“Nano-sized and Nano-structured Materials for Hydrogen Storage or Catalytic Purposes”

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VETEC

(formerly “TEMAV” S.p.A. and
“Centro Ricerche Venezia” of ENIRISORSE- ENI group;

Shareholders: ENI-tecnologie; InPACT; Parco VEGA)

For 20 years: R & D on

- **technologies,**
- **industrial process (chemistry ; metallurgy)**
- **innovative materials**

Many (positive) examples or case histories of
“scaling up”

(pilot plants starting from our laboratories; patents)

Some case studies:

- ***procedure for production (10^1 Kg-scale) of micrometer sized SOL GEL spheres of ZrO2 + additives for catalysis***

- ***Double side polishing and EPI-ready surfaces for 2 inch InP Wafers***

- ***VETEC sells ingots (Kg scale) of pure In 6 - 7 N's grade***

- ***VETEC is the first Italian producer of InP ingots and wafers of monocrystalline InP of n, p and SI – type; supplies polycrystalline InP for a French company***

MATERIALS in the Fuel Cells field

From 2000's:
With different Mechanical Alloying systems :
Rotating Ring MILL,
Planetary MILL and
Attrition MILL,

supplies, under request, alloys (dozens-Kg scale) and composites (with rare earths) for MCFC (Molten Carbonate Fuel Cells) both for electrodes and the electrolyte.

A scaling up from Kg to Tons is being considered now.

In the last 5 years at VETEC:

- **“micro”- plant for the production of “batches” of graphite nano - fibres**

- **R&D on Mg hydrides and “catalytic phases” for Mg hydrides; production at Kg scale**

NANO-FIBRE

Promising data on the “storage” in nano-fibres, with a “herringbone" nano-structure, were reported :

67 wt.% (if activated at 120 atm) at 25℃
OBELIN, ENDO and KOYAMA, *J. Cryst. Growth* (1976)

Later on, after new measurements, there was a strong controversy concerning the true capacity.

Recently:
3.8 wt.% (69 bar) at T room
LUEKING, YANG, RODRIGUEZ and BAKER, *Langmuir*, (2004)

VETEC:

own apparatus and method for:

synthesis of batches of nano-fibres by

catalytic decomposition of ethylene

in the presence of H2

Purposes:

i) **to study different synthesis procedures both of the catalyst and graphite nano-fibres in order to control diameter and morphology;**

ii) **to characterise the materials and**

iii) **to measure their hydrogen storage properties.**

A) Synthesis of the catalysts

Fe-Cu and Ni-Cu bimetallic catalysts

were synthesized by four different procedures:

A) coprecipitation,
B) reduction-precipitation,
C) reverse microemulsion,
D) incipient wetness of a high surface area silica support.

B) Synthesis of the nano-fibres

The synthesis of graphite nanofibers was carried out in a catalytic microplant made of:

i) a Lenton tubular furnace with a fused silica tubular reactor;

ii) process gases lines + “Brooks” mass flow controllers;

iii) an in-line gas cromatograph (Agilent 6890) for measuring the ethylene conversion during the synthesis

Synthesis procedure - A typical procedure is:

A given quantity of catalysts is placed on a quartz boat inside the fused silica tube

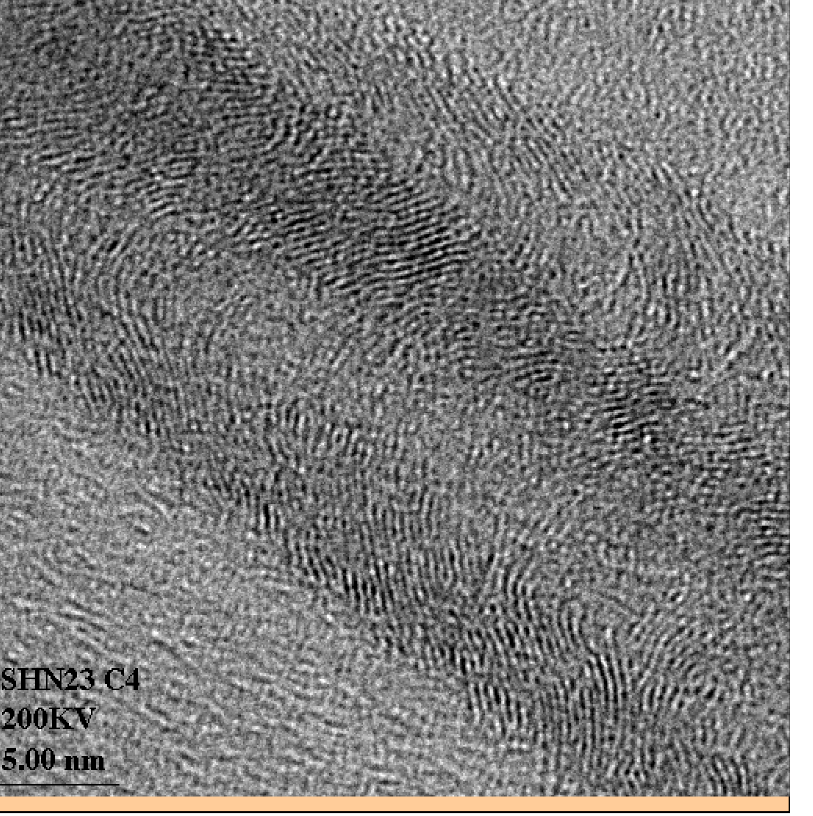
The catalysts are calcined in He and reduced "in situ" with H_2 flow

The reaction of synthesis of the nano-fibres begins when a mixture $C_2H_4 : H_2 = 1 : N$ is fed into the reactor for a given t

The reactor is cooled down to T room in flowing He.

Products: NANO-FIBRE batches for different procedures and different catalysts

SEM-SE



EniTecnologie's **HRTEM :**

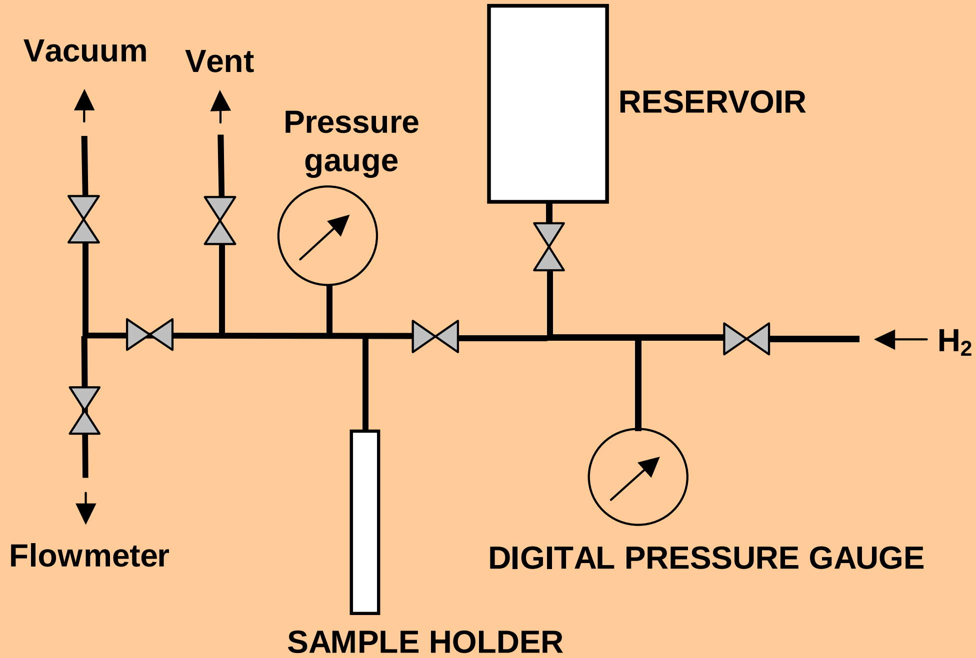
Jeol JEM 3010 200 kV

(max. resolution: 0.16 nm)

“True” nano fibres : 5 - 15 nm diameter

HRTEM

The “storage” capacity was measured with a self-made volumetric apparatus (able to reach 160 bar and 450°C; Dr. E. Sentimenti and collaborators)



The yield of reaction is for some of the procedures very high:

e.g. 50 g nano-fibres / g catalyst.

(mainly in the case of Ni-base catalysts with higher activity in comparison to Fe-base catalysts,

and to the high surface area of catalyst nanopowders)

Results concerning “storage”:

after testing different conditions for the activation "in situ”

----> the nano-fibres do not store significant

quantities of H (activated at near 100 bar) at Troom

In fact: values of “Adsorbed H_2 “

ranging from 0.10 - 0.33 [gH_2 /g(H_2+sample)] %

are obtained

Furthermore: In order to promote a "spillover"

function action some batches were doped with

2 wt.% Pd

-----> after activation at 77 bar :

a “storage” of 1.4 +/- 0.3 wt.% was established

Catalytic Purposes

Batches of grafite Nano-fibres can be supplied by VETEC for **Catalytic Processes**

In fact, as indicated in:

- United States Patent 5,626,650 (1997)
Nano-fibres are used for the separation of one or more components from a multi-component gaseous stream

- Anderson et al. WM'00 Conf. (2000)
Nano-fibres have the ability to adsorb Organic Molecules, for enviromental applications

- R&D on Mg hydrides and "catalytic phases" for Mg hydrides

From 2002's VETEC has a collaboration program with CAB - Centro Atòmico Bariloche, Atomic Energy Commission of Argentina, in order to develope catalytic phases (alloys, compounds) for the improvement of the behaviour of the standard MgH2 material or other hydrides

Catalytic phases: induction and arc furnaces
(NANO – MICRO sized particles)

Hydrides: Planetary Mill; "Australian" Mill
(NANO structured - particles)

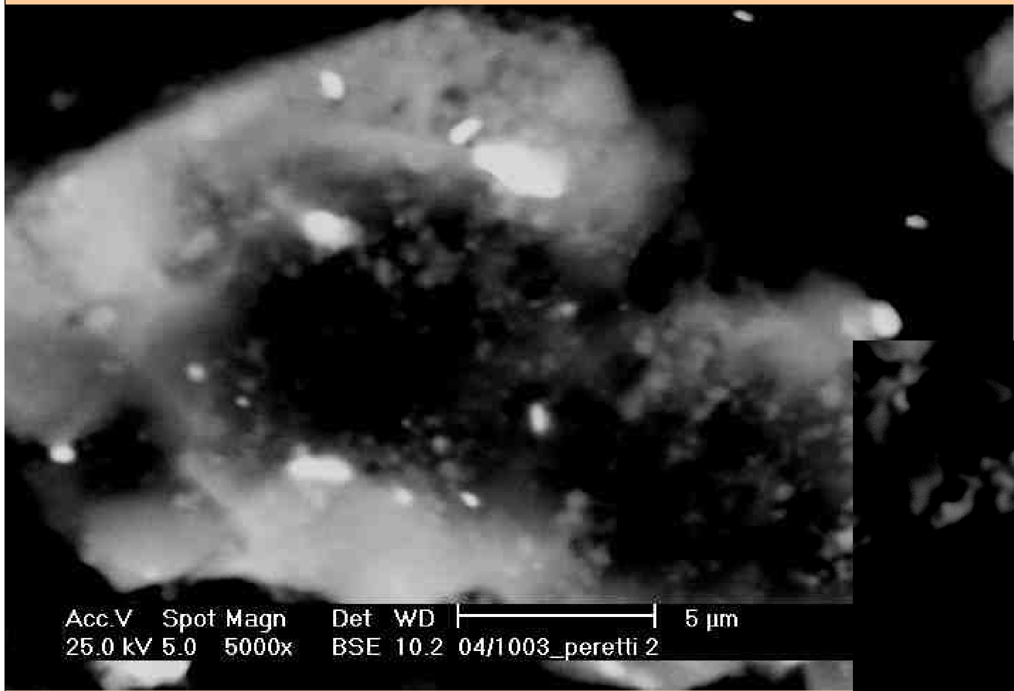
Measurements: by means of a volumetric VETEC apparatus (and a volumetric CAB apparatus)

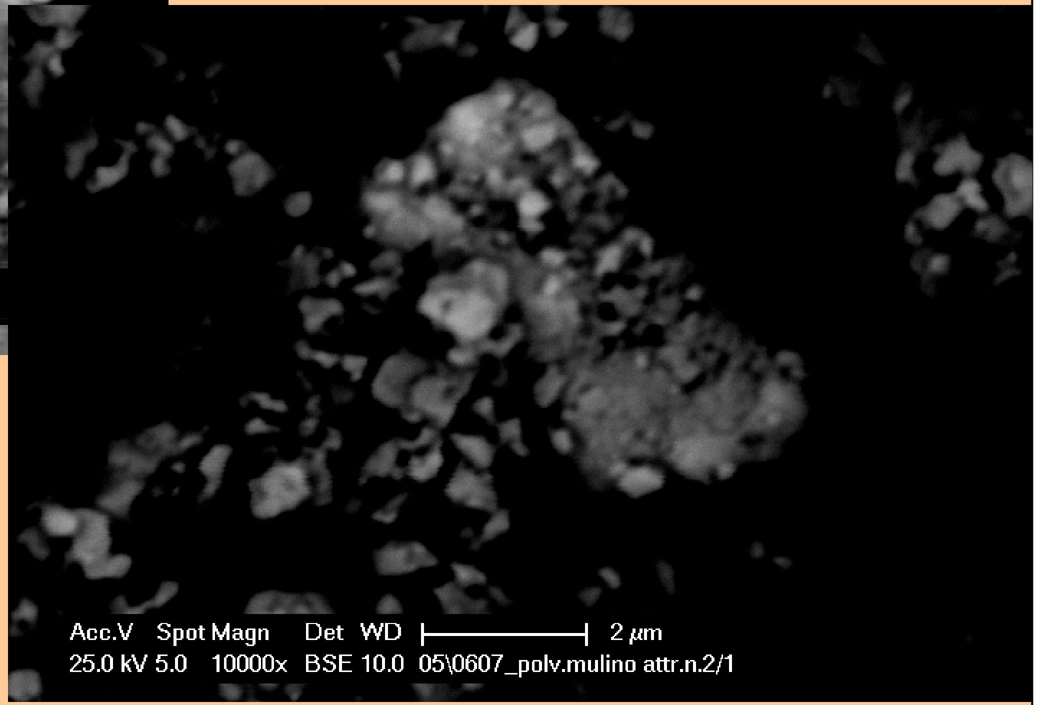
Container for the activation at high p

of hydrides (hundreds of grams)

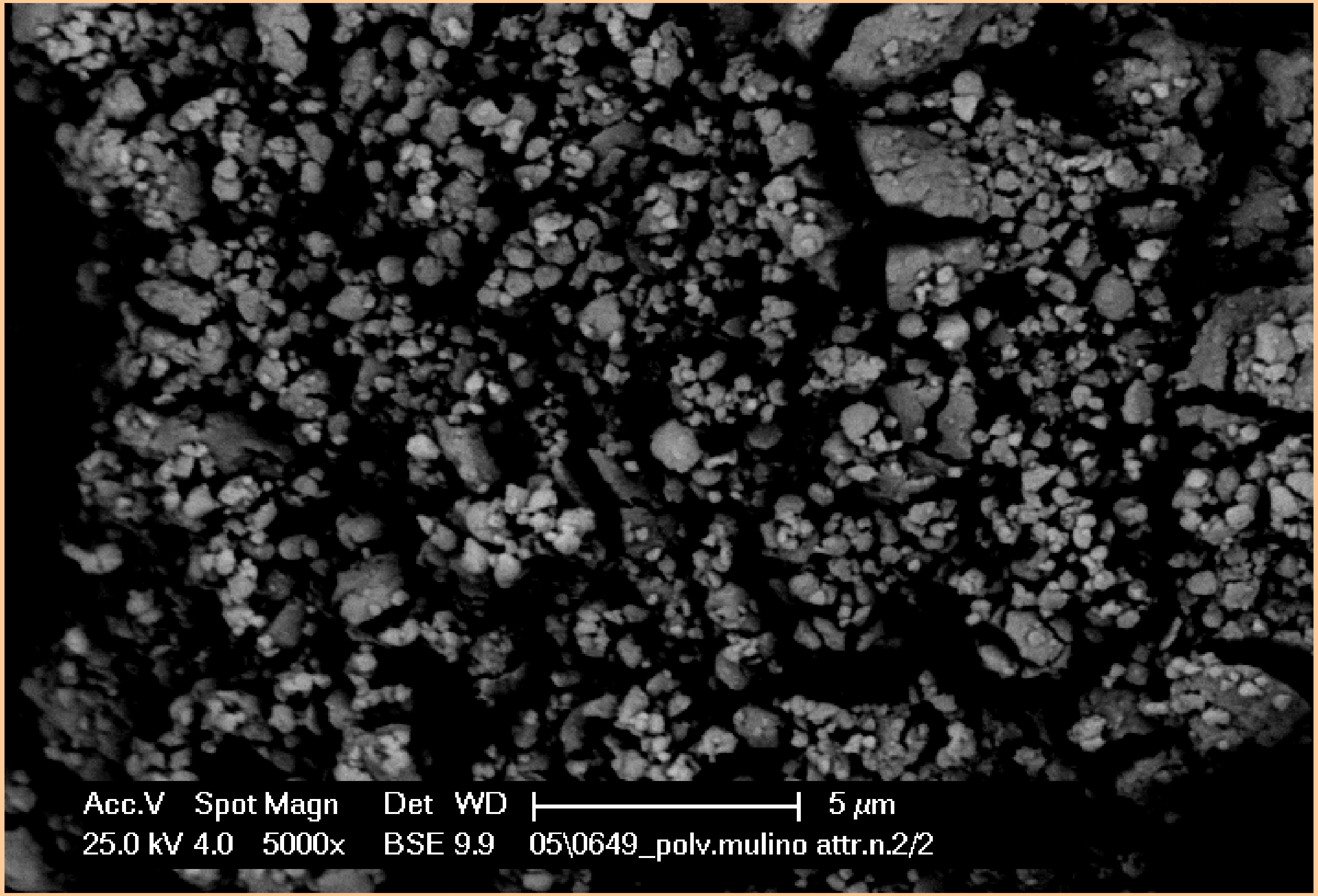
Case study 1: **MgH2 hydride + CAB's catalytic phase**
Morphology after 24 hours milling: second phase size<500nm

SEM-BSE





Morphology after 48 hours milling: second phase size < 50-100nm



SEM-BSE

Case Study 2: R&D works in collaboration with
UNIPD: University of Padua-Centro Idrogeno

SCALING UP with Attrition MILLING

Material to be considered: MgH2+ 5% wt Nb2O5

a) "Attritore 72 h": MgH2+Nb2O5 (VETEC)

(procedure and composition: UNIPD)

Checked against the "reference" material
b) "Spex 20 h" : MgH2+Nb2O5 ;
Spex 8000 Mill (University of Padua)

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“SZEGVARI” Attrition Mill :

Capacity:

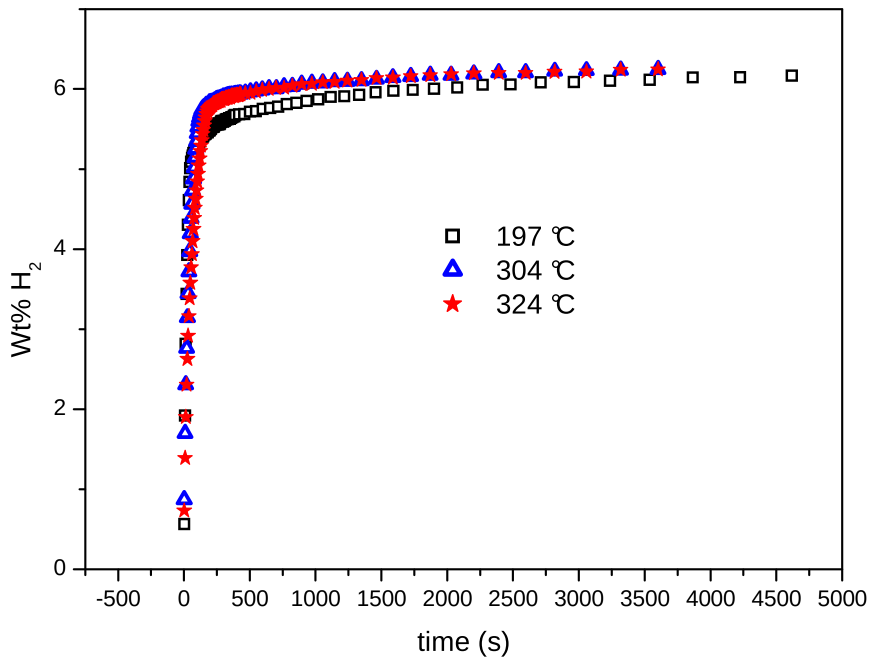
15 litres ; 0.5-1.5 Kg /batch

about 1 ton /year

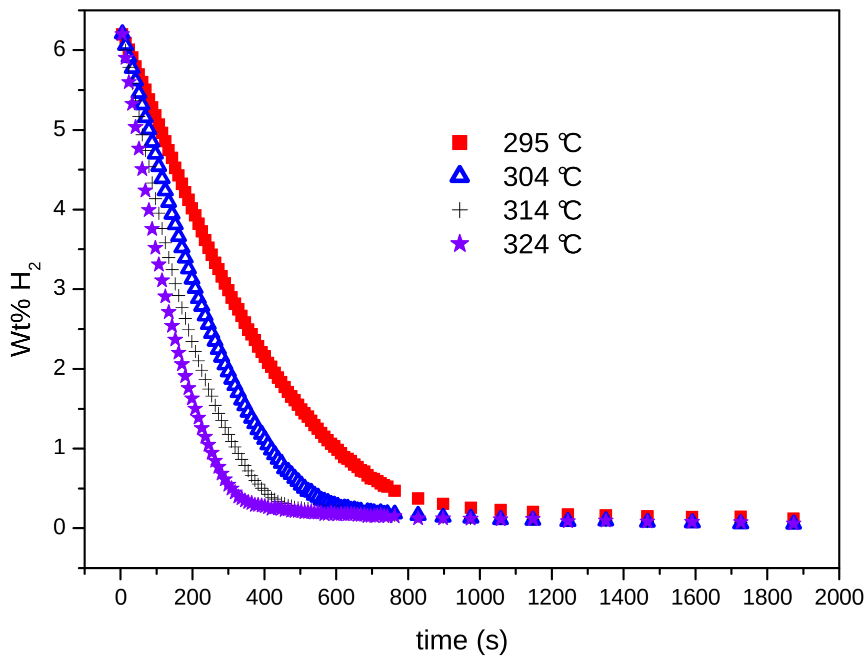
Milling and pick up of sample: under Ar

Characterisation: University of Padua

Material : “Attritor 72 h”



Soak at various temperatures after activation

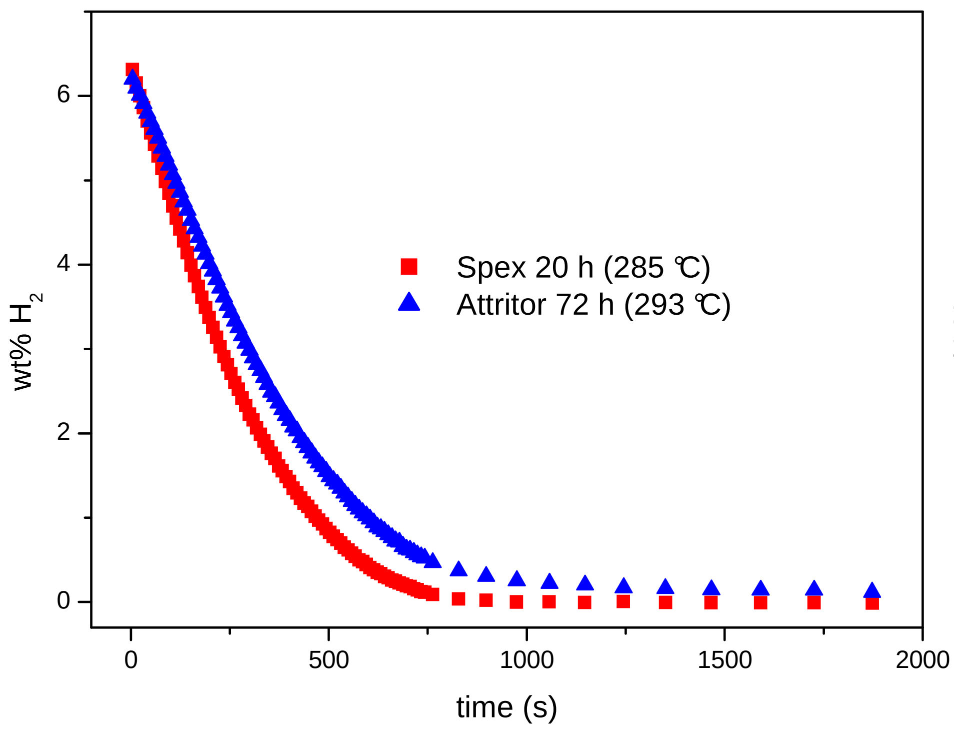


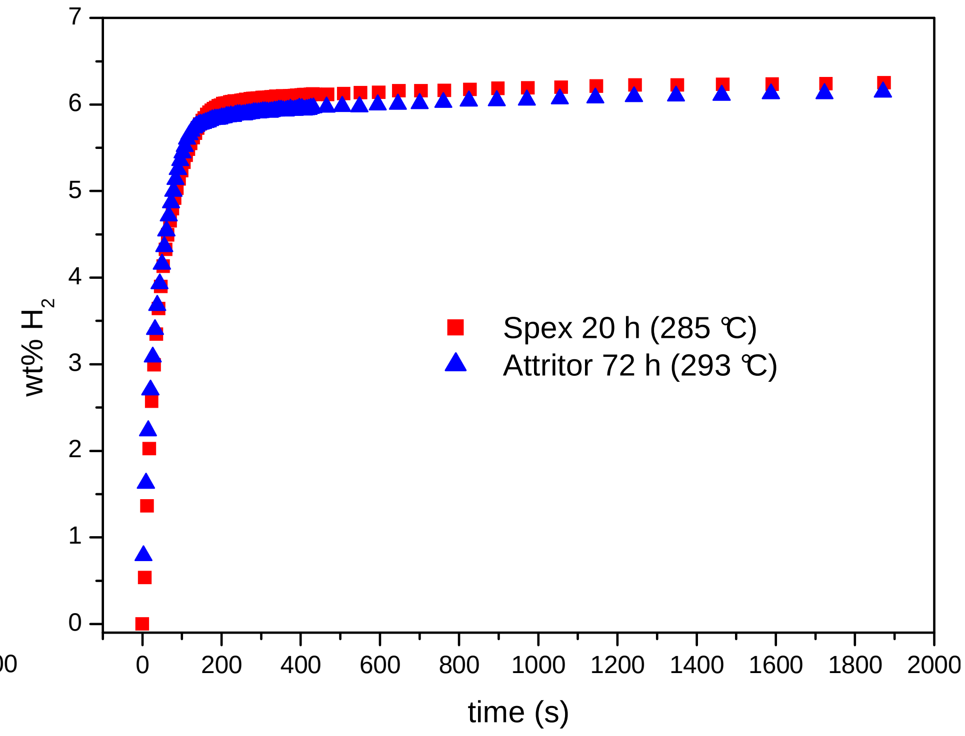
Release at various temperatures.

The maximum hydrogen content for “Attritor 72 h” is 6.2 wt% H_2

Release for “Attritor 72 h” : it reaches 93 % of the maximum hydrogen content in 400 s

Comparison between "Attritor 72 h" and "Spex 20 h"





The maximum hydrogen contents are:

6.2 wt% H_2 for Attritor 72 h and

6.3 wt% H_2 for Spex 20 h.

Soak and release: roughly same behaviour

Results concerning Hydrides:

The "SCALING UP" of the hydride MgH2+Nb2O5

from grams up to about 1/2 Kg exhibits:

- **same or similar wt%**
  (maximum storage)
- **same or similar soak-release behaviour**

CONCLUSIONS:

the product “VETEC - Attritor 72 h”

is good enough for practical applications

As for example: For a two-stage (2 hydrides) reservoir for vehicles

as demonstrated in :

“New solid state hydrogen reservoir for vehicular applications”

Giovanni Principi, Milo Petris, Amedeo Maddalena, Petru Palade, Sabrina Sartori, Eliseo Settimo, Bernardo Molinas, and Sergio LoRusso

Exhibition – Congress : Mostra-Convegno “Automovili e Motori High-Tech”, Modena, luglio 2005

FORECASTS

In the next 3-5 years VETEC will be involved in:

- the application of nano-structured hydrides together with "standard" hydrides for ships ("vaporetti") in the Venice Lagoon

- same or similar mixture of hydrides to be applied to light vehicles

A CRAFT project has been presented to the EC (September 2005):

"Equipment of ecological light vehicles with a functional hydrogen metal hydride reservoir"

Partner

CELCO-Profil di Vigonovo (VE, Italy),
Salvio Busquets S.A (Spain),
Hygear B.V. (The Netherlands),
Fiedler Mobil GmbH (Germany),
Università di Padova (PD, Italy),
Università di Ancona (AN, Italy),
Leibniz Institute IFW Dresden (Germany),
VETEC (VE, Italy)

- It will be useful to work around the "nano-structured" concept: a true nano-sized second phase (additives) should be created for hydrides in order to improve their performance.

- Regarding nano-fibres

Future applications on the environmental applications will be explored.
"Perhaps one of the most attractive applications of these materials in the near future would be in the REMOVAL of OIL-spills from OCEAN" (Anderson et al. WM'00 Conf.)