ETRI Energy Technologies Research Institute

The University of Nottingham
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Solid State Hydrogen Storage for Stationary Renewable Energy Systems

Gavin Walker

Director, Energy Technologies Research Institute

Content

- Introduction
  - Energy at Nottingham
- Solid state storage
  - Metal hydrides
  - Thermodynamic tuning
- Stationary applications
  - Thermal Energy Storage
  - Community Energy
  - Indian renewable energy systems
  - Solid state compressors

ETRI Overview

- Leading centre for energy RD&D
- £60M research portfolio
- > 100 researchers
- 9 Priority research themes
- Dedicated building
- Partnerships
- Industrial Advisory Board
- 5 Key activities

Energy Technologies Building

ETRI Research Themes and Champions

Society, Economics and Policy
Alison Mohr

Fossil Energy and Carbon Capture and Storage
Hao Liu

Energy Vectors and Storage
Seamus Garvey

Efficient Energy Buildings
Mark Gillott

Renewable Energy
Bioenergy - *Greg Tucker*
Solar – *Richard Campion*
Wind/ marine – *Seamus Garvey*

Smart Grids
Mark Sumner

Advanced Materials for Energy
David Amabilino

Energy Systems
Gavin Walker

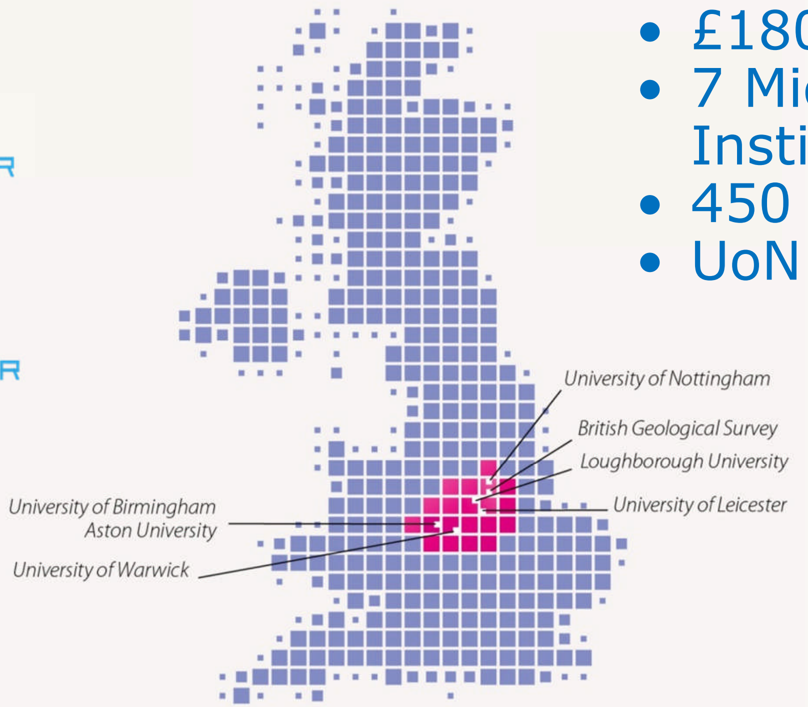
Horizon – Energy
Alexa Spence

ERA ENERGY RESEARCH ACCELERATOR

TERA ENERGY RESEARCH ACCELERATOR

IERA ENERGY RESEARCH ACCELERATOR

GERA ENERGY RESEARCH ACCELERATOR



- £180M Project
- 7 Midlands Research Institutes
- 450 Academics
- UoN Theme Lead

UNIVERSITY OF BIRMINGHAM · The University of Nottingham · THE UNIVERSITY OF WARWICK · Loughborough University · Aston University · University of Leicester · British Geological Survey

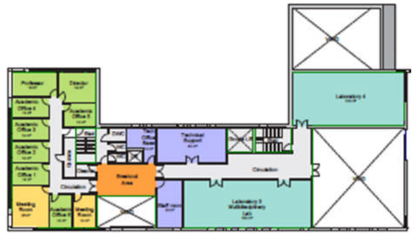
Cross-ERA activity

- **Community Energy**
- Trent Basin - Europe’s second largest regeneration scheme
- 140 home Community Energy Demonstrator
- Lighthouse project for the UK, leading advances in community energy storage, multivector smart grids and energy management for the benefit of the community and as a service for the grid.

G-ERA RAD Building

- **Research Acceleration and Demonstration building**
  - Office and lab space
  - ERA and ETC team
  - High Performance Compression and Expansion
  - Hydrogen Systems Test Bed
  - Carbon Capture Demonstrator
  - Multidisciplinary Research Lab

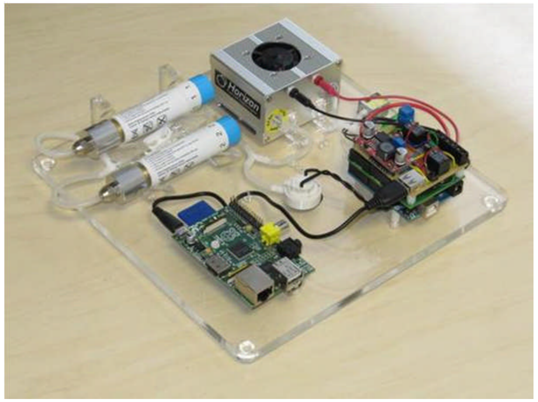
CGI visual of anodised aluminium cladding



Hydrogen for sale

What’s on the market?

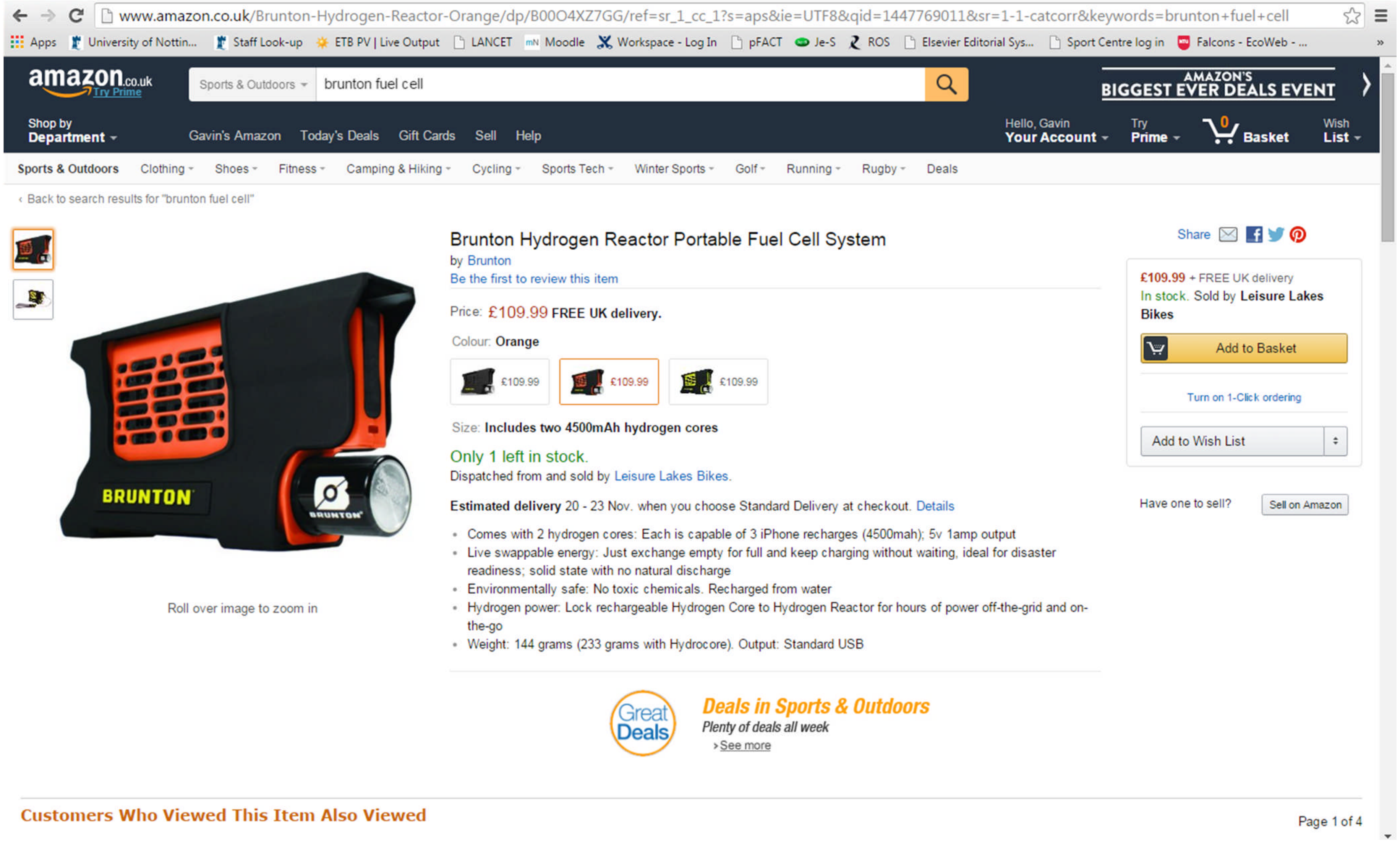
- Educational kits



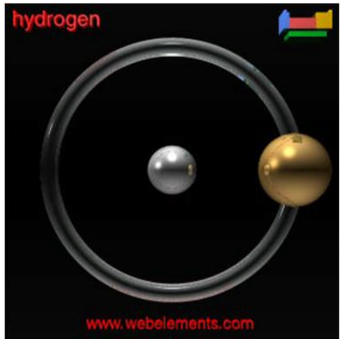
- Battery Chargers

- Fuel Cell Electric Vehicles

What's on the market?



Properties of Hydrogen



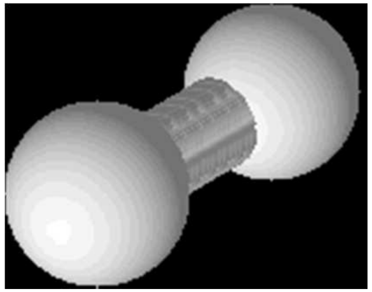
- Highest energy density by mass
  - lower heating value (LHV):

  120 MJ/kg (*cf.* petrol: 43 MJ/kg)

  33.2 kWh/kg (*cf.* petrol: 12.4 kWh/kg)

- Clean burning

  $2\ H_2 + O_2 \rightarrow 2\ H_2O$

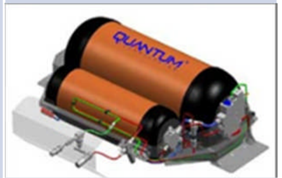
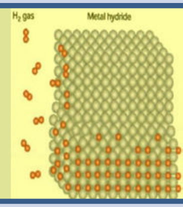
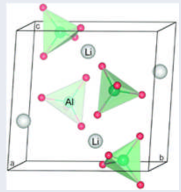
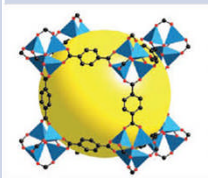


- Low density gas at room temperature
  - 0.09 g/L (*cf.* air 1.2 g/L)
- Boiling point: 20 K (equal to -253°C)
  - density of liquid: 70.8 g/L (*cf.* water: 1000 g/L)
- Melting point: 14 K (equal to -259°C)

Hydrogen economy

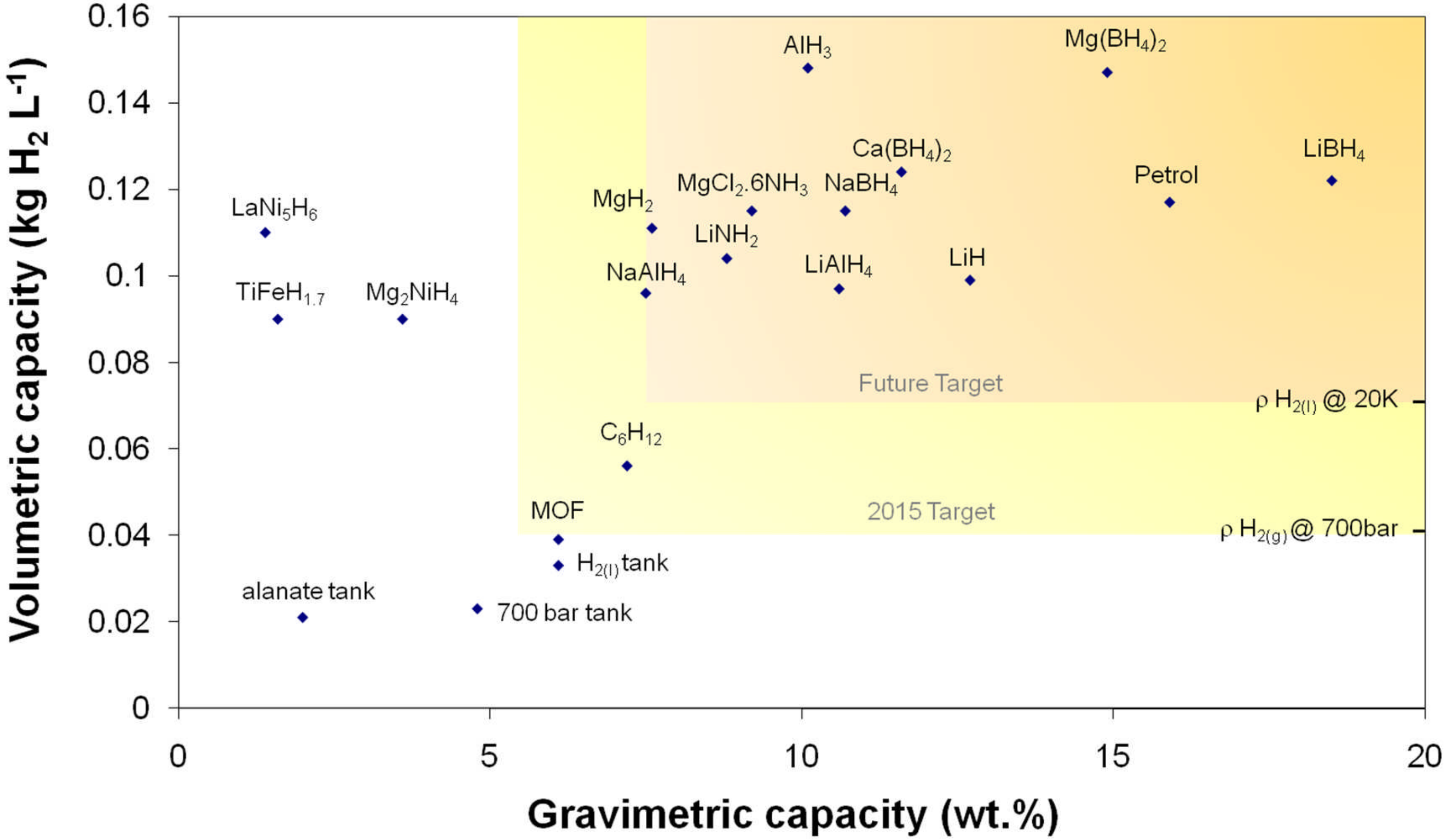
- Is a hydrogen economy a new concept?
  - The UK was using “town gas” until 1973
  - replaced by cheap natural gas
- Gasification or steam reforming of coal producing a H_2/CO gas mix.
- Used for lighting, domestic heating/cooking, etc.

Hydrogen storage options

Method	Gravimetric capacity (wt %)	Pressure (bar)	Temperature (°C)	Energy density (kg/m³)	Issues	
Compressed hydrogen	100	700	RT	30	High pressure	
Liquid hydrogen	100	1	-253	70	Boil off	
Metal hydrides (AB_2, AB_5, AB, MgH_2,etc.)	1.3 – 6.6	1-50	RT – 300	95 – 160	Low capacity	
Chemical hydrides ($NaAlH_4$, $LiBH_4$, $LiNH_2$, etc.)	5 - 25	10-60	150 – 400	50 - 150	High temperature, Reversibility	
Porous materials (MOF, CNT, etc.)	6 - 14	1- 150	- 196	40 -90	Low temperature, High pressure	

Solid State Hydrogen Storage

- Stationary applications – volumetric capacity and cost are more important
- Solid state storage offers higher volumetric capacities
- Want to avoid expensive metals

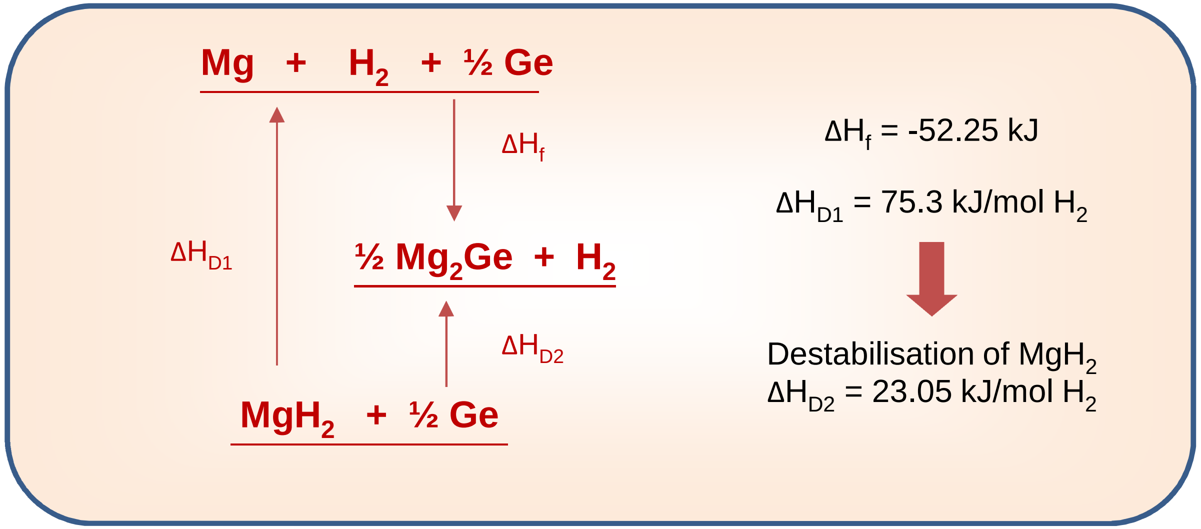


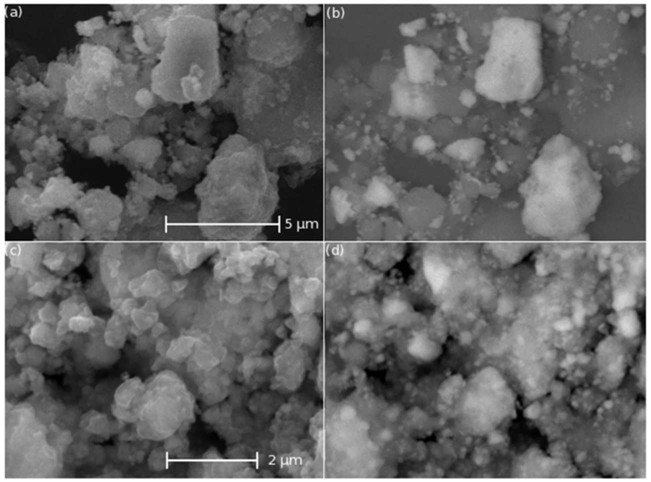
G S Walker, Public Service Review - UK Science and Technology, 1 (2010) 136.

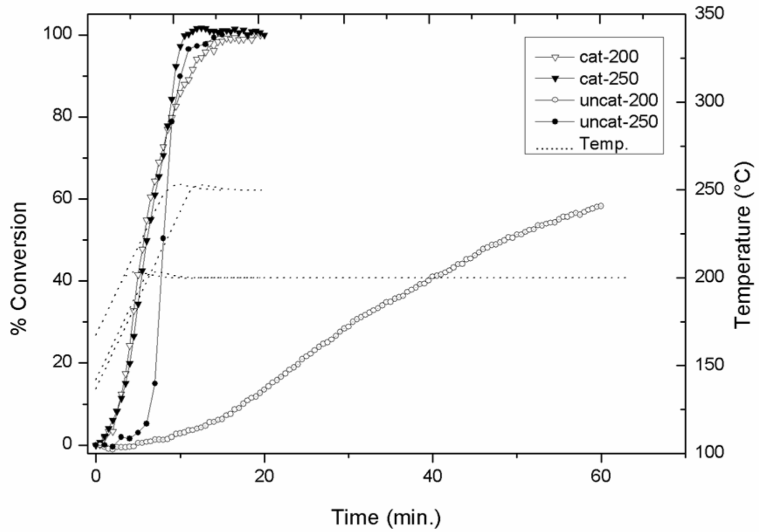
Reducing the temp of operation: Thermodynamic Tuning

MgH_2 Multicomponent Systems

- $2MgH_2$ + Si slow dehydrogenation kinetics (>5h at 250°C)
- Ge ⇒ fast kinetics





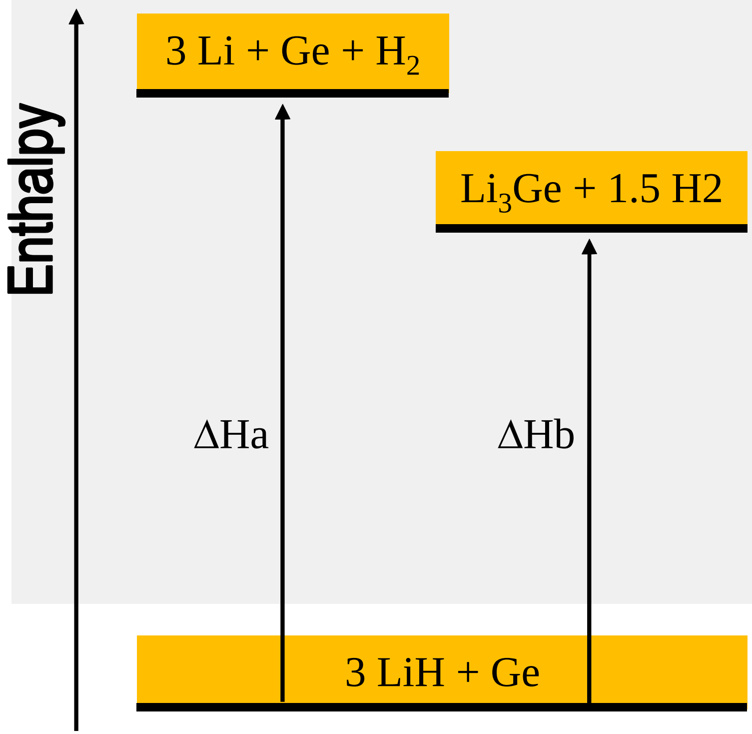


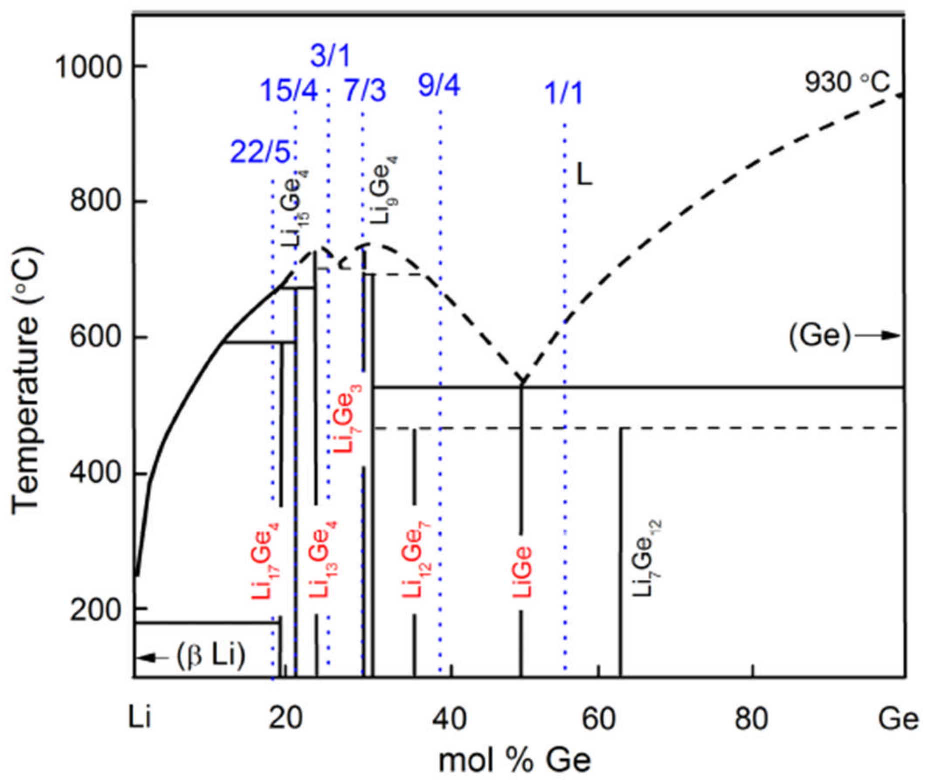
- T_{dehyd} < 150°C
- Capacity = 3.2 wt.%
- Reversible

Chem. Commun, **47** (2011) 8001.

3 LiH + Ge

- 3LiH/Ge system
- 3.1 wt.%





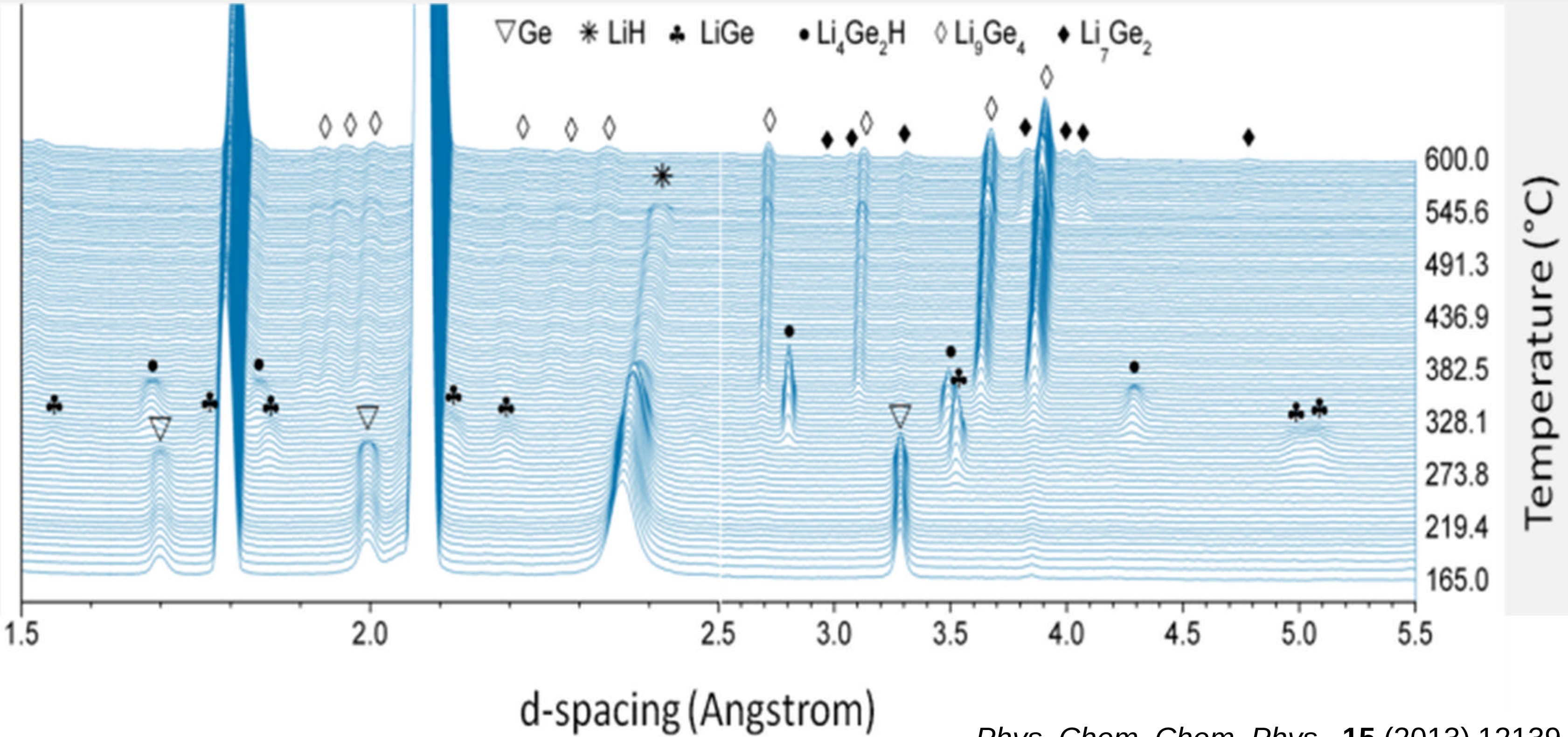
- Potential to increase capacity

Sangster, J Phase Equ., 1997, **18**, 289

3 LiD + Ge

in situ Neutron Powder Diffraction

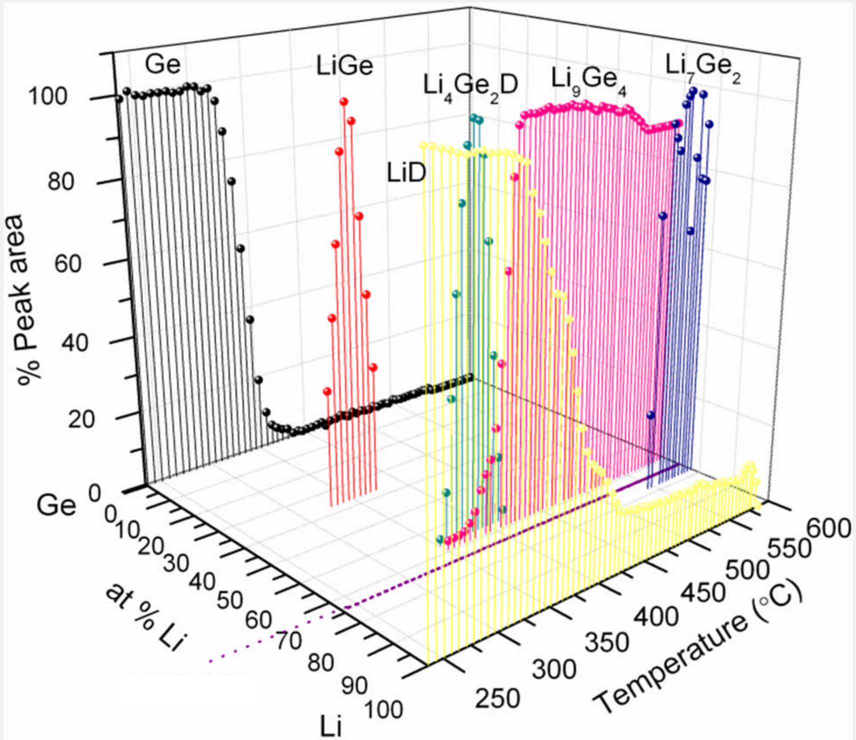
- 5 h BM sample
- Dynamic vacuum



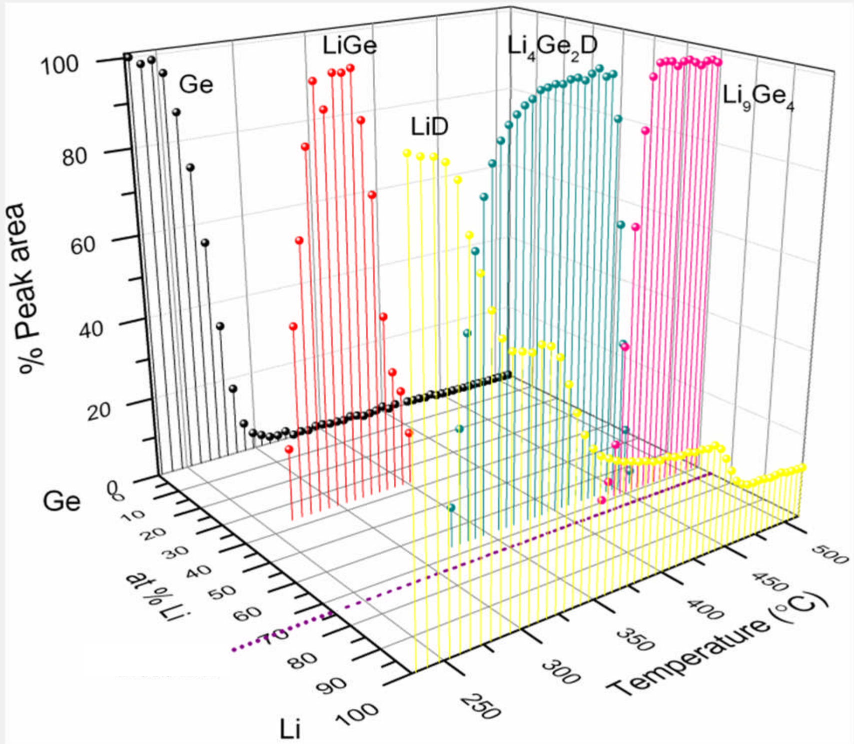
Phys. Chem. Chem. Phys., **15** (2013) 12139-12146

3 LiD + Ge

- Evolution of phases



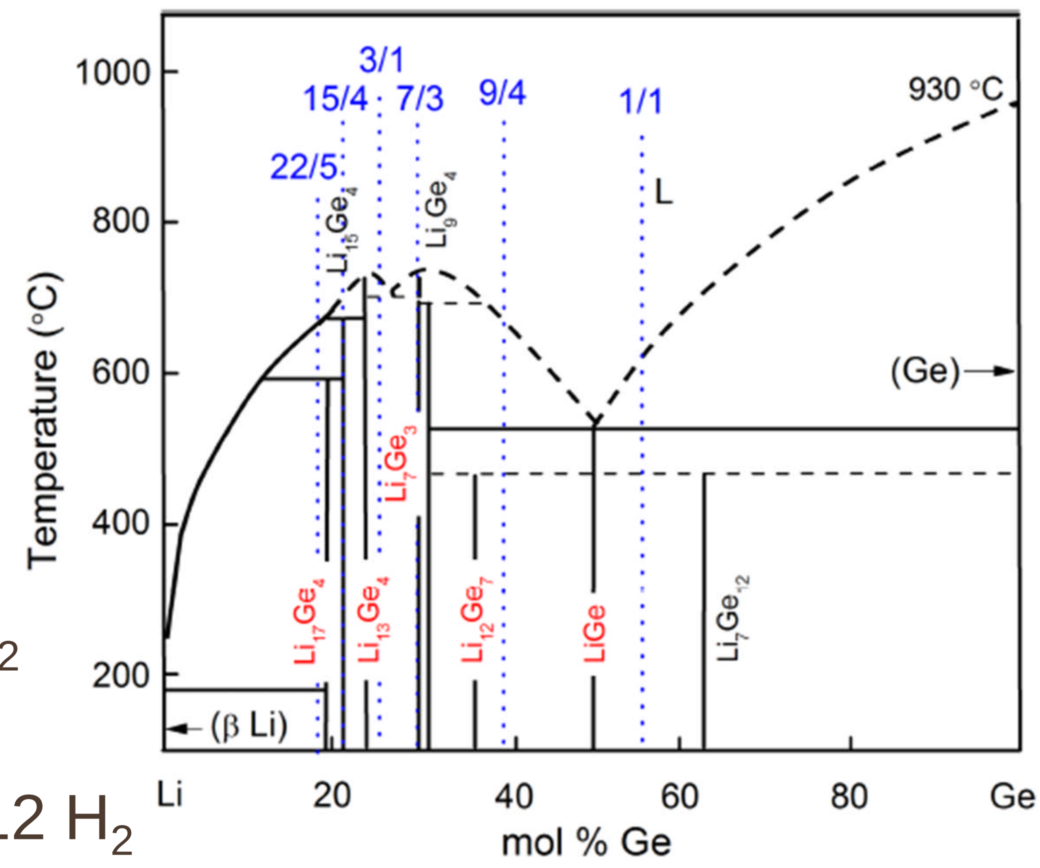
Dynamic vacuum



Self generated atmosphere (p_0 = 0 bar, p_{max} = 3.5 bar)

Phys. Chem. Chem. Phys., **15** (2013) 12139-12146

3 LiH + Ge



Reaction sequence

$3\ LiH + Ge$

↓

$2\ LiH + LiGe + 0.5\ H_2$

↕

$LiH + 0.5\ Li_4Ge_2H + 0.75\ H_2$

↕

$0.75LiH + 0.25\ Li_9Ge_4 + 1.12\ H_2$

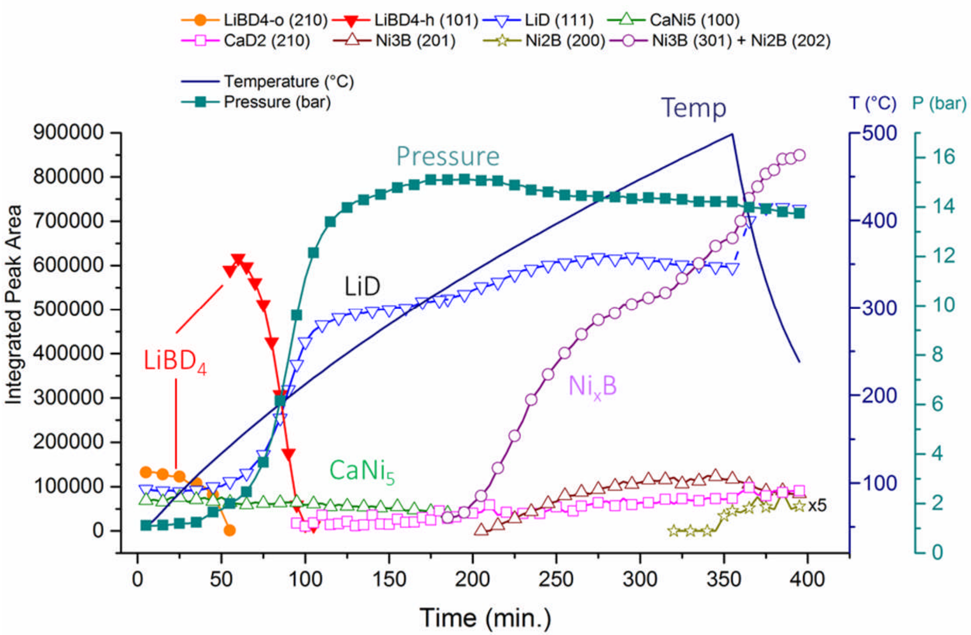
↕

$0.1\ Li_9Ge_4 + 0.3\ Li_7Ge_2 + 1.5\ H_2$

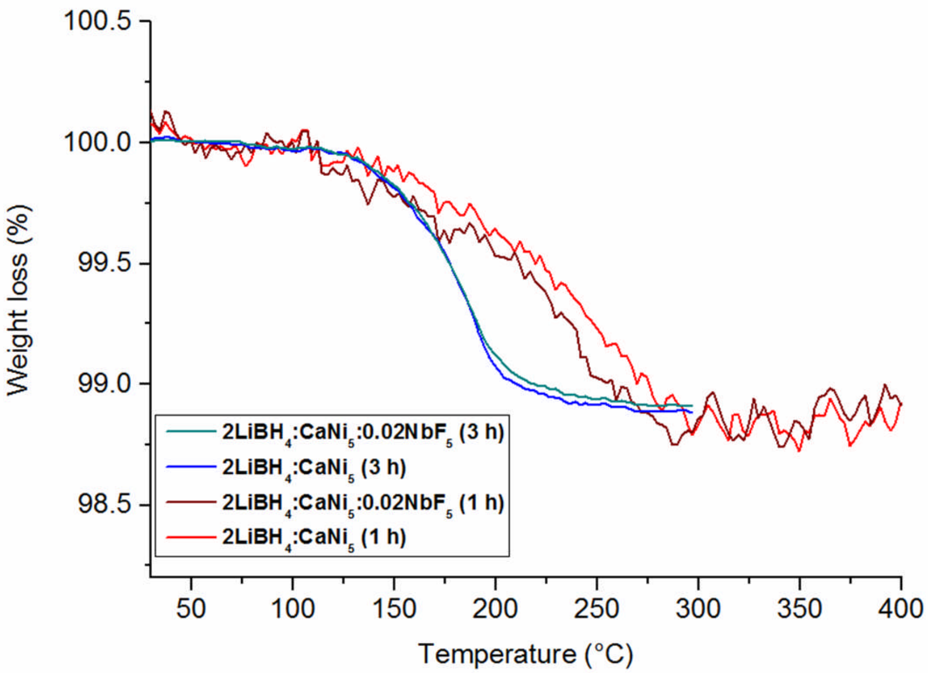
Phys. Chem. Chem. Phys., **15** (2013) 12139-12146

$2LiBH_4 : CaNi_5$

- Neutron diffraction



- TGA
  - H_2 release below 150ºC



- Investigating the decomposition route in order to improve capacity

Stationary Hydrogen Systems

Thermal Energy Storage (TES) for Concentrated Solar Power (CSP)

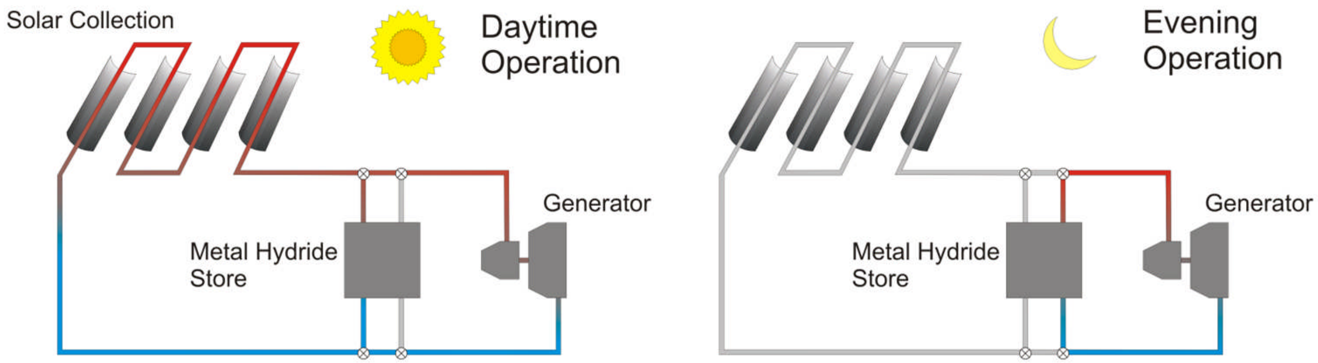
Andasol III (Spain)
50 MW, 7.5 hrs storage

MHx TES

- Concentrated solar power (CSP) has the potential to be a major renewable energy source.
- Has advantage that storing heat is much cheaper than storing electricity:

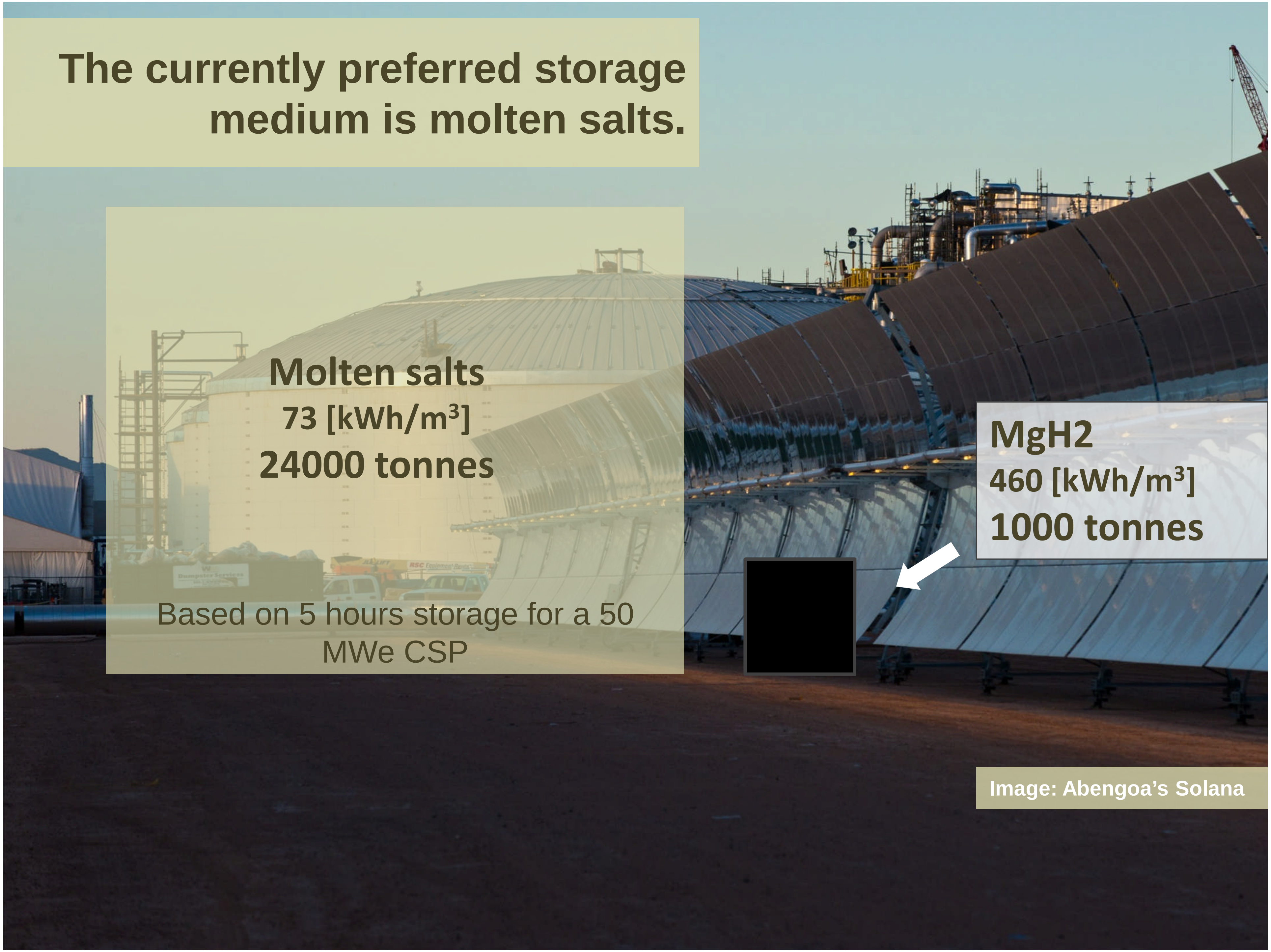
  Hydride thermal storage ~ £3 – £4 /kWh   Li-ion electrical storage ~ £500 /kWh

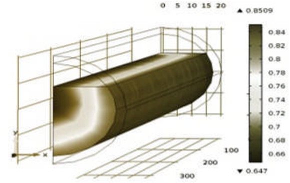
- However, such thermal storage is essential for widespread deployment of (CSP).
- It will bring together the periods of peak electrical generation and peak demand.



- The Mg-MgH2 system is a strong candidate for the storage medium:
  - High enthalpy of formation (-74.5 kJ/mol H2).
  - Suitable pressures in the CSP operating temperature range.
  - Abundance of Mg at low cost.

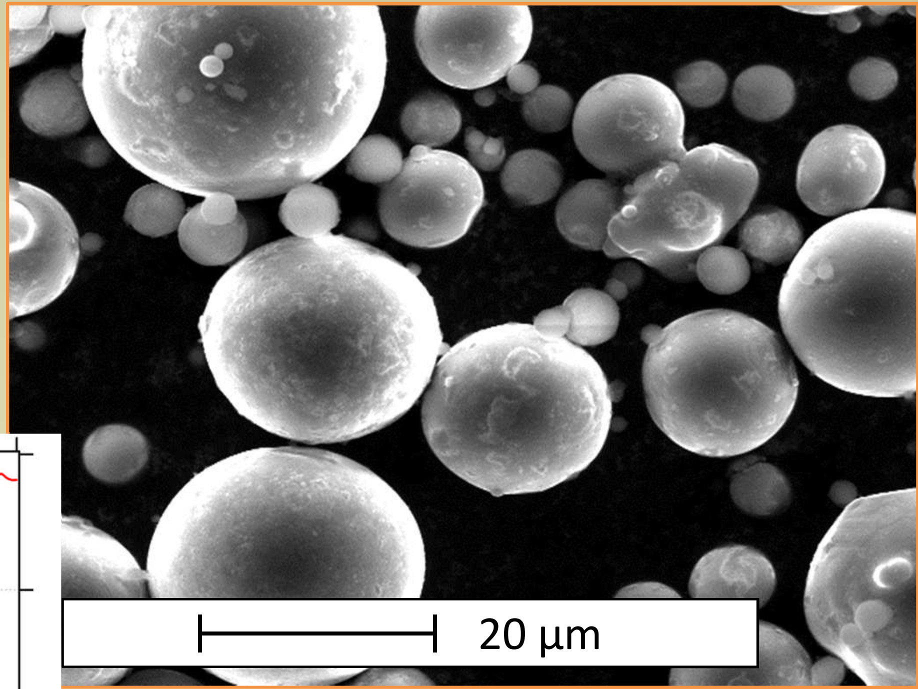
The currently preferred storage medium is molten salts.

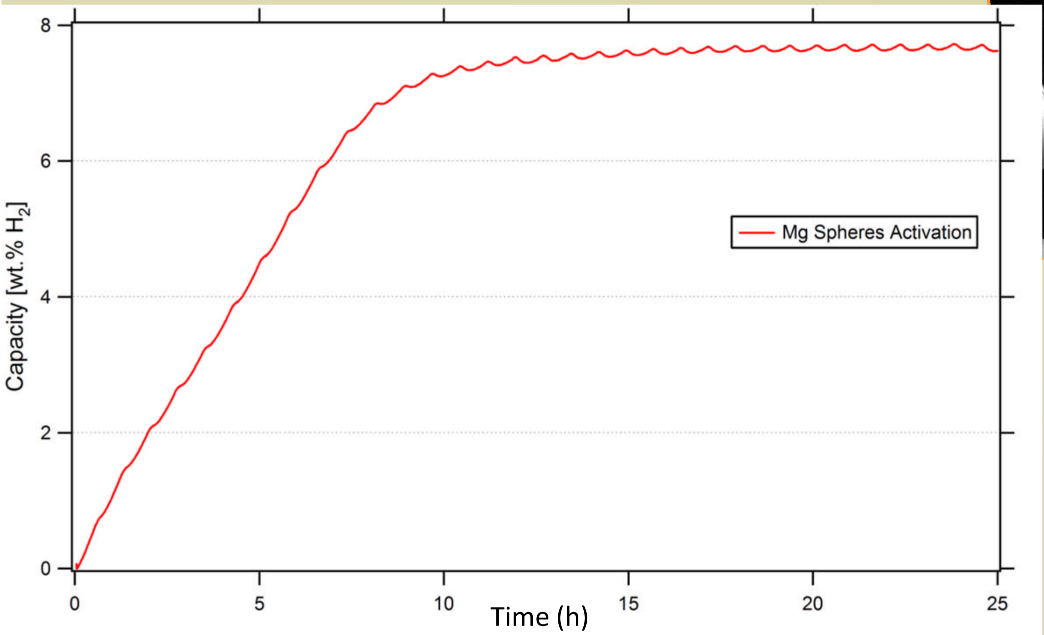




Cost Reduction

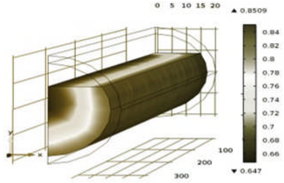
- Two main avenues to reduce fabrication cost of porous material.
  - Start with Mg instead of MgH_2.
  - Remove the milling stage.
- Atomised Mg powder tried as benchmark.
- Activated at 400 ° C under 40 bar H_2.
- Immediately cycled without milling.





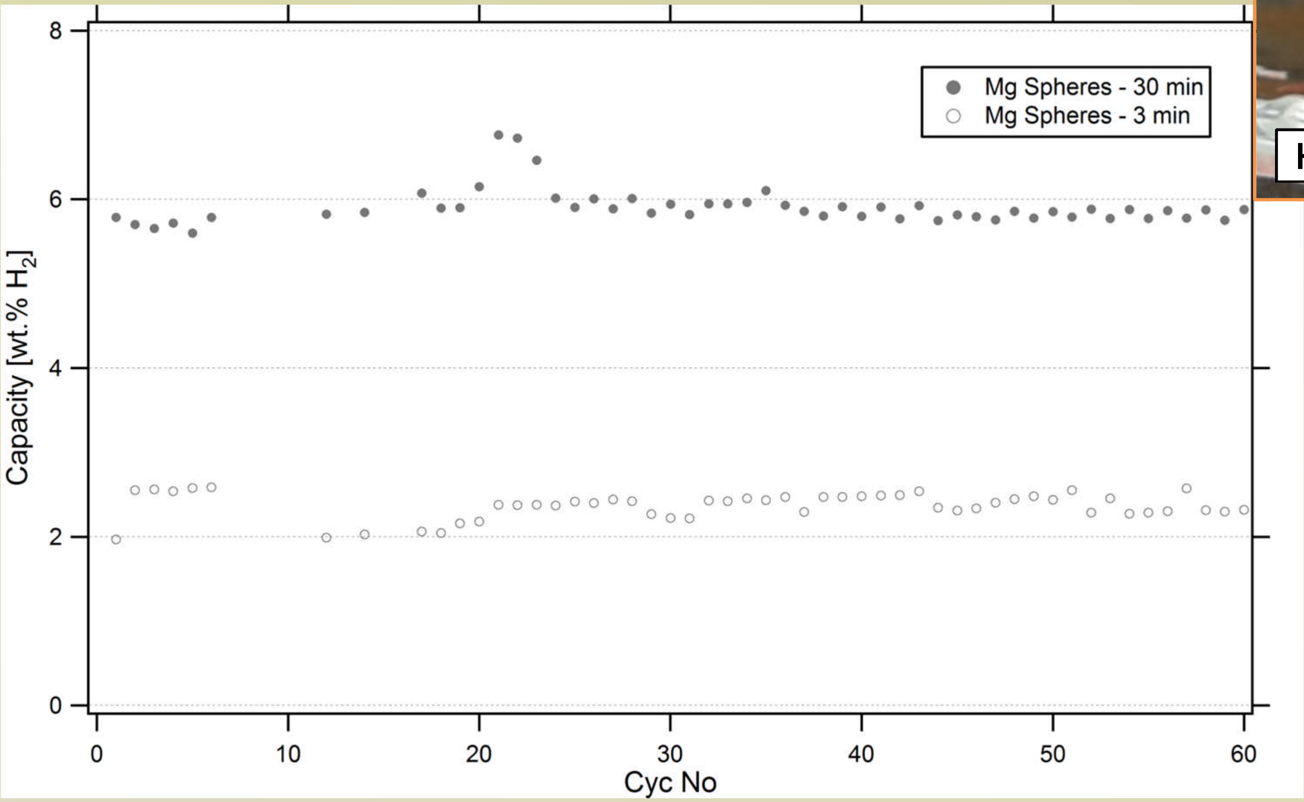
Average particle diameter = 26 µm.

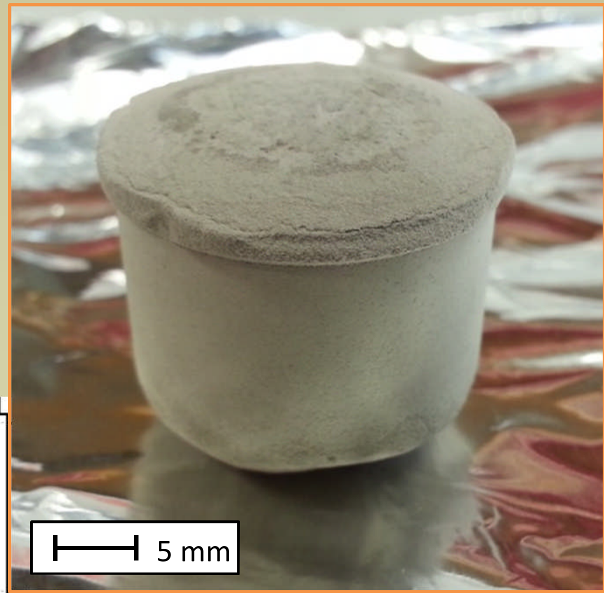
Activated to max. capacity within 1 day.

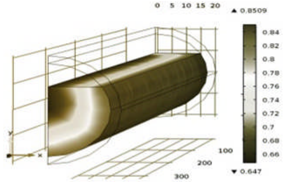

Cost Reduction

- 5 g sample cycled 60 times.
- Sufficient to develop porous structure.
- Capacity stabilised at 6.0 wt.% H_2 by cycle 60.





- Slightly slower kinetics then ball milled sample

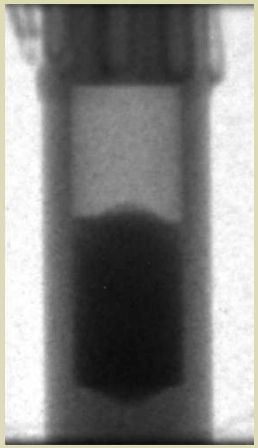




Bed Expansion

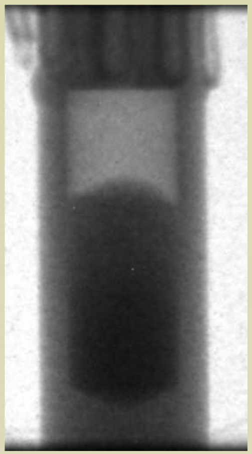
- Radiography undertaken at NIST

- Bed volume increased with each cycle

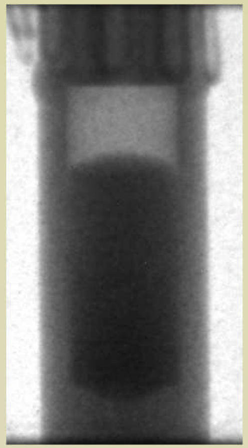
Sample mass: 2.2 g
Porosity: 0.7
Volume of vessel: 2.4 cm^3
Temperature: 400 ^oC
Pressure: 30 bar
Cycle length: 30 minutes



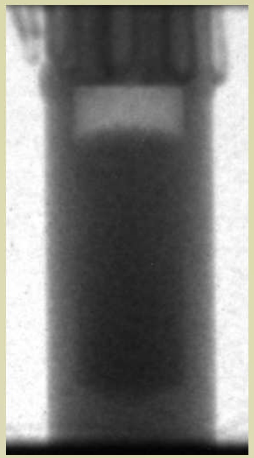
Cycle 1



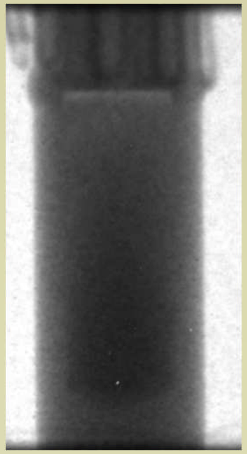
Cycle 2



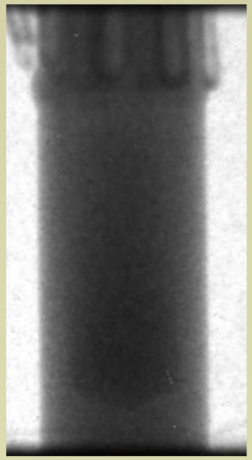
Cycle 5



Cycle 10



Cycle 20

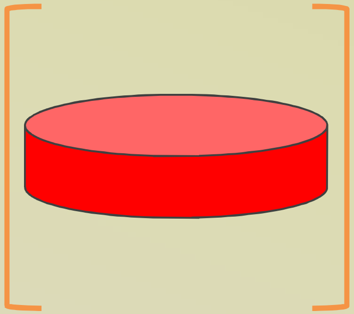


Cycle 30

X-ray μCT

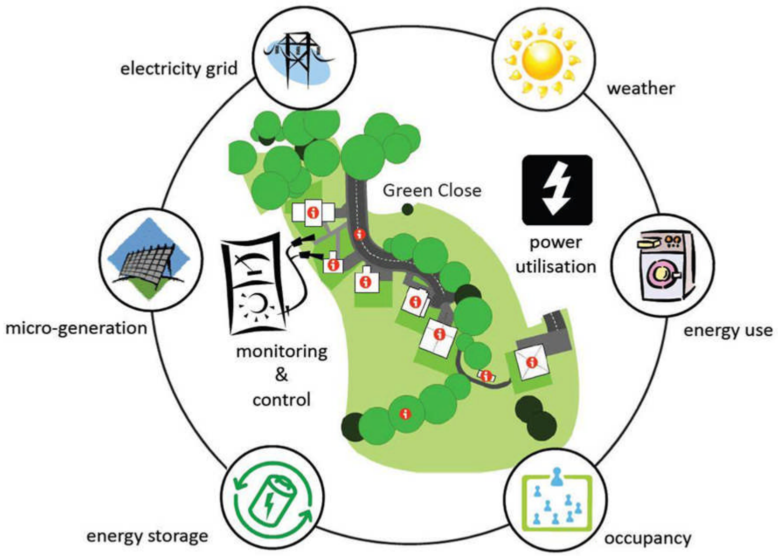
- Porous cylinder scanned and reconstructed to observe internal structure.

Porous Sample



Intelligent smart energy community (ISEC) project

David Parra, Mark Gillott, Gavin Walker



Smart Grid

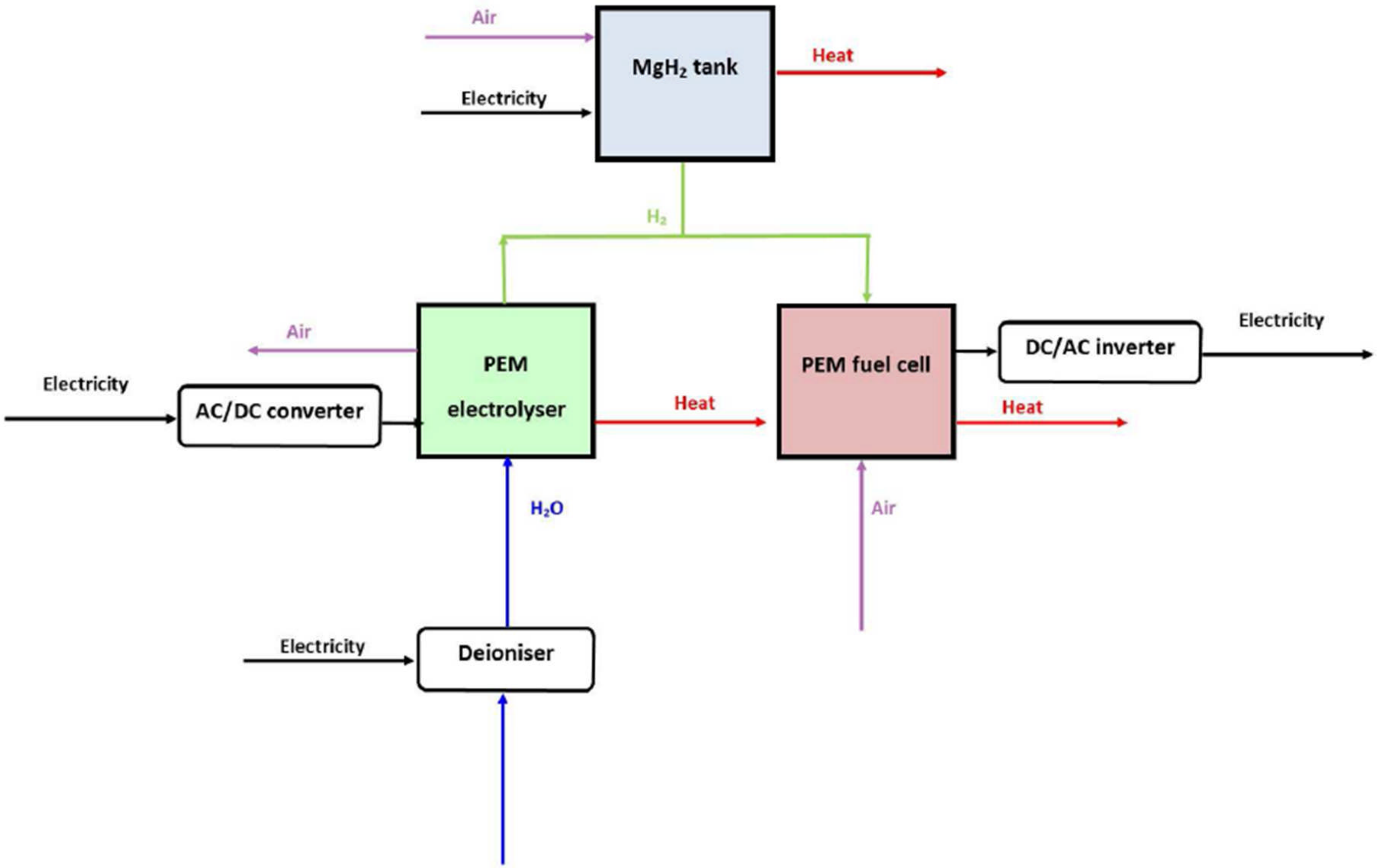
Creative Energy Homes

Applied Energy **137** (2015) 576-587

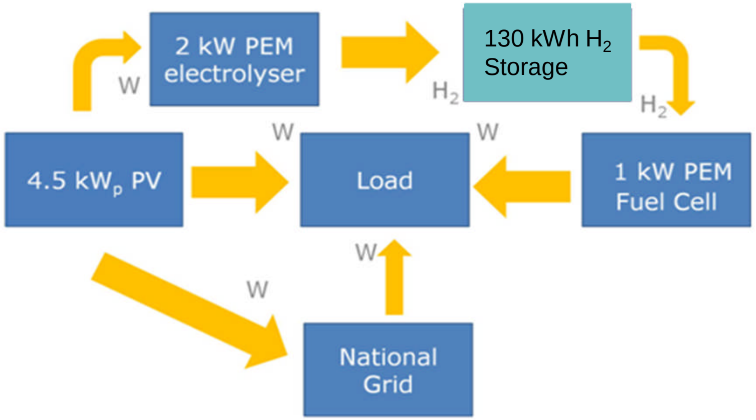
Project Part-Financed by the European Union

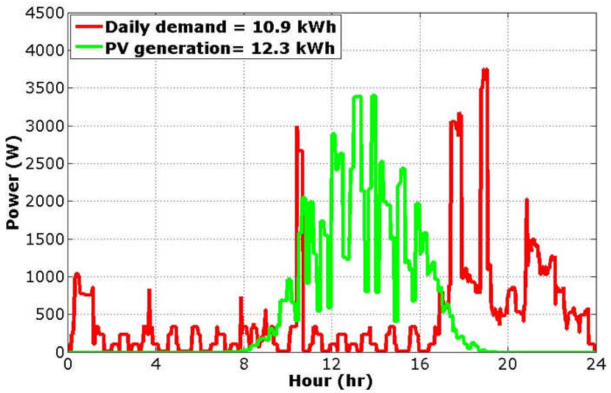
European Regional Development Fund

H_2 Community Energy Storage System



ISEC project





Daily energy mismatch

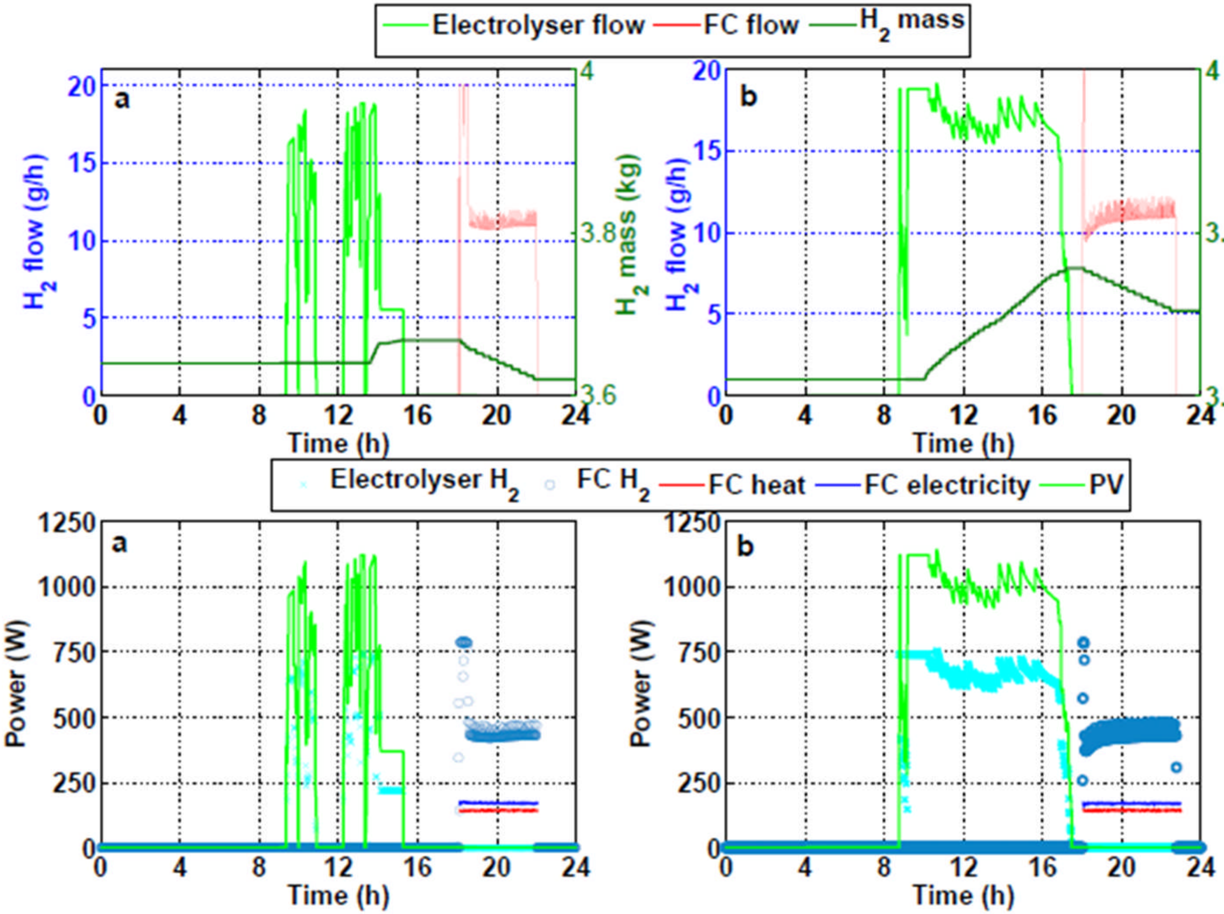
Hydrogen infrastructure

ITM HBox Solar
McPhy Store
Ballard PEM-FC

IJHE **41** (2016) 5215-5229

Project Part-Financed by the European Union
European Regional Development Fund

PV time shift



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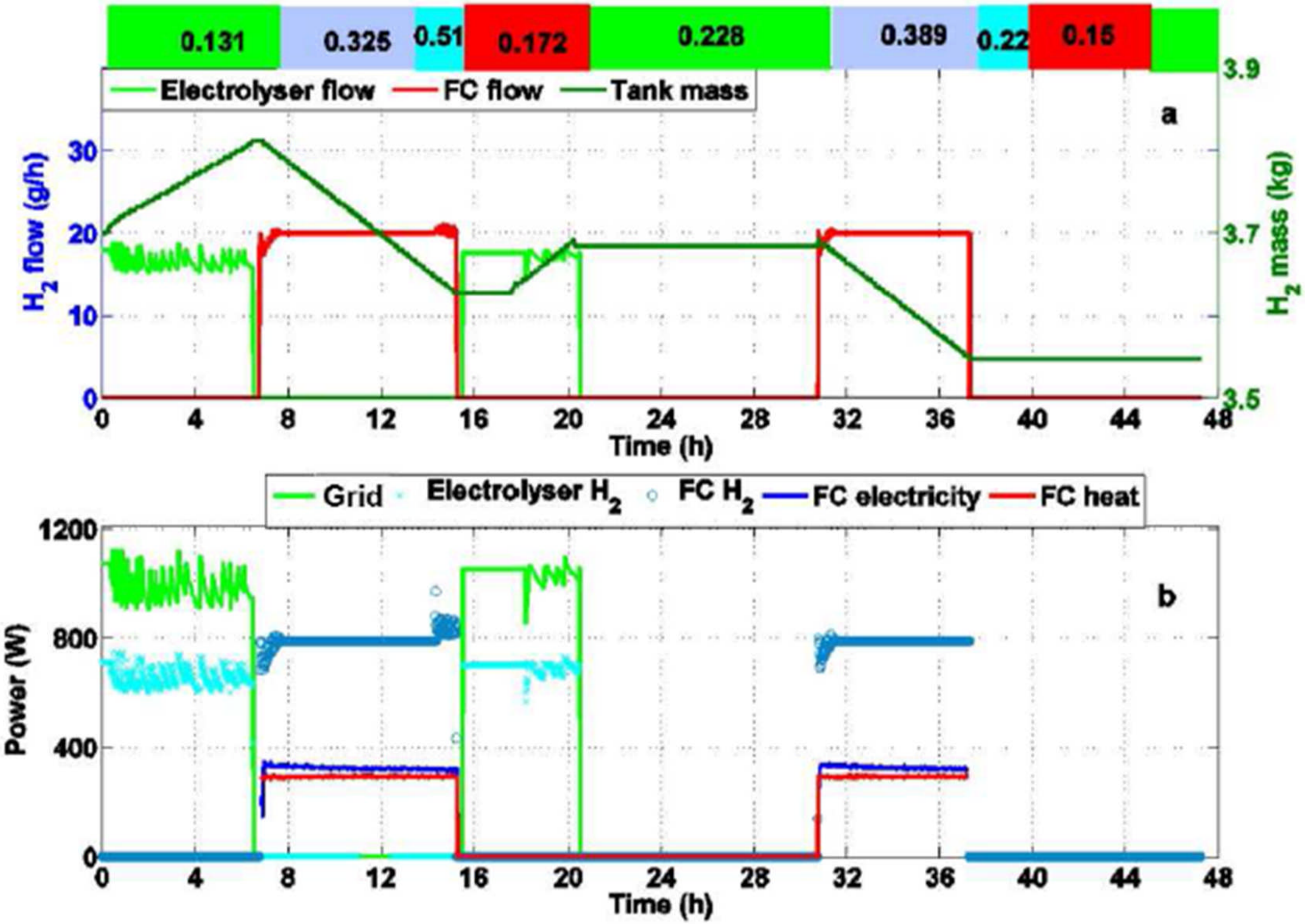
Demand Load Shift



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ISEC project

System Efficiency

- Partial loads and intermittency for PV time shift reduces system efficiency
- Partial loading – storage unaffected (ca. 20 W power demand), but reduces the efficiency of the electrolyser (64-66%) and Fuel Cell (38-40%)
- Electrical roundtrip efficiency of the system 26%
- CHP roundtrip efficiency of the system 52%
- Combined use doubled utilisation of hydrogen system

Variable Tariff

- Night off-peak (x); day off-peak (2x); peak (3x)
- Profitable to load time-shift peak to night off-peak

Longer term storage

- No charge leakage

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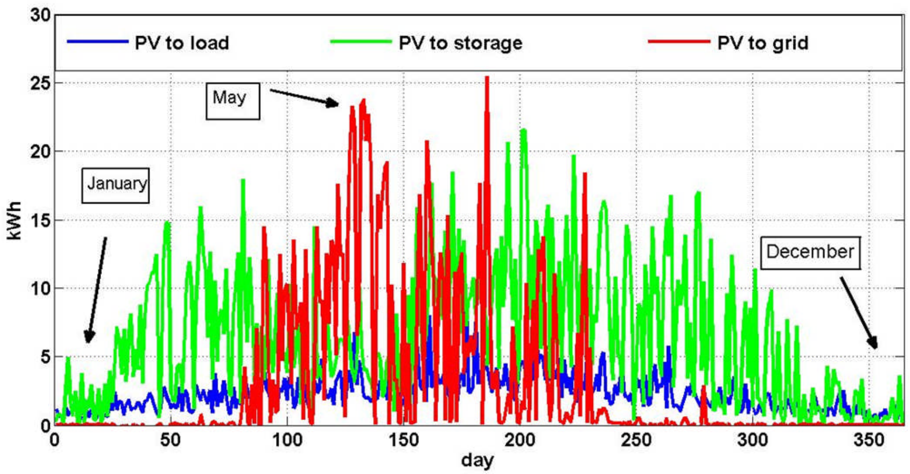
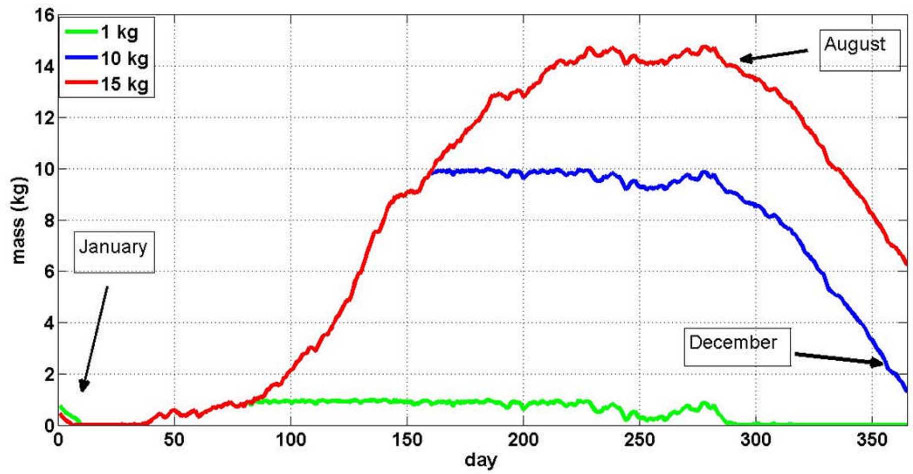
Longer term PV time shift



Annual PV generation distribution



Hydrogen Seasonal storage

- Makes sense to utilise heat as well (CHP)
- Space heating and hot water *ca*. 60% of energy demand
- No self discharge
- Parasitic losses for McPhy systems too large for longer term storage
- Requires an ambient temperature MHx

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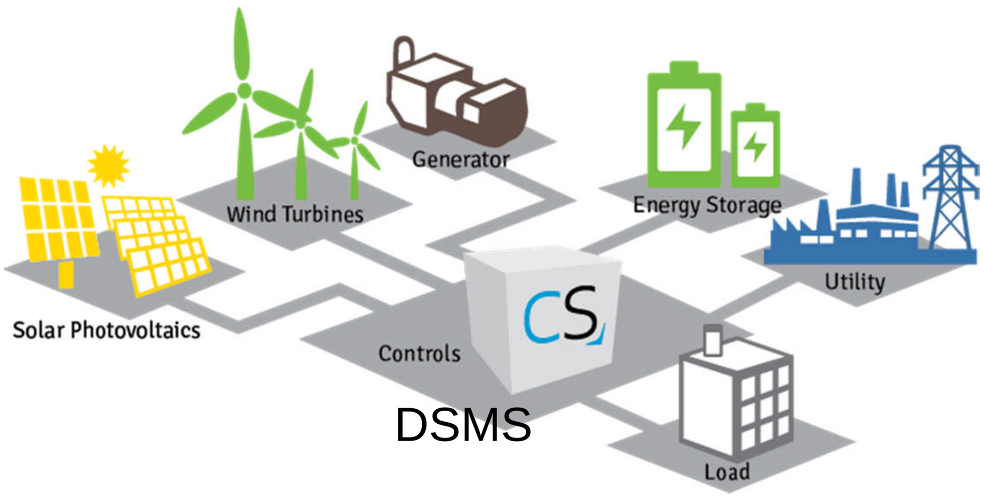
Intelligent Microgrids with Appropriate Storage for Energy (IMASE)
UK-India Project

Microgrid:
It is a small scale power supply network that is designed to provide power for a small community.

- Local power generation for local loads.
- Highly flexible and efficient.
- Connected to utility grid
- Energy storage
- Excess power can be sold to the utility grid.
- Size from housing estate to municipal community.

Microgrid



Government of India
Department of Science and Technology
सत्यमेव जयते

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Research Councils UK
Energy
For a Low Carbon Future

IMASE

Aim:

- Optimise the microgrid in order to maximise the efficiency of the microgrid while maintaining the quality and security of supply.
- Integration of electricity generation, storage, and transmission/distribution components.

1. Industry
2. Local school
3. Community houses

→

- Intelligent DSMS
- Storage technology

→

Intelligent Microgrid solution

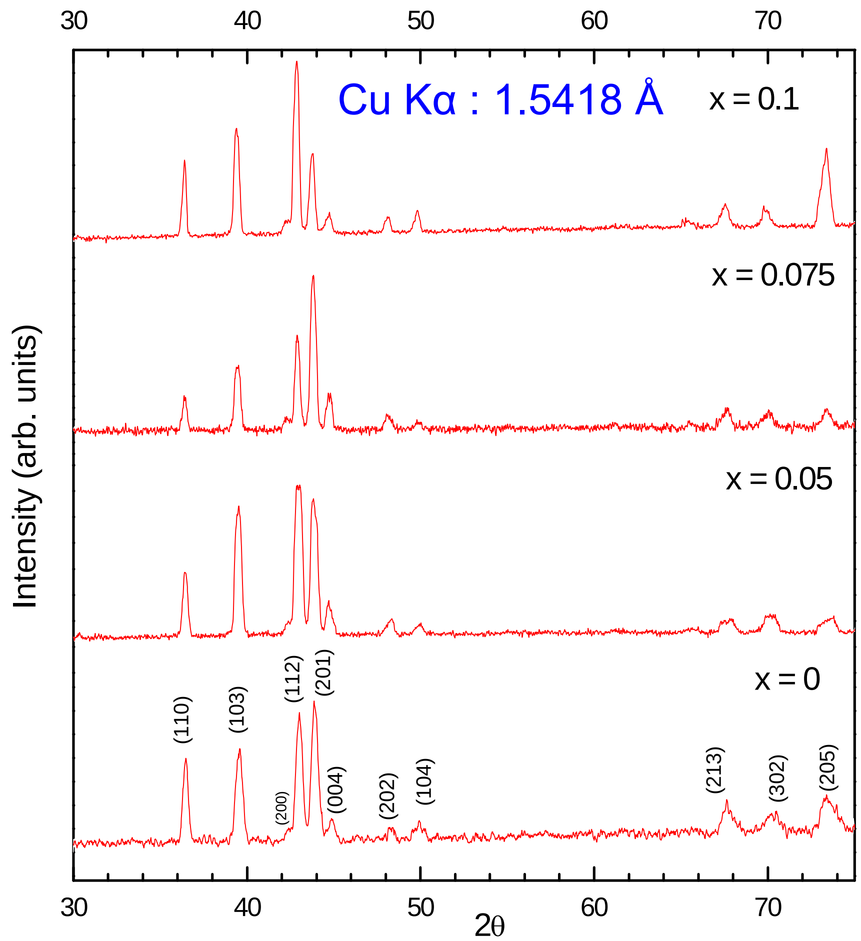
Develop suitable low cost hydrogen storage system for medium and long term storage for microgrid applications.

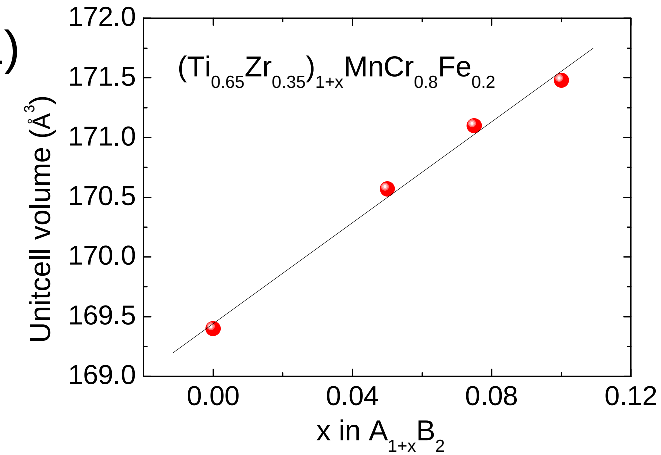
Objectives

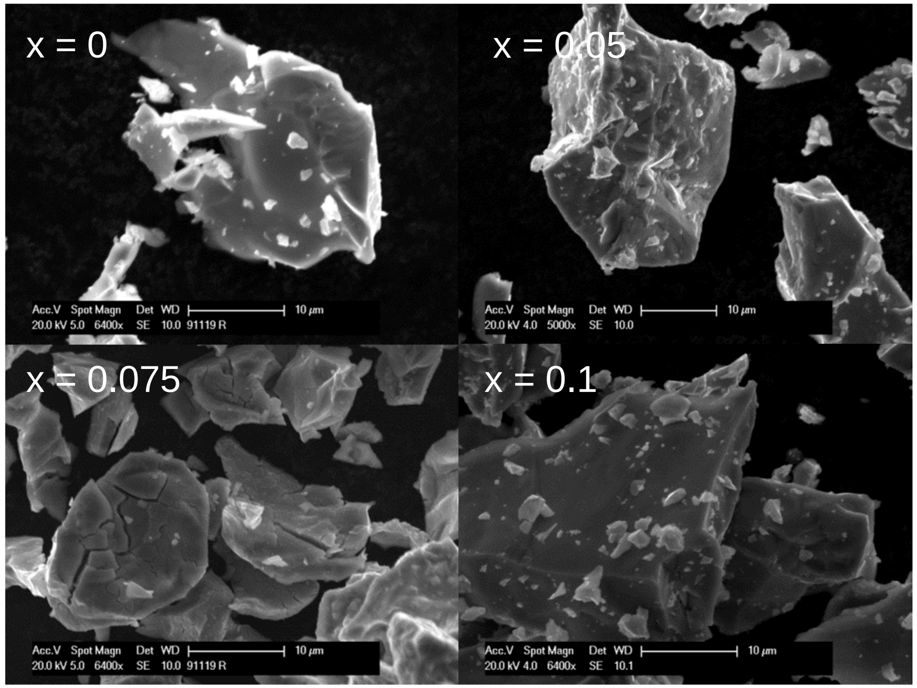
- Identify a suitable material for stationary hydrogen storage application
  - Working conditions: 25 ^{o}C to 35 ^{o}C and 1-30 bar
  - Good reversible storage capacity
  - Acceptable kinetics (4hrs)
  - long cycle life (10 years)
  - Cost effective
- Design and development of prototype hydrogen storage system
  - Storage capacity: 10.5 kWh
  - heat management: passive vs active
  - Acceptable kinetics

Material

$(Ti_{0.65}Zr_{0.35})_{1+x}MnCr_{0.8}Fe_{0.2}$ (x = 0, 0.05, 0.075 and 0.1)







- Single phase formation
- Hexagonal structure (C14)
- space group $P6_3/mmc$

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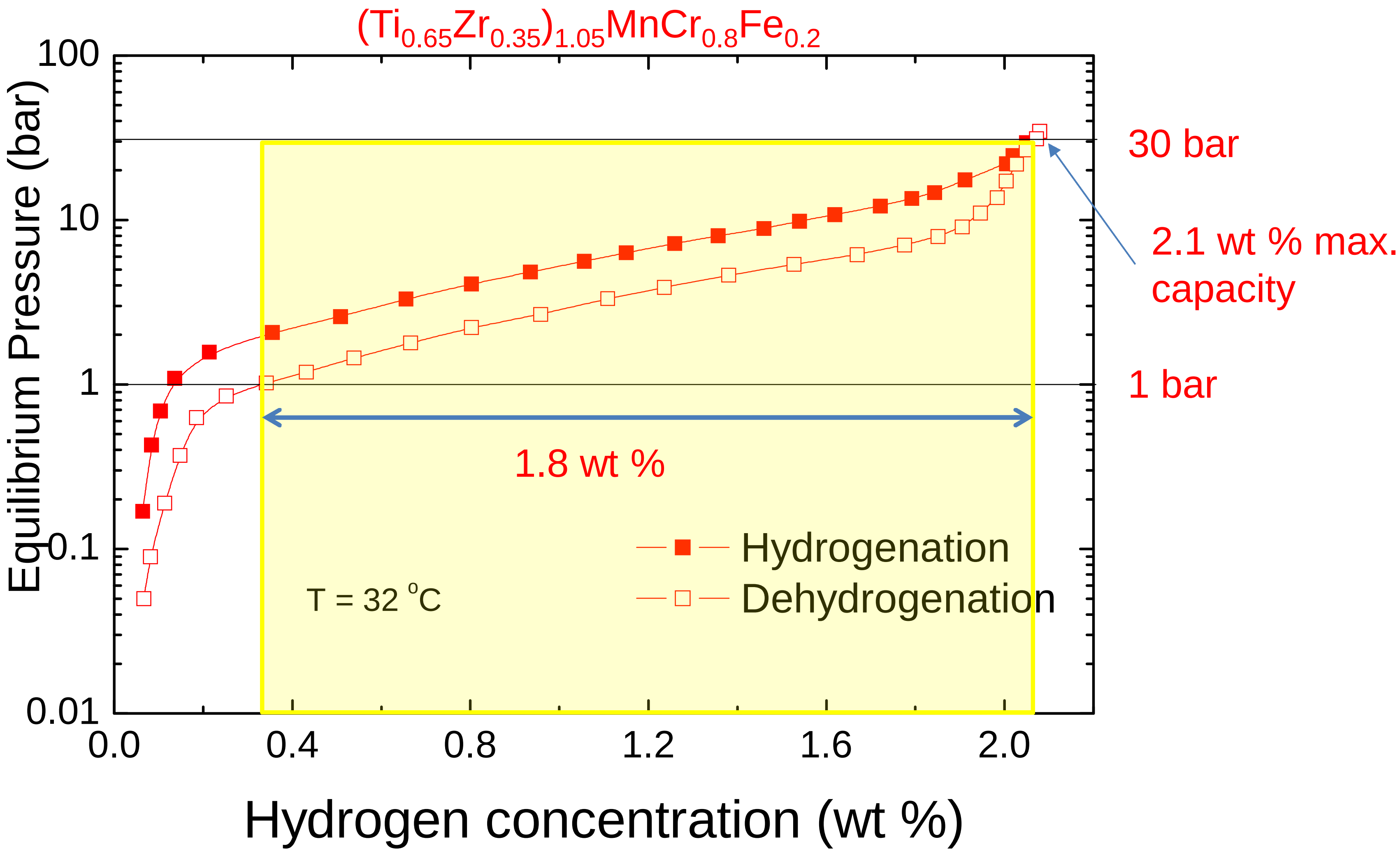
Pressure – Composition Isotherms



Working capacity (1 to 30 bar) at 32 °C ~ 1.8 wt %

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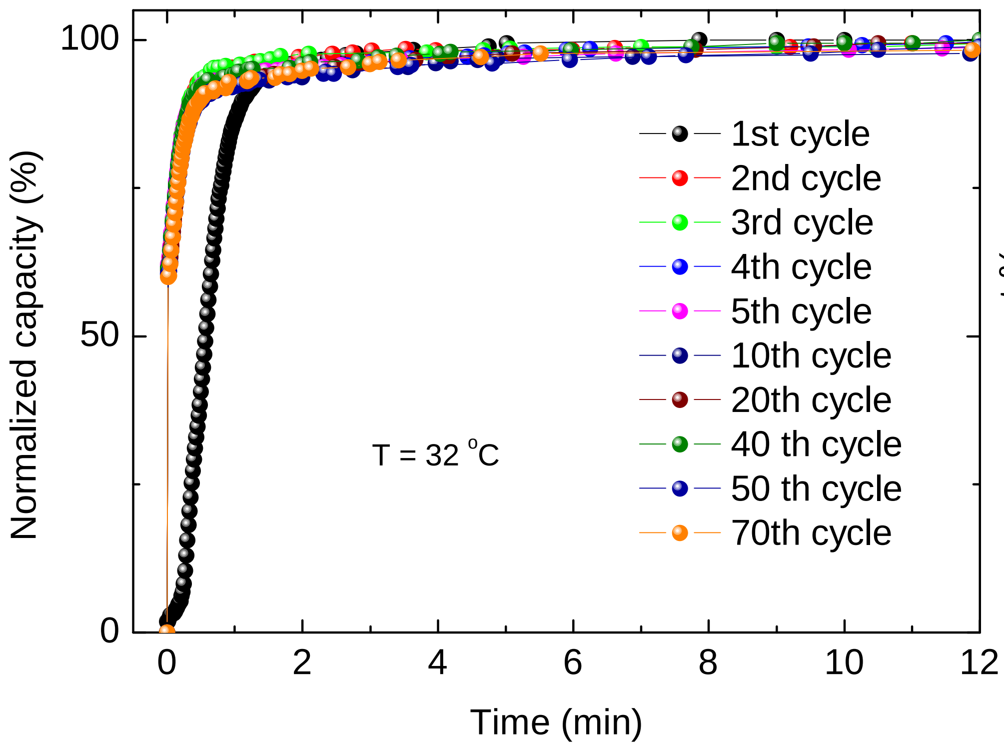
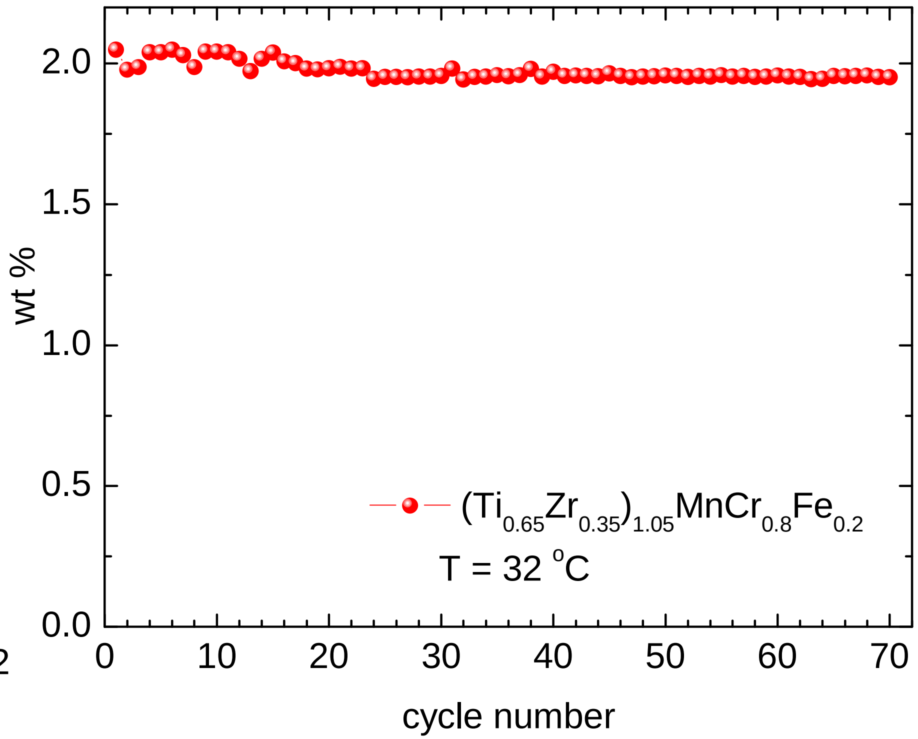
Kinetics & Cycle life

$(Ti_{0.65}Zr_{0.35})_{1.05}MnCr_{0.8}Fe_{0.2}$





95 % of capacity reached within 5 min and good cyclic stability

Capacity stabilizes at 1.95 wt % over 70 cycles

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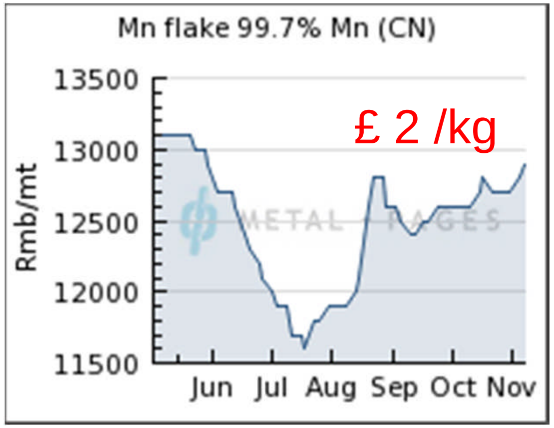
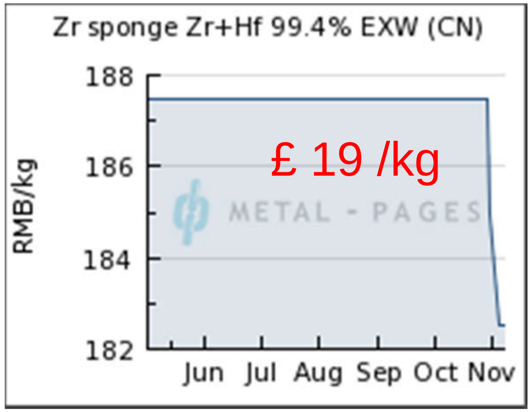
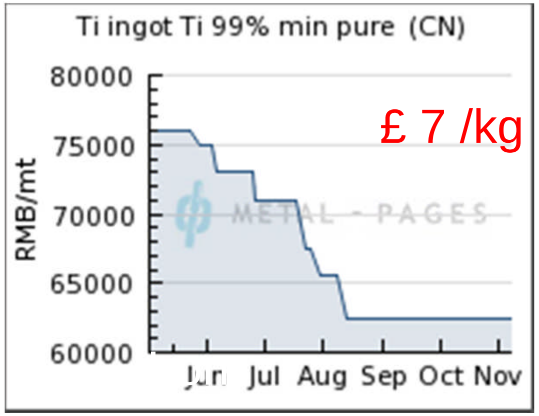
Cost analysis

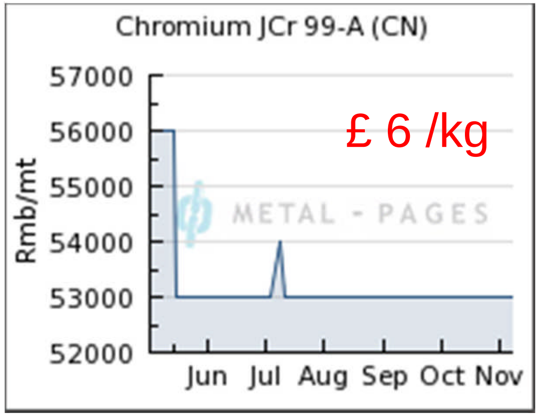




Iron
Commercial Price: £10
1kg
www.pureiron.co.uk/price_list.htm

Vanadium
Commodity price : £ 327 per kg





Commercial Hydralloy C

Commodity price : £ 48 /kg

Commercial price : £ 45-50/kg @1000 kg

Energy storage: £81 /kWh

Nottingham AB_2 alloy

Commodity price : £ 9 /kg

Cost of energy storage: £13 /kWh

Design of a prototype store

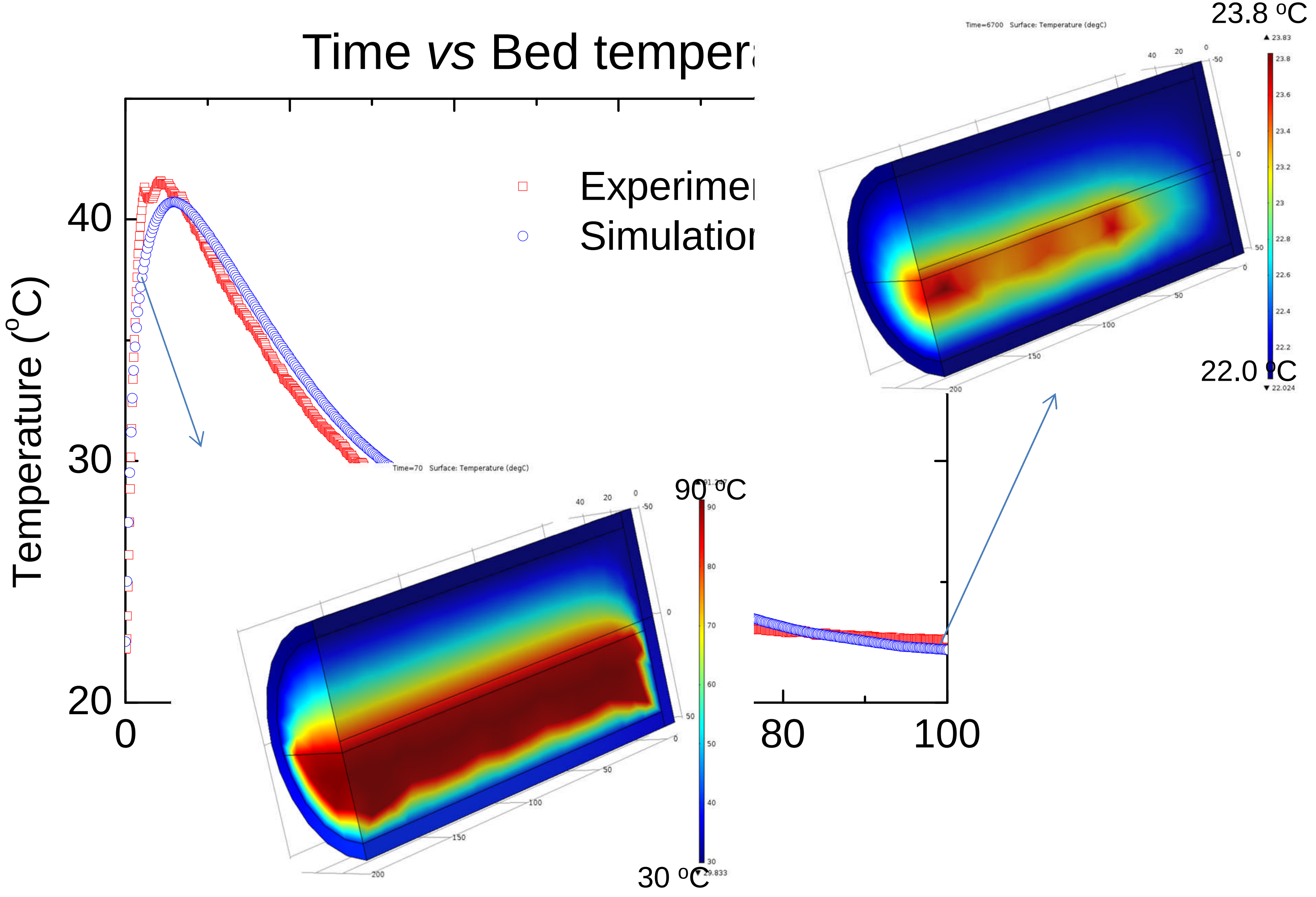
- Aluminium alloy (6061 T6) cylinders procured from Luxfer cylinders
- Better corrosion resistance (scuba diving)
- Better heat transfer effect than stainless steel cylinders
- Working pressure range of 200 bar at 15 °C

Prototype system : Objectives

- ❖ Effect of Air flow
- ❖ Effect of initial pressure
- ❖ Effect of external fins

Simulation results

Comparison between the expt. data and simulation



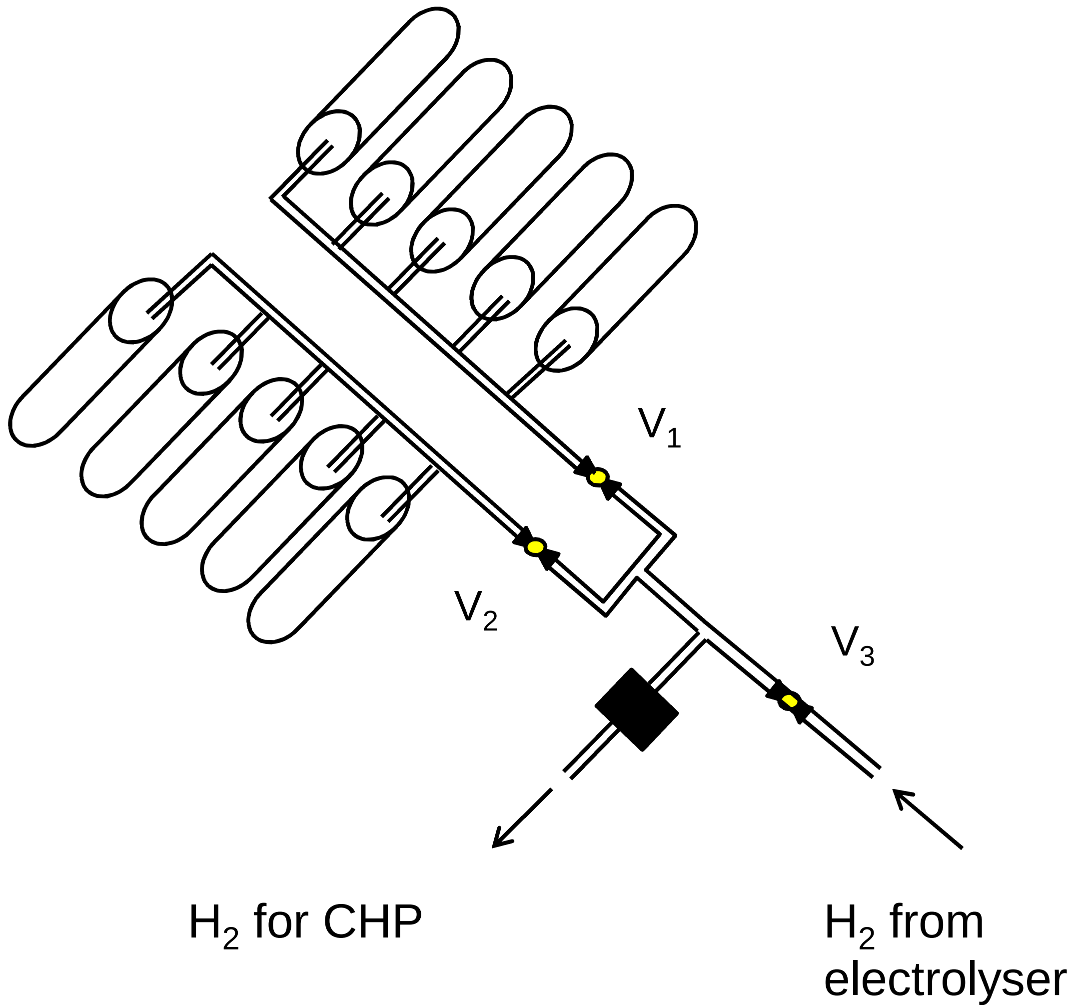
Full scale system

Modular design
Ten Al alloy (6061 T6) cylinders;
15 kg of AB_2 alloy
10.5 kWh energy stored

Hydrogenation kinetics : 2 hrs
Dehydrogenation kinetics : 4 hrs

Larger vessels will require:

- Better heat management
- Internal / external fins



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Engineering Safe and Compact Hydrogen Energy Reserves (ESCHER)

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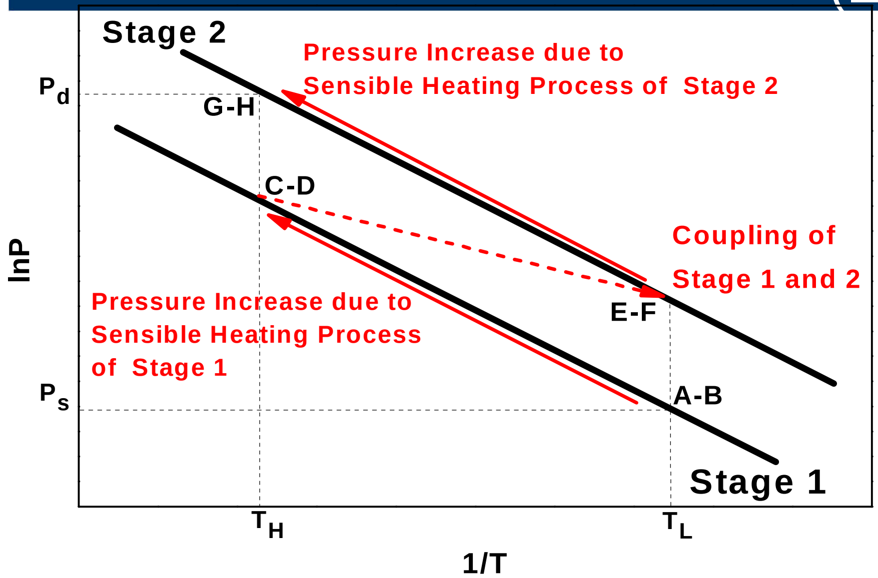
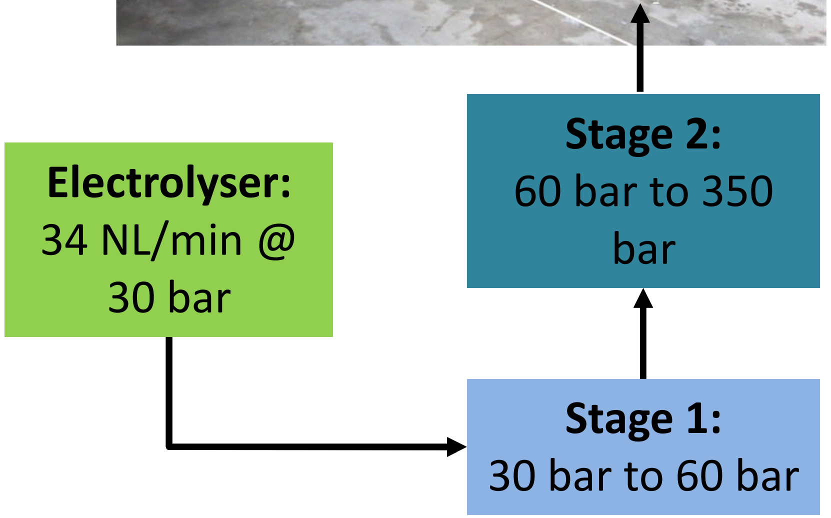


Target H_2 production	600 g
Total charging time	<10 h
Number of overnight cycles	10
H_2 storage capacity of each stage	60 g
Length of each cycle	50 mins
Mass powder per stage	Ca. 4 kg



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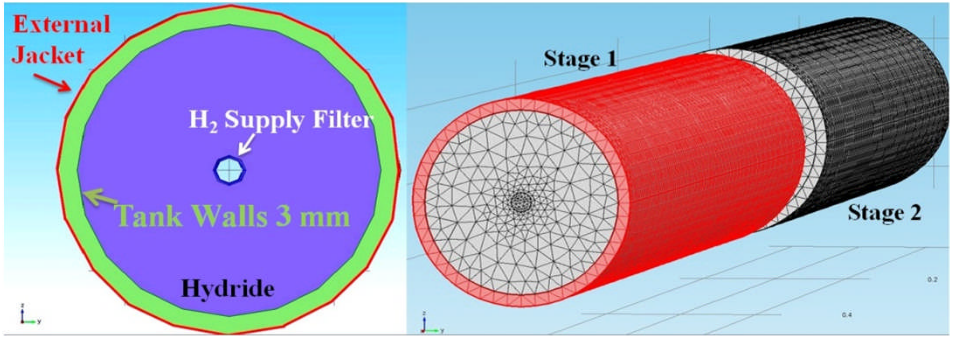
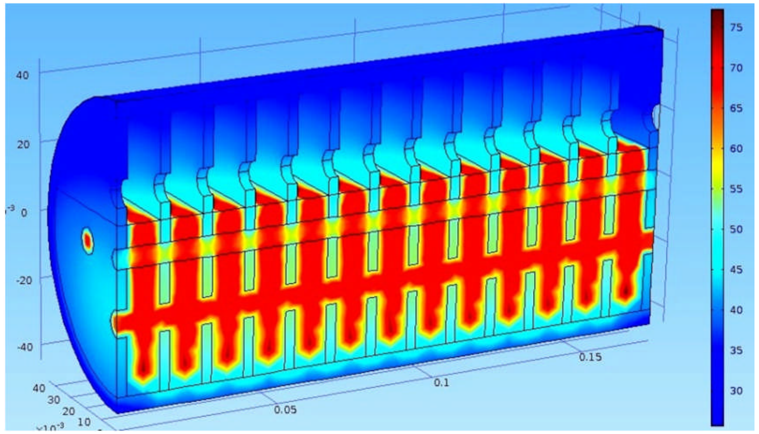
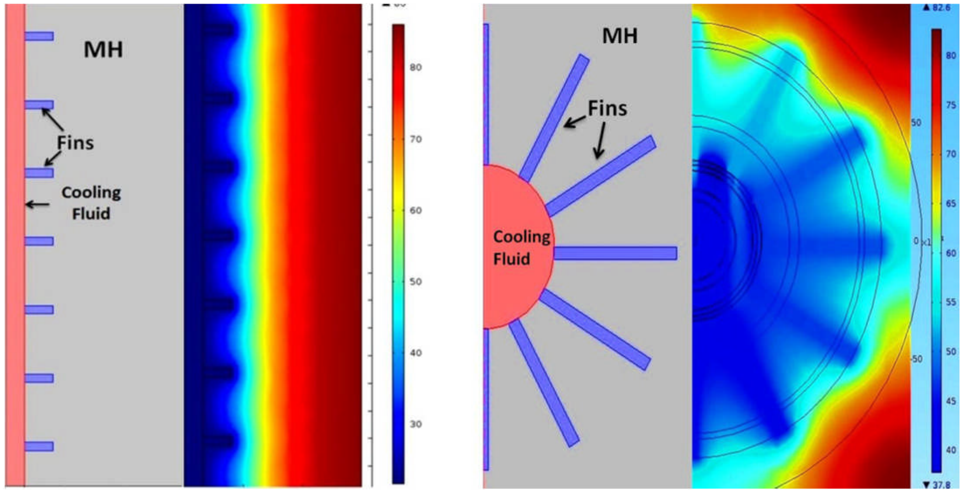
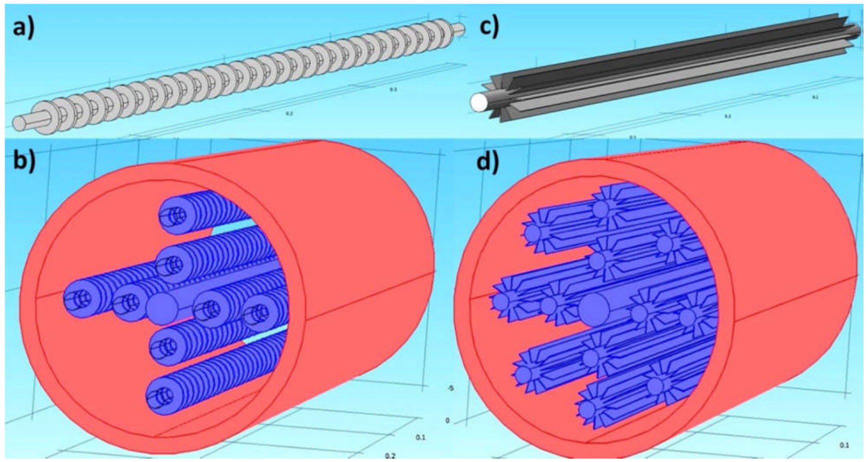
H2FCSUPERGEN
THE HYDROGEN AND FUEL CELL RESEARCH HUB

Internal fin designs









E.I. Gkanas, D.M. Grant *et al* doi:10.1016/j.jallcom.2015.03.123
E.I. Gkanas, D.M. Grant *et al* 10.1016/j.ijhydene.2016.04.035

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TANK Project

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Electrolyser

MHx Store

Hymera PEM-FC

- Feasibility project - off the shelf hydrogen stores for small 0.5kg to large applications 100kg hydrogen
- Designing a prototype pressure vessel with interior architecture to allow passive heat management
- Operation between 2 and 30 bar

arcola energy

Luxfer Gas Cylinders

ITM POWER Energy Storage | Clean Fuel

Innovate UK Technology Strategy Board

TANK

Island Hydrogen

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Technology Strategy Board

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- Green hydrogen generation
  - powered by Renewables
- Nott Hydrogen refuelling station
  - 30 kg hydrogen at 350 bar
- Optimising the system
- 100 kg a day refueller
- > 200 kg on site storage
- H-ICE Boat and harbour refueller

Sheffield M1 Wind-Hydrogen fuel station opened Sept 2015

- Opportunity for MHx stores – reduce the quantity of high pressure hydrogen stored on site.

ITM POWER
Energy Storage | Clean Fuel

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Innovate UK
Technology Strategy Board