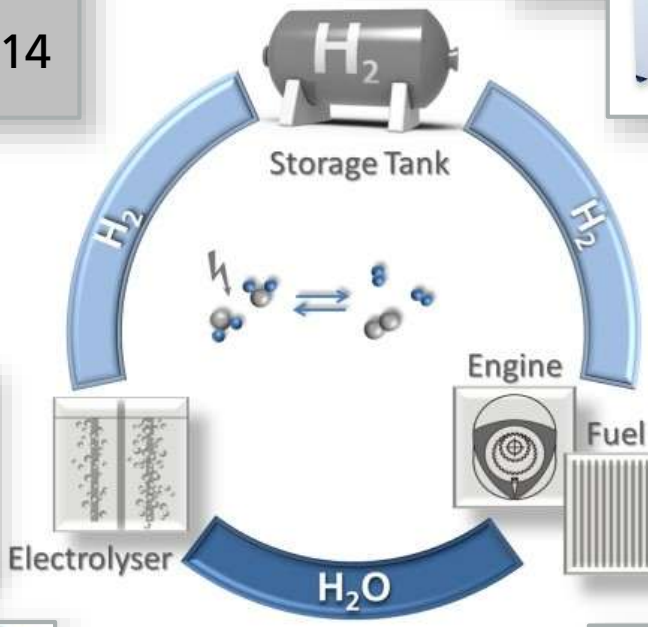
Innovative Materials & Manufacturing Technologies for H_2 Production and H_2 Storage

Dr. Lars Röntzsch
Berlin, 24 June 2014



Fraunhofer
IFAM

Fraunhofer-Gesellschaft

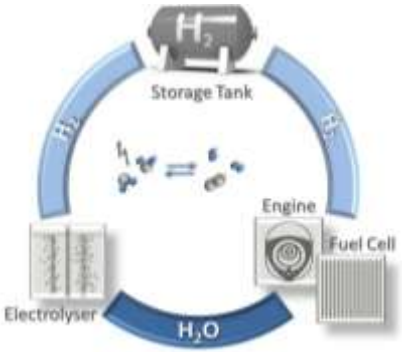
- largest organization for applied R&D in Europe
- 67 institutes at 42 locations in Germany
- affiliated international research centers
- about 23,000 employees
- annual budget:
  - > 2 bn. EUR
  - 1.7 bn. EUR via contract research

Fraunhofer IFAM

- about 400 employees
- budget: 43 million EUR p.a.
- 4 locations:
  Bremen, Dresden, Oldenburg, Stade

Fraunhofer IFAM Branch Lab Dresden

Hydrogen Technology @ Fraunhofer IFAM

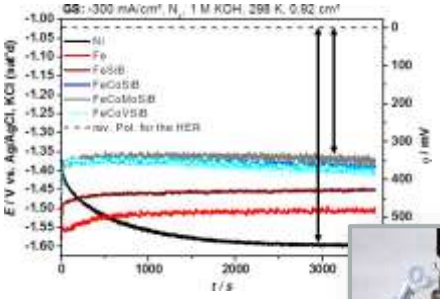


1 1.0079
H
HYDROGEN

density (0°C):
90 g/m³
boiling point:
-253°C

Electrolysis

- Nanocrystalline electrodes with reduced overvoltage
- 3D electrodes
- Cell design & testing

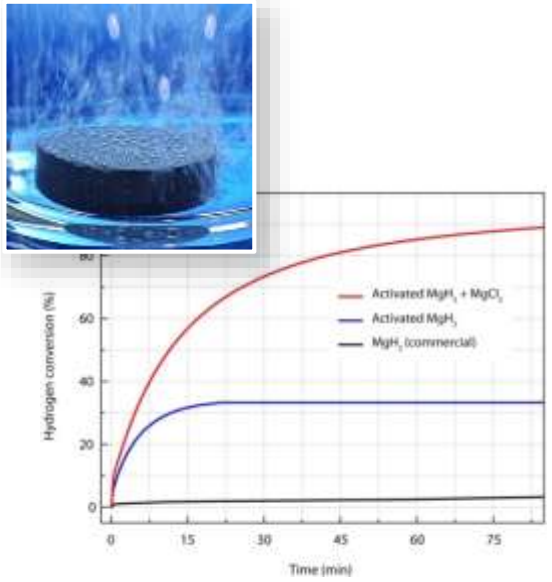


Solid H_2 Storage

- Hydrides (absorption)
- MOFs (adsorption)
- Matrix Composites
- Processing technologies
- Tank development

Hydrolysis

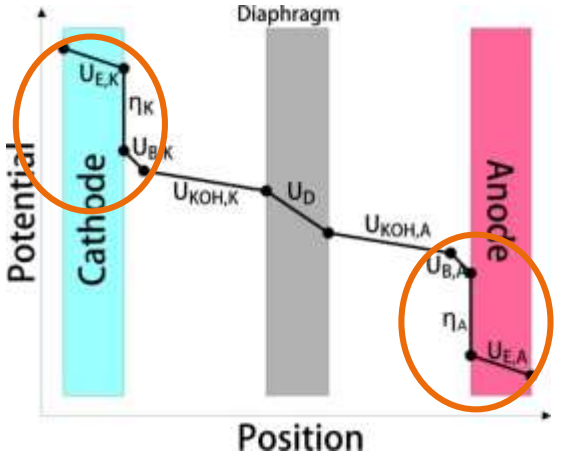
- Simple & robust on-demand H_2 generation
- Reaction control by additives
- 100% conversion in 90 min



Fraunhofer IFAM Branch Lab Dresden

Electrode Materials for AEL

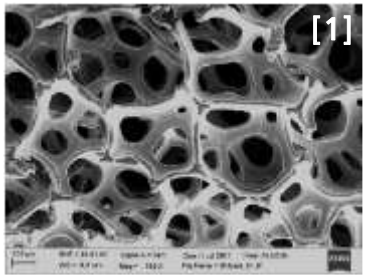
- **Low Voltage** at a **High Current Density**
  - ↳Energy
  - ↳H_2 production rate
- Demands
  - **Stability**
    - Degradation < 3 µV/h*
    - Life-Time Stack > 90 000 h (10 a)
  - **Electrochemical Activity**
    - Cell-voltage 1.8 – 2.2 V (< 0.6 A/cm²)*
  - **Costs**
    - Investment costs AEL system < 1000 €/kW_{el}*
  - **Corrosion Resistance**
    - Depends on the mode of operation
  - **Active Gas Bubble Management**
    - Hierarchically structured electrodes

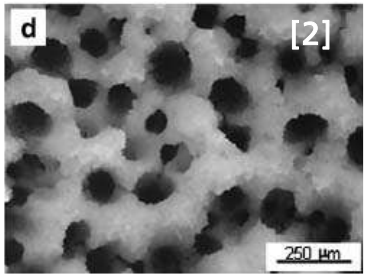


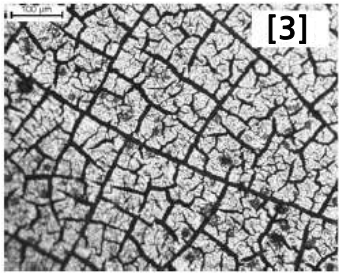
*Smolinka et al., NOW Studie, 2011.

Electrode Materials for AEL

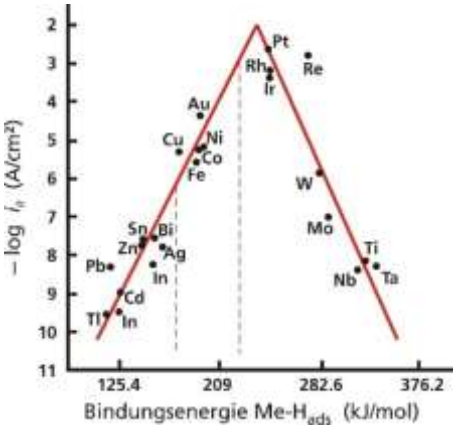
- Two issues have to be considered
  - High surface area → High density of reaction sites
    - Roughened and porous structures: Raney-Ni, 3D-Foams, 2D-Meshes …







  - Highly reactive surface species → Low excess energy for the H_2 and O_2 evolution reaction
    - Depends on electrode material: Pt, Ni, NiMo, NiCo, FeCo …

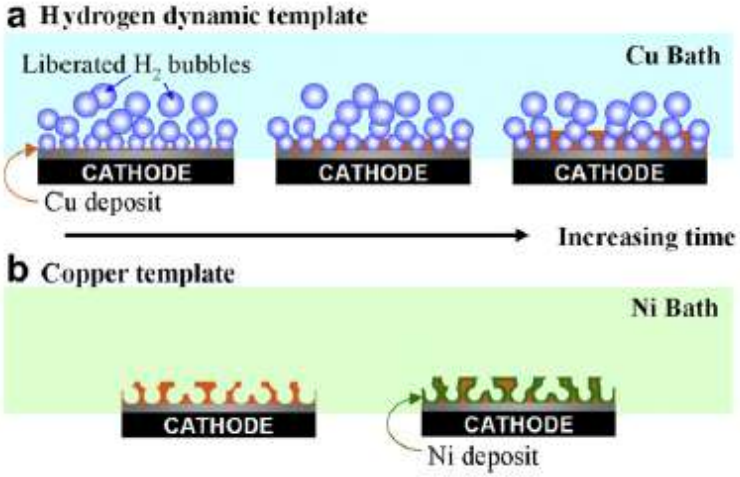


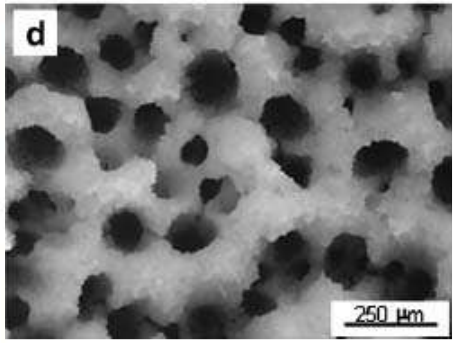
[1] Allebrod et al., *Journal of Power Sources* **2013**, *229*, 22–31.
[2] Herraiz-Cardona et al., *Int. J. Hydrogen Energy* **2012**, *37*, 2147–2156.
[3] Herraiz-Cardona et al., *Electrochim. Acta* **2011**, *56*, 1308–1315.

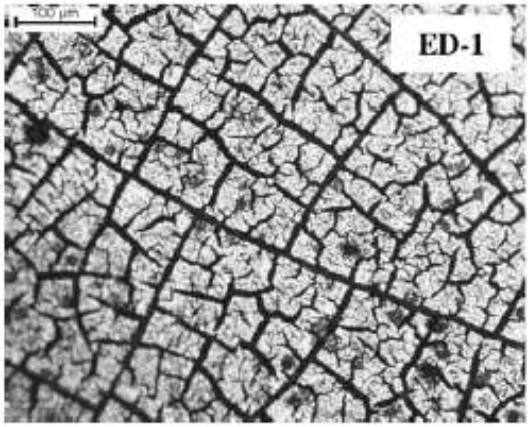
Production Processes

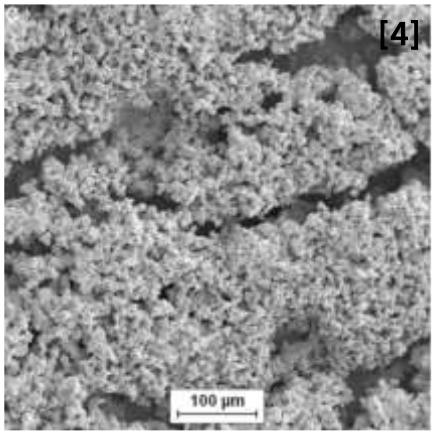
- Macro- and micro-structured surfaces
  - Deposition methods
    - Chemical
    - Electrochemical
      - Galvanic

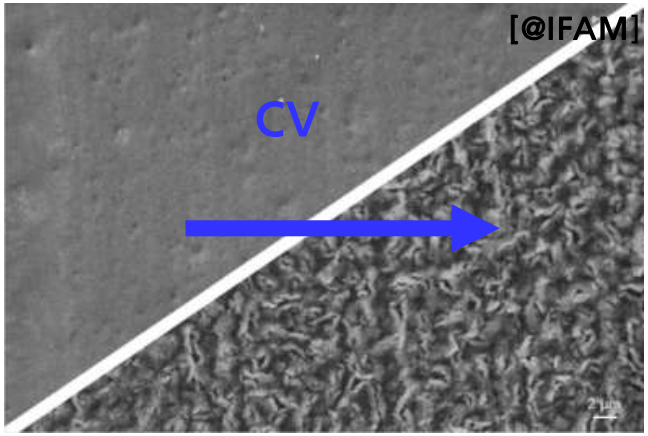
      → mostly Raney-Ni







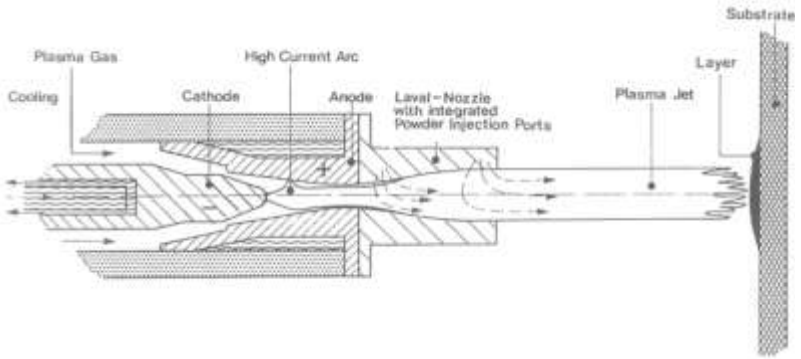


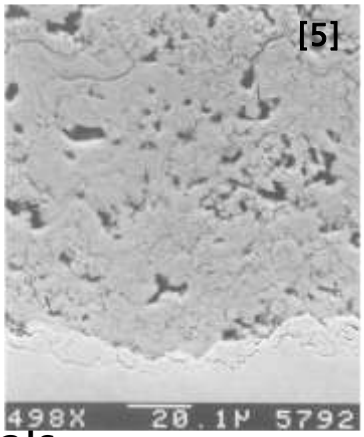


[4] J. Kubisztal et al., *Int. J. Hydrogen Energy* **2007**, *32*, 1211–1218.

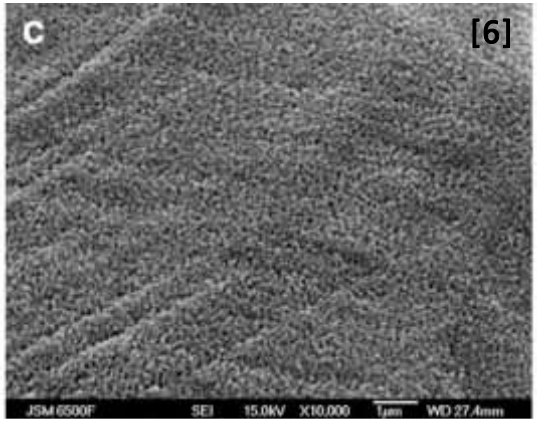
Production Processes

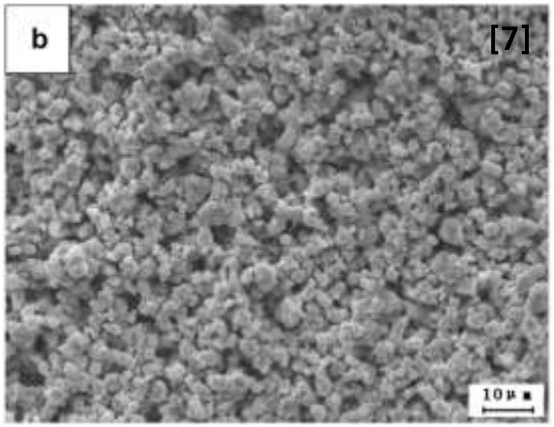
- Physical
  - Vacuum plasma spraying





  - Sputtering, Sintering of powdery materials

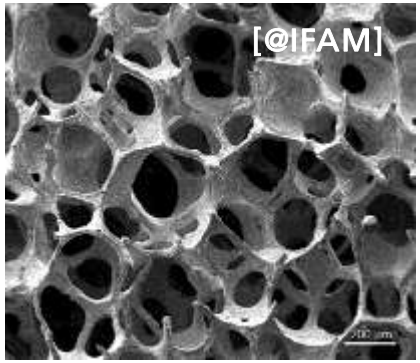


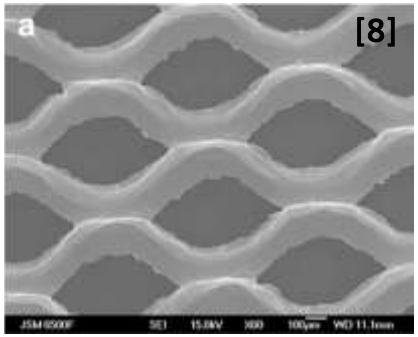


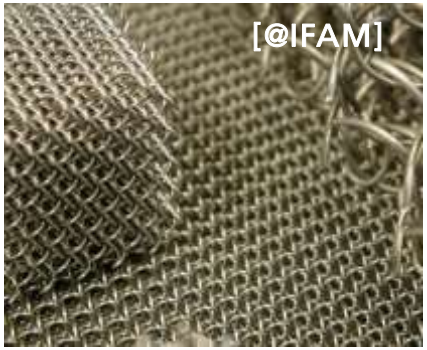
[5] G. Schiller, R. Henne, V. Borck, *J. Therm. Spray Techn.* **1995**, *4*, 185–194
[6] D. Pletcher, X. Li, S. Wang, *Int. J. Hydrogen Energy* **2012**..
[7] H. Dong, T. Lei, Y. He, N. Xu, B. Huang, C. T. Liu, *Int. J. Hydrogen Energy* **2011**, *36*, 12112–12120.

Production Processes

- 3D-Structures: foams, fleeces, meshes …

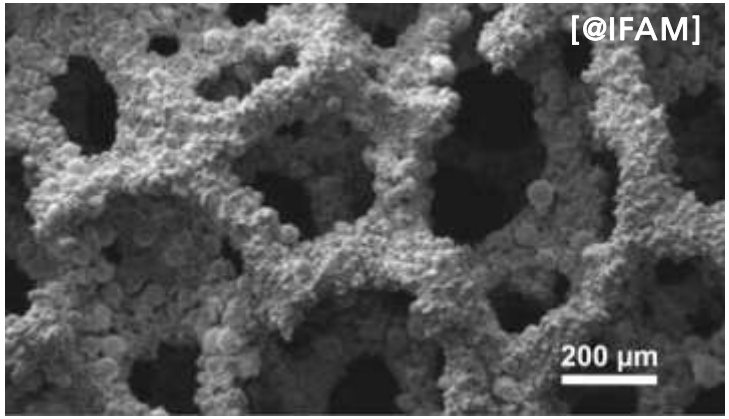


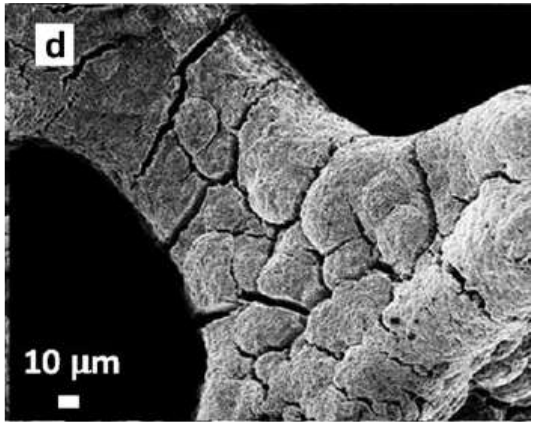


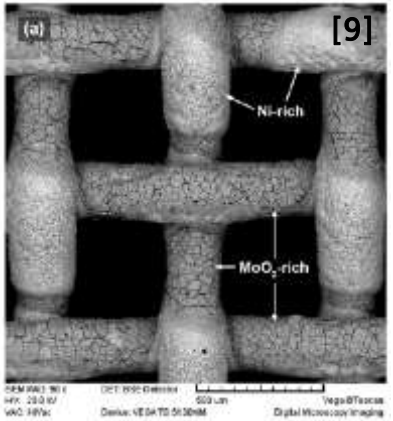


- Combination of different methods

  → Multi-hierarchical structures



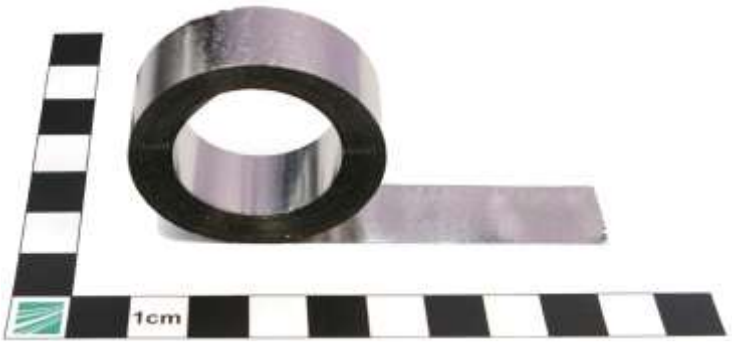


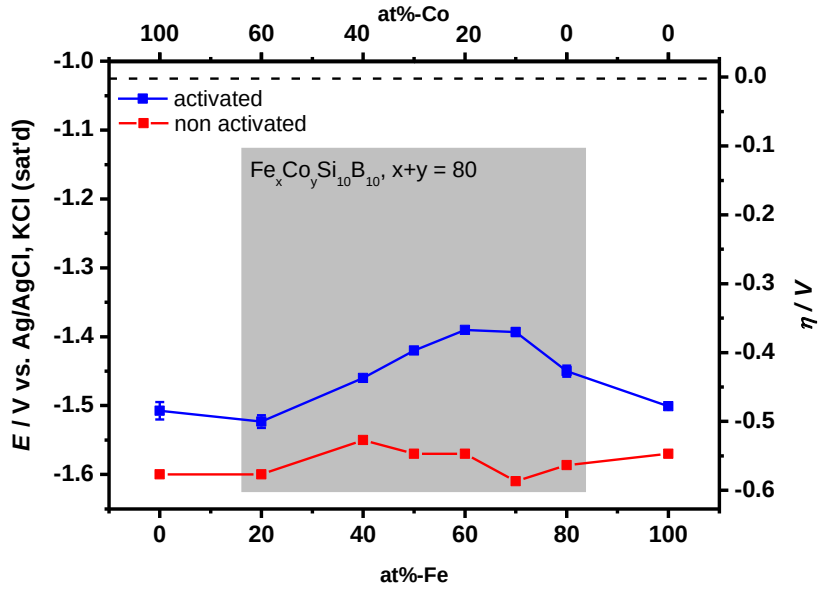


[8] D. Pletcher et al., *Int. J. Hydrogen Energy* **2012**.
[9] U. Lačnjevac et al., *J. Electroanal. Chem.* **2012**, *677-680*, 31–40.

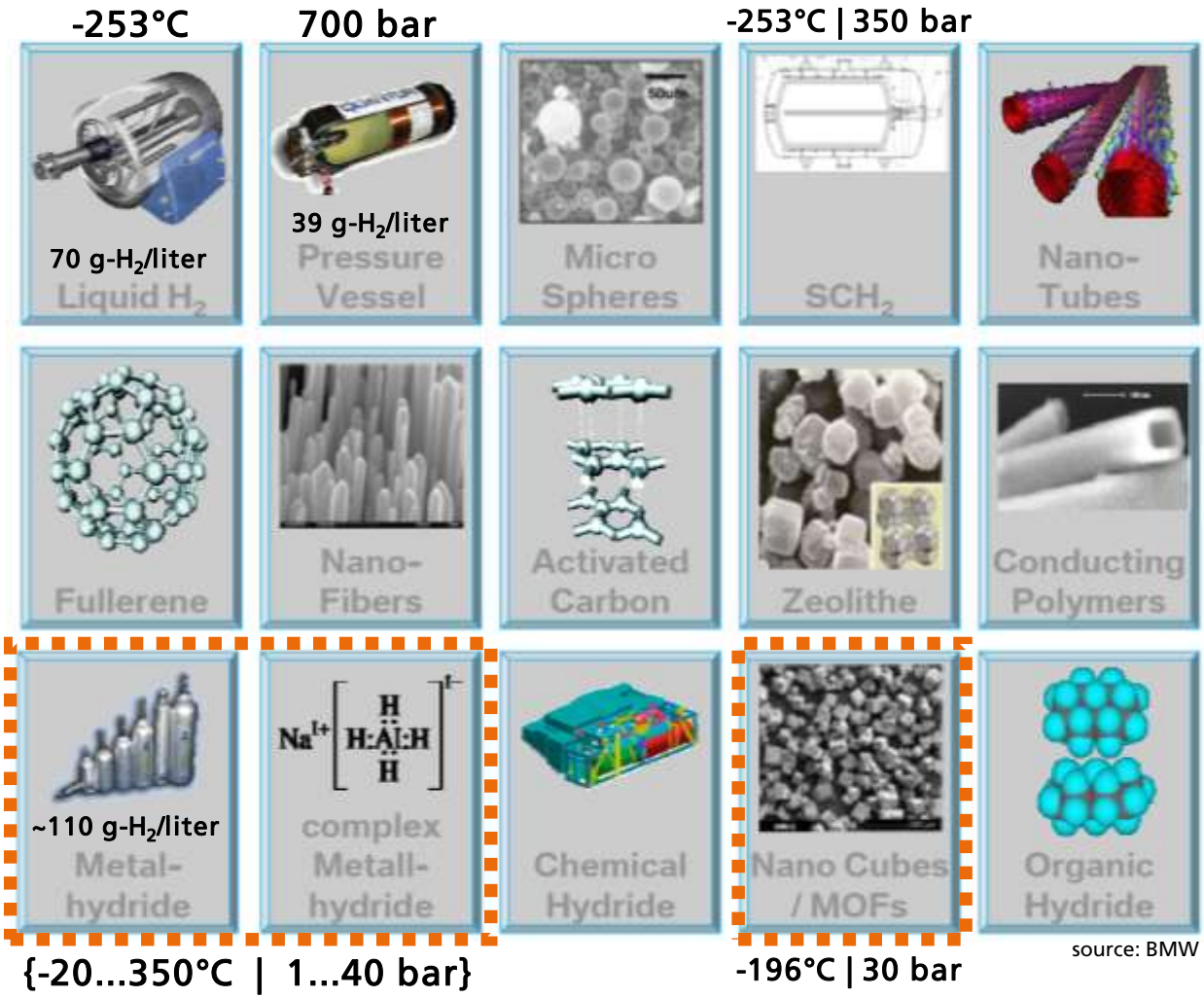
Electrochemical Activity

- Efficiency of electrolysis depends strongly on the activity of the catalyst
  - Chemical composition
    - Cathode: Pt, Ni, NiMo, FeNiMo, FeCo …
    - Anode: Ni, RuO_2, NiCo, FeNi …
  - Microstructure: Crystal size (10 nm … 100 nm … 1 μm)
  - Low cost, e.g. Fe-alloys (developed @IFAM):
    - Energy consumption reduction ~ 0.44 kWh / Nm^3-H_2





Methods of Hydrogen Storage

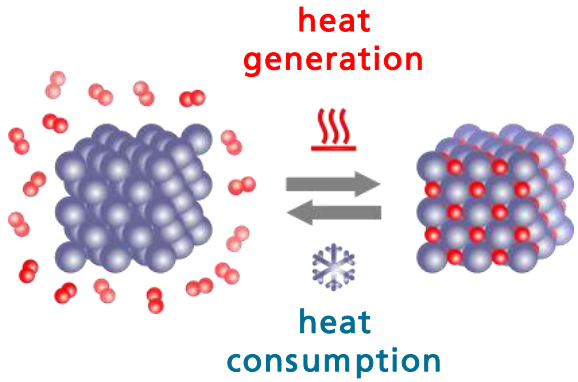


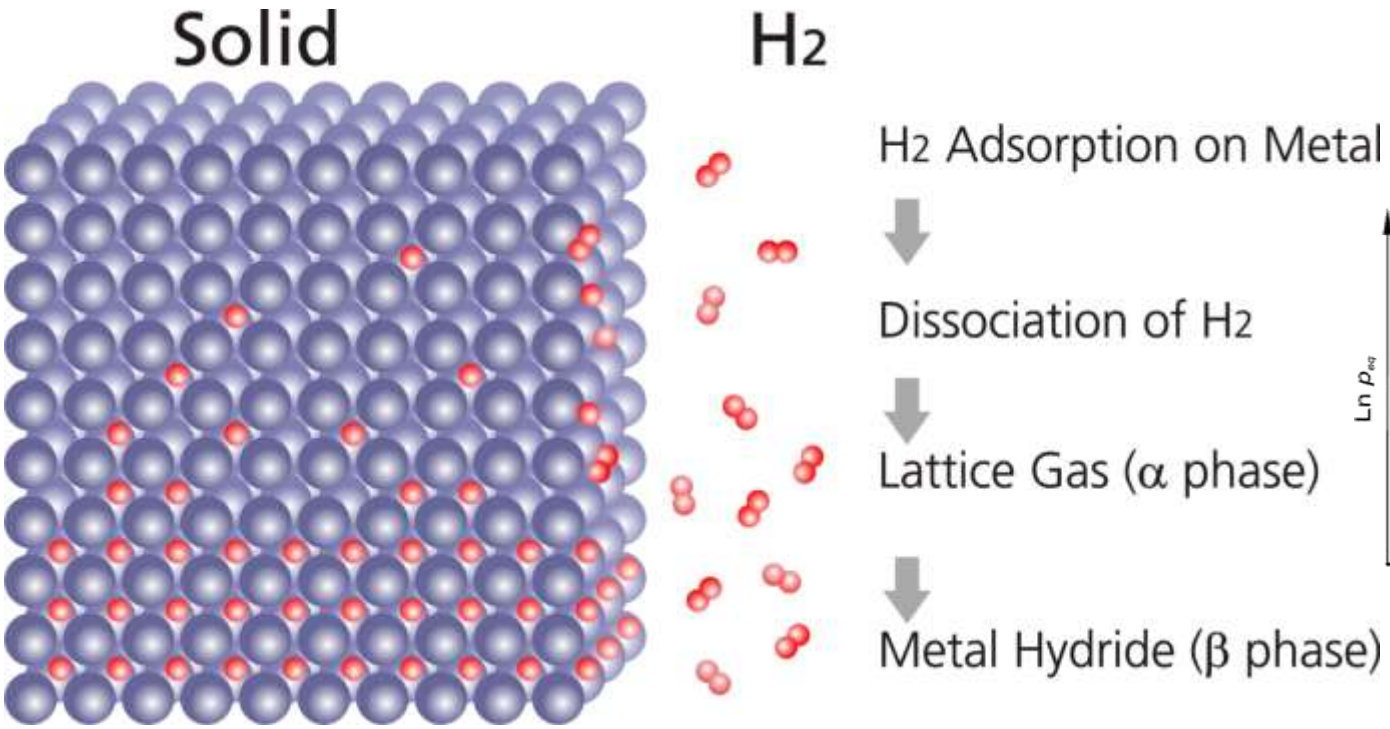
1 1.0079 H HYDROGEN
density (0°C): **90 g/m³**
boiling point: **-253°C**

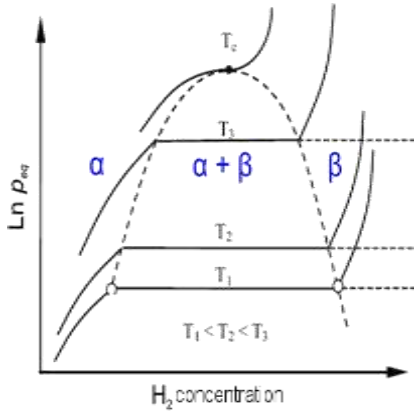
- Physical:
  - Compression
  - Liquefaction
  - Cryo-compression
- Chemical:
  - Absorption → Metal hydrides
  - Adsorption → MOFs, zeolites ...
  - C-H, N-H, B-H

Metal Hydride Formation

Metal + H_2 ⇌ Metal Hydride + Heat

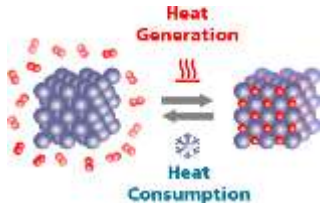


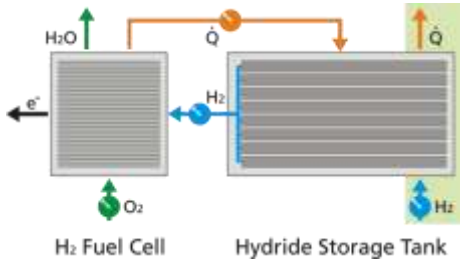


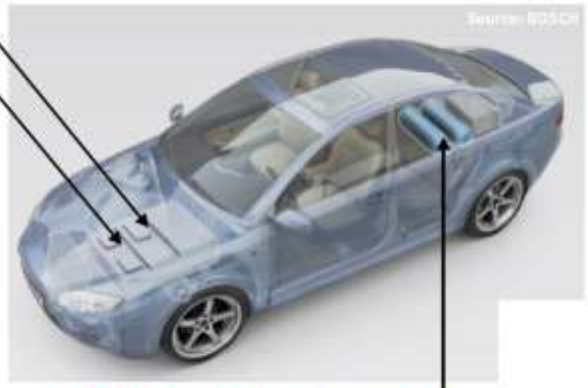


Applications of Metal Hydrides

- **H_2 storage** (mobile, portable, stationary)
- **H_2 generation** (hydrolysis)
- **Heat storage (e.g. CSP generation)**
- **Heat generation (e.g. thermoboosters)**
- Hydride-based cooling
- Hydride-based H_2 compressors
- Separation of H_2 from gas mixtures (e.g. CH_4 | H_2)
- Electrochemical applications (e.g. battery electrodes)
- Thin film applications (e.g. sensors)

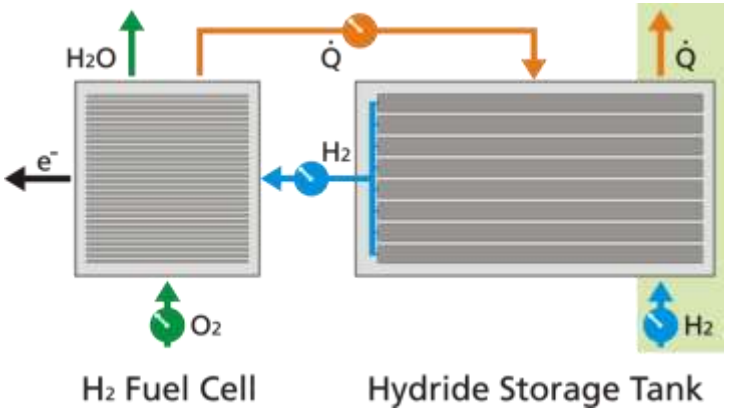






Optimal Metal Hydride → "Materials Design"

- High hydrogen capacity
  - gravimetric
  - volumetric
- Fast reaction kinetics (hydrogen uptake/release) → fine crystallinity
- Adjusted pressure-temperature regime with H_2 converter
  - dehydrogenation close to exhaust heat temp. of FC / ICE operation pressure
- Low price of base materials
- Easy and safe to produce
- Fast migration of hydrogen through hydride powder bed (diffusion, flow)
- Fast heat transport inside reaction zone → tank design
- Long cycle life
- Non-flammable, non-toxic
- Recyclable



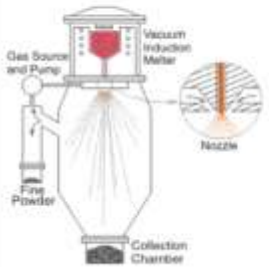
Materials Processing: Powder Technology Route

History: Densified Hydride Beds
- various patents 1980s
- Kim *et al.* IJHE 2001
- Sanchez *et al.* IJHE 2003
- Chaise *et al.* IJHE 2009
- Pohlmann *et al.* IJHE 2010

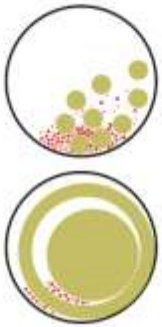
Materials Synthesis

Melt Spinning

Atomization



Milling

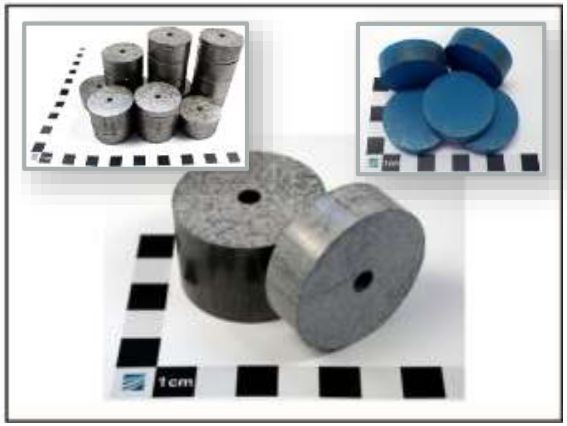


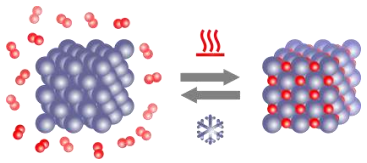
70% porosity → ~30 g-H_2/liter
λ < 1 W/(mK)

Blending

Secondary Phases:
- Metal powders (Al, Cu, …)
- Graphite
- Cellular metals

Compaction

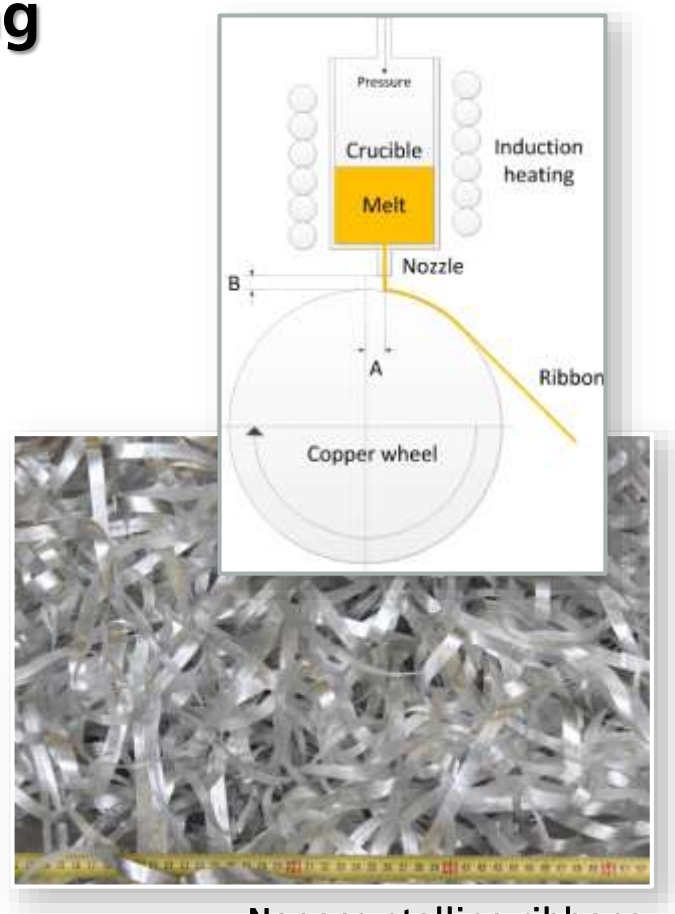




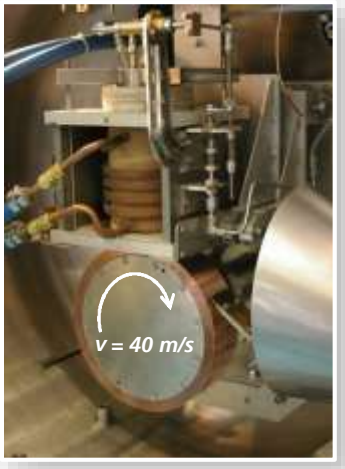
25% porosity → ~80 g-H_2/liter
λ >> 1 W/(mK)

Materials Synthesis by Melt Spinning

- Rapid solidification of the metallic melt ('shock-freezing', cooling rate 10^6 K/s)
- Homogenous distribution of elements (TMs, REs)
- Far-from-equilibrium processing:
  - Metastable state
  - Strongly exceeding equilibrium solubilities
- Up-scaling and high-yield production possible (10^2 – 10^3 kg/h)
- Processing in inert atmosphere (gassing of nozzle)



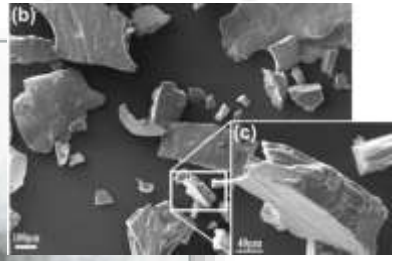
Nanocrystalline ribbons (thickness ~30 µm)



Melt spinning device at IFAM-Dresden

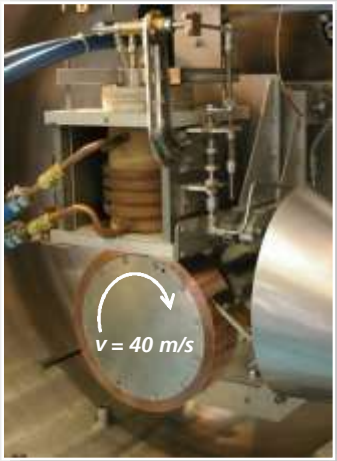
Dr. Lars Röntzsch

Materials Synthesis by Melt Spinning



Chopped melt-spun flakes
(thickness ~30 µm; width < 1 mm)

Nanocrystalline ribbons
(thickness ~30 µm)

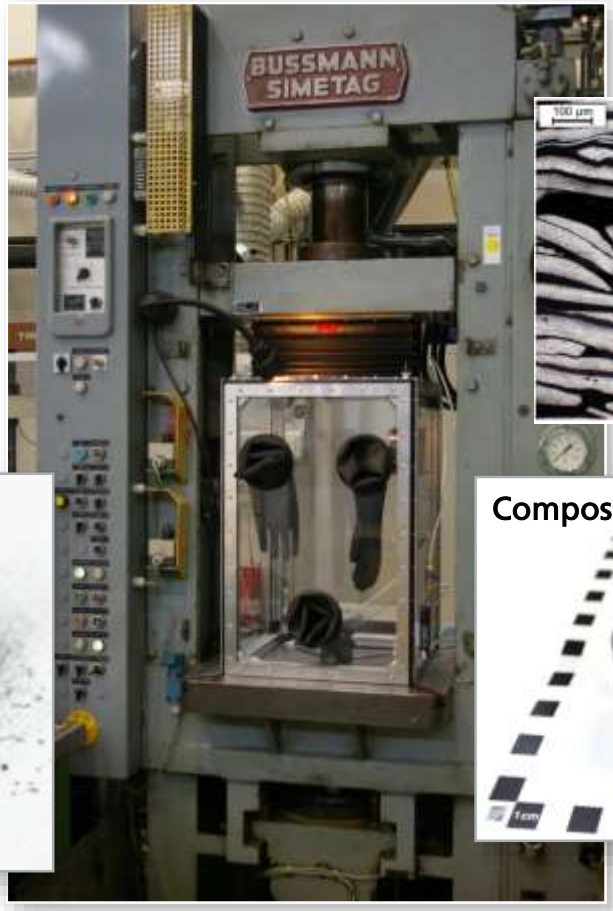


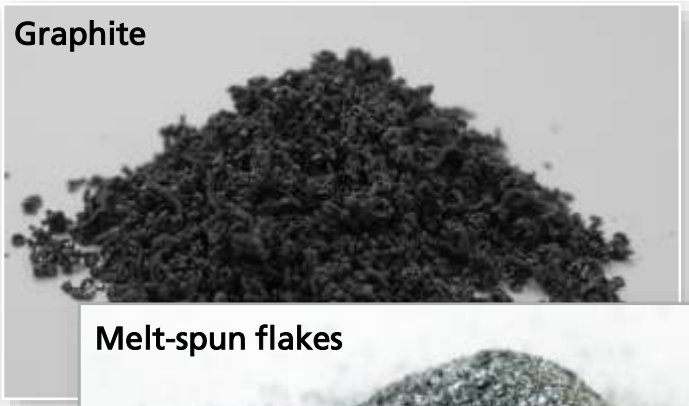
Melt spinning device at IFAM-Dresden

Dr. Lars Röntzsch
24.06.2014

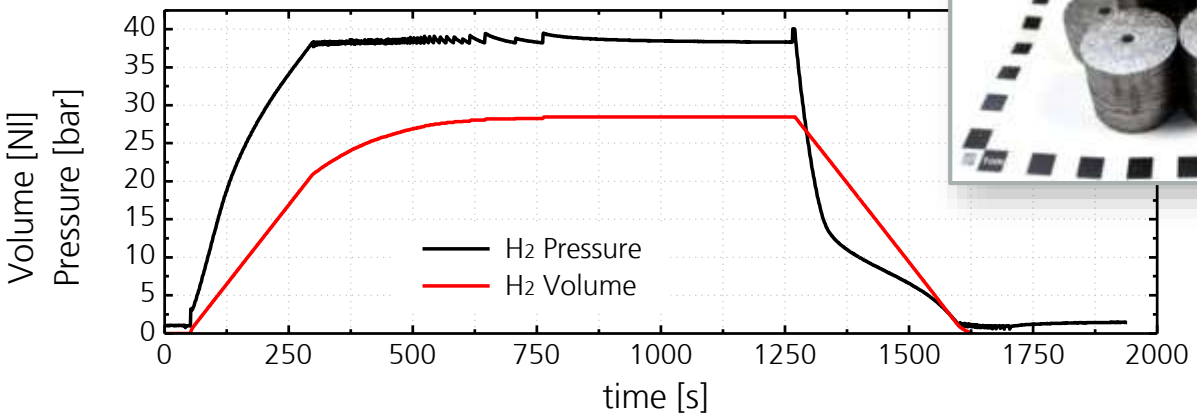
Tailoring Heat Conduction

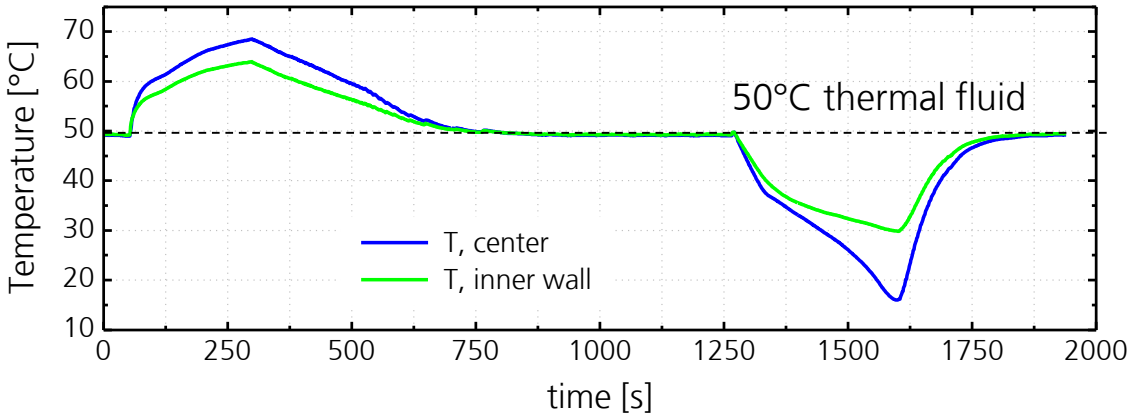
- Mixing hydride powders or flakes
  with secondary phase, e.g. Cu, Al, graphite, porous metals (some vol.%)
- Uniaxial compaction (> 50 MPa)
- Example: Graphite





Example: MH-Graphite Composite





MH-composite after cycling

Hydrogen, a Business Case for the `*Energiewende*´? Dream or Reality?

- `Green Hydrogen´ is not profitable yet; e.g. H_2 production costs at E.ON Power Plant Falkenhagen (AEL) about 30 ct/kWh$_{H2}$ [R. Schoof, 2014]
- Hydrogen as energy carrier (fuel) is not widely available yet
- Most hydrogen energy products are still expensive, thus, they are not widely used by endusers thus far
- Hydrogen has to compete strongly with traditional energy carriers (no powerful pro-H_2 incentives)

→ Very weak driving force for the hydrogen energy market thus far

→ Continuation / acceleration of H_2 infrastructure ramp-up is a **must**

→ Hydrogen technology development programs are badly needed to achieve cost reductions

→ Hydrogen energy product stimuli to trigger powerful markets beyond today's isolated niche markets

Thank You!

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