מגמות חדשות בחומרים המשמשים לאגירת מימן

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רותם תעשיות בע"מ
24.12.06

Outline

- Overview of the global energy challenge
- Overview of the hydrogen Economy
- Metal Hydrides and IMC
- Complex Hydrides (Alanates)
- AlH_3 (Aluminum Hydride)
- Nano materials
- Carbon Nano Tubes
- Borohydrides

Motivation

- World energy demand (30-60 Terawatts) by 2050
- Demographic expansion: 8.9 Billion by 2050.
- Global Climate warming
- Hydrogen economy (Energy carrier)
- Transportation in 2040 : 150 mega tonsH_2/y
- On-board storage for vehicular applications.

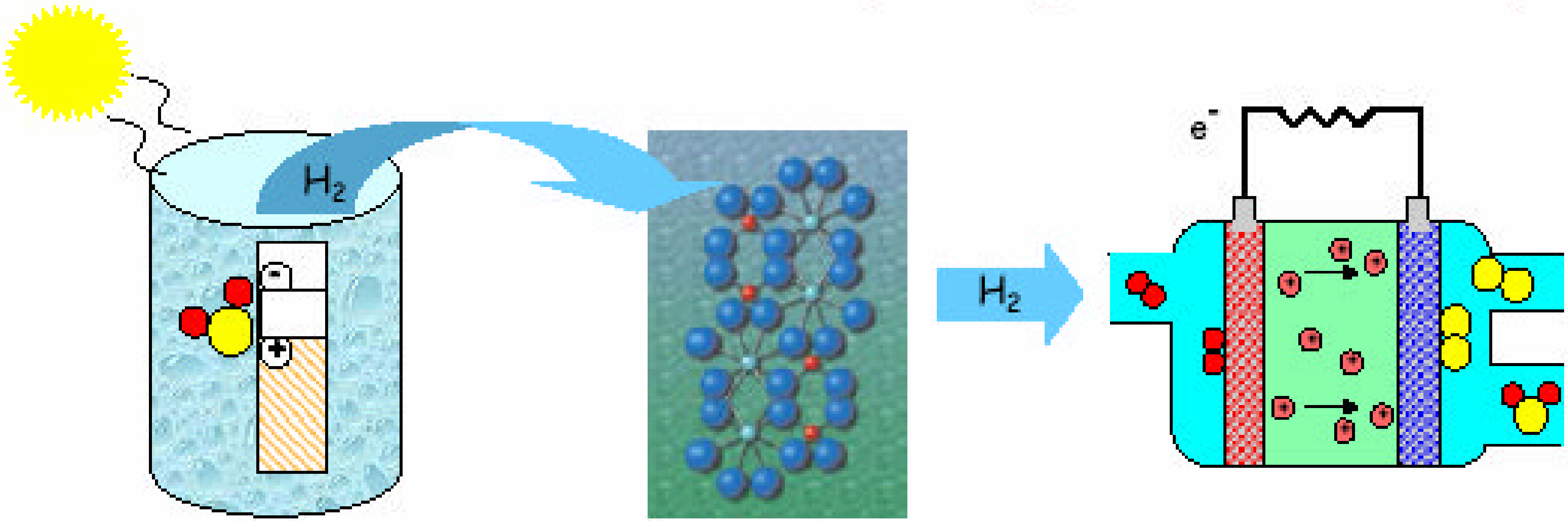
DOE targets for on-board

Feature \ Year	2010	2015
Hydrogen weight %	6%	9%
kWh/kg	2	3
kWh/L	1.5	2.7
Fill time – minutes/5kg hydrogen	3	2.5
Cost - $/kWh	4	2

Hydrogen Economy bottlenecks

- Production
- Storage
- Transportation shipping and handling
- Infrastructure

Outlook: the Mature Hydrogen Economy



production:
split water renewably

storage:
solid state materials

use:
fuel cells

high impact on energy challenges
supply, security, pollution, climate

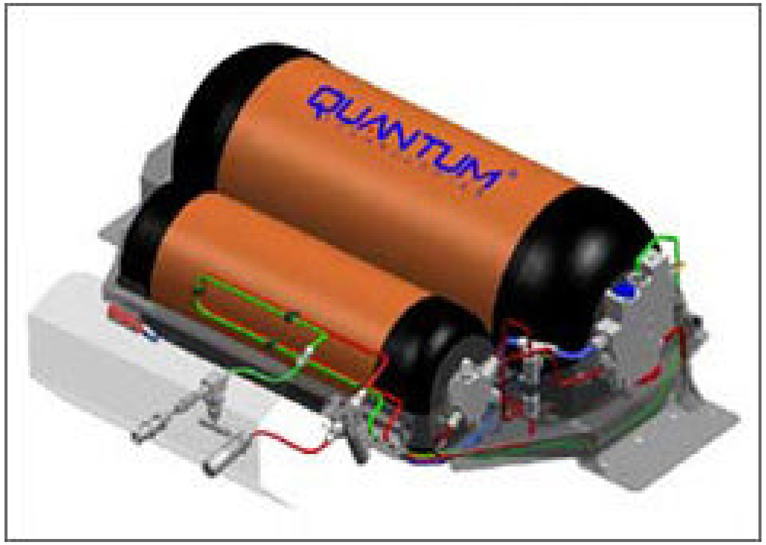
science within reach
breakthrough research discoveries
catalysis, membranes,
nanoscale architectures, bio-mimetics

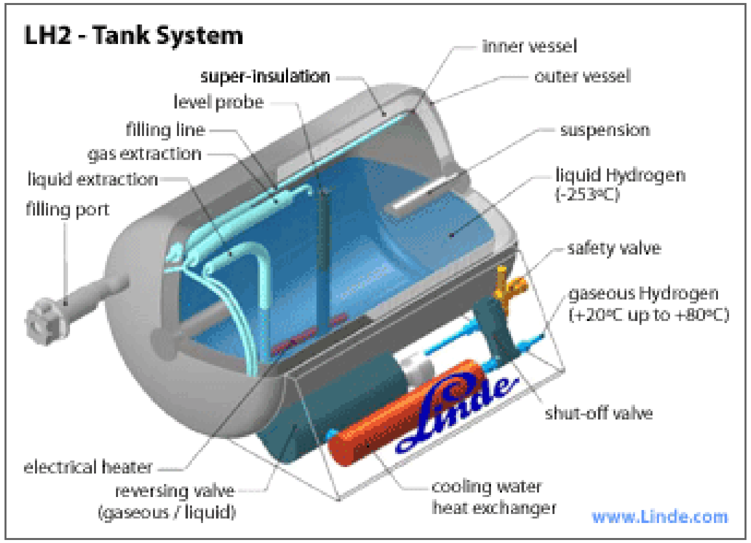
Hydrogen Storage

Compressed gas tanks

Cryogenic liquid cylinder

Storage in materials





Hydrogen Storage in Materials

Reversible solid-state materials regenerated on-board:

1. Alloys and intermetallic compounds (IMC).

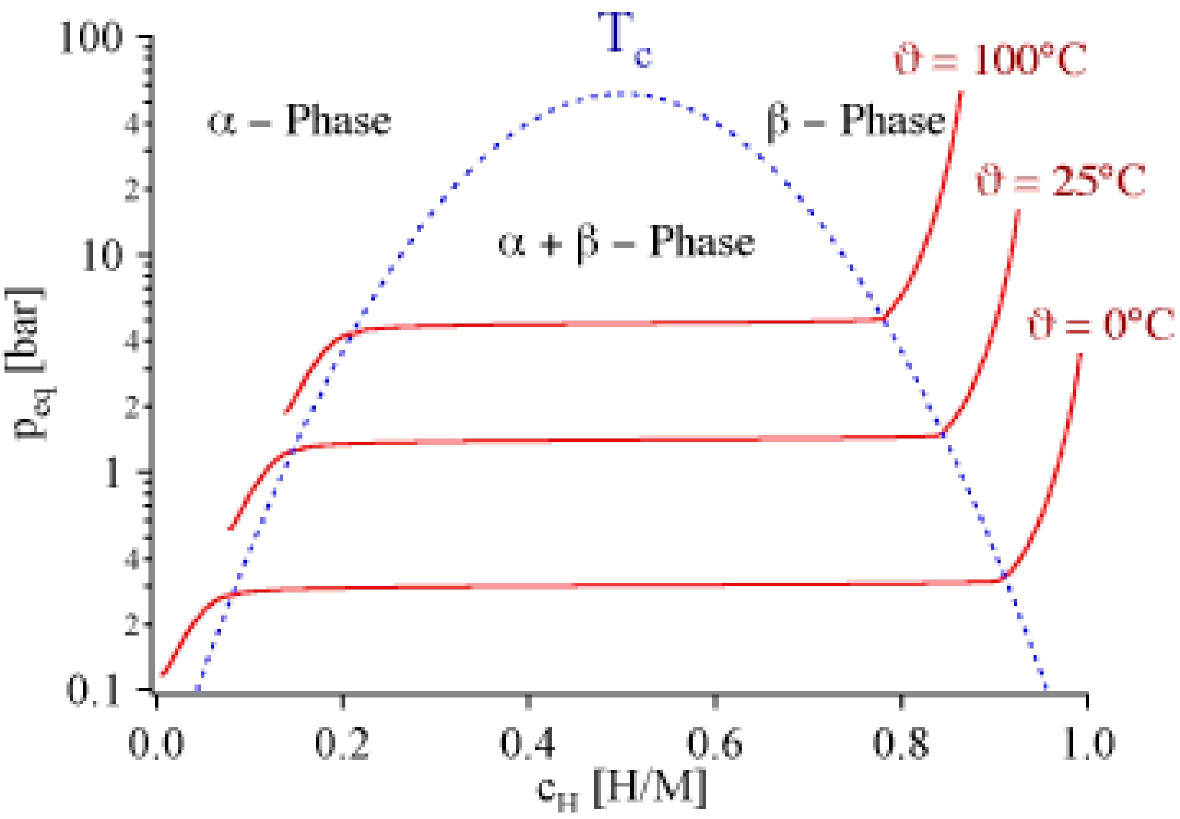
$$\text{Metal} + H_2 \Leftrightarrow \text{Hydride}$$

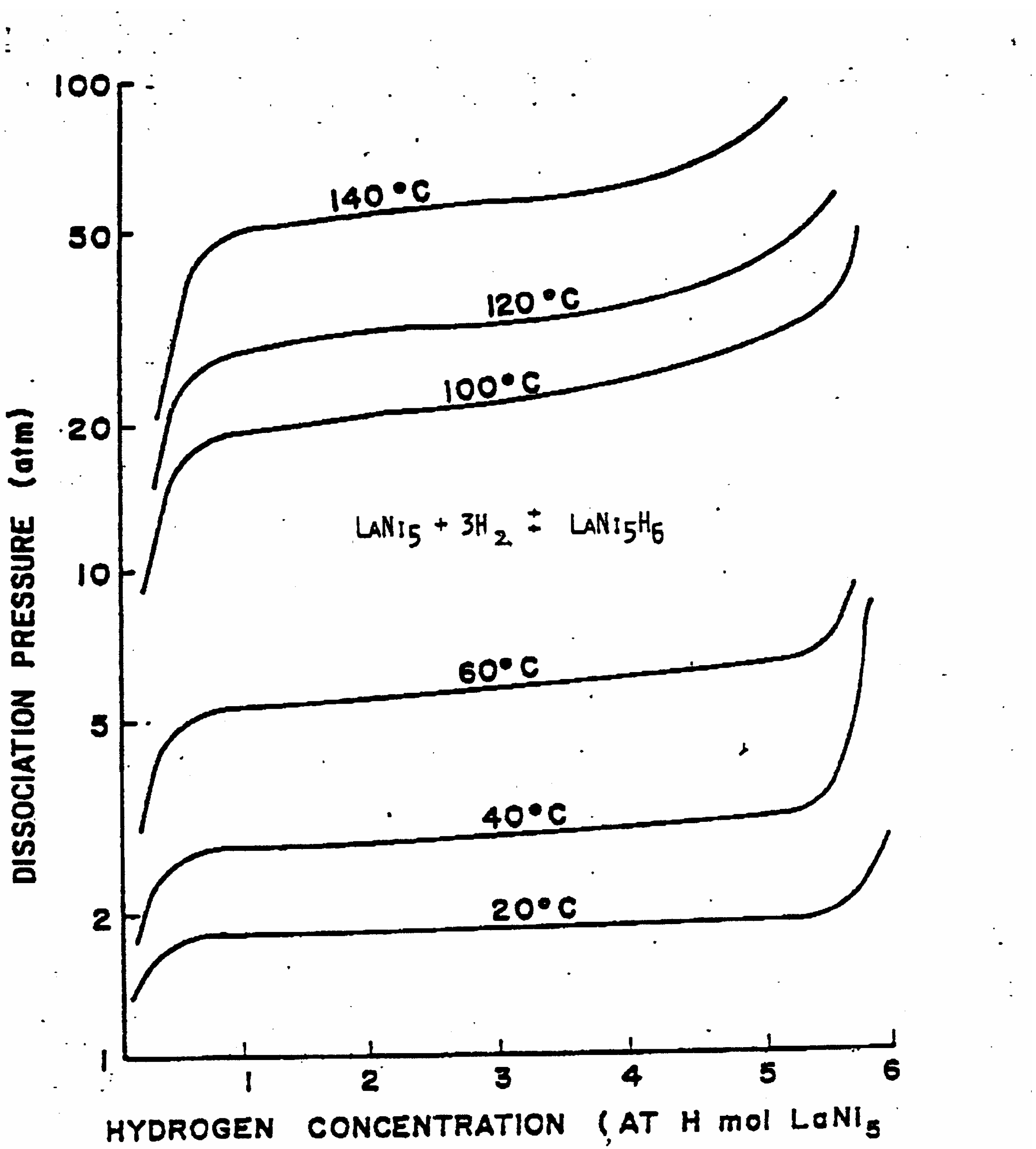
Gravimetric and Volumetric H-Densities

Hydride	wt % H	N_H
H_2 Gas (at 100ATM)	100	0.5
H_2 Liquid (20°K)	100	4.2
LiH	12.7	5.9
MgH_2	7.6	6.6
LaH_2	2.1	6.8
ZrH_2	2.2	7.3
UH_3	1.3	8.4
TiH_2	4.0	9.1

$N_H \times 10^{22}$ = Number of H atoms/cm^3

Pressure - Concentration - Isothermes




DISSOCIATION PRESSURE (atm)
100
50
20
10
5
2
1
140 °C
120 °C
100 °C
60 °C
40 °C
20 °C
LaNi5 + 3H2 ⇌ LaNi5H6
1
2
3
4
5
6
HYDROGEN CONCENTRATION (AT H mol LaNi5

Hydrides properties

- Pressure –Composition-Temperature Isotherms.

- Themodynamics:
  - Van't Hoff plot (InP vs.1/T)

$$LnP = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

ΔS and ΔH are negatives:
Hydriding – exothermic
Dehydriding - endothermic

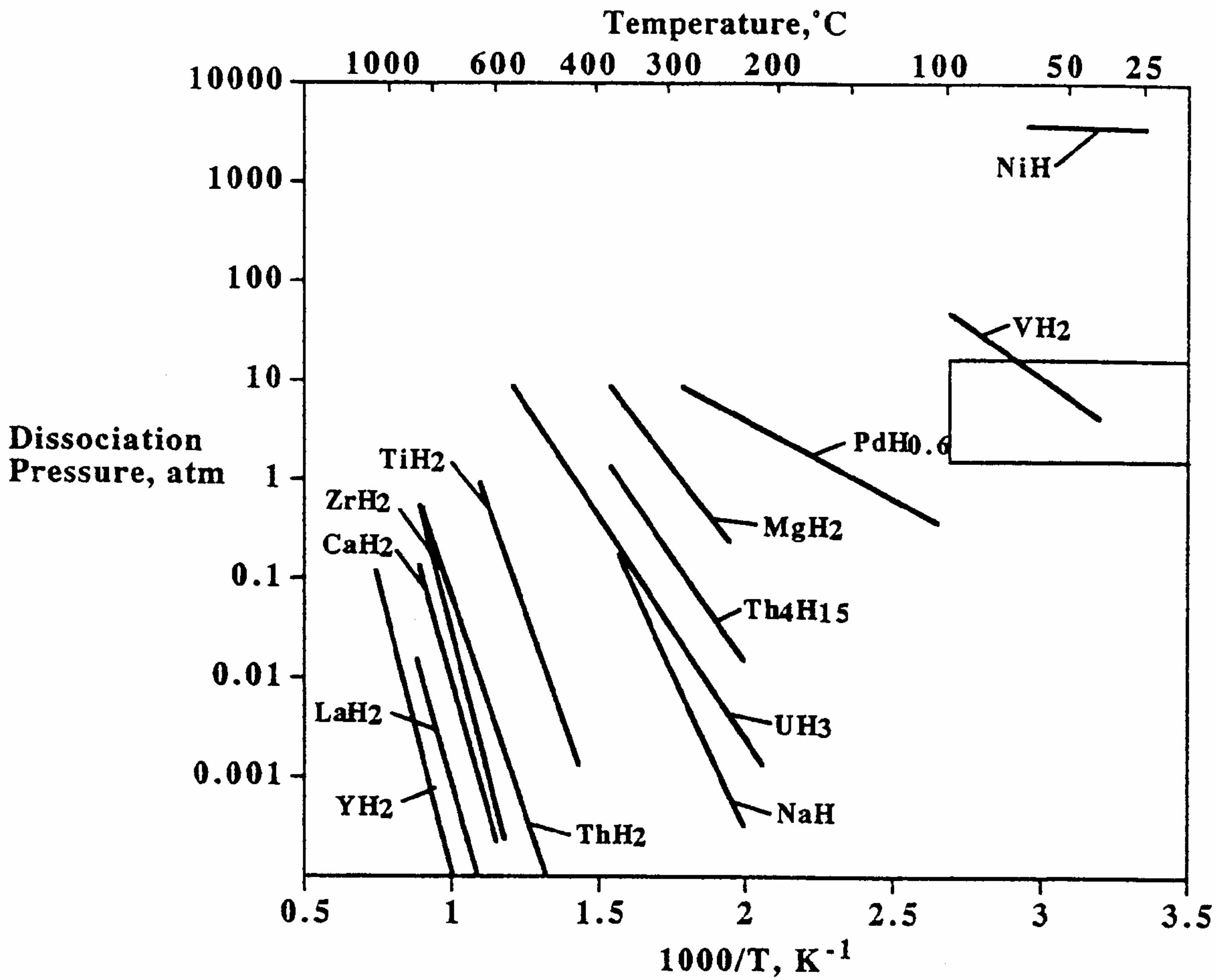


Fig. 3. Van't Hoff lines (desorption) for elemental hydrides. Box indicates 1-10 atm, 0-100°C ranges.

Hydrogen Storage Challenges:

Weight and volume
Cost
Efficiency
Life cycle
Refueling time (heat problem)
Codes and standards

•Magnesium Hydride

•MgH_2

7.6 wt% of hydrogen (851 liter H_2 STP / Kg)

Reversible hydride

Life cycles

low cost

Environmental friendly material

Established know-how of over 2 decades at Rotem's laboratories

BUT

$\Delta H = -18.5$ Kcal/mole H_2

Peq = 1 atm at 300°C

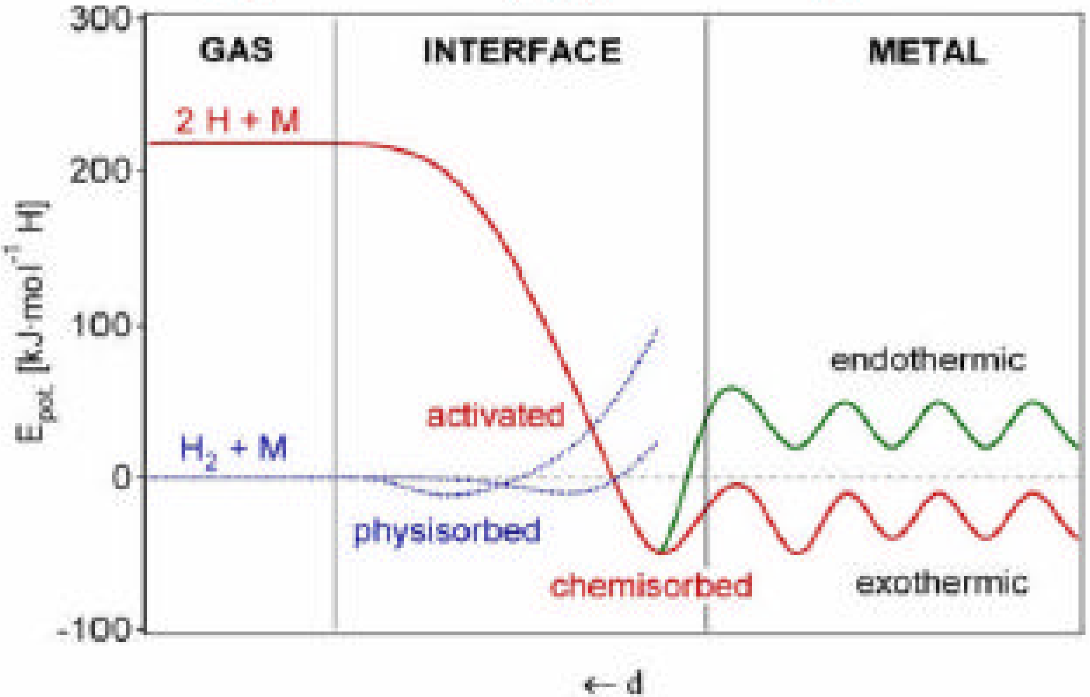
Destabilization by alloying

Mg_2NiH_4 Peq = 1 atm at 280°C

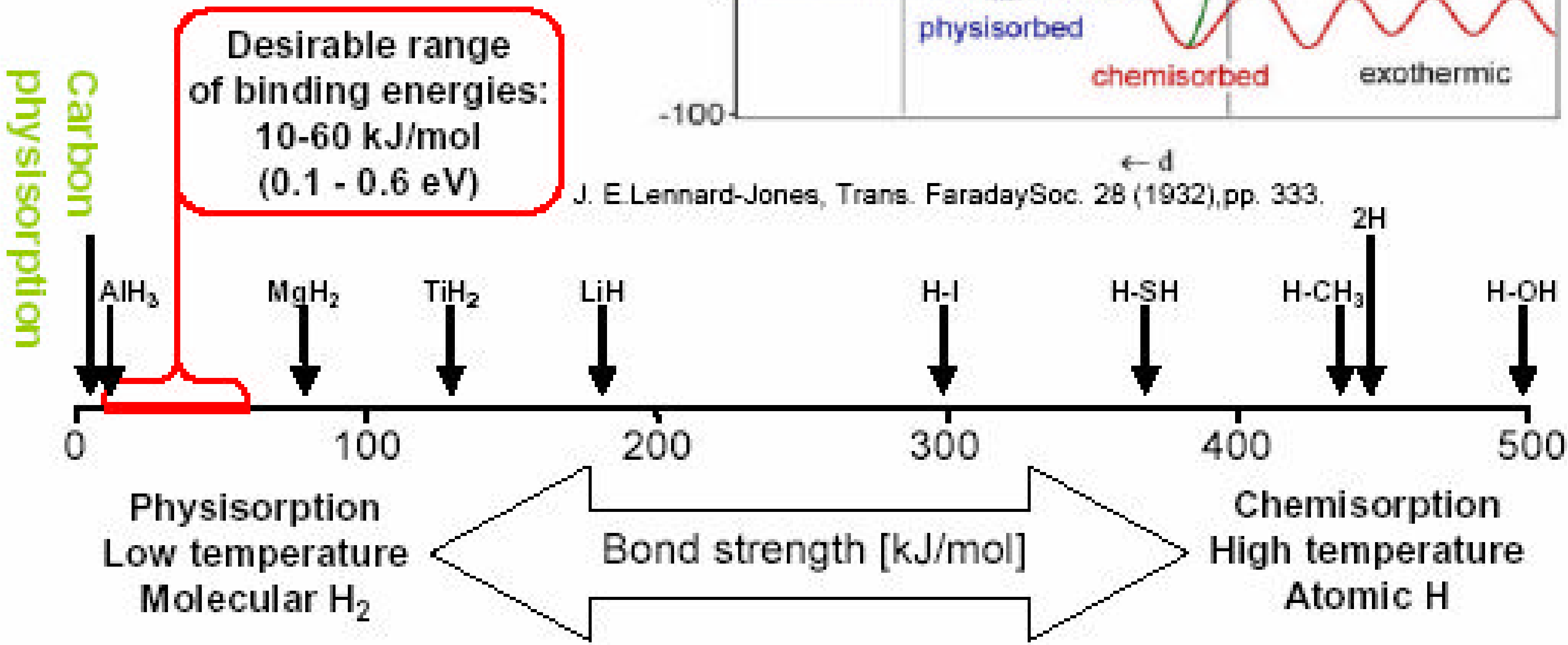
combination of electrochemical and nanotechnology ??

Desired binding energy range

Potential energy for molecular and atomic hydrogen absorption



J. E.Lennard-Jones, Trans. FaradaySoc. 28 (1932),pp. 333.



H Content various alanates

Alanate	H, wt. %
$NaAlH_4$	7.4
$LiAlH_4$	10.5
$Mg(AlH_4)_2$	9.6
$LiBH_4$	18.5
$NaBH_4$	10.7

Destabilization by doping

7.4 wt.% H total,
¾ or 5.6 wt.% usable

9% of H-content
Is irreversibly lost!

$$\underbrace{NaAlH_4}_{\text{7.4 wt.\% H total, 3/4 or 5.6 wt.\% usable}} + 0.03TiCl_3 = \underbrace{0.91NaAlH_4 + 0.09NaCl + 0.09Al + 0.03[Ti]^0}_{\text{6.2 wt.\% H total}} + \underbrace{0.18H_2}_{\text{9\% of H-content is irreversibly lost}}$$

6.2 wt.% H total,
¾ or 4.7 wt.% usable: ~16% loss of reversible capacity

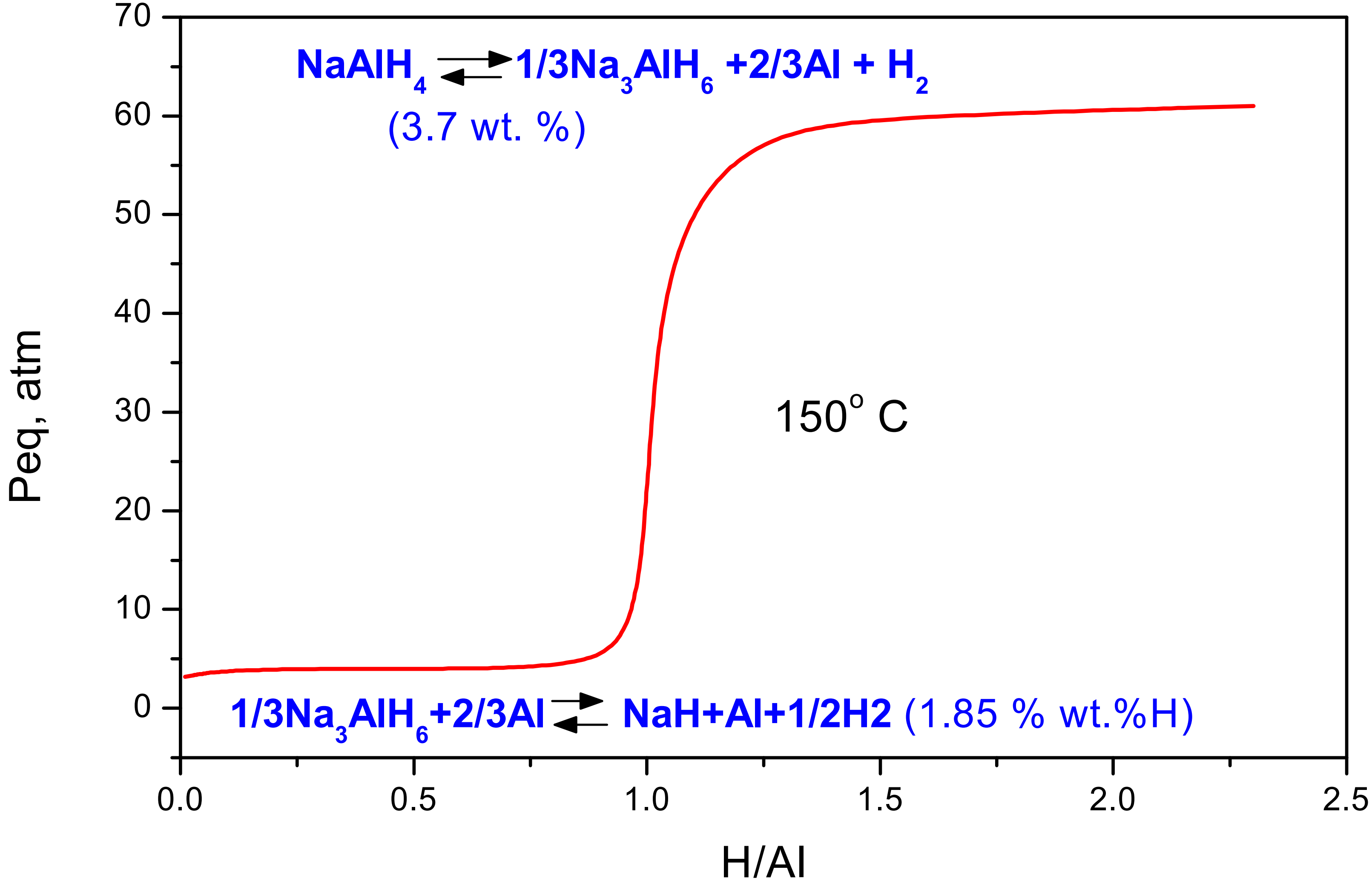
10.5 wt.% H total,
¾ or 7.9 wt.% usable

9% of H-content
Is irreversibly lost!

$$\underbrace{LiAlH_4}_{\text{10.5 wt.\% H total, 3/4 or 7.9 wt.\% usable}} + 0.03TiCl_3 = \underbrace{0.91LiAlH_4 + 0.09LiCl + 0.09Al + 0.03[Ti]^0}_{\text{8.5 wt.\% H total}} + \underbrace{0.18H_2}_{\text{9\% of H-content is irreversibly lost}}$$

8.5 wt.% H total,
¾ or 6.4 wt.% usable: ~19% loss of reversible capacity

PC Isotherm; Ti catalyzed $NaAlH_4$



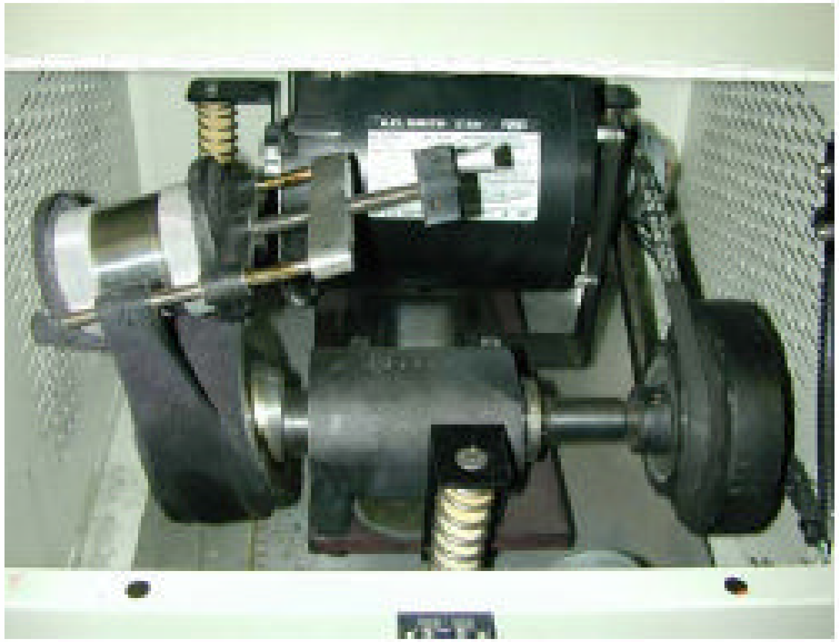
B. Bogdanovic et al. J. Alloys & Cpds. 302, 36, 2000.

Complex Hydrides – A New Frontier for Future Energy Applications

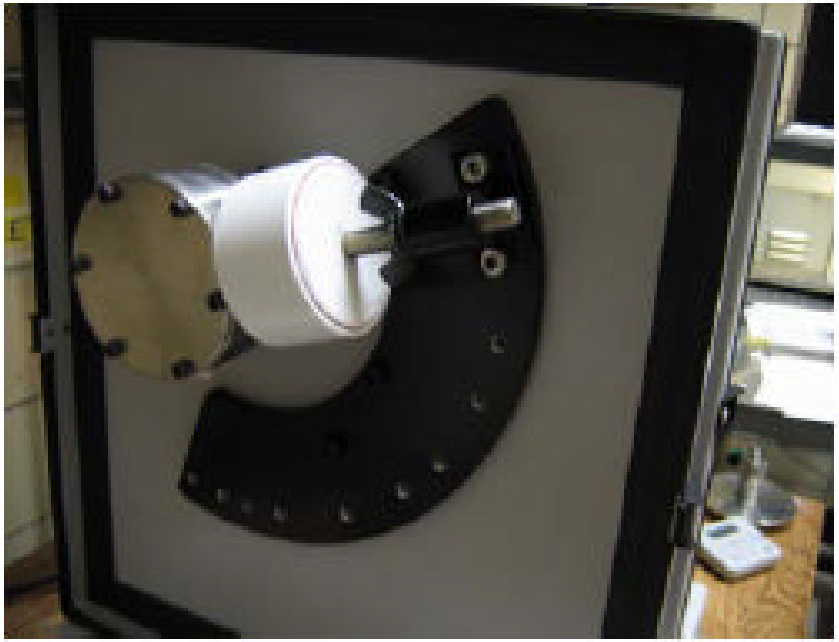
Vitalij K. Pecharsky et al, Iowa State University, Ames,

- **<u>Program Scope</u>**
- **Synthesize** an array of **novel non-transition metal-based complex hydrides.**
- **Mechanochemical technique** starting from several parent **light-element hydrides**.
- Fully **characterization** using **state-of-the-art experimental** techniques.

Mechanochemistry

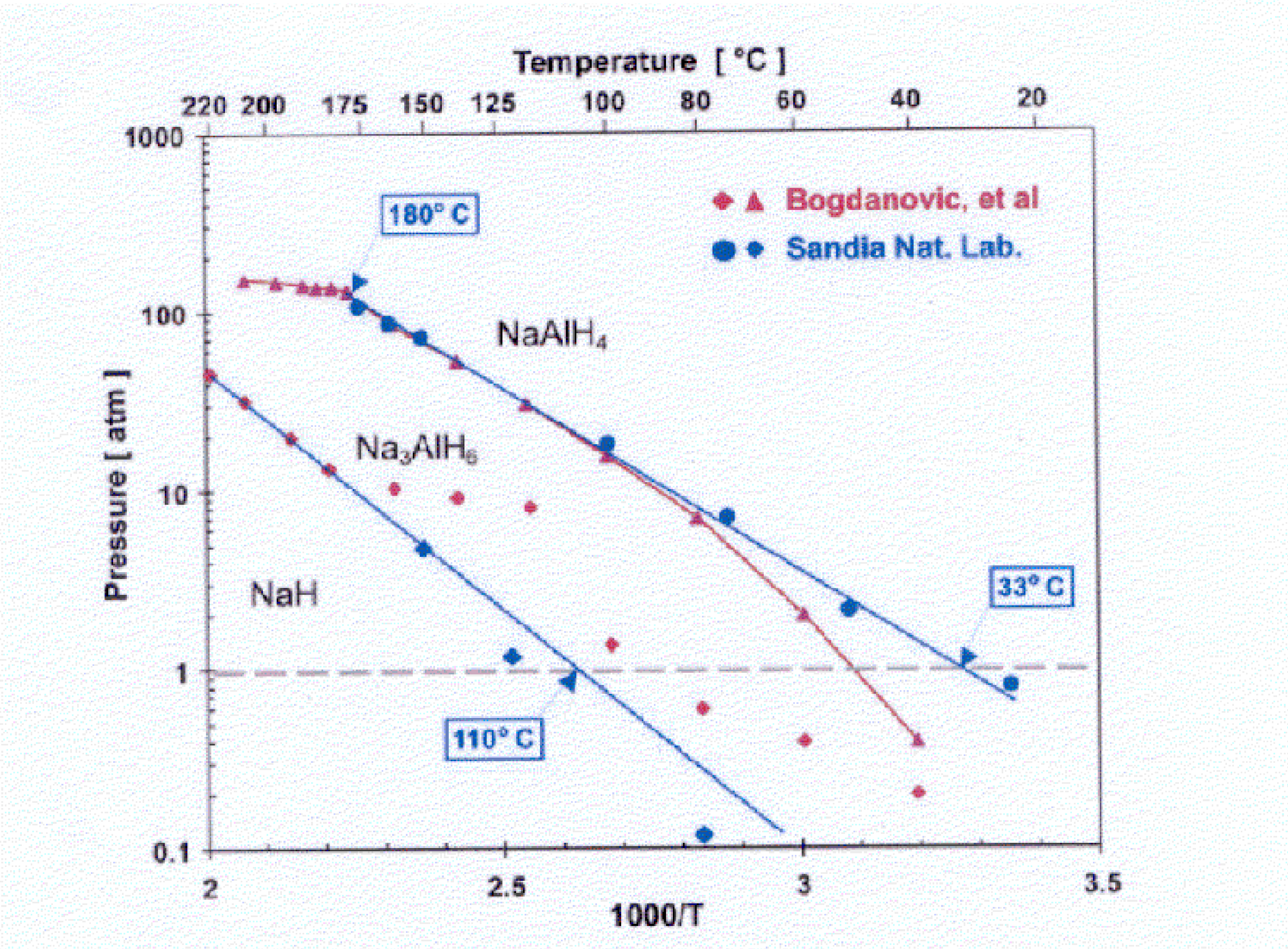


SPEX: high energy; control by balls-to-material mass ratio



Magnetic: variable energy; control by rpm and positioning of the magnets

Van't Hoff Plot for 2 alanate phases



K. J. Gross et al. Proc. Of 2000 DOE/NREL Program Review

Nanotechnology and the Hydrogen economy

Hydrogen storage in carbon nanotubes

- Storage of H_2 in single wall carbon nanotubes (SWNT) of 98% purity.
- M. J. Heben (NREL): SWNT with internal dimensions of 1-2 nm shows 6.5 wt% H-capacity at R.T.

High Throughput Screening of Nanostructured Hydrogen Storage Materials

Mildred S. Dresselhausa et al
Massachusetts Institute of Technology

- **combinatorial** materials synthesis approach, to identify high **capacity hydrogen storage fast kinetics**.
- **Nanostructured metastable** hydride materials for storing hydrogen by chemisorption and physisorption mechanisms, and with kinetics, enabled by the **small size** and **good heat transfer** characteristics.
- Development of **nanoporous** hydride materials through the synthesis of nanocomposite materials with finetuning of the process conditions.
- Development of **materials characterization techniques**.
- Development of **models** and **simulations** for understanding of size effects on the thermodynamics, kinetics, heat transfer in nanostructured hydrogen storage materials.

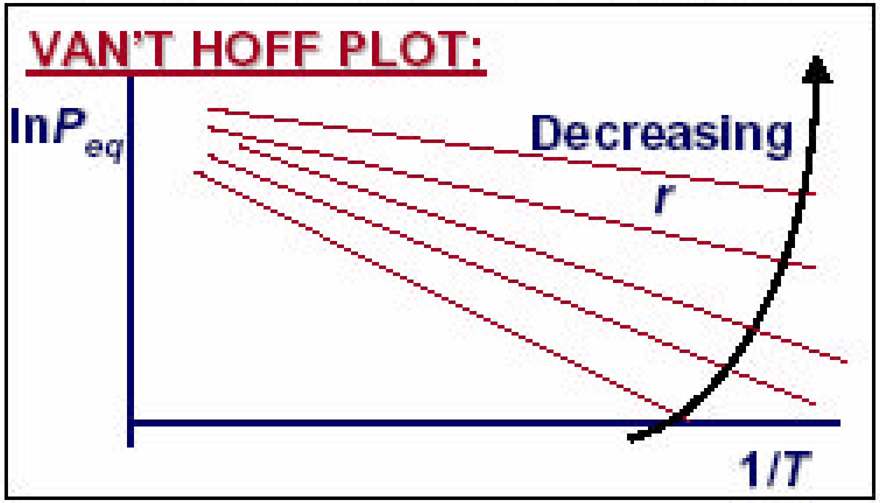
Size Effects on Thermodynamic Properties

Assuming the following reaction

$$M + H_2 \rightarrow MH_2$$

- At the nanoscale, the surface energy becomes important and it modifies the free energy.
- If the surface energy term Δ is positive, enthalpy of formation will be reduced for smaller particles.

Van't Hoff plot for a model MH_2 hydride



Bulk molar free energy of formation

$$\boxed{\Delta G = \Delta G_o + RT\ln\left(\frac{a_{MH}}{a_M P_{H_2}}\right)}$$

Van't Hoff relation

$$\boxed{\ln P_{H_2}^{eq} = \frac{\Delta H_o}{RT} - \frac{\Delta S_o}{R}}$$

Nanoparticle molar free energy of formation

$$\boxed{\Delta G(r) = \Delta G_o(r) + RT\ln\left(\frac{a_{MH}}{a_M P_{H_2}}\right) + \frac{3\overline{V_M}\Delta(\gamma_{Mg}, \gamma_{MgH_2}, r)}{r}}$$

Nanoscale Van't Hoff relation

$$\boxed{\ln P_{H_2}^{eq} = \frac{\Delta H_o}{RT} + \frac{3\overline{V_M}\Delta}{rRT} - \frac{\Delta S_o}{R}}$$

AlH_3

<u>Mission Statement:</u> *To develop and demonstrate a safe and cost-effective light-metal hydride material system that meets or exceeds the DOE goals for on-board hydrogen storage.*

Decomposition of AlH_3

$AlH_3 \rightarrow 3/2H_2 + Al$ (Temp. = 60° – 100° C)

H-capacity (g) = 10.1 wt% (DOE 2010 Storage-Target = 6.0)

H-capacity (v) = 149 kg/m3 (DOE 2010 Storage-Target = 45)

ΔH_{des} = 7.6 kJ/mol H2 (only 20% of NaAlH4)

AlH_3 Polymorphs

- A total of seven AlH_3 isomers are known to exist:
  - α, α', β, δ, ε, γ, ζ
- With exception of α-AlH_3, little is known about these polymorphs
- α, β, and γ phases can be grown using an organo-metallic synthesis method

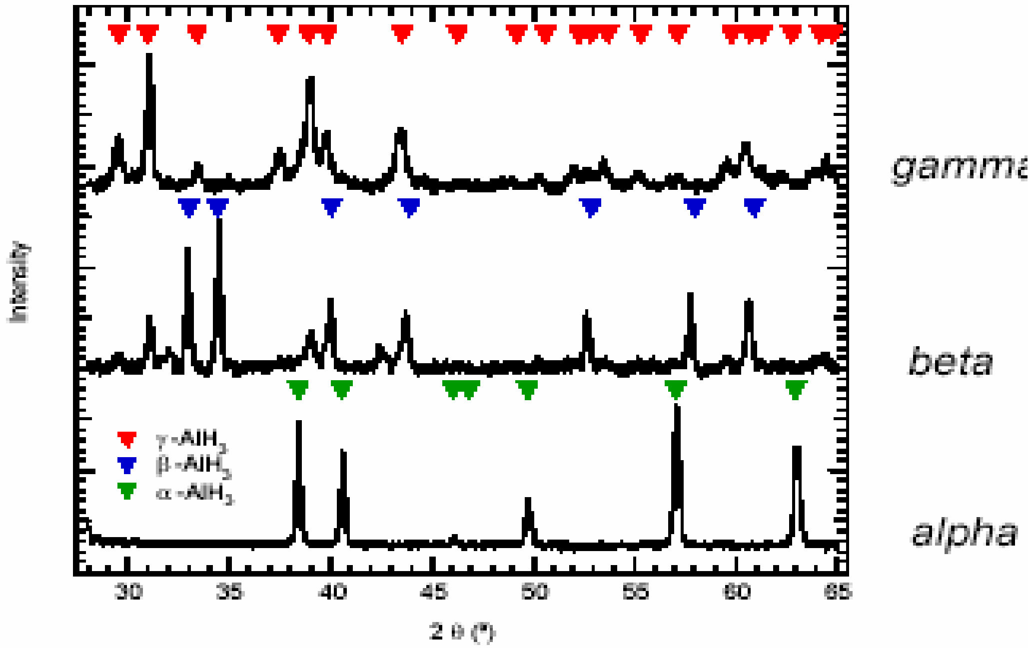
$$3LiAlH_4 + AlCl_3 + ether$$

$$\downarrow \text{(filter)}$$

$$4AlH_3 + 3LiCl + ether$$

$$\downarrow \text{(remove ether)}$$

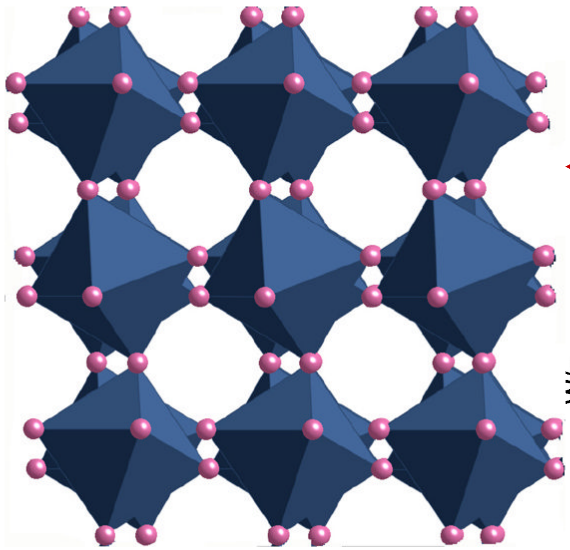
$$4AlH_3$$



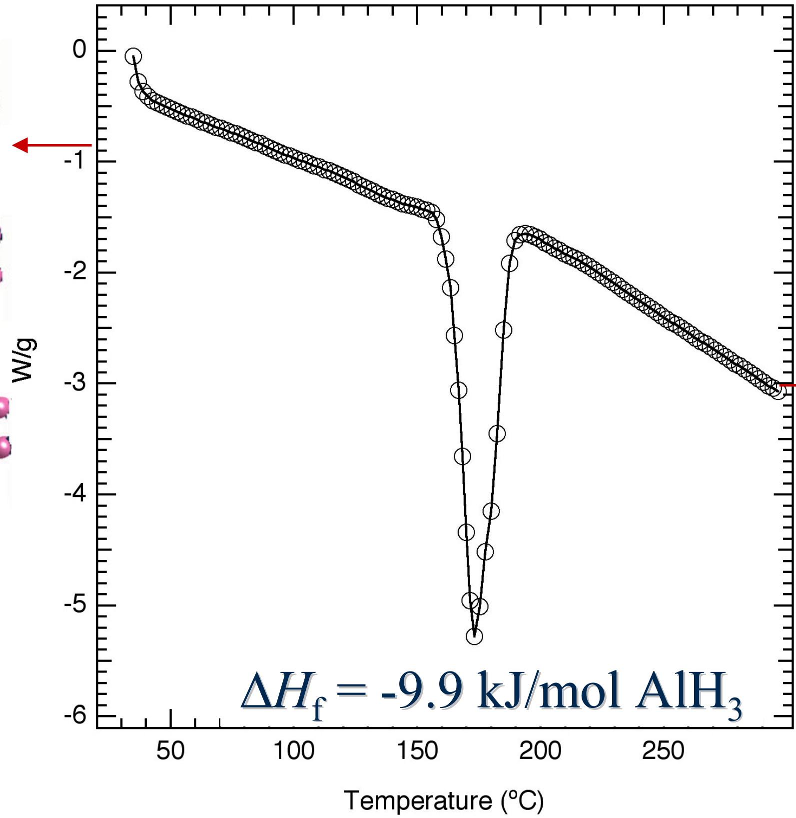
Thermodynamics of α-AlH_3

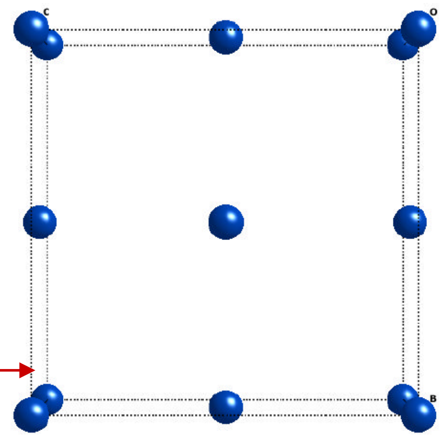
- Differential scanning calorimetry 30 - 300° C at 10° C/min
- Large endothermic peak at ~160°C from decomposition reaction:

$$\alpha\text{-}AlH_3 \rightarrow Al + 3/2\ H_2$$



α-AlH_3 (R-3c)



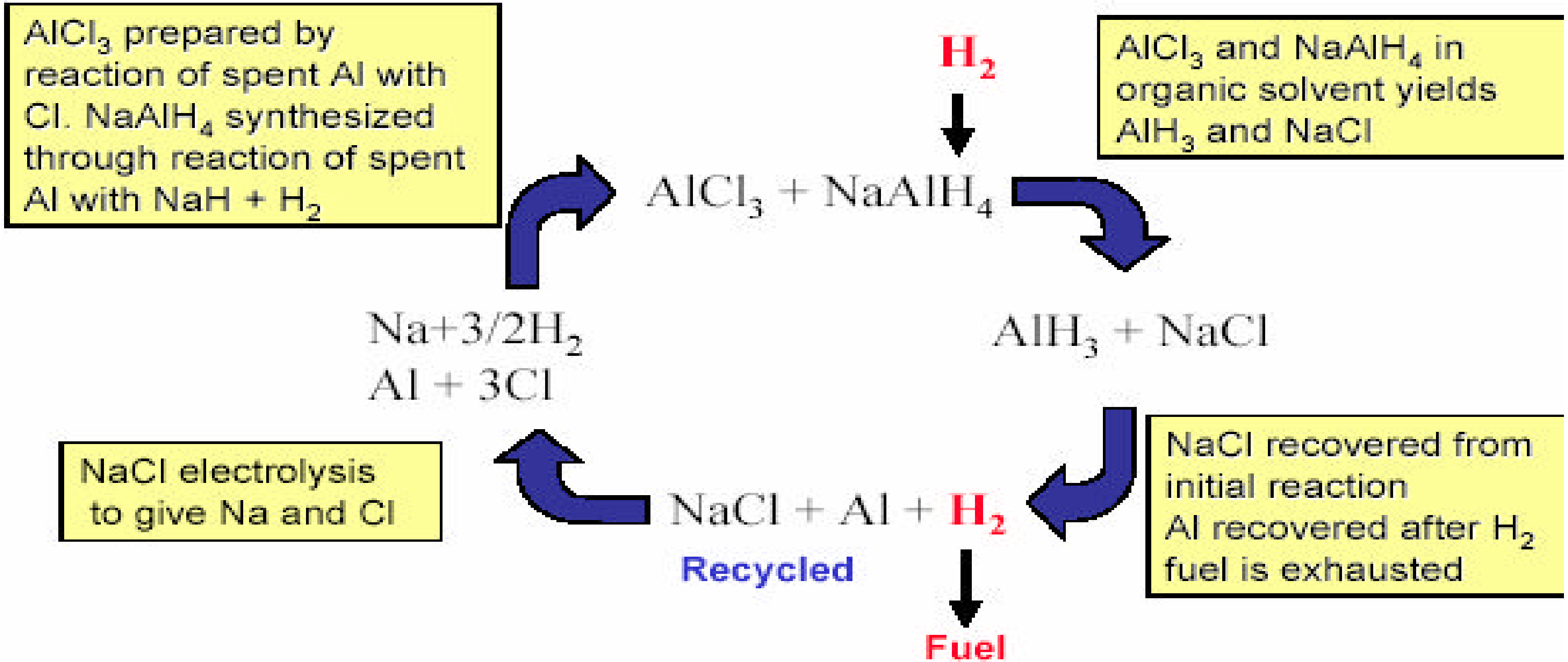


Al metal (fcc)

J. Graetz, et al., *J. Alloys. Comp.* (2006)

Reversible AlH_3

- AlH_3 may be regenerated from recovered products after hydrogen fuel is spent



Note: system is "reversible" since all products are recovered and re-used (except hydrogen).

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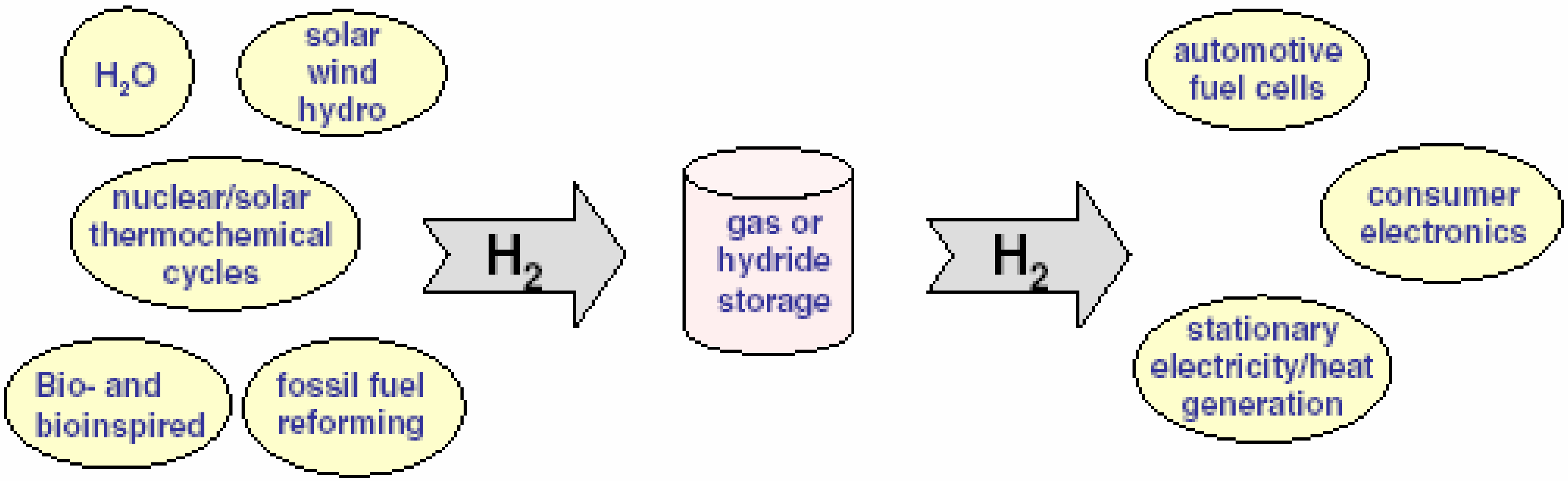
The Hydrogen Economy – The Technology Gaps



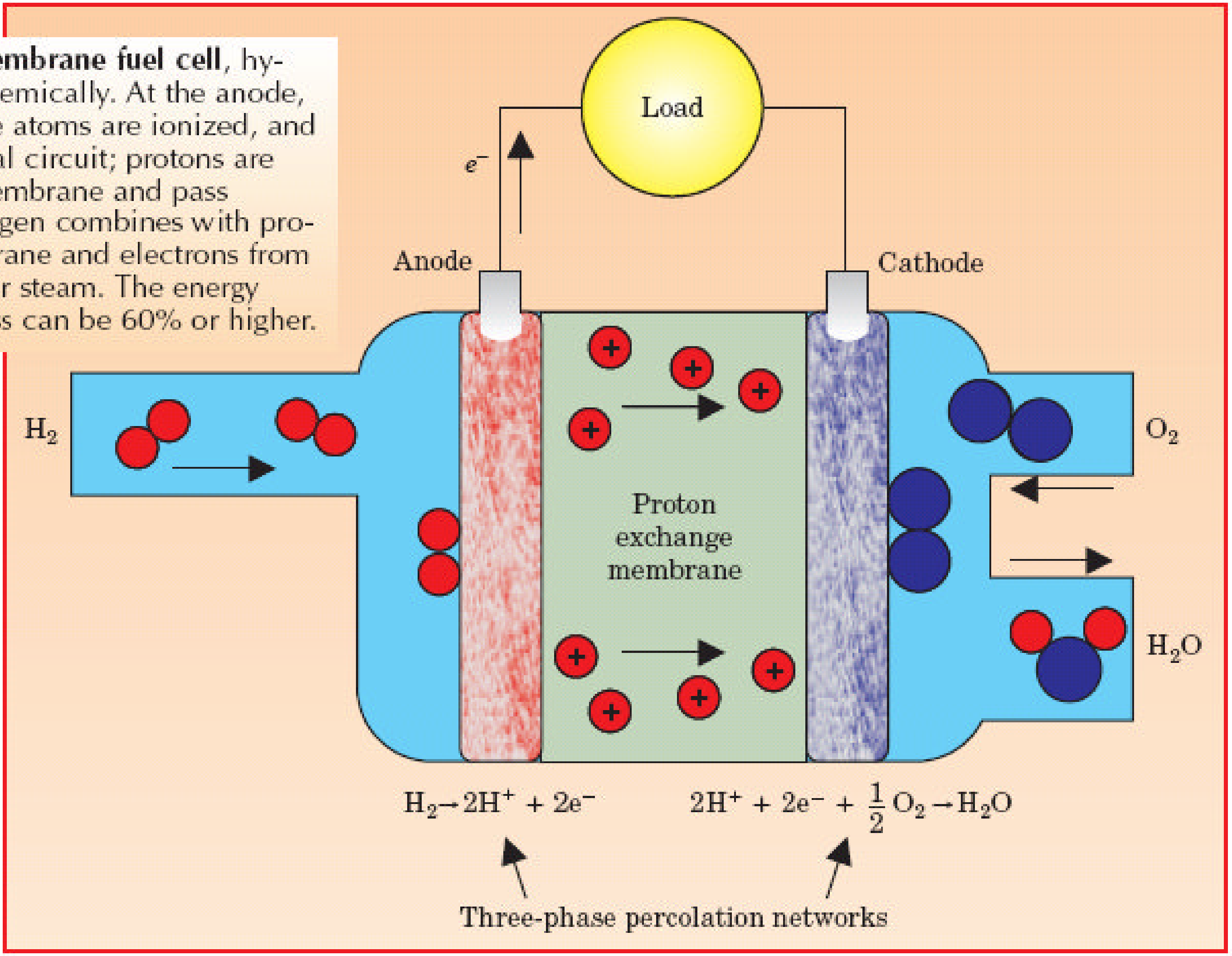
production	*storage*	*use (in fuel cells)*
9M tons/yr	4.4 MJ/L (Gas, 10,000 psi) 8.4 MJ/L (LH2)	\$200-3000/kW
Gap	Gap	Gap
150M tons/yr (Light Cars and Trucks in 2040)	9.7 MJ/L (2015 FreedomCAR Target)	\$30/kW (Internal Combustion Engine)

Applications

- Fuel cells.
- Nickel metal hydride batteries.
- Getters.
- Sensors.
- Sorption cryocoolers.
- Heat Pumps

PEM Fuel Cell

Figure 5. In a proton-exchange-membrane fuel cell, hydrogen and oxygen react electrochemically. At the anode, hydrogen molecules dissociate, the atoms are ionized, and electrons are directed to an external circuit; protons are handed off to the ion-exchange membrane and pass through to the cathode. There, oxygen combines with protons from the ion-exchange membrane and electrons from the external circuit to form water or steam. The energy conversion efficiency of the process can be 60% or higher.



מכוניות מונעות במימן

- בעולם יש 200 מכוניות לניסוים ולבדיקות.
- F-cell מתוצרת מרצדס

מונעת במימן דחוס (350 Atm) מהירות 140 קמ״ש.טווח 100-160 ק״מ.

- בתהליך המילוי בעיה קריטית של פינוי חום (רדיאטורים ומאווררים).
- קילוגרם של מימן מספיק תיאורטית ל-100 ק״מ.
- מחיר ק״ג מימן 2.7Eur .
- בעיית תשתית הובלה, חלוקה ותחנות תידלוק.
- הדור הבא F-600

לחץ 700Atm, טווח 400 ק״מ, מהירות קמ״ש 170

תאוצה 11sec ל-100 קמ״ש.

- מכוניות מונעות במימן נוזלי.

METAL HYDRIDE ELECTRODES

- AB_5:

$$AB_5 + 6H_2O + 6e^- \Leftrightarrow AB_5H_6 + 6OH^-$$

  – $LaNi_5H_6$=372mAH/g
- AB2:

$$AB_2 + 3H_2O + 3e^- \Leftrightarrow AB_2H_3 + 3OH^-$$

  – VTiZrNiCrCoMnAlSn alloys (Ovonics)=440mAH/g
- 1000 cycles
- Degradation and corrosion in 6M KOH.

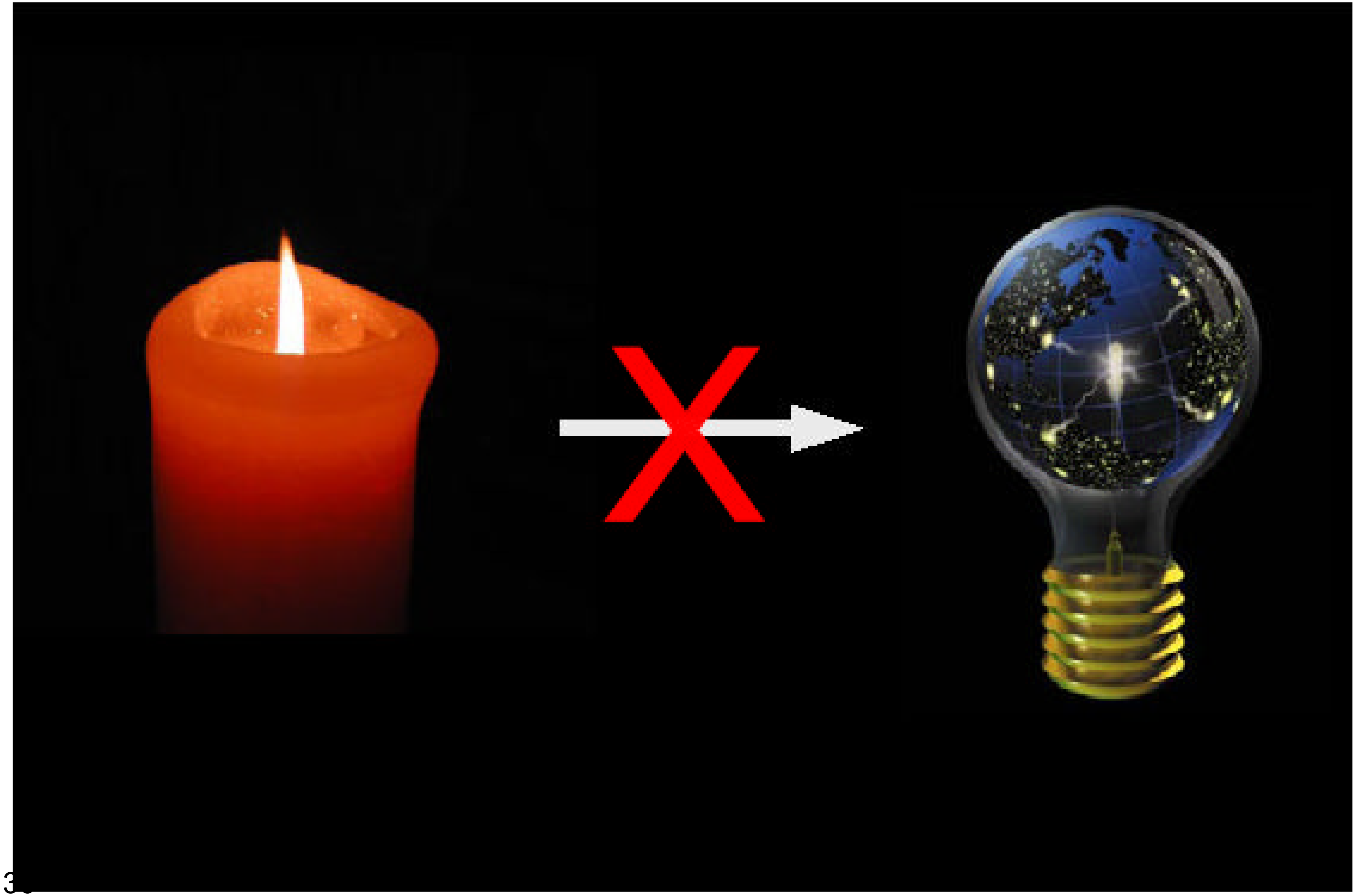
Future Directions

- Reversible complex hydrides
- Modification of alanates
- Low-temperature reversible amides
- Reversible borohydrides move from $NaBH_4$ to $LiBH_4$.

- Aluminum hydride:

Determine the optimum AlH_3 phase
Perfect the metallurgical stimulation approach to achieve >8 wt.% H_2 desorption at <100°C;
Develop an off-board process to rehydride spent Al at a cost less than the 2010 DOE target.

... but electricity was not discovered via incremental improvements to the candle



Applications

- Fiber optic sensors: color change WO3-H2 (NREL – DCH Technology).
- Permanent magnet production (Nd-Fe-B)
- Chemical catalysis.
- Ammonia synthesis

My activities

- Dilatometric and Electrochemical studies of metal hydrides:
  - H_2 transport through oxide layers (CeO_2, RuO_2, Gd_2O_3).
  - Hydrogen sensing by the above technique.