# Advanced Nanostructured Materials for Solid State Hydrogen Storage

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GKSS Research Centre Geesthacht, Germany

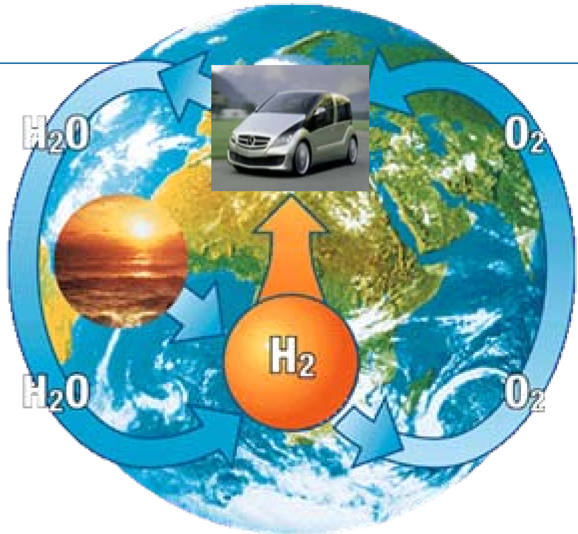
**EuroNanoForum 2009**

**Workshop „Nanomaterials for Energy“**

**Prague, June, 2nd, 2009**

# Challenges of Hydrogen Technology

GKSS FORSCHUNGSZENTRUM




Hydrogen is the ideal future energy carrier

- **Zero emission vehicles**
- **Decentralised energy supply**
- **Portable electronics**
- **...**

Key issues

| $H_2$ production/separation/conditioning | $H_2$ storage | Conversion to power |
| --- | --- | --- |
|  |  |  |
| high selectivity + efficiency | low weight + volume | low cost + high efficiency |

# Overview

- **Introduction** to solid state hydrogen storage

- **Nanostructured Materials** for hydrogen storage
  - **Reactive Hydride Composites**
  - **Anion substituted materials**
  - **Nanoscaled scaffolds** and **frameworks**

- Future **challenges** of research

# Efficient Hydrogen Storage Methods ?

Densification required !

# Challenges

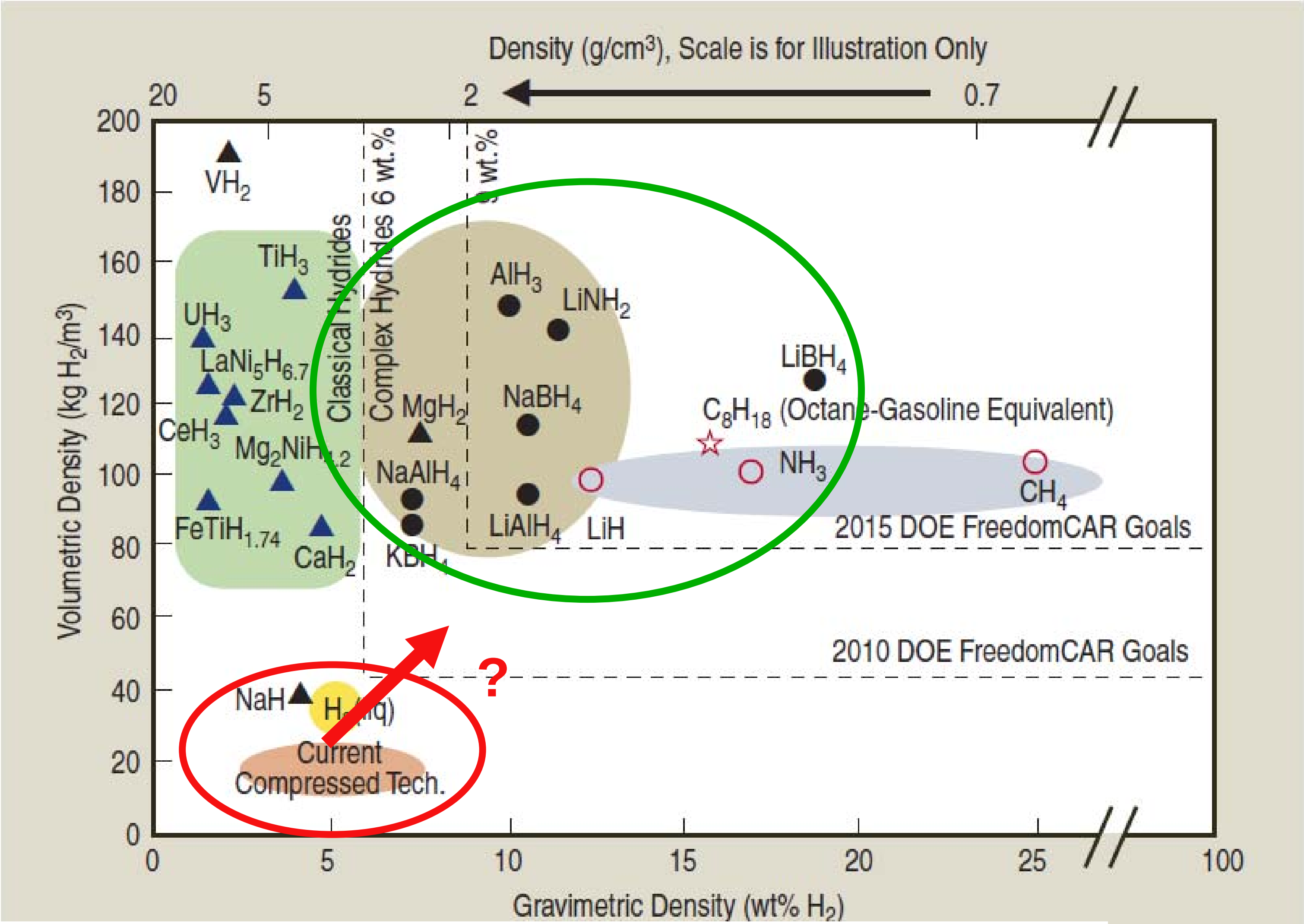
- **Vehicles are being designed by OEMs that can achieve > 300 miles**
  - **350 or 700 bar $H_2$ pressure demonstrated**
  - **1 to 4 tanks**
  - **Specified range from ~200 to > 350 miles**

- **But**
  - **Performance / life time**
  - **Space on-board**
  - **Safety**
  - **Cost**

  **are still challenges for mass market penetration…**

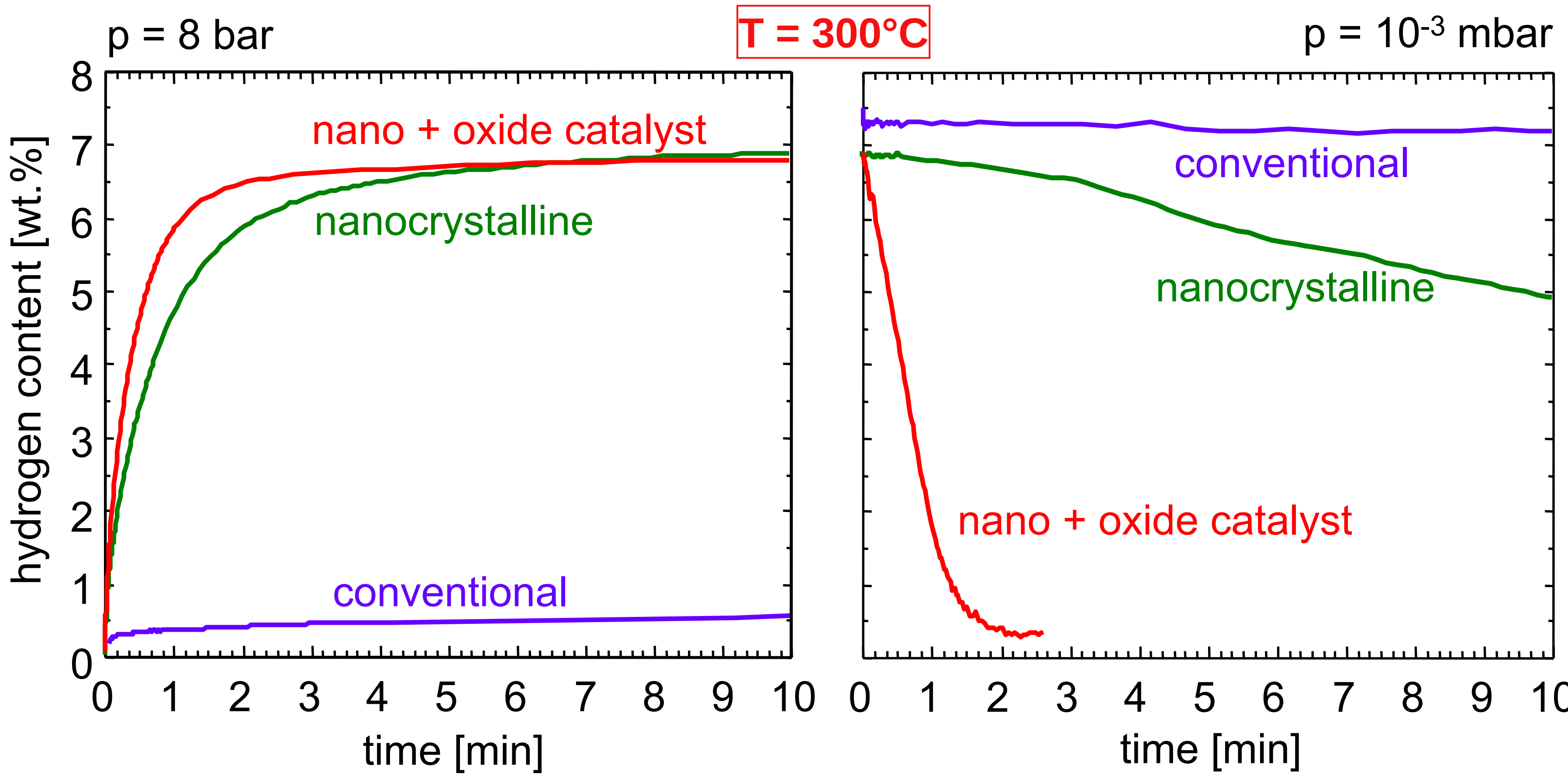
- **Is there a low pressure alternative?**

# Hydrogen Storage Capacity




Chandra, Reilly, Chellappa - Metal Hydrides for Vehicular Applications: The State of the Art – Journal of the Minerals, Metals and Materials 58, 2 (**2006**) 26 – 32, DOI; 10.1007/s11837-006-0005-0

# Kinetics: Achievements by Nanostructure

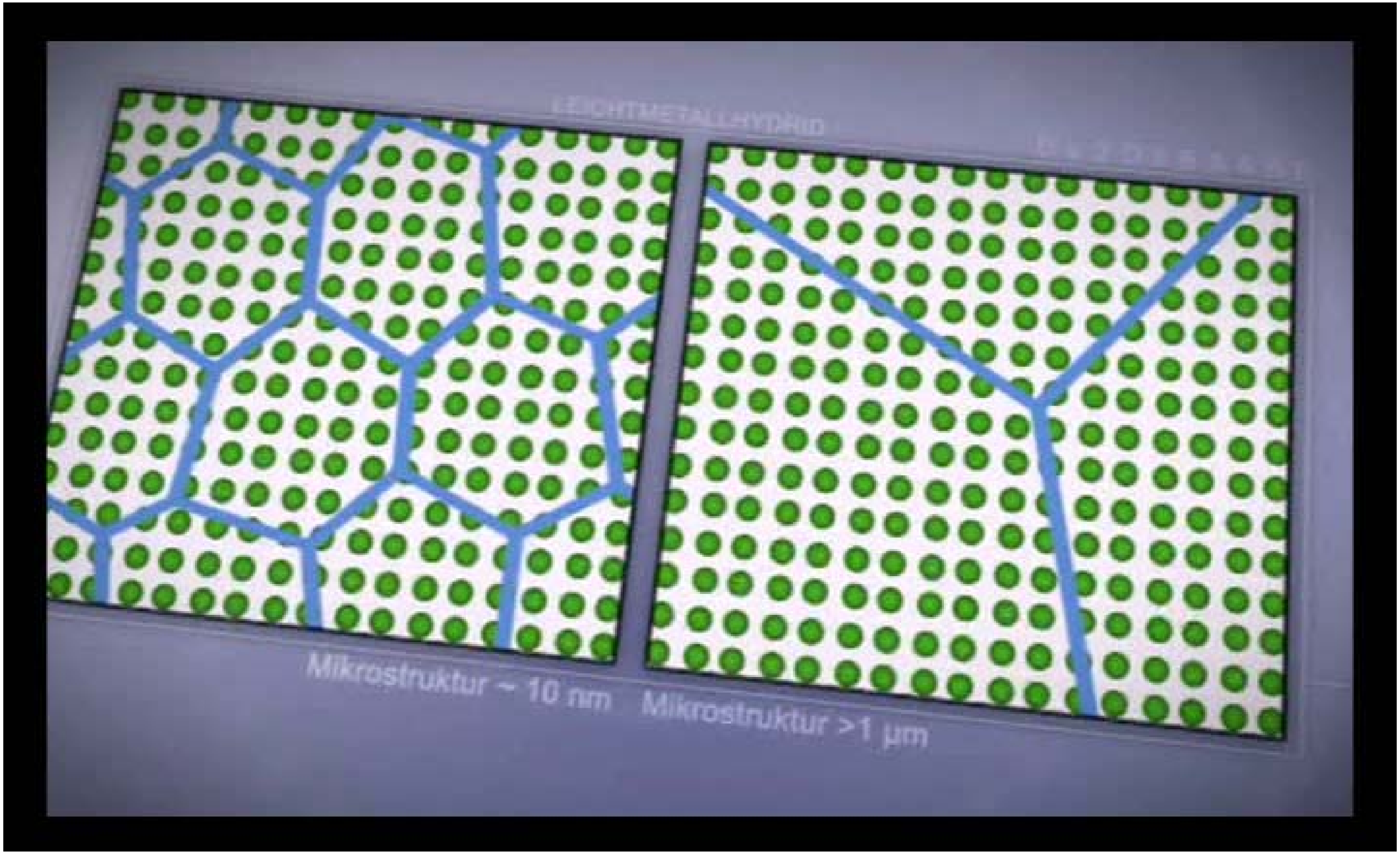



nanocrystalline $MgH_2$ + catalyst GKSS FORSCHUNGSZENTRUM ⟹ technological breakthrough in kinetics

Oelerich et al. JAC 322 (2001), L5; EP 1165434 A1 (2000)

HELMHOLTZ ASSOCIATION

# Reaction Scheme of Solid State Hydrogen Storage Materials



# Challenges for Solid State Hydrogen Storage

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**Industry goals:** > 6.0 wt.%, 42 kg $H_2/m^3$ ⇒ **low weight and volume**

$T_{Op.}$ < 150 (200°C) ⇒ **PEM Fuel Cells**

$\Delta H$ = 25 - 40 kJ/mol $H_2$ ⇒ **low heats of reaction**

⇒

new compounds, composites and modifications:

- **Reactive Hydride Composites**
- **F substitution**
- **nanoscale scaffolds and frameworks**

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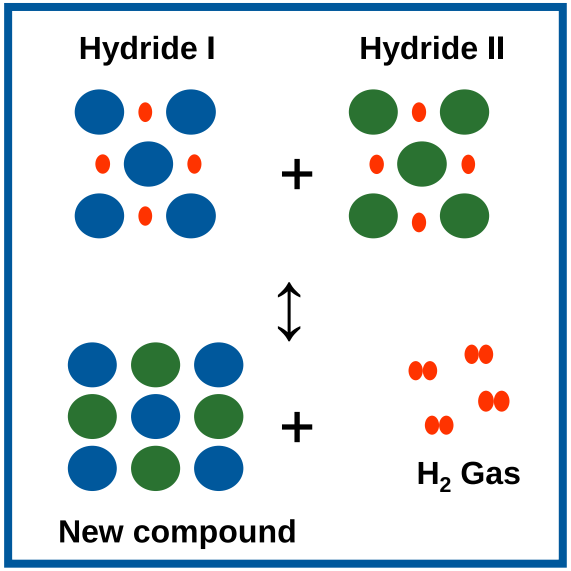
# Reactive Hydride Composites

# Reactive Hydride Composites*

two hydrides in a **composite react exothermally** while releasing hydrogen




HRL-Laboratories

Thermodynamics ✓

Kinetics ☞

COSY
Complex Solid State Reactions for Energy Efficient Hydrogen Storage

- High capacity
- Low reaction enthalpy / heat of reaction

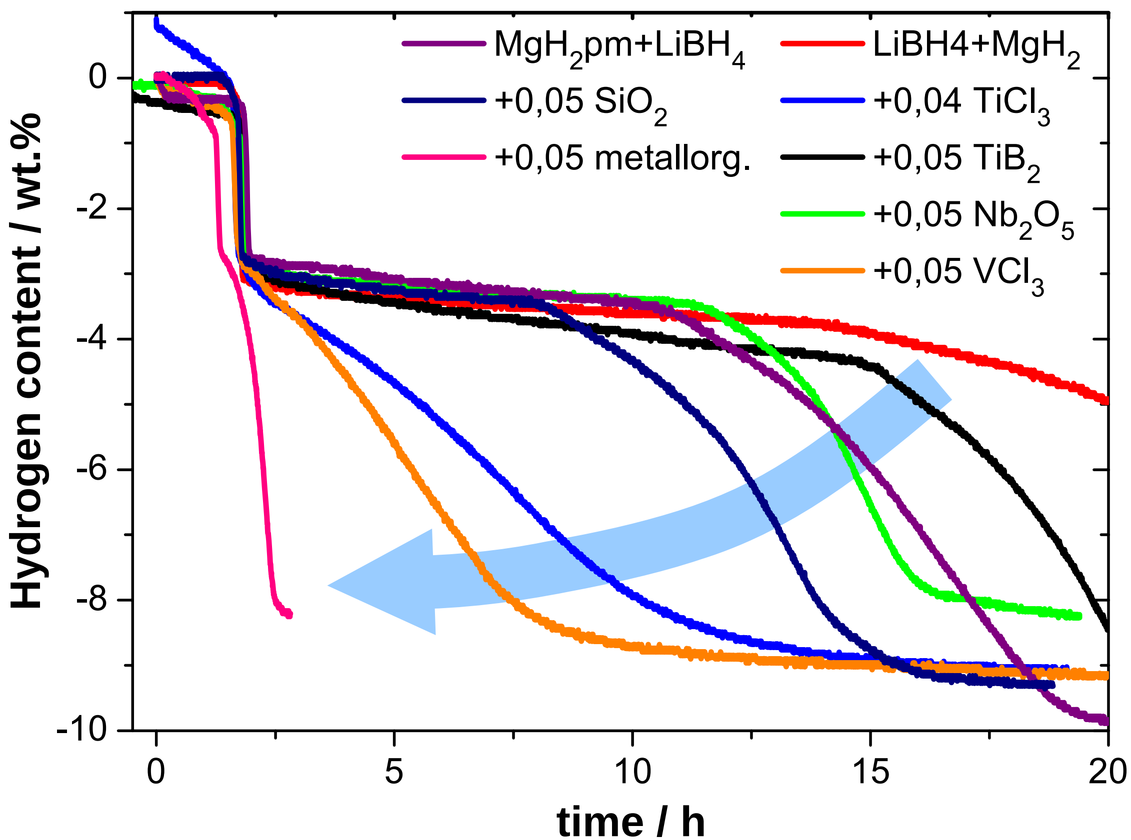
* G. Barkhordarian et al.: patent application 2004, J. Alloys & Compounds 440 (2006)

J.J. Vajo et al.: patent application 2004, J. Phys. Chem. B 109 (2005)

# RHC Desorption Kinetics with Various Additives

$$2LiBH_4 + MgH_2 \Leftrightarrow 2LiH + MgB_2$$

400°C, 5 bar $H_2$




- Suitable **additives** and preparation parameters accelerate desorption

- (One) critical parameter: **formation of $MgB_2$**

- nucleation of $MgB_2$ enhanced by **additive Borides**

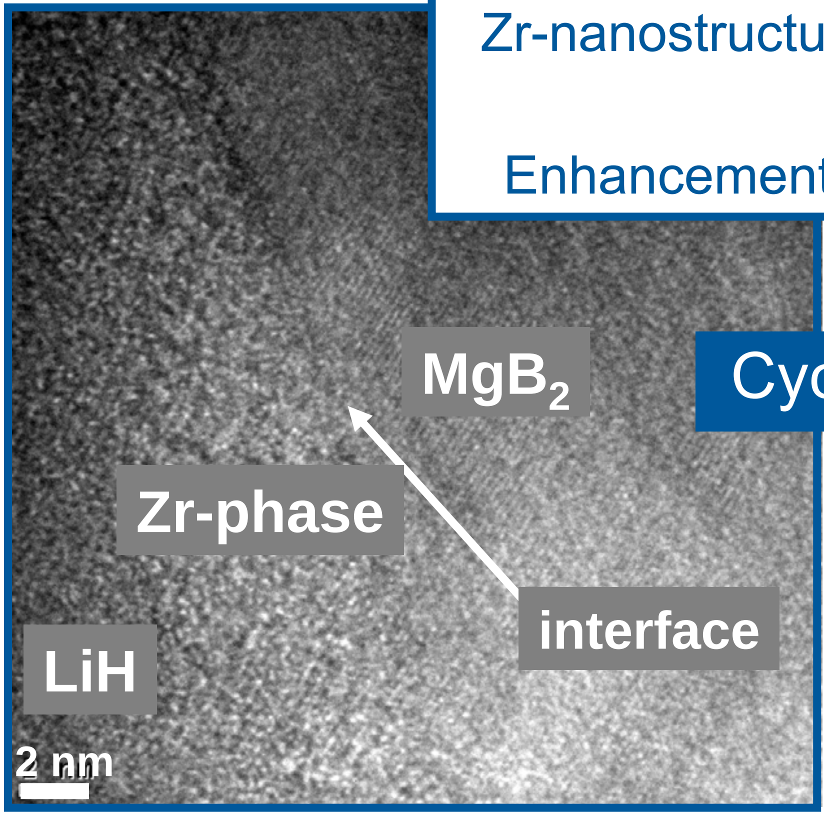
U. Bösenberg et al. GKSS Forschungszentrum, Acta Materialia 55 (2007)

# Location of Zr-structures (TEM)

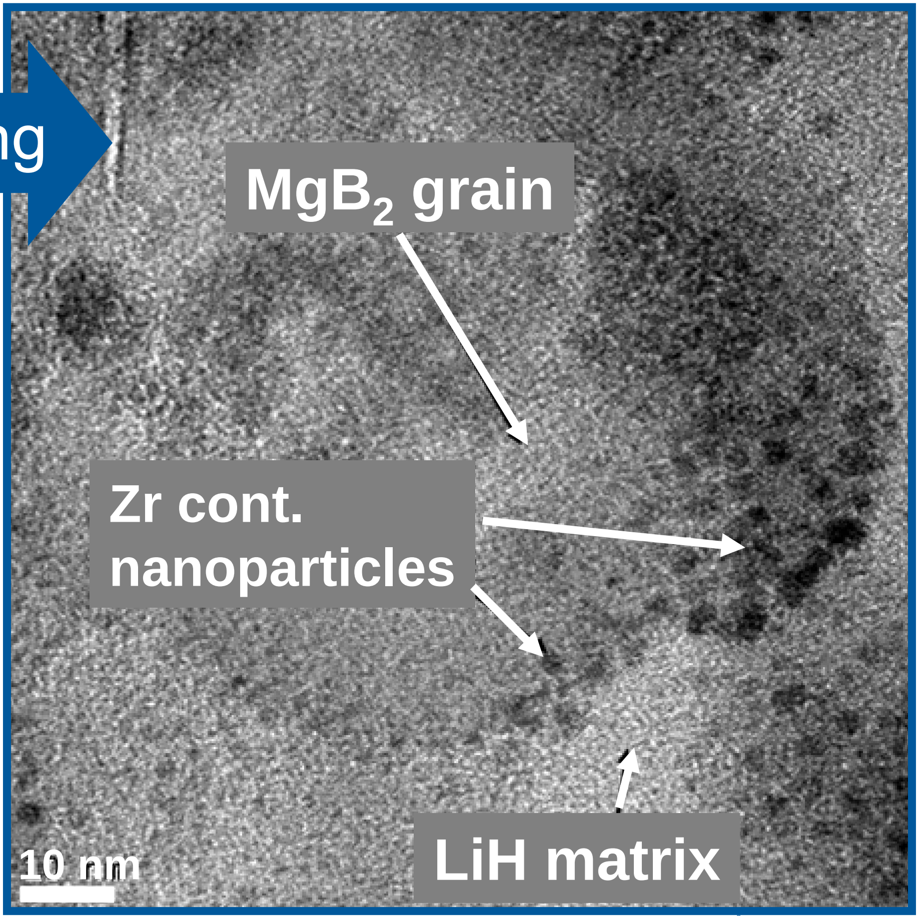
Zr-nanostructures at the interfaces

$\Rightarrow$

Enhancement of $MgB_2$ formation




Cycling




In cooperation with
Young Whan Cho et al., Seoul National University
and the Korean Institute of Science and Technology

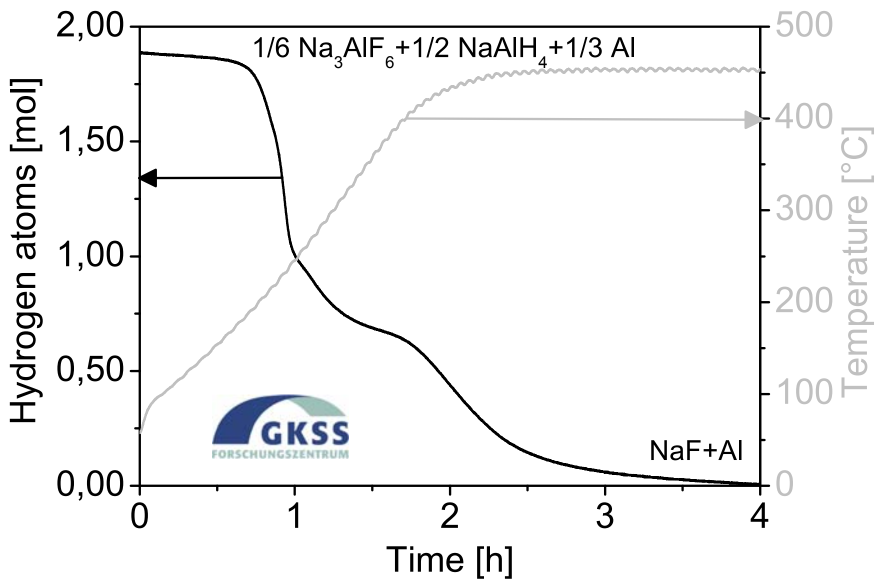
# Anion Substion in Hydrides

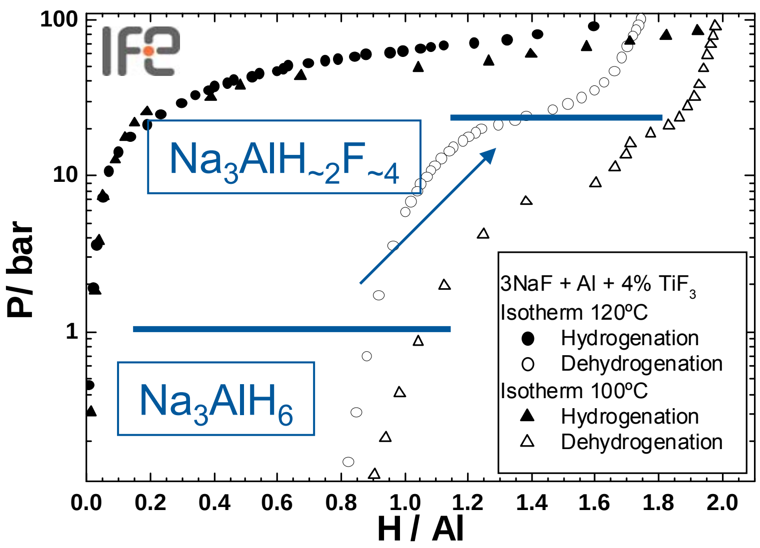
# Destabilization by Anion Substitution

**Hydrides** ⇔ **Fluorides**: often **similar** structures, **different** thermodynamics

⇒ possible to form mixed compounds with **reduced heat of reaction?**

**YES**





1) IFE Patent pending, Brinks, Fossdal, Hauback (2008)
Hendrik W. Brinks, Anita Fossdal, Bjørn C. Hauback - J. Phys. Chem. C 112 (2008), 5658
2) GKSS Patent pending, Eigen, Dornheim, Bormann (2008)
N. Eigen, U. Bösenberg, J. Bellosta von Colbe, T.R. Jensen, Y. Cerenius, M. Dornheim, T. Klassen, R. Bormann - Journal of Alloys and Compounds, 477 (1-2) (2009), Pages 76-80,

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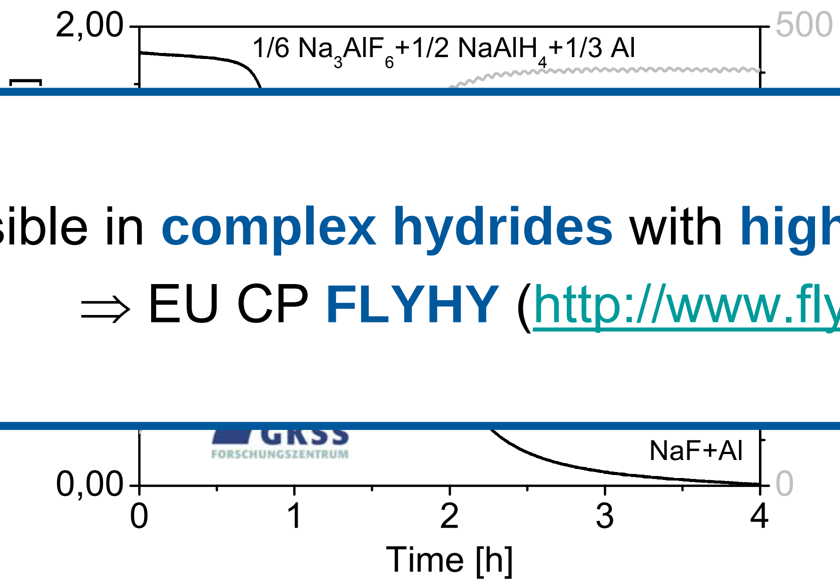


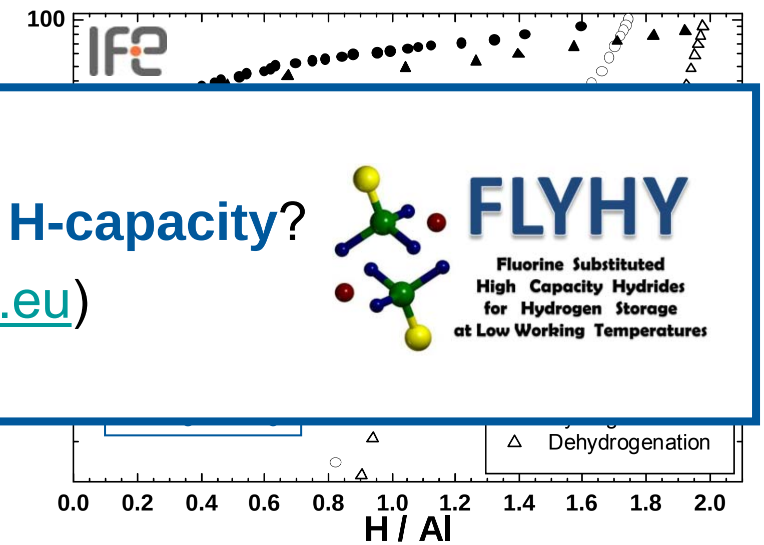


Possible in **complex hydrides** with **higher H-capacity**?

⇒ EU CP **FLYHY** (http://www.flyhy.eu)

FLYHY
Fluorine Substituted High Capacity Hydrides for Hydrogen Storage at Low Working Temperatures

1) IFE Patent pending, Brinks, Fossdal, Hauback (2008)
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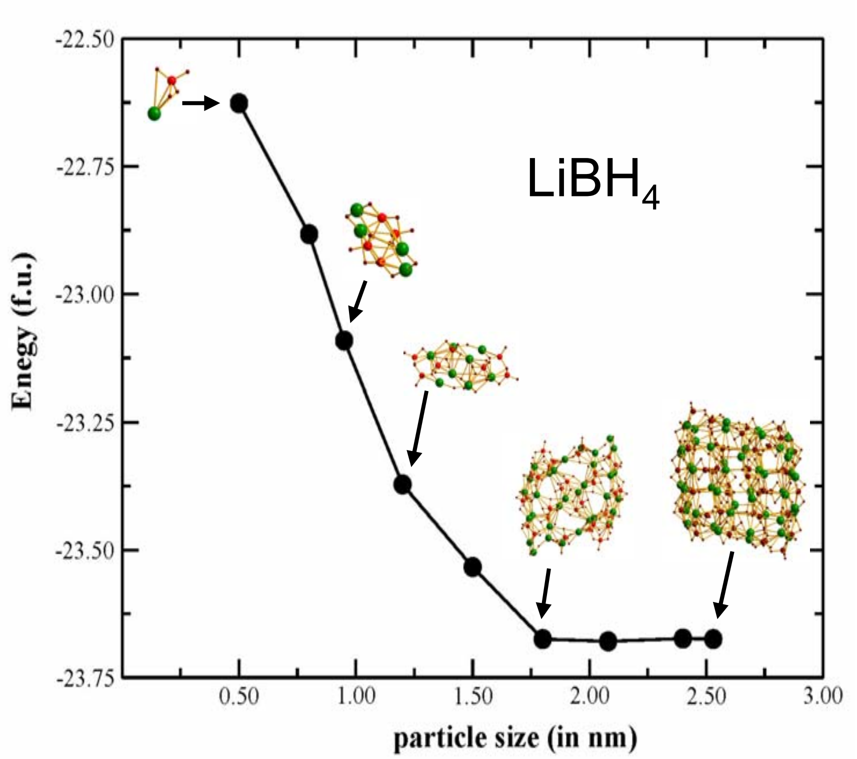
# Nano Scaffolds and Frameworks

# Nanoscale phenomena in H storage materials / Results

Karlsruhe Institute of Technology

NANOHy
Novel Nano Composites for Hydrogen Storage Applications

## Modelling



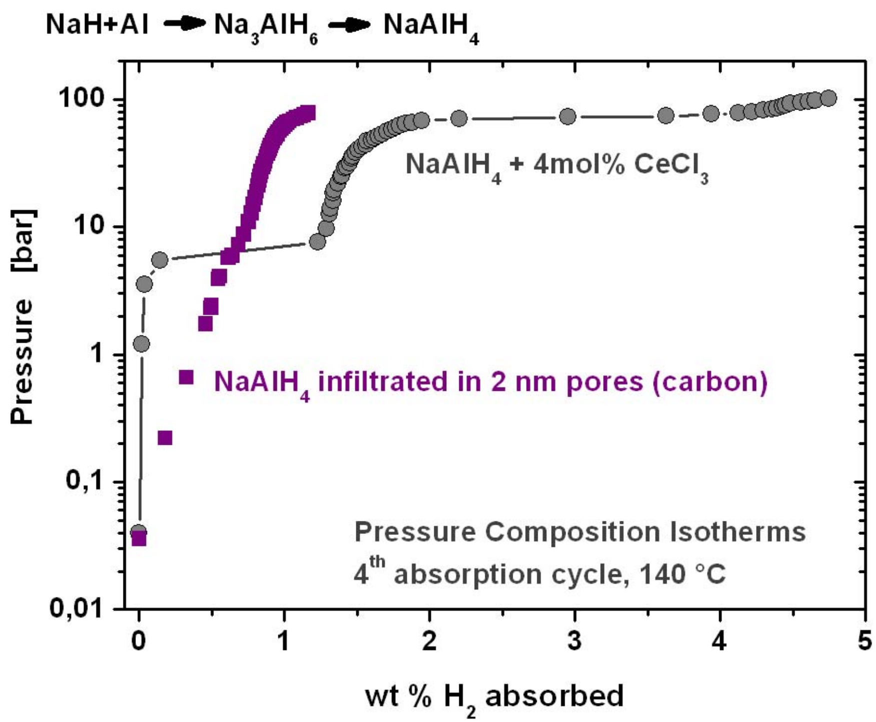

**Critical size of complex hydride particles**

P. Vajeeston et al., Small (2009)

SMN
SENTER FOR MATERIALVITENSKAP OG NANOTEKNOLOGI

## Thermodynamics

### Equilibrium pressures




**Solubility of H enhanced by 1-2 orders of magnitude in a nanocomposite**

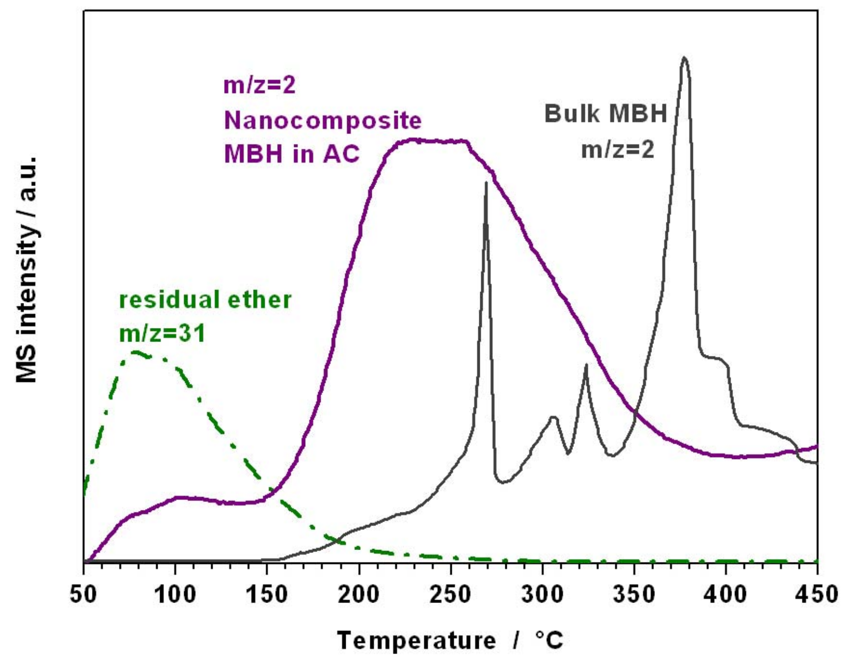
M. Fichtner et al., MH 2008 Symposium; submitted (2009)

# Nanoscale phenomena in H storage materials / Results

NANOHy
Novel Nano Composites for Hydrogen Storage Applications

## Kinetics

### TDS-MS

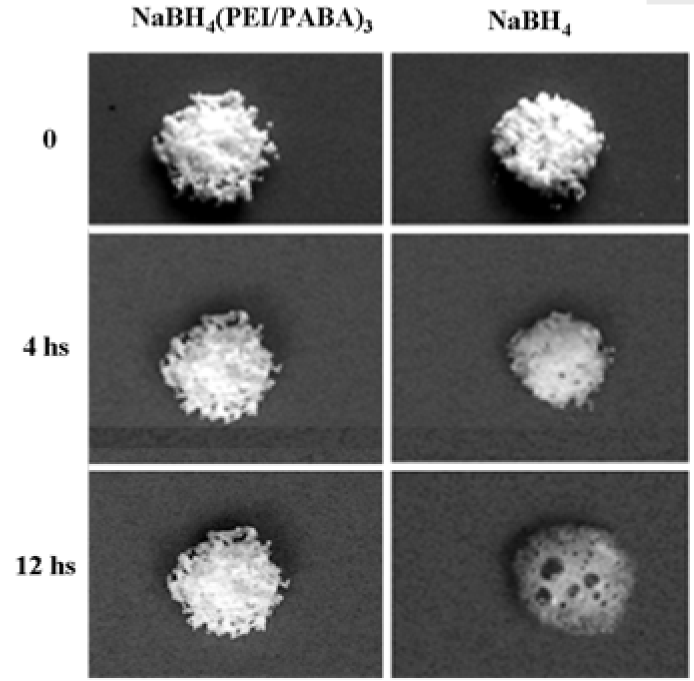



Lowering of desorption T of $H_2$ by >100 K

M. Fichtner et al., Nanotechnology (2009)

Forschungszentrum Karlsruhe

## Safety




Safe encapsulation of complex hydride by self-assembled layer technique

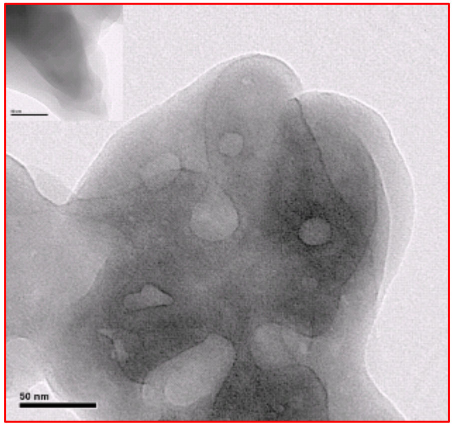
D. Shchukin et al., submitted (2008)

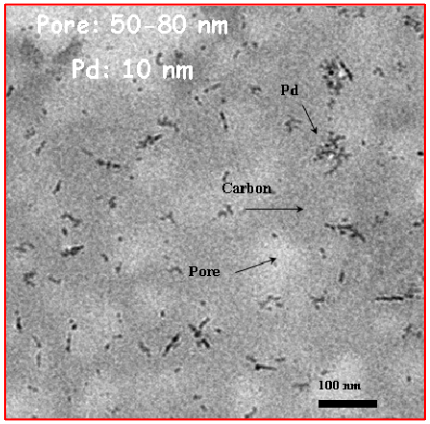
Max Planck Institute of Colloids and Interfaces

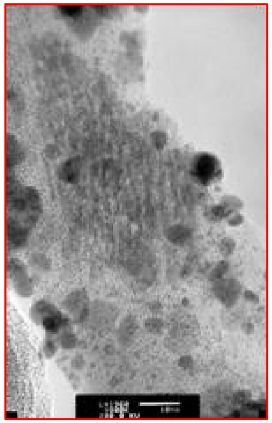
# Framework Materials

✓**Nanoporous structures → Metal-doped carbons:**

- Novel carbogenic foams with high surface spin concentration
- Pd/C foam nanocomposites to exploit "spillover effect" → $H_2$ uptake > 2 wt% at 298 K
- Pd-alloy/C foam nanocomposites → Enhanced $H_2$ uptake (> 4 wt%) at 298 K
- Mixing with other promising framework materials (MOFs, etc)
- Volumetric Densities? Working Pressures?





*Carbon*, **45** (2007) 852-857

# Tank Design

NESSHY
Novel Efficient Solid Storage for $H_2$

# Upscaling & Storage systems

## ✓Mg-based Tanks:

- Large scale production of improved Mg based hydrides
- 10 kg $MgH_2$ tank under development

Industrial scale Milling

**2 kg $MgH_2$** tank**, ≈ 5 kWh**

**(120 gr - 1344 NL $H_2$)**

External volume : 3 l = **40 kg/m³**
Weight ≈ 12 kg => **1 wt.%**
Max Pressure: 1.5 MPa

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

# Hydrogen Storage Tank of Complex Hydrides

## (Model) Material: Sodium Alanate $NaAlH_4$

- ✓ Gravimetric capacity: 4,5 wt.%
- ✓ Good kinetics, adequate thermodynamics

⇒ **Optimisation** of tank design by

- **Light-weight** construction
- **High capacity** storage materials

## Upscaling

0.1g
1x

1g
10x

5g
50x

250g
2500x

8 kg = 400 g $H_2$
**~20 l Tank**
for **4500 l $H_2$**
**0,9 wt.%, 22 kg/m$^3$**
80.000x

# Nanomaterials for Hydrogen Storage

Significant **advantages** vs. CGHS and LHS

- **High volumetric densities** well above DOE targets
- **Low working pressures** (< 200 bar)
- **Inherently safe**: self "cooling" effect during hydrogen release

Main **directions of research** to be pursued

- Fundamental **understanding** of effects ⇒ **Engineering** on the **nanoscale**
- Challenges:
  - Working **temperatures < 200°C**
  - Fast reaction **kinetics**
  - **Hydrogen quality**
- Cost effective **materials production**
- **Tank design, simulation** and **construction, heat management**

⇒ Overall **energy efficiency**

- **Codes and Standards**

# Acknowledgements


**GKSS Research Centre**

- M. Dornheim, G. Barkhordarian, C. Bonatto Minella, R. Bormann, J. Bellosta v. Colbe, U. Bösenberg, N. Eigen, R. Gosalawit, T. Klassen, G. Lozano, O. Metz, C. Pistidda

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- M. Fichter, W. Lohstroh, C. Frommen, and colleagues

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- Athanassios Stubos and colleagues

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- MC RTN **COSY** (MRTN-CT-2006-035366)
- CP **NANOHY** (GA 210092)
- CP **FLYHY** (GA 226943)

**thank you for your interest!**