IEA Hydrogen TCP Task 32
Subtask: Application of Hydrides in Hydrogen Storage and Compression
Dr. Martin Dornheim, Helmholtz-Zentrum Geesthacht

16th International Symposium on Metal-Hydrogen Systems
Guangzhou, Oct. 28th – Nov. 2nd
## Application of Hydrides in Hydrogen Storage and Compression

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Application of Hydrides in Hydrogen Storage and Compression: Achievements, Outlook and Perspectives

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Submitted for publication in IJHE
Fuel cell train
Activities on Hydrogen Storage Systems

• Materials and Concepts

• Cost Analysis & System Analysis

• Scale up materials production – ball-milling, cold rolling etc.

• Tank development and testing

• Large Scale Testing Infrastructures

• Integrated Systems / Applications
  • Mobile
  • Stationary
  • Metal Hydrid Compressors
Optimization of storage tanks requires knowledge of processes inside tank

High sensitivity of neutrons towards hydrogen
Compaction in Pellets
Neutron imaging of FlexiStore storage tank

Tank designed for *in situ* studies of medium & high temperature metal hydrides

- Steel body for \( p \leq 100 \text{ bar}, T \leq 400 \, ^\circ\text{C} \)
- Monitoring of temperature, pressure and hydrogen flow
- Neutron radiography using of fission neutrons at NECTAR at MLZ:
  60 mm pellet, Exposure time: 250s, Field of view: 28 cm x 28 cm, Pixel size: 0,28mm x 0,28mm
Neutron imaging of metal hydrides / Reactive Hydride Composites (RHC)

→ Sodium alanate:
   \[ \text{NaH} + \text{Al} + \frac{3}{2} \text{H}_2 \leftrightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 \leftrightarrow \text{NaAlH}_4 \]

→ Li-RHC: \[ 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2 \leftrightarrow 2\text{LiBH}_4 + \text{MgH}_2 \]

→ Study of dominant driving forces for heterogeneous hydrogen distribution:

Material packing density

Temperature gradient

Hydrogen distribution
Demonstration project: HyFill-Fast
Aarhus Universitet, Danmark, Torben R. Jensen (coordinator),
Danish Technical University,
Helmholtz-Zentrum Geesthacht, Germany, Martin Dornheim
Nel Hydrogen Fuelling, Danmark,
Korea Institute of Science and Technology, Seoul, Sydkorea, YoungWhan Cho

HyFILL-FAST – A new concept

- Aim: (1) develop ionic liquid hydrogen compressor; (2) New concept for combined hydrogen gas (700 bar) and solid state hydrogen storage; (3) Materials that absorb hydrogen and/or heat; Metal hydride hydrogen compressor for advanced diffraction experiments to study hydrogen release and uptake.
- Develop more energy-efficient hydrogen compression and cooling, faster vehicle refueling, larger hydrogen storage capacity, longer vehicle driving range, improved general energy efficiency.

Synthesis Scale-up

Process development

→ Requirement of novel additives
→ Contamination prevention
→ New safety concepts

Material cost reduction

→ Use of cheaper catalysts (3TiCl₃·AlCl₃, …)
  → Properties comparable or improved
  → Sensible material cost reduction
→ Use of hydrides synthesized from waste
  (MgH₂, NaAlH₄, from Mg and Al, …)
→ Very good kinetics and reversibility
  → Slightly reduced H₂ capacity

Pistidda C. et al., Hydrogen storage systems from waste Mg alloys, J. Power Sources, 270 (2014), 554
Siebtechnik ball-mill

- bis zu 10 kg Pulverchargen
- hochskalierbar bis in den Tonnenmaßstab
- kontinuierlicher Betrieb möglich
Symoloyer CM100

Industrial scale production costs

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<th>CM100</th>
<th>CM400</th>
<th>CM900</th>
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<tr>
<td>powder production</td>
<td>[kg/h]</td>
<td></td>
<td></td>
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<td>production capacity</td>
<td>[to]</td>
<td></td>
<td></td>
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<tr>
<td>~processing costs</td>
<td>[€/kg]</td>
<td>2.09 €</td>
<td>0.98 €</td>
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rotary v feeders

starting materials a + b

side channel turbine SKV**

dustgasfilter SGF**

pilot cyclone ZK**

air lock

product -ab-

charge- & drain-gratii Bska**/As
Research in Progress in KIST: Solid H₂ storage for stationary applications

- Mg + Fe mixture by vertical roll milling process
- Mg-Ni eutectic alloys by melting and pulverization
- Lab-scale tank under testing

Mg-Ni alloy powders

Lab-scale vertical roll mill

Lab-scale tank (300 g powder)
The storage material

The material chosen for this tank is **Hydralloy C5** from GfE GmbH, an intermetallic hydride type \( \text{AB}_2 \) (TiMn\(_2\)) with C14 Laves phases structure:
- \( \text{H}_2 \) gravimetric capacity **1.83 wt.%**
- \( \text{H}_2 \) volumetric capacity **115 g/L**

Exact composition:
- Mn 52.0 \%
- Ti 27.5 \%
- V 14.1 \%
- Fe 3.0 \%
- Zr 3.0 \%
- Al 0.3 \%
The storage system

1 Module:
- 0.285 L and 960 g of hydride
- ~17 g H₂ stored
- Positive results
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5 Modules:
- 4720 g of hydride and ~85 g of H₂
- Relief valve added

10 Modules:
- ~10 Kg hydride and ~170 g H₂
- Positive full scale testing
The storage system

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- 0.285 L and 960 g of hydride
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Frame and casing:
- Stable and robust
- Ancillaries and connections
Hydrogen storage test tanks based on NaAlH4


Applied research: heat pump based on AB$_5$ alloys
LCA H2 tanks

T3 and T4: type III and type IV compressed gas tanks

SS: mixture of metal and complex hydrides \((\text{LaNi}_{4.3}\text{Al}_{0.4}\text{Mn}_{0.3} + 2\text{LiNH}_2 - 1.1\text{MgH}_2 - 0.1\text{LiBH}_4)\)

SS tanks have similar environmental performances than T3 and T4

APU installed on IVECO Daily

M. Baricco. et al., J. Power Sources 342 (2017) 853
Assembly of Metal Hydride Based Hydrogen Storage Reservoir

**Single Hydride Tube**
Optimized tube design from single tube tests

**Hydride Tube Array**
- Staggered 5 x 8 array of 2” diameter tubes.
- Maximizing number of rows/column improves heat transfer
- Baffles used to alternate fluid flow.

**Hydride Reservoir**
Dimensions: 470mm x 700mm x 370mm. Hydrostatically pressure tested to 1,500 psi (2x op. press.)
Integration of Metal Hydride Based Hydrogen Storage Reservoir with PEM Fuel Cell Power Pack

- Fuel Cell Power Module
- Power Electronics
- Hydrogen Reservoir
- Ultra Capacitors
- Radiator
Final Integration and Field Testing

Final integration of the metal hydride based hydrogen storage system, fuel cell and forklift carried out at Greenway Energy in 2015.

Trouble shooting and field testing of the fully integrated system carried out with funding from the US DOE Small Business Vouchers pilot at SRNL 2017 -2018.

Forklift before and after replacement of the 48 V battery system by the integrated fuel cell and MH hydrogen storage system
Stationary applications of metal hydrides in Japan

Resort hotel

H2One™ Family

Portable container

Load leveling

H2One installed in 2016

Installed at a resort hotel

Metal hydride is used for seasonal energy storage

Hydrogen capacity: 1000Nm³

Small size H2One on two 4ton Trucks

Expected for emergency use with 250Nm³ of hydrogen

Mobile

Tohoku Power Company installs for load leveling

Storage capacity of MH: 220Nm³ of hydrogen

Load leveling

The system for 1000m² building

PV cell of 20kW and 300kg of TiFe base alloy contains 40Nm³ of hydrogen

PV cell supplies energy for lightning and other usage at the baseball stadium

Hydrogen capacity: 200Nm³

P2G at baseball stadium

NEDO project at Yamanashi

Renewable energy from PV power stored in AB5-type hydride

Capacity: 52Nm³ in AB5-type at preset

However, installation of large scale TiFe storage is planned

NEDO project at Sendai

At a water filtration plant hydrogen is used for emergency power supply

Capacity for three day operation: AB5 hydride 240Nm³ and Gas cylinder 240Nm³ (8 bar in 30Nm³ tank)
Microgrid:
It is a small scale power supply network that is designed to provide power for a small community.

• Intelligent Microgrids + Appropriate Storage for Energy (IMASE) UK-India Project

• Intelligent smart energy community - UK (ISEC) project
Heat management of hydride stores

For small and large stores heat management can be critical to effective operation

E.I. Gkanas, D.M. Grant, A. Stuart et al doi:10.1016/j.jallcom.2015.03.123
E.I. Gkanas, D.M. Grant A. Stuart et al 10.1016/j.ijhydene.2016.04.035
ESCHER – Non mechanical compressor based on metal hydrides
MIRE group: Hydrogen storage systems for mobile and stationary applications
Realistic simulation in a single stage hydrogen compressor based on AB₂ alloys

A.R. Galvis E, F. Leandini, J. Bodoga, J.R. Aras, J.F. Fernandez

MME-Group, Esc. Física de Materiales, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049, Madrid, Spain

For instance:

• 10⁻²<P<200b
• Based on AB₂ alloys
• 3-stages and fast kinetics
• 0.25 mol H₂/compressed

Current/Future research:

• Coupling the compressor with a photocell: Improvement of the first stage

• Use of compressor to investigate the thermodynamic and kinetic properties of non-stable hydrides.
Metal Hydrides Compression Cycle

Compression Steps:
1 – 2: Absorption ($T_1$)
2 – 3: Heating up
3 – 4: Desorption ($T_2$)
4 – 1: Cooling

The batch process can be automatized by combining two compression units in parallel.
**GRZ HyCo**

- **Maximal Pressure [bar]**: 150
- **Maximal Outlet Flow Rate [Nml/min]**: 400
- **Storage Capacity [Nl]**: 70
- **Refueling pressure [bar]**: 8
- **Ramp-up time [min]**: 6
- **Dimensions L x W x H [mm]**: 350 x 250 x 170
Small-Scale Demonstrator Compressor

5 – 50 bar
20 – 110° C
Max. Flow at 50 bar: 50 g\textsubscript{H}_2/h

Small-scale demonstration of the conversion of renewable energy to synthetic hydrocarbons, N. Gallandat et al., RSC Sustainable Energy and Fuels, 2017
HYMEHC-5

- Capacity: 5 Nm³/h
- Input pressure: 6 bar
- Output pressure: 200 bar
- 2-stage compressor system

HYMEHC-10

- Capacity: 10 Nm³/h
- Input pressure: 10 bar
- Output pressure: 200 bar
- 2-stage compressor system
Hydrogen Tank Testing Facility (HTTF) Schematic overview

- Flow controller
- Data recording
- Process control

- Test chamber
- Hydride tank
- Vacuum pumps

- Thermal generator
- Heating and cooling
- Thermal fluid
New Hydrogen Tank Testing Facility (HTTF2)
- Office and lab space
- ERA and ETC team
- High Performance Compression and Expansion
- Hydrogen Systems Test Bed
- Carbon Capture Demonstrator
- Multidisciplinary Research Lab
Solid State Hydrogen Storage @ Helmholtz-Zentrum Geesthacht

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500 bar Hydrogen Tank Test Facility II