Hydrogen as an Energy Carrier: A Materials Perspective

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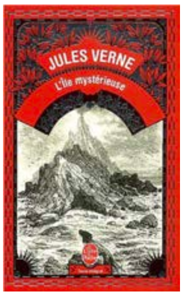
Hydrogen economy : History

- ”Mystery Island” Jules Vernes 1874

The engineer says: *“je crois que l'eau sera un jour employée comme combustible, que l'hydrogène et l'oxygène, qui la constituent, utilisés isolément ou simultanément, fourniront une source de chaleur et de lumière inépuisables”*



- H - economy 1970 by J. Bocris

H_2

- High energy density : H_2 142 MJ kg^{-1}, liq. HC 47 MJ kg^{-1}
- Can be used to store and transport energy
- Abundant
- Secondary energy source - production

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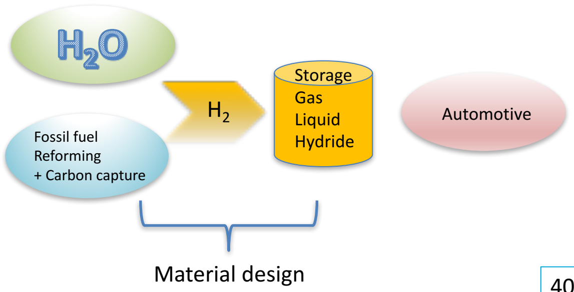
Hydrogen as an energy carrier

- Production
- Transport & Storage



400 km
Combustion: 24 kg petrol or 8 kg H_2
Fuel cell: 4 kg H_2

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Hydrogen production

€ x3

Image by courtesy of David van Nunen

Electrolysis of H_2O

www.hysep.com/basic-info/index.html

from fossil fuel by
Steam Methane Reforming

90% of H_2

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Hydrogen production from fossil fuel

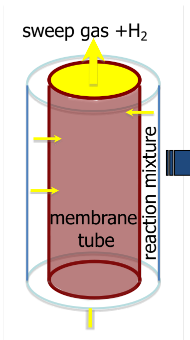
Steam reforming: $CH_4 + H_2O \rightleftharpoons 3\,H_2 + CO$ (ΔH = 206 kJ/mol)

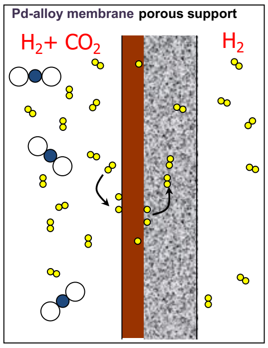
Water-gas shift: $CO + H_2O \rightleftharpoons H_2 + CO_2$ (ΔH = - 41 kJ/mol)

$CH_4 + 2\,H_2O \rightleftharpoons 4\,H_2 + CO_2$

Energy efficient by removing H_2 from reaction mixture

Membrane reactor





•Process Conditions

T: 550 – 950 K
P: 10 - 50 bar

•Stable alloy

- *delamination*
- *embrittlement*
- *segregation*

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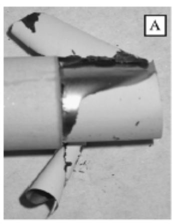
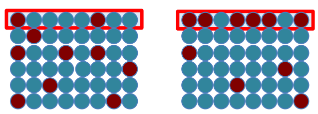
Metal membranes for gas separation

Microstructural changes	Surface poisoning
o Thermal expansion mismatch o β–hydride formation below T_C	o H_2S, H_2O, CO, CO_2 o Surface segregation



vacuum gas environment



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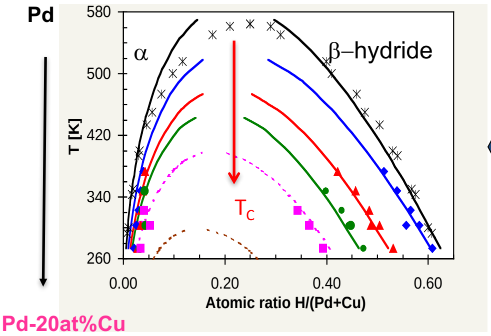
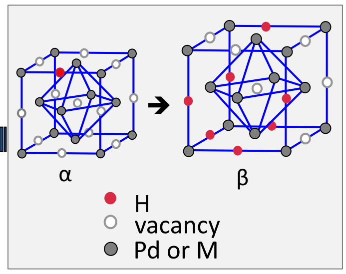
Y. Huang et al., *Thin Solid Films* 515 (2007) 5233

Optimise composition for stability

Modelling $Pd_{(100-x)}Cu_x$-H systems



Cluster Variation Method - CVM



ΔV/V~0.1

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Nanu et al. Adv. Funct. Mater., 18, (2008) 898

Pekelharing, Böttger et al. Met.Mat. Trans. A (1999) 1945s

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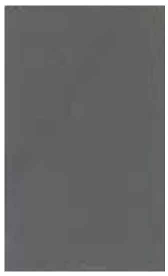
Pd : nano-structuring & embrittlement

Single H_2 loading – deloading cycle

Pd-compact morphology



Pd loose nano-sized structure

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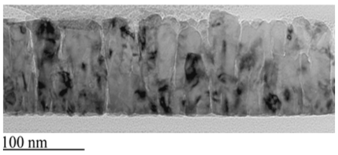
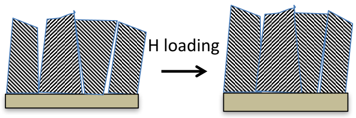
Optimise microstructure for stability

- Nano-structuring
  - Quasi-free expansion

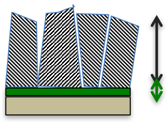


Brush membrane concept



Loose nano-sized columnar structure : sputter conditions

  - adhesive layer:



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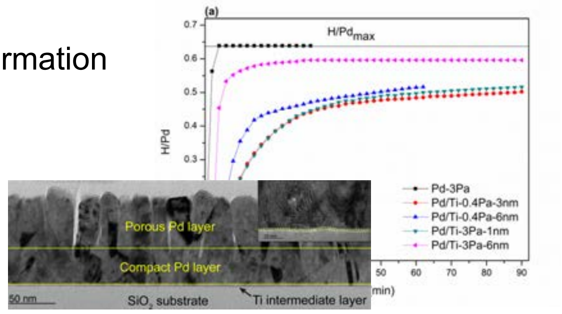
Improve adhesion

- Hydrogen loading and de-loading cycles
- Analysis of:
  - Phase transformation
  - Stress
  - Texture



Pd film

5 cycles

Pd on Ti film

Pd on PI film

20 cycles

20 cycles

20 cycles

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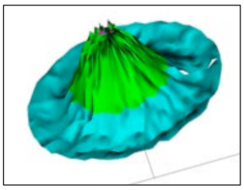
Optimal film performance

Pd on PI : good adhesion – no delamination
high performance – solubility and kinetics

- Resulting optimal film characteristics:
  - Open nano-structure
  - Texture: 'weak' 111-texture 1,5 x random
  - Stress: ~ 100 MPa



Pd on PI film

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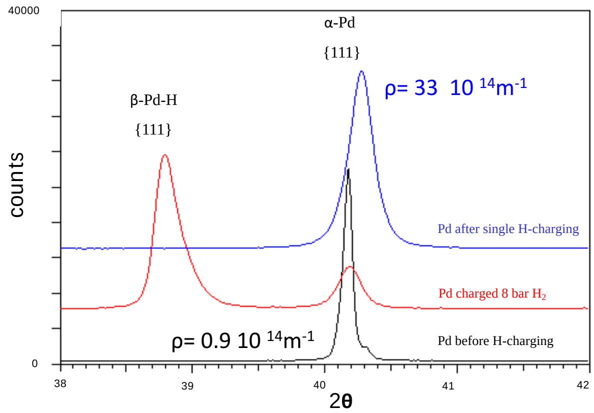
Phase transformation and damage

Effect of hydrogen loading on dislocation density



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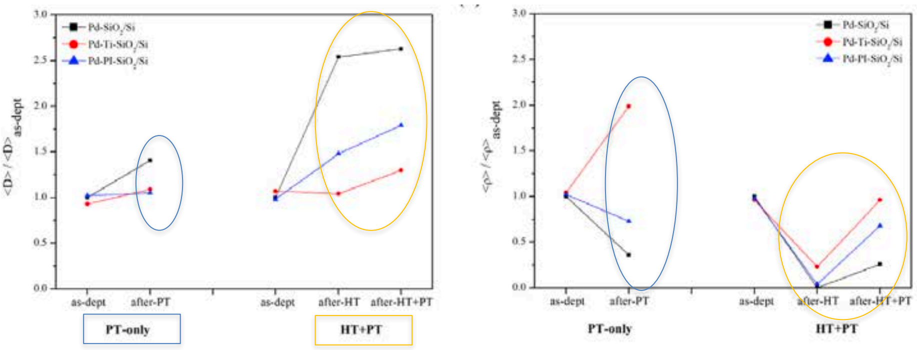
Pd - hydrogen absorption experiment 12

Phase transformation and damage

Crystallite size

Dislocation density



Hydride formation (T< 353 K)

Heating up to 625 K + Hydride formation

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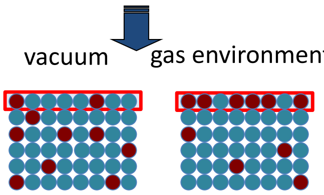
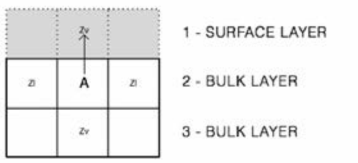
Segregation

- Segregation in binary alloys
  - o H_2, CO, CO_2 (H_2S, H_2O)
  - o Surface segregation

vacuum gas environment





regular solution model - in vacuum

$$Q_{seg} = \underbrace{(\gamma_A\sigma_A - \gamma_B\sigma_B)}_{\text{surface}} + \underbrace{2\omega Z_l(X_A^b - X_A^s) + 2\omega Z_V(X_A^b - \tfrac{1}{2})}_{\text{configurational}}$$

$$\omega = \varepsilon_{AB} - \left(\frac{\varepsilon_{BB} + \varepsilon_{AA}}{2}\right)$$

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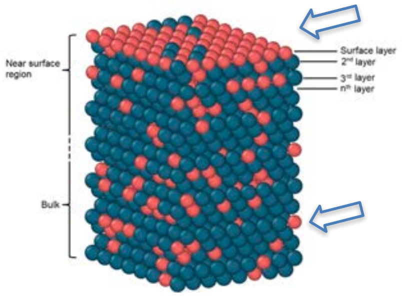
Surface segregation



Solid lines includes elastic strain

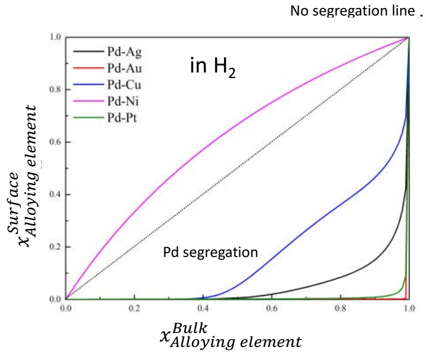


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Image by courtesy of J.Postma -2020

Meng et al. Int.J. Hydr. Ener. 43 (2018) 2212s

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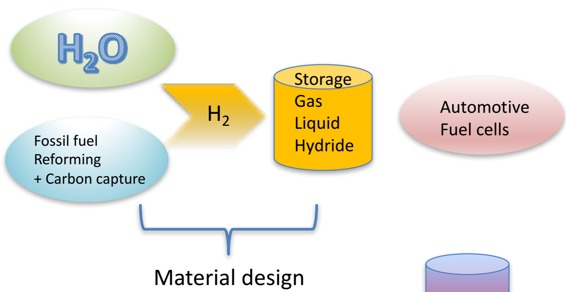
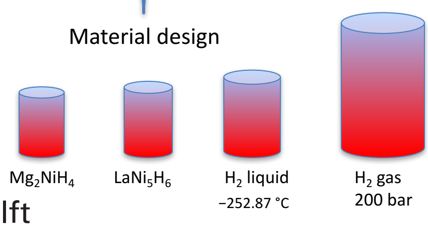
Hydrogen as an energy carrier

- Production
- Transport & Storage





400 km
Combustion: 24 kg petrol or 8 kg H_2
Fuel cell: 4 kg H_2

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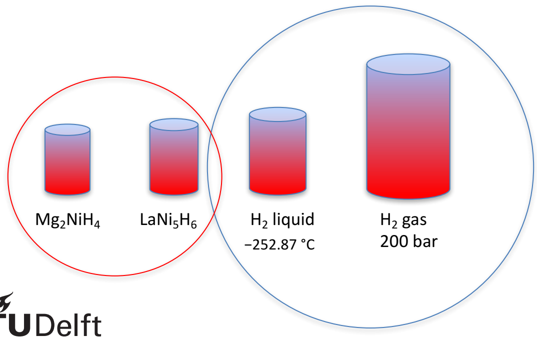
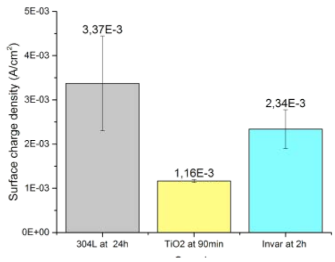
Hydrogen transport & storage

Capacity (mass, volume)
Reversible – (P-C-T) P, T moderate
Kinetics (absorption/desorption)
Lifetime



Existing infrastructure
LNG tanks for liquid H_2?



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Conclusion

- Materials design needed for
  - Efficient & low cost green hydrogen production
  - Existing infrastructure H-proof
  - Storage in solids (solubility, kinetics)

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Thanks to

Vanya Uluc
Xiao Zheng
Daniel Enciso
Frans Tichelaar
Diana Nanu
Ruud Hendrikx
Meng Zhao
Shunli Shang
Neha Verma
Katherine Encalada
Richard Huizenga

ZEF
materials innovation institute
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NWO Netherlands Organisation for Scientific Research
LUXEMBOURG INSTITUTE OF SCIENCE AND TECHNOLOGY LIST
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