4 MHz)
HI emission line in radio astronomy:
- Gas temperature

- Magnetic field strength

- Structure and kinematics of galaxies/clusters



› **Biology & Chemistry**

^{1}H-NMR spectroscopy (nuclear spin ^{1}H: I = ±1/2):

- Structure elucidation of (bio)molecules

› **Electrochemistry**

Normal hydrogen electrode

- Reference electrode in CV, coulometry, and so on

› **Medicine**

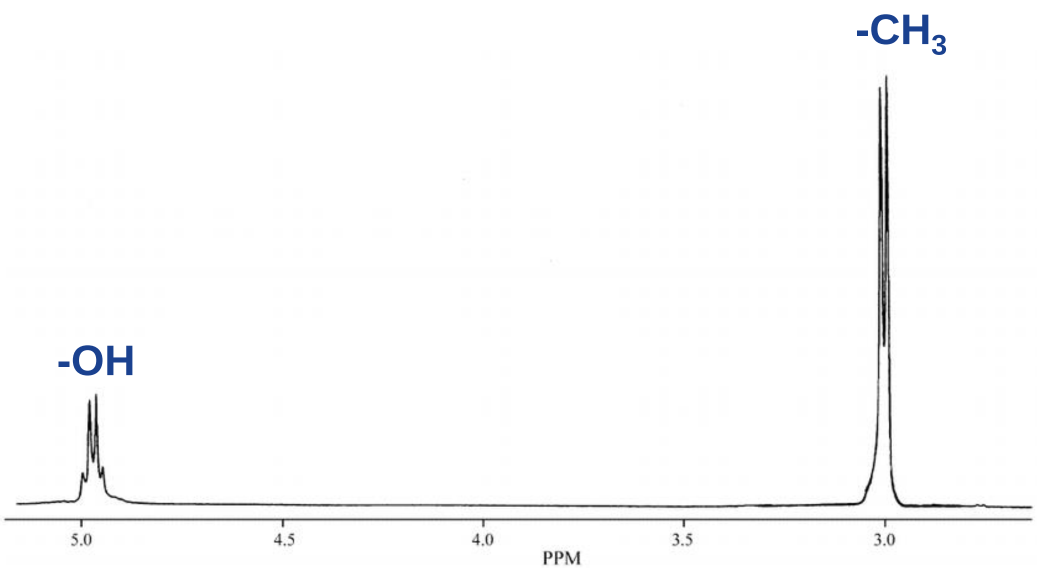
Magnetic resonance imaging (MRT, T1-Relaxation)

- Imaging in diagnostics

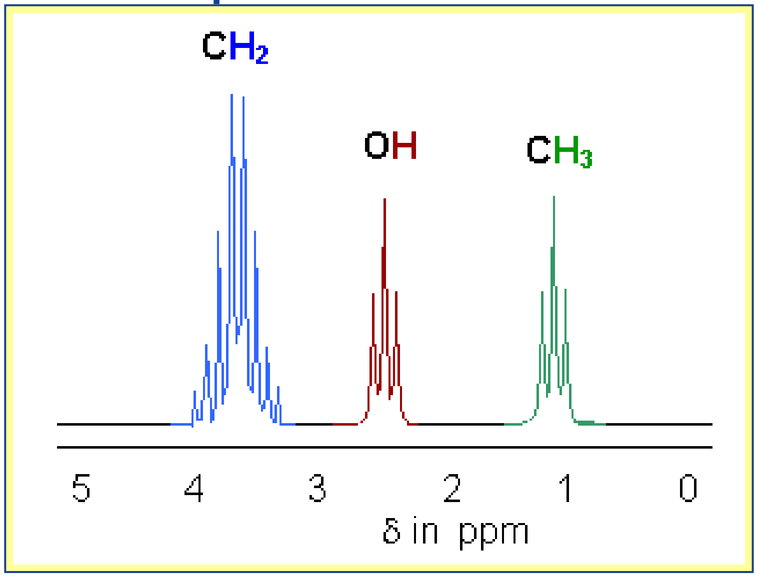
Analytics

^{1}H-NMR Spectroscopy

^{1}H-NMR spectrum of methanol at 253 K



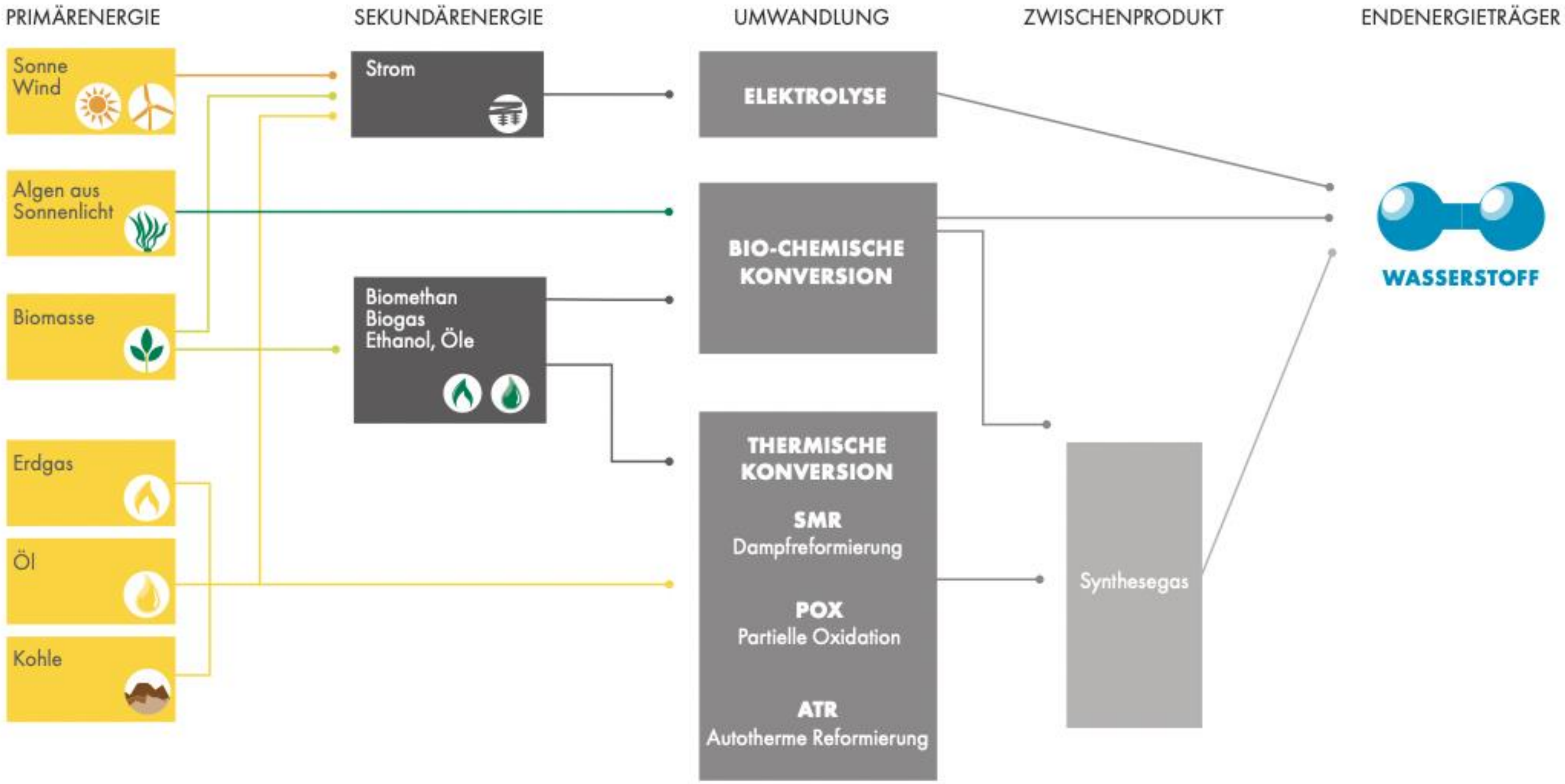
^{1}H-NMR spectrum of ethanol at 77 K



1. Each type of proton gives its own NMR signal, here 2 or 3 types
2. NMR signals split into M lines through interaction with the neighboring protons: M = (n+1)*(m+1) with n, m = number of equivalent adjacent protons

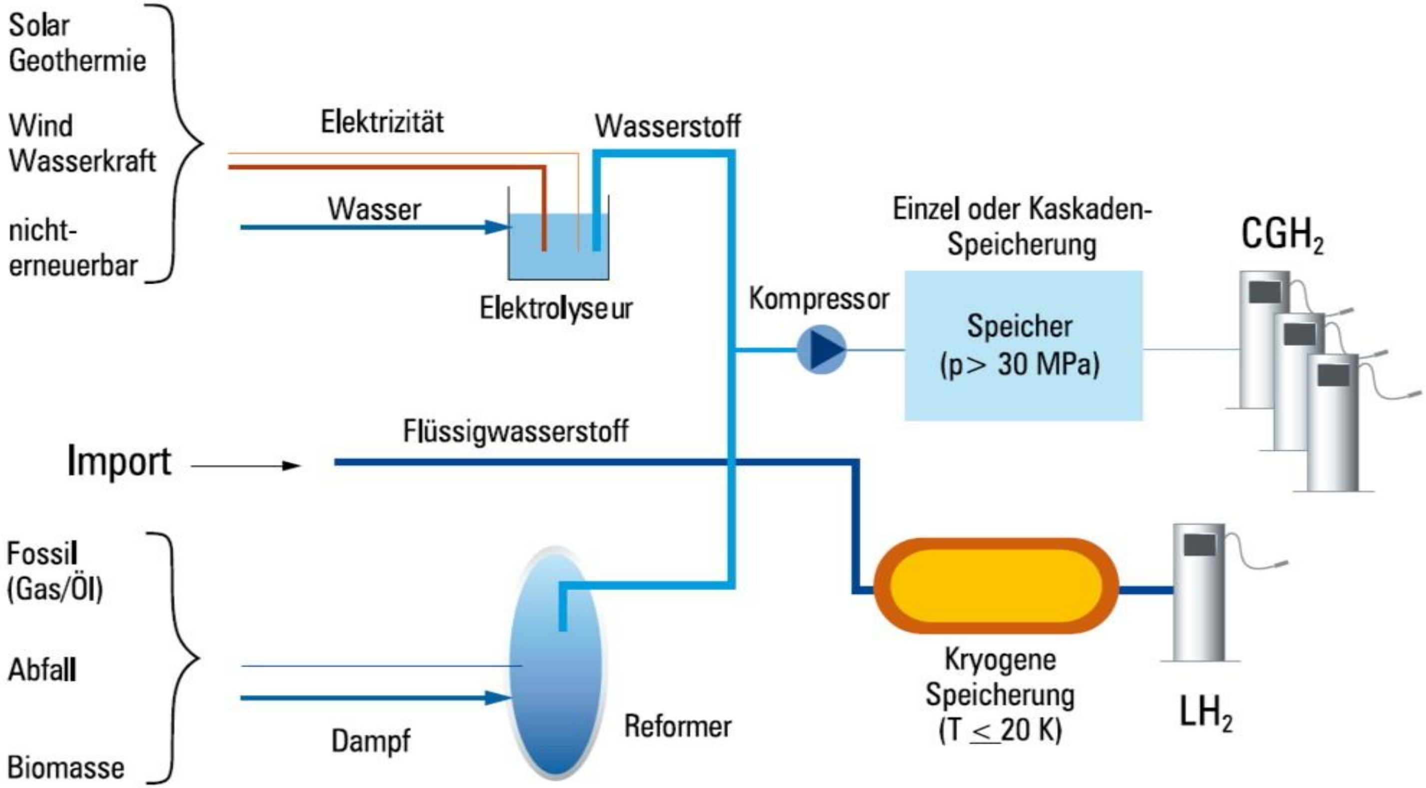
Hydrogen Production (Overview)

Ref.: J. Adolf, C. H. Balzer, J. Louis, U. Schabla, M. Fischedick, K. Arnold, A. Pastowski, D. Schüwer, Shell Wasserstoffstudie, Energie der Zukunft?, Hamburg, 2017



Hydrogen: Unde venis – Quo vadis?

Source: Deutscher Wasserstoff- und Brennstoffzellenverband „Woher kommt die Energie für die Wasserstofferzeugung - Status und Alternativen“: http://www.hyweb.de/Wissen/docs2006/DWV_Woher-H2_NOV2006.pdf



Hydrogen through Steam Reforming

48% H_2 worldwide from natural gas, methane (CH_4)

$$CH_4 + H_2O \rightarrow CO + 3\,H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

→ High energy consumption and CO_2-formation

Advantage: centralized production enables CO_2 sequestration or carbon capture and storage (CCS)

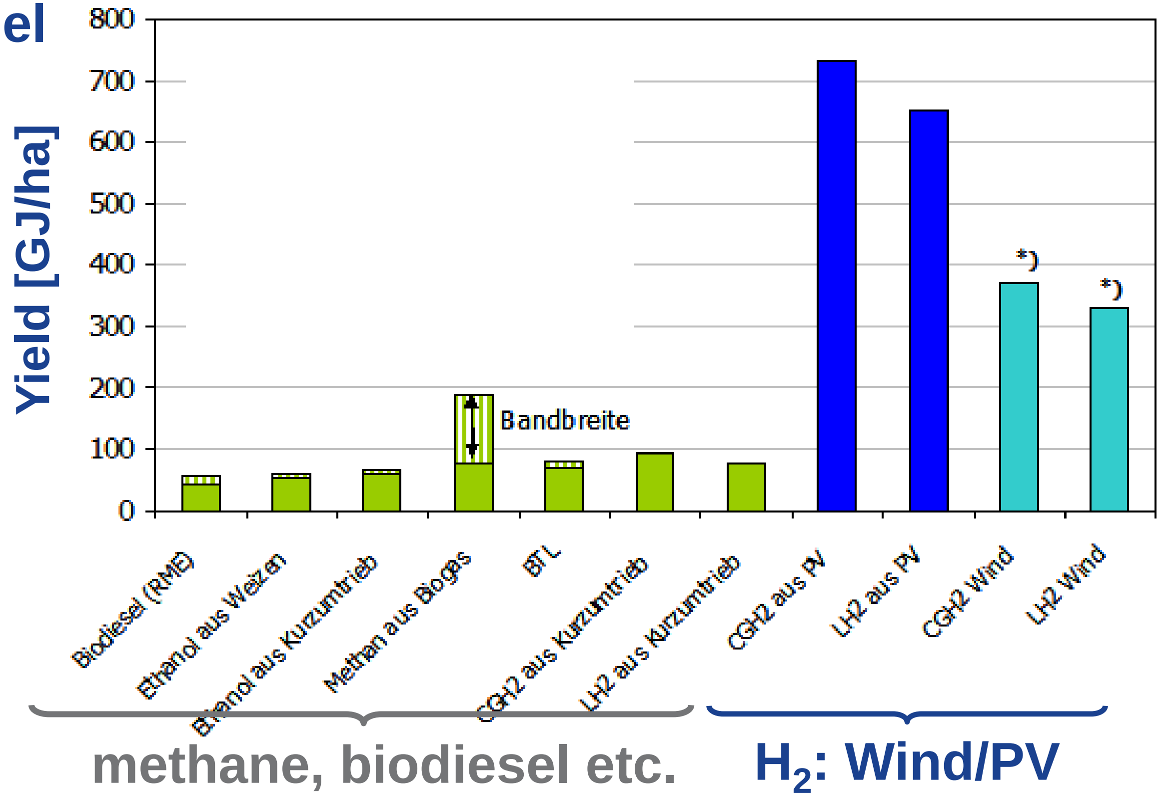
R&D: New catalysts for microreformers

Steam reforming plant in Brunsbüttel (Linde AG)

Hydrogen from Biomass

Study by Ludwig Bölkow Systemtechnik GmbH 2007

If you produce hydrogen from photovoltaic or wind power plants on a field instead of producing biofuels on the same area, you get about 10 times more fuel



Source: http://www.hyweb.de/Wissen/docs2007/LBST-Analysis_Biofuels-vs-H2-wind-PV-yield_09OCT2007.pdf

Electrolytic Hydrogen Production

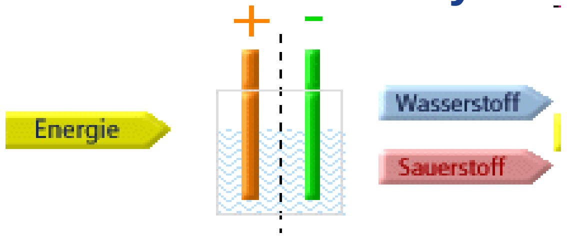
Total reaction: $2\ H_2O \rightarrow O_2 + 2\ H_2$

OER (Anode): $4\ OH^- \rightarrow O_2 + 2\ H_2O + 4\ e^-$

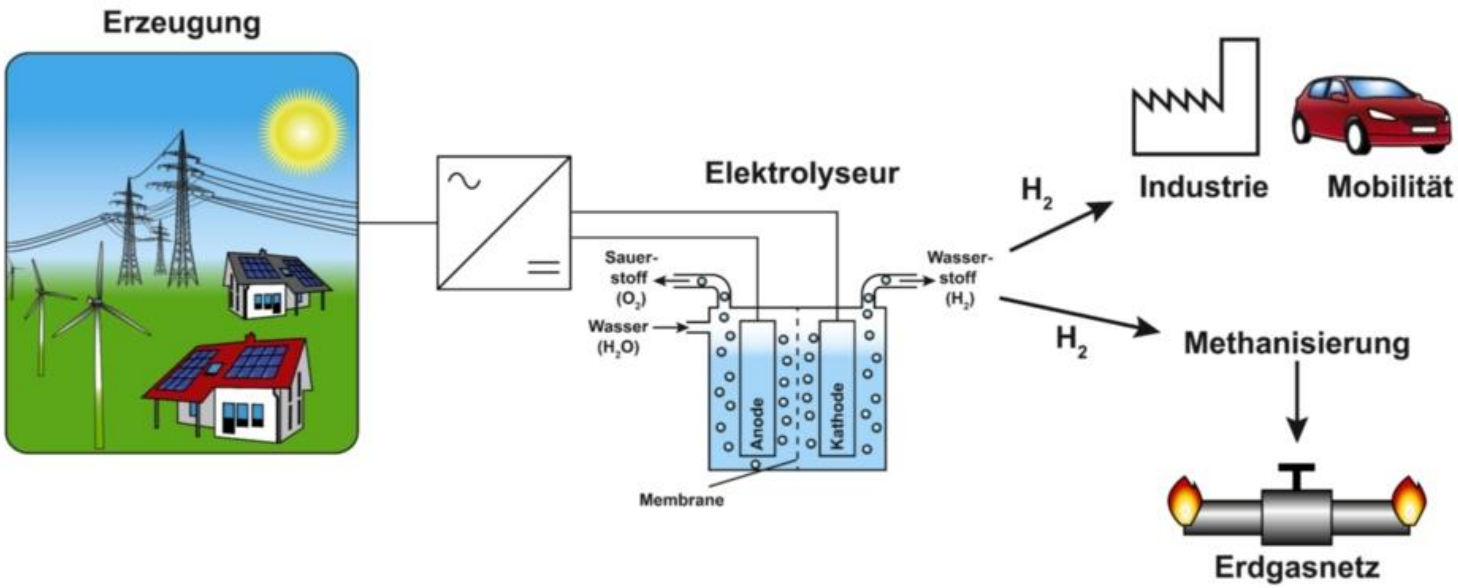
HER (Cathode): $4\ H_2O + 4\ e^- \rightarrow 4\ OH^- + 2\ H_2$

Efficiency: 60 – 85%

PEM water electrolyzer



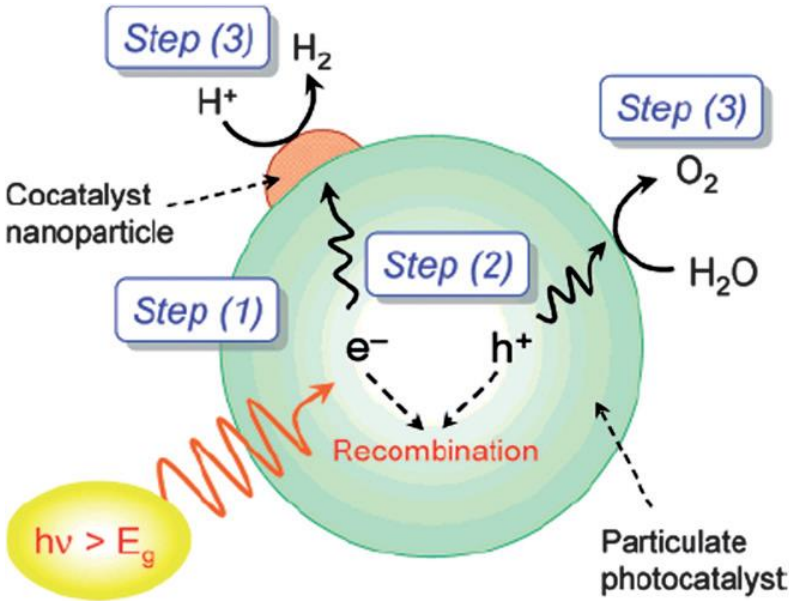
Process: Alkaline electrolysis, membrane electrolysis, HT vapor electrolysis

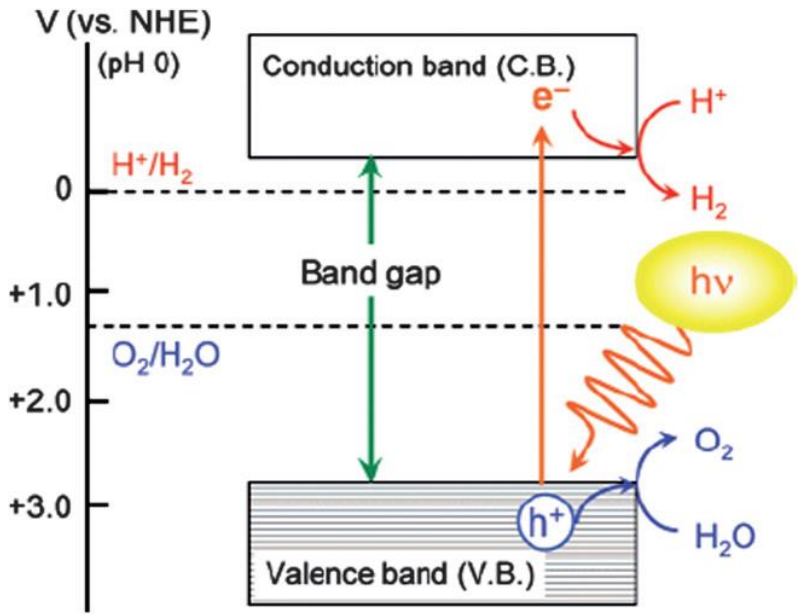


Solar Hydrogen Production: Photocats

First system demonstrated in 1971 → TiO_2 with Pt as co-catalyst
Ref.: A. Fujishima and K. Honda, Nature 238 (1972) 38

Water splitting theoretically possible from approx. 1000 nm (1.23 eV), in real systems the required energy is 690 nm (~1.8 V) due to overvoltage caused by interface effects





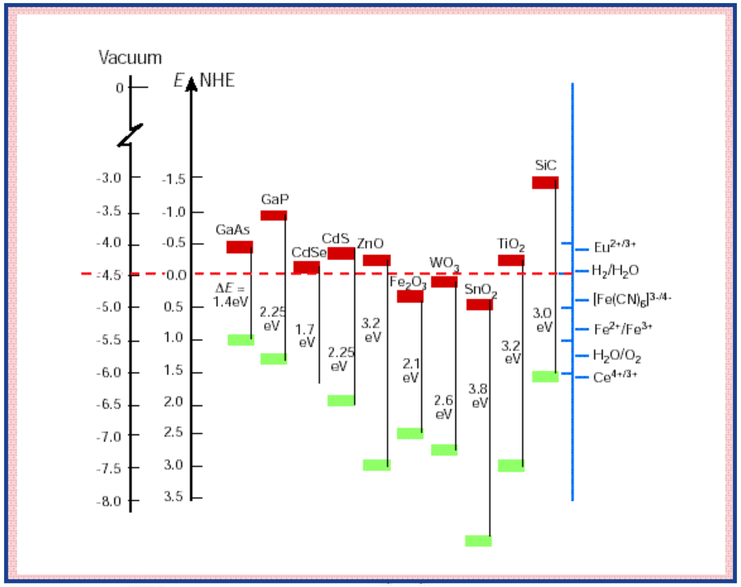
Solar Hydrogen Production: Photocats

Boundary conditions for inorganic materials

Band gap 2.0 – 3.0 eV

VB ~ -6.0 V below vacuum level

CB ~ -4.0 V below vacuum level



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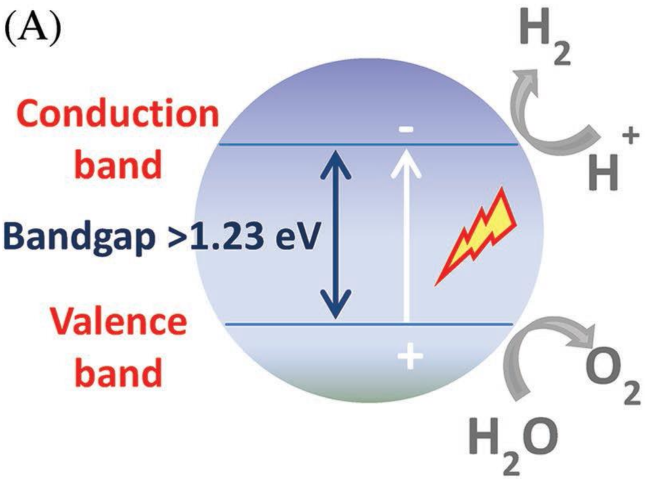
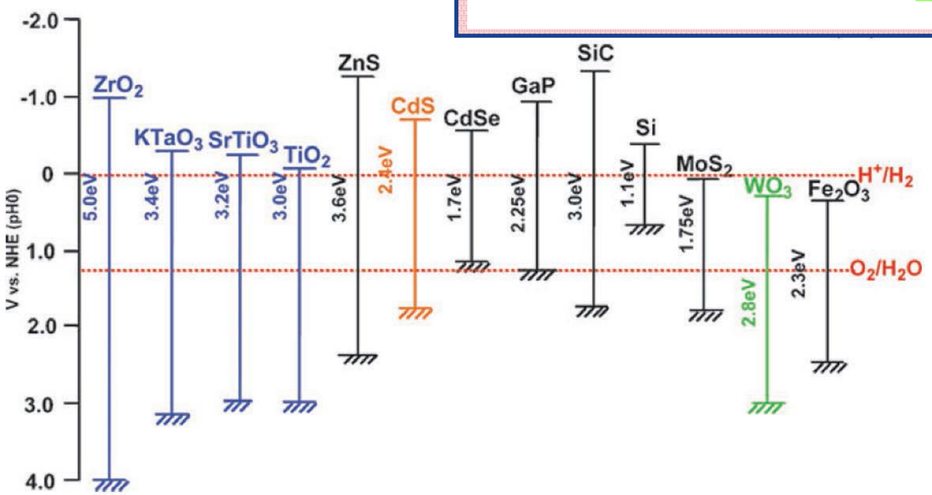
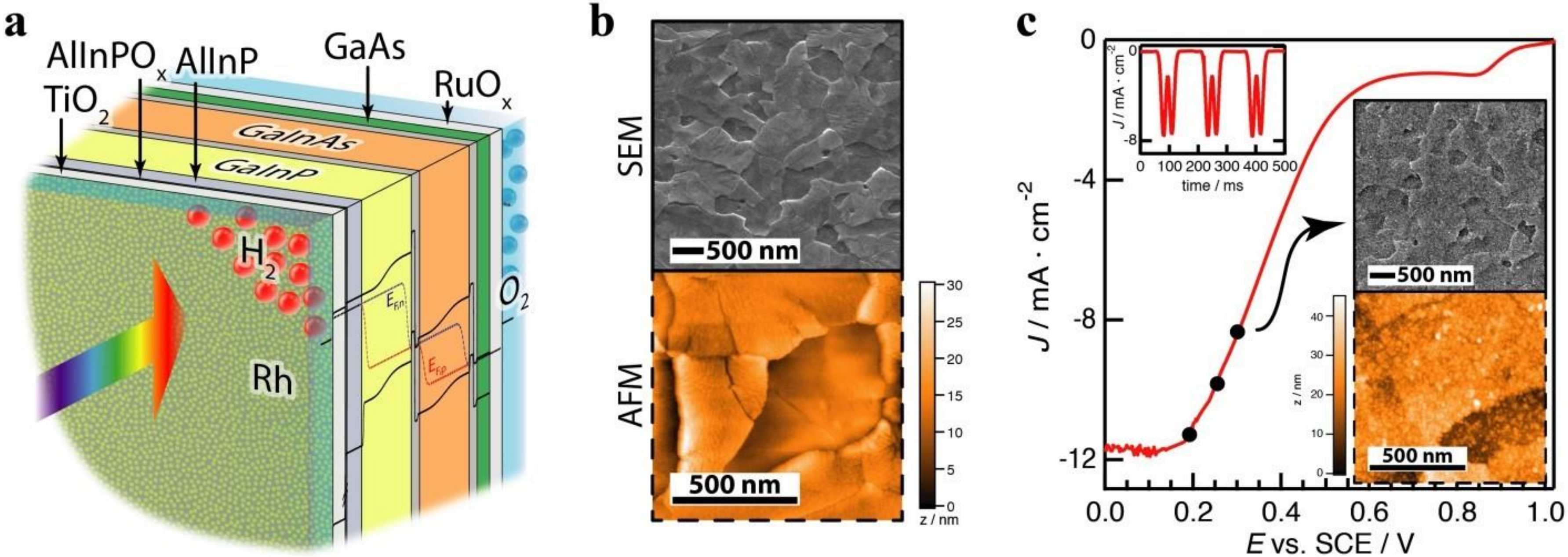




Solar Hydrogen Production: Record

Ref.: ACS Energy Letters 3 (2018) 1795, „Monolithic Photoelectrochemical Device for Direct Water Splitting with 19% Efficiency"



Cathode: Rh $2\ H^+ \rightarrow H_2\uparrow$

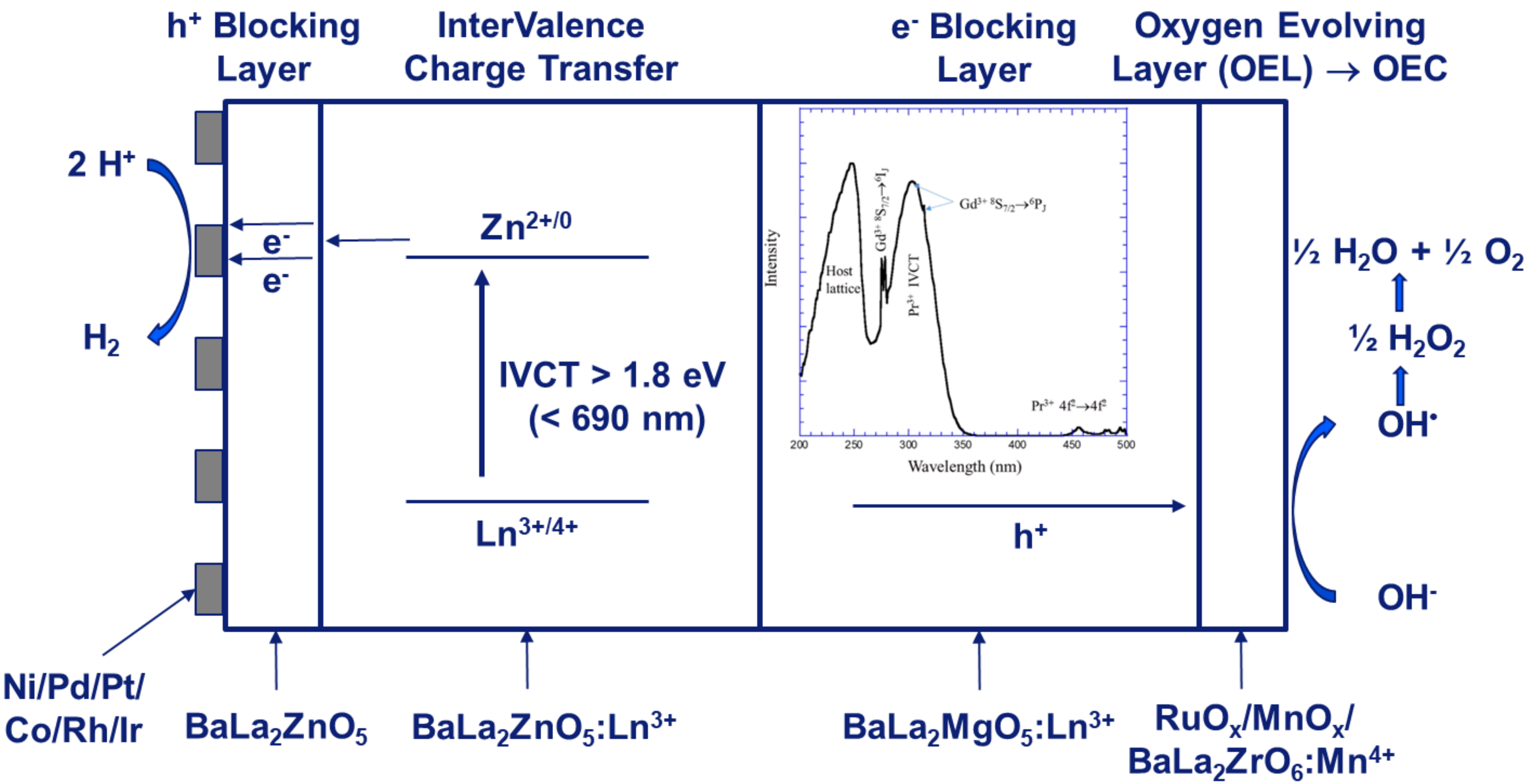
Anode: $Ru^{II/III/IV}O_x$ $2\ OH^- \rightarrow O_2 + 2\ H^+ + 4\ e^-$

Problems: Stability of electron & hole conductors (Ga,In)(P,As) → PH_3, AsH_3

Absorption edge of TiO_2 ~ 3.2 eV

Solar Hydrogen Production: Ceramics

Composite ceramic perovskites → $Ba_2La(Mg,Zn)O_5:Ln^{3+}$ (Ln = Ce, Pr, Tb)



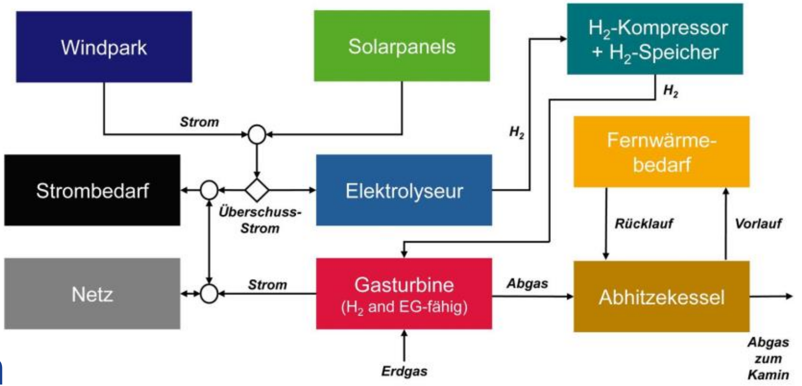
Summary

Hydrogen is the primary energy fuel in the universe

- Fusion of hydrogen to helium and metals (up to about Fe/Ni) in the stars provides energy for billions of years
- Fusion products: Heat + light + the elements of the periodic table

Hydrogen is an important reducing agent in the chemical industry and metallurgy

- Basis of ammonia and fertilizer production
- The future of steel production

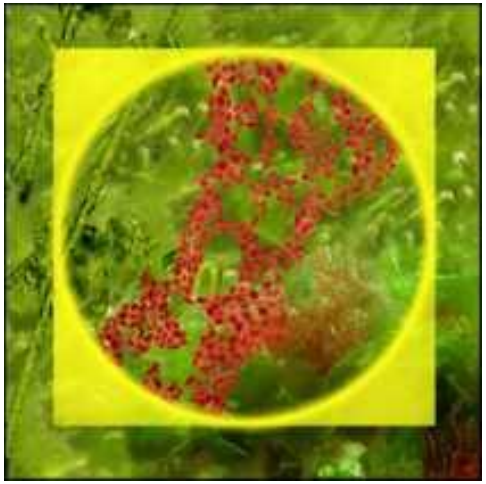


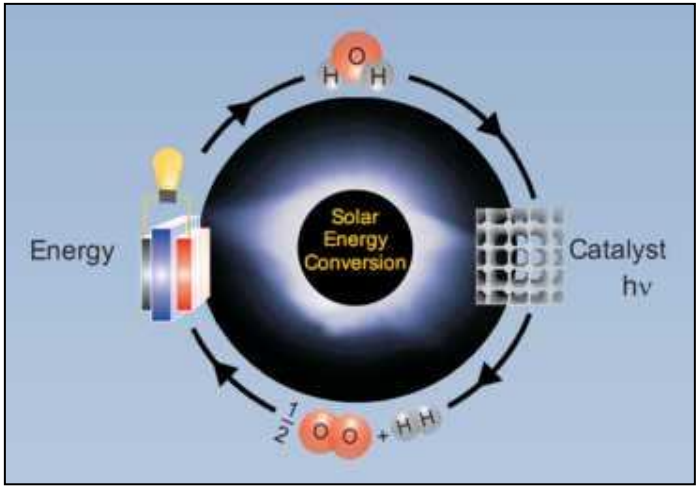
Hydrogen is the energy carrier of the future

- Fuel cells: Electricity generation
- Gas turbines: Electricity and heat generation
- Hydrogen combustion engines: Mobility
- Fusion reactors: Central power and heat generation

Outlook

Hydrogen as the basis of a global energy economy without polluting the earth's atmosphere with greenhouse gases (Ergo: entropy neutral!)





Photobiological H_2 generation with $[Mn_4Ca]^{n+}$-Cluster approx. 1 billion years development time

Photocatalytic H_2 generation with inorganic oxides R&D for about 50 years

Proposal: New global Manhattan Project of the 21st century

→ H_2 photoreactors as a "weapon" against the climate crisis

Let solar light do the job (Science 315, 2007, 789; PNAS 103, 2006, 15729)

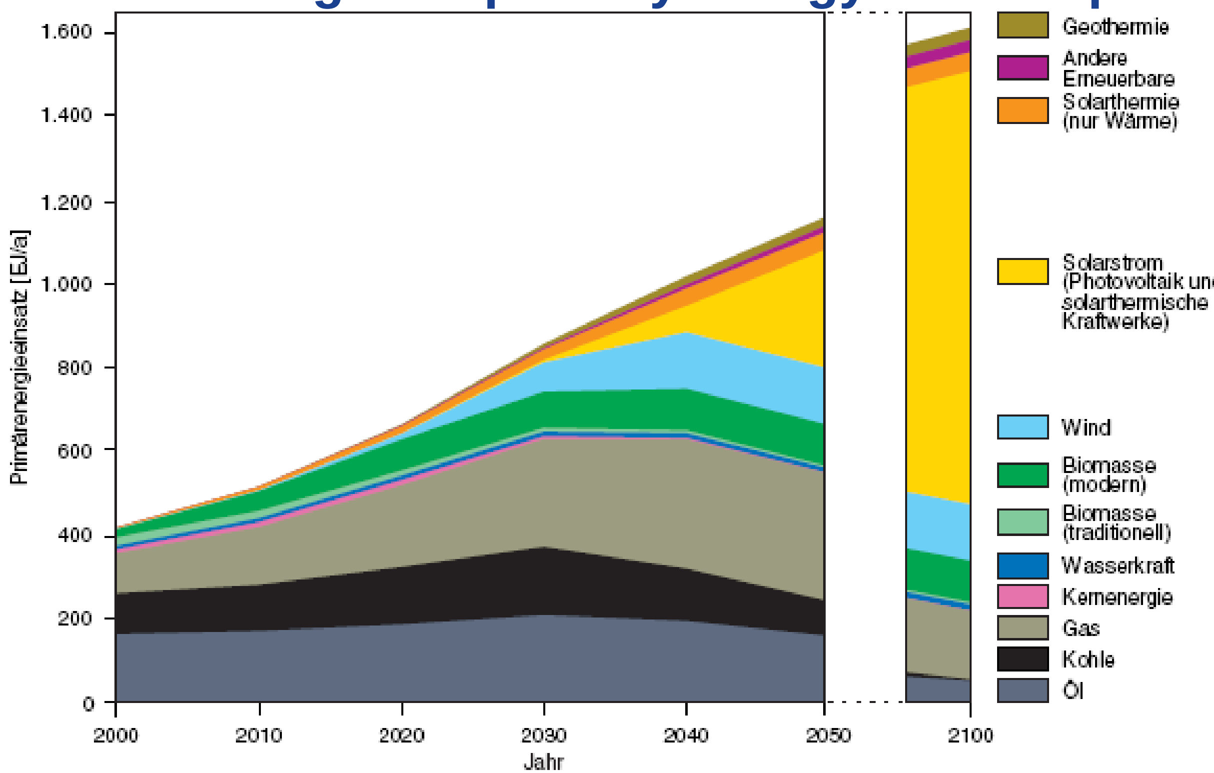
Outlook

„Its time to act“

Date	Daily CO_2
April 2013	398 ppm
April 2022	420 ppm
April 2023	423 ppm
April 2024	427 ppm
AGR	~ +4 ppm/y
April 2033	~ 463 ppm
April 2053	~ 550 ppm
April 2100	~ 750 ppm

~ 2 °C goal with a 50% probability no longer achievable

Increase in global primary energy consumption



2000: 400 EJ/a → 2015: 580 EJ/a → 2100: 1200 EJ/a

References

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