

# Hydrogen in metals and hydrogen storage

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School on Pulsed Neutron Sources Trieste - Italy, 17 - 28 October 2005



# Content

- 1. Primer for hydrogen in metals
- 2. A deeper insight
- 3. Neutron studies
- 4. Hydrogen economy
- 5. Hydrogen storage materials







# 1. Primer for hydrogen in metals





## 1. Step: Dissociation, Physisorption, Chemisorption



 $M + \frac{1}{2}xH_2 \leftrightarrow MH_x$ 







Ref.: J. E. Lennard-Jones, Trans. Faraday Soc. 28 (1932), pp. 333.
L. Schlapbach, Chapter 1, L. Schlapbach (Ed.) in Intermetallic Compounds I, Springer Series Topics in Applied Physics, Vol. 63, Springer–Verlag, 1988, p. 10.



## 2. Step: Diffusion into the metal

Three diffusion types:

V

1. Classical jump diffusion:

2. Thermally activated tunneling:

3. Self trapping through lattice relaxation:











#### 3. Step: Occupation of interstitial sites in metals







## 4. Step: Volume change

Lattice parameter change due to point defects:

$$\frac{\Delta a}{a} = \frac{1}{3} \frac{\Delta V}{V} = \frac{1}{3} \frac{\Delta v}{\Omega} c_H$$

 $\Delta v = \Delta V / N_D$  = defekt strength  $\Omega = V/N_H = a^3 / 2$  = volume of hostatom







#### 5. Step: Chemical equilibrium

1





Equilibrium condition between external  $H_2$  - pressure and dissolved H in metal:

$$\frac{1}{2}\mu_{H_2}(gas) = \mu_H(metal)$$

$$\ln \sqrt{\frac{p_{H_2}}{p_0}} = \frac{\Delta H}{RT} + \ln \left(\frac{c_H}{1 - c_H}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

Solution enthalpy:

$$\Delta H = E_B - \frac{1}{2}E_D < 0$$





## Solubility isotherms for hydrogen in metals



The linear dependence  $(p_{H2})^{1/2} \sim c_H$  is a direct consequence of hydrogen dissociation in the metal.





#### Solubility isotherms and phase transition









# 2. A deeper insight





## **Dissociation at the surface**



Projected DOS (arb. units)

- 1. H<sub>2</sub> molecule bonding and antibonding state relative to the metal d-band
- 2. Coupling matrix element between molecular orbitals in metal d-band
- 3. Filling of the molecule surface antibonding state





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## Hydrogen in Metals: Lattice gas with interaction



acher's Ansatz for the free energy (1937):  

$$F = -\frac{1}{2}J\tau_{H}^{2}N_{0} - k_{B}T\ln\frac{N_{0}!}{(N-N_{0})!N!}$$

$$\mu_{H} = \Delta H + k_{B}T\ln\left(\frac{\tau_{H}}{1-\tau_{H}}\right),$$

$$\Delta H = \underbrace{E_{B} - \frac{1}{2}E_{D}}_{H-Metal} - \underbrace{J\tau_{H}}_{H-H}}_{interaction}$$

What is the binding energy  $E_B$  and the interaction energy J due to?





# **H-H** elastic interaction



H-H interaction is mediated by long range strain fields = elastic interaction.

$$E_{el} = \frac{1}{2} \sum_{m,n} u_m J_{mn} u_n$$

Strain field:  $\vec{u}_m(\vec{r}) = \frac{\Delta v}{4\pi C_{11}\kappa_T} \frac{\vec{r}}{r^3}$  For

J follows: 
$$J = \eta B \frac{(\Delta v)^2}{\Omega} c_{\text{max}}$$

- $\Delta v$  = volume change per hydrogen atom.
- $\Omega$  = volume per host metal atom
- B =bulk modulus
- $\eta$  =short range electronic parameter
- $c_{max}$  = maximum hydrogen concentration

The H-H interaction is only attractive, if the system is finite and has free surfaces.





# Energetics

Westlake criterion: Size for hydrogen site: r > 0.37Å D. G. Westlake, J. Less-Common Metals **91** (1983) 275

Switendick criterium: Minimum distance between two hydrogen atoms d > 2.1 Å A. C. Switendick, Z. Phys. Chem. N.F. 117 (1979) 89





Maximum hydrogen density in metals is then ~ 200 kg/m<sup>3</sup> as compared to 70 kg/m<sup>3</sup> in the liquid state.





#### Effective embedding theory





J.K. Nørskov, Phys. Rev. B 26, 2875 (1982)



## Local band structure semiempirical model





R Griessen, Phys. Rev. B 38, 3690 (1988)



#### **BINARY HYDRIDES**



Ref.: Gottfried Brendel, "Kapitel: Hydride", Ullmanns Encyklopädie der technischen Chemie, 4. neubearbeitete und erweiterte Auflage, Band 13 (1977), pp. 109-133, Verlag Chemie Weinheim New York

C##,	Pres. Pres.	NAN, NAN,	Pm	SteH <sub>2</sub> SteH <sub>2</sub>	Eurit,	Gan, Gan,	760) 760)	Dy44; Dy44;	Holik, Holik,	808) 200	Trotty Trotty	(*141 <sub>2</sub> ) *1443	€uH; EuH;
1.985	1.87	187		1.27	1.81			1.38	1.40	1.83	* **		8.94
<b>78:85</b> ,	Patt,	QH,	Nijolikij Nijolikij	Padis Padis	A911, A911,	Cm	Bk	Cf	Es	Fm	Md	No	Lr
1.11	1.5%	¥ 222	1.22	1.222	14								

# Pressure-composition isotherms for the determination of phase diagrams and solution enthalpies



Equilibirium or dissociation pressure







## Metal-hydrogen phase diagram







#### Dynamics and diffusion of a lattice gas







## Phonon dispersion of Ta with H



Acoustic modes are little affected by H New optic modes due to local hydrogen vibration.



A. Magerl et al. J. Phys. C 10 (1977) 2783



## Local hydrogen vibration

50

100

150





J. Rush et al.



## Local hydrogen vibrational potential



FIG. 2. Calculated energy vs displacement curves for hydrogen in Nb. The displacements of the hydrogen for the tetrahedral site are (0,0,a) [t-o in Fig. 1(a)] for the left-hand portion of the curve and (0,a,0) [t-y in Fig. 1(a)] for the right-hand portion.



K.M. Ho, H.J. Tao, X.Y. Zhu, PRL 53 (1984) 1584



#### Quasi-elastic neutron scattering: Scattering function for continuous diffusion in a liquid







Quasi-elastic neutron scattering:  
Scattering function for jump diffusion  

$$S_{inc}(\vec{Q},\omega) = \frac{1}{\pi\hbar} \frac{f(Q)/\tau}{(f(Q)/\tau)^2 + \omega^2}; \quad \Gamma_{inc} = 2\hbar f(Q)/\tau$$

f(Q) is an oscillatory structure factor:

$$f(Q) = \frac{1}{n} \sum_{i=1}^{n} \left( 1 - \exp\left(-i\vec{Q} \cdot \vec{l}_i\right) \right)$$

The incoherent line width oscillates in case of jump diffusion, and for a Bravais lattice is:

#### Hydrogen diffusivity in Pd single crystals



Only O-O jumps are consistent with measurements

QENS allows to determine self-diffusivity and geometry of jump vectors



J.M. Rowe et al. PRL 29 (1972) 1250



## Gorsky effect or anelastic relaxation for the study of diffusion in solids



Relaxation time and diffusion constant:

$$\tau_{anel} = \tau_{0,anel} \exp(U_D / k_B T)$$
  
$$\tau_{0,anel} = d^2 / \pi^2 D_0; \quad D = D_0 \exp(-U_D / k_B T)$$

G. Alefeld et al. PRL 22, 697 (1969)





## Hydrogen diffusivity



 $D_0 = 5 \times 10^{-4} \text{ cm}^2/\text{s}$ ; U = 0.106 eV for H in Nb and T > 300K









1. Production





- 1. Production
- 2. Storage





- 1. Production
- 2. Storage
- 3. Transport





- 1. Production
- 2. Storage
- 3. Transport
- 4. Uses of hydrogen





## 1. Production of Hydrogen




• Water vapor over hot coal





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- Thermal Dissociation of carbon hydrides (Steam-reforming of oil and natural gas produces 9M tons H<sub>2</sub>/yr)





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- Photobiological production









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  - ♦ methanol (CH<sub>3</sub>OH)





# Requirements of hydrogen storage materials identified by DOE panel

- •High gravimetric and volumetric density (10 wt %)
- •Fast kinetics
- •Favorable thermodynamics
- •Reversible and recyclable
- •Safe, material integrity
- Cost effective
- Minimal lattice expansion
- •Absence of embrittlement





### Further requirements

- Ambient temperature for charge and discharge
- Low hysteretic losses
- Sensitivity to impurity gases
- Multi-cycle stability
- Activation procedure
- Large-scale production possibility at low cost





### Some classical metal-hydrides for storage

Alloy	Weigth % H <sub>2</sub>	Rel. Volume density	Dissociation temperature (°C)
LH <sub>2</sub>		1	
MgH <sub>2</sub>	7.6	1.8	290
Mg <sub>2</sub> NiH <sub>4</sub>	3.6		250
TiFeH <sub>1.9</sub>	1.8	1.8	50

Target of International Energy Association (IEA):

- $\geq$  5% hydrogen capacity
- Desorption temperature  $\leq 80^{\circ}C$  at 1 bar





# LaNi<sub>5</sub>-based intermetallic Alloys

- Produced by high-energy mechanical alloying
- LaNi<sub>5-y</sub>Sn<sub>y</sub>
  - Sn:
    - to reduce the plateau pressures for absorption and desorption
    - to decrease the hysteresis between the pressure for hydride formation and decomposition (side effect: decreases the hydrogen storage capacity)
  - An activation cycle is not necessary for the powders to absorb H.
  - Nanocrystalline powder are less affected by the volume change variation due to H charging.





#### Typical hydrogen absorption-desorption curves



absorption-desorption cycle around 300°C with rapid rates.





# Pressure-composition isotherms for micro- and nanocrystalline FeTi Alloys



Nanocrystalline Fe<sub>50</sub>Ti<sub>50</sub> has:

- a lower pressure plateau
- a reduced capacity
- a much easier activation
- Pd addition: enhance the adsorption kinetics





# **Mg-based Alloys**

- Advantages:
  - Light weight
  - High hydrogen capacity
- Mg<sub>2</sub>Ni, 20-30nm by mechanical alloying, adsorb H without activation at temperature <250°C (Mg<sub>2</sub>NiH<sub>4</sub>)
  - Pd addition: enhance the adsorption kinetics
- Mg<sub>2</sub>Ni-H system, by milling in a hydrogen atmosphere
  - much higher absorption capacity (1.6wt%) at ambient temperature
  - much lower dehydriding temperature (440K) (Mg<sub>2</sub>NiH<sub>4</sub> 520K)





#### Surface coating for faster hydrogen charging



Inactive surface Diffusion barrier



catalytic H<sub>2</sub> dissociation, oxidation protection, hinders poisening of surface





#### Storage of hydrogen in metal alloys

# Cylinder storing 20 liters of hydrogen at normal pressure in a metal alloy







# Hydrogen storage in graphite nanotubes









# Volume comparison for storage



4kg hydrogen in/as Mg\_NiH4 LaNi<sub>5</sub>H<sub>6</sub> liquid H<sub>2</sub> H<sub>2</sub> at 100atm





#### Volumetric and gravimetric H<sub>2</sub> storage capacity







#### U. S. DOE Goals and Current Status of Hydrogen Storage Technologies (Milliken, June 2003)







# 3. Hydrogen Transport





# 3. Hydrogen Transport

Pipelines for gas or liquid





# 3. Hydrogen Transport

Pipelines for gas or liquid

Tanks
on trucks,
on ships,
or trains









1. Fertilizers (presently largest use)





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- 2. Fuel in combustion engines





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- 3. Fuel cells for electrical power




### 4. Uses of hydrogen

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- 4. Tuneable and switchable optical and magnetic materials





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- 5. Sensors





## Hydrogen: from production to use













Production of hydrogen by wind or water and its use in internal combustion engines may be the most efficient hydrogen economy.....

## Comparison

	All electric economy	Hydrogen economy
Primary source	Oil, gas, coal, renewables	Wind, water, sun, renewables
Storage	Pumped reservoir, batteries	Pressurized tank, LH <sub>2,</sub> metal hydrides
Transport	High voltage power lines	Tankers, pipelines
Advantages	Clean, safety standards established	Clean, good storage potential, use in combustion engines
Disadvantages	Firm supply, electrical road not applicable to aircraft, ships	Unfamiliar, danger of explosion, new infra- structure required





#### Messages

- Enormous gap between present state-of-the-art capabilities and requirements that will allow hydrog to be competitive with today's energy technologies
  - production: 9M tons ⇒ 40M tons (vehicles)
  - storage: 4.4 MJ/L (10K psi gas) ⇒ 9.72 MJ/L
  - fuel cells:  $3000/kW \Rightarrow 35/kW$  (gasoline engine)
- Enormous R&D efforts will be required
  - Simple improvements of today's technologies will not meet requirements
  - Technical barriers can be overcome only with high risk/high payoff basic research
- Research is highly interdisciplinary, requiring chemistry, materials science, physics, biology, engineering, nanoscience, computational science
- Basic and applied research should couple seamlessly





http://www.sc.doe.gov/bes/ hydrogen.pdf



#### The five priority research areas for the future identified by the DOE panel

Five high-priority research directions will be the focus of the solicitations:



- Novel Materials for Hydrogen Storage
- Membranes for Separation, Purification, and Ion Transport
- Design of Catalysts at the Nanoscale
- Solar Hydrogen Production
- Bio-Inspired Materials and Processes

http://www.sc.doe.gov/bes/hydrogen.pdf







# Thank you for your attention



