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Nano-Structured Hybrid Hydrogen Storage Materials for Small Scale Energy Supply Technologies

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(Start Date – 1 July 2007, Duration of Project – 3 years)

Joule Funding Budget: £341,256

Grant Holders Seminar
Joule Centre for Energy Research in the North West
University of Salford, Greater Manchester, 2 October 2008

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Opening Thoughts:

Children,
if you're watching… At school tomorrow, if you got a science lesson, and the teacher says: "Today we are going to do storage of hydrogen", pay attention: Because whoever works that out is going to be the richest person the world has ever seen!

Jeremy Clarkson,
***Top Gear*, BBC2**
2nd December 2007

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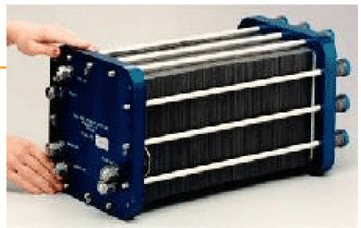
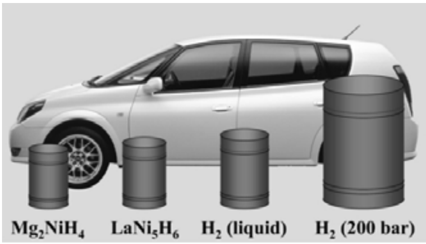
Opening Thoughts:



Fuel cells react hydrogen with oxygen (from the air), releasing energy and producing water as a by-product.

$$H_2 + \tfrac{1}{2}O_2 \xrightarrow[-285.83kJ]{} H_2O$$

Governed by electrochemistry rather than thermodynamics, fuel cells are typically more than 75% efficient. This compares favourably to 60% max. efficiency of current car engines.



However, compact hydrogen storage is a challenging problem. Volumes required to store 4kg of hydrogen in various forms is illustrated left.

Image from:
L. Schlapback & A. Zuttel, Nature, **2001**, *414*, 23

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Project Objectives

Our project is based around 3 broad objectives:

1. The preparation of a carbon-based framework with high surface area and controllable porosity, with assessment of currently available materials.

2. Development of a method to deposit light metallic elements or compounds (e.g. lithium or lithium imide/amide) that may promote hydrogen sorption or other effects e.g. spillover catalysis.

3. Discovery of novel methods to create lithium (imide/amide) inclusions within the structure of materials.

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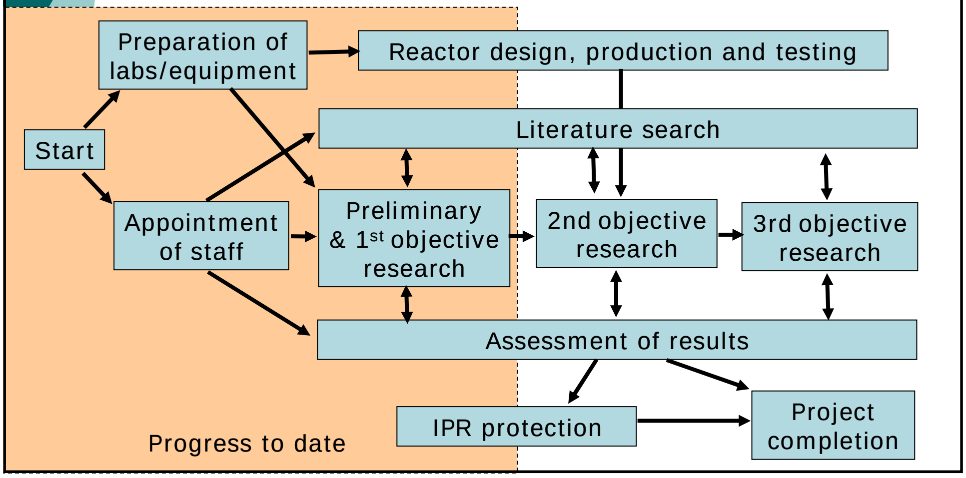
Project Objectives



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Preliminary Research

http://www.chemvironcarbon.com

Carbon materials from our commercial partner Chemviron Carbon, and carbonised Purolite materials are currently being assessed for suitability as candidates for material which fulfils requirements of being:

•Lightweight.

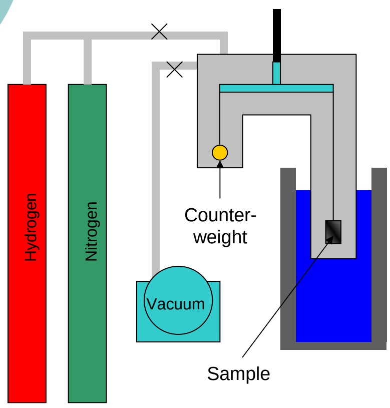
•High specific surface area (SSA).

•Pre-determined pore size distribution (PSD).

Assessment of these characteristics is done using IGA

Preliminary Research

Experiments are carried out using IGA (Intelligent Gravimetric Analyser), which allows assessment of a sample's gas sorption ability.



Preliminary Research

Hiden Analytical, Europa Boulevard, Warrington.

http://www.hidenanalytical.com

Analysis of this information determines Specific Surface Area (SSA) Pore Size Distribution (PSD) and hydrogen sorption uptake.

(Visual assessment of surface porosity also pending using electron microscopy.)

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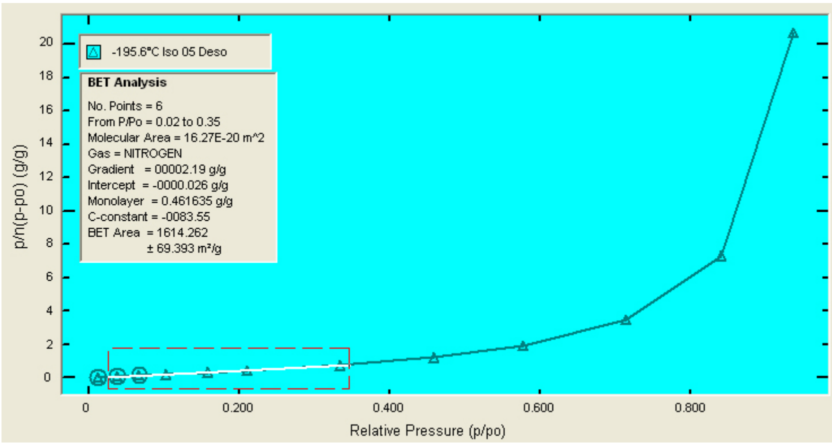
Preliminary Research

Chemviron Carbon Sample: Petroleum Coke Briquette

BET Specific Surface Area = 1614 m^2/g



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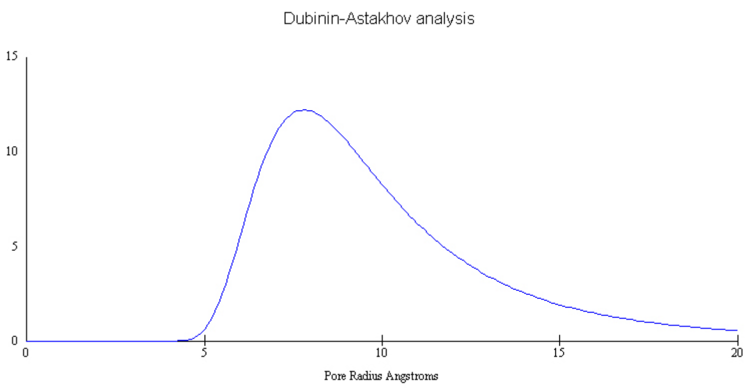
Preliminary Research

Chemviron Carbon Sample:

Modal average pore size = 7.6 Angstroms (0.76nm)



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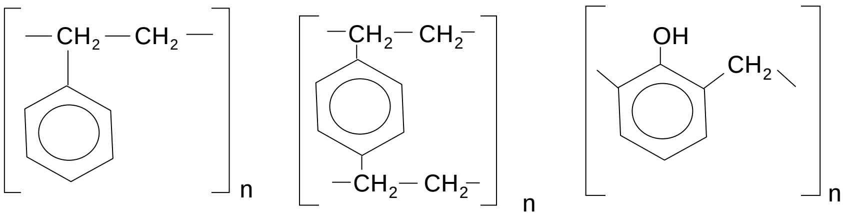
1st Objective Research

Initial experimental work focused upon the creation of polymer sample that, when pyrolysed, give high yields of carbonaceous remains. These are then assessed for PSD and SSA.

Literature review suggested 3 candidate classes of polymer

Poly(styrene) classes	Poly(divinyl-benzene) classes	Phenolic Resins



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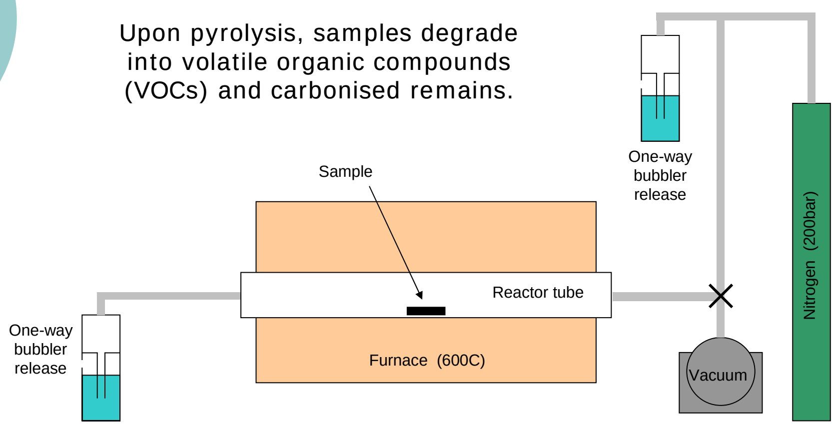
1st Objective Results

Upon pyrolysis, samples degrade into volatile organic compounds (VOCs) and carbonised remains.



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1st Objective Results

Sample:	Furnace Temp:	Ramp time	Time at temp	Solid remains
Poly(Styrene)	600C	20 min	60 min	Negligible *
		180min	60 min	Negligible *
Poly(Divinylbenzene)	600C	20 min	60 min	21-25%
		180 min	60 min	24-25%
Phenolic resin	600C	20 min	60 min	52-58%
		20 min	60 min	55%

* Upon pyrolysis, poly(styrene) completely disintegrated into constituent organic molecules. Subsequent mass spectroscopy determined these included monomers, dimers, trimers (90%), benzene based ring compounds (5%) and other organic matter (5%)

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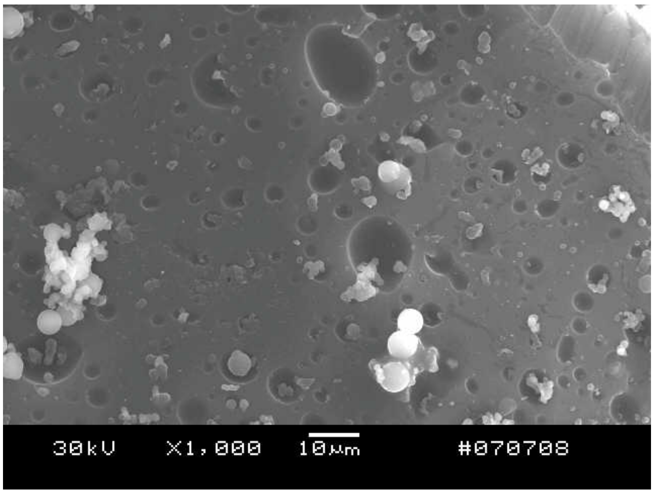
1st Objective Results

SEM images of pyrolysed remains of poly(divinylbenzene)



1st Objective Results

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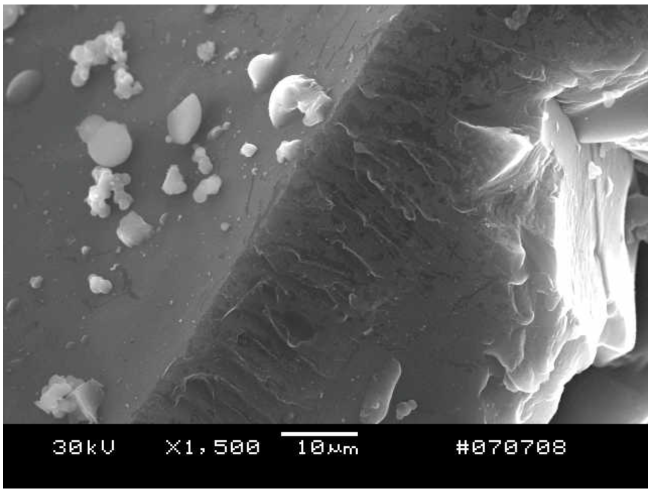
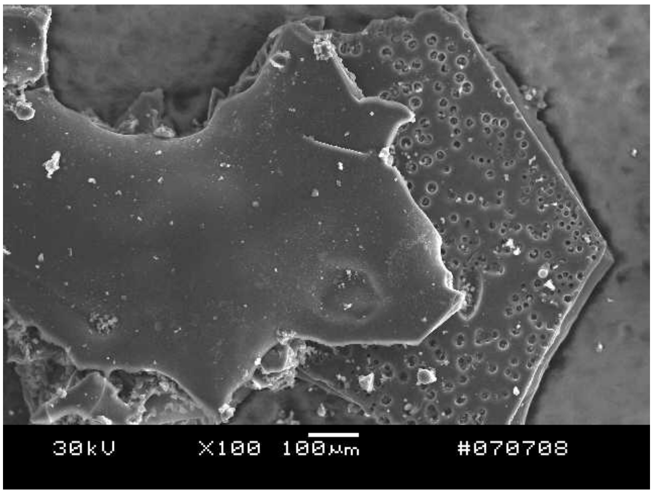


1st Objective Results

SEM images of pyrolysed remains of poly(divinylbenzene)



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1st Objective Results:

- Greater degrees of crosslinking during polymerisation leads to better carbonaceous yields after pyrolysis

- Controlling rate of temperature increase gives control over extent of porosity

Focus moved to 'hyper-crosslinked' polymers referred to in the literature: vinylbenzylchloride derived polymers and isoprene/divinylbenzene co-polymers

Production of isoprene/divinylbenzene co-polymers was attempted, but could not be synthesised via free-radical, UV or natural light initiation.

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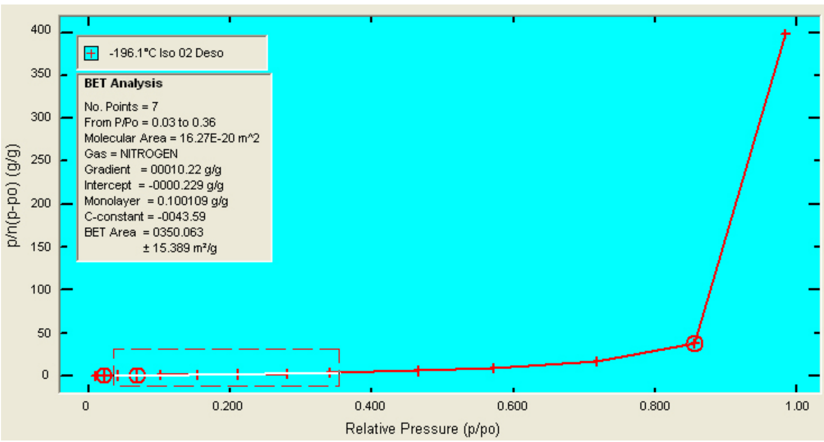
1st Objective Results

Novel Polymer-based Material:

BET Specific Surface Area = 350 m^2/g



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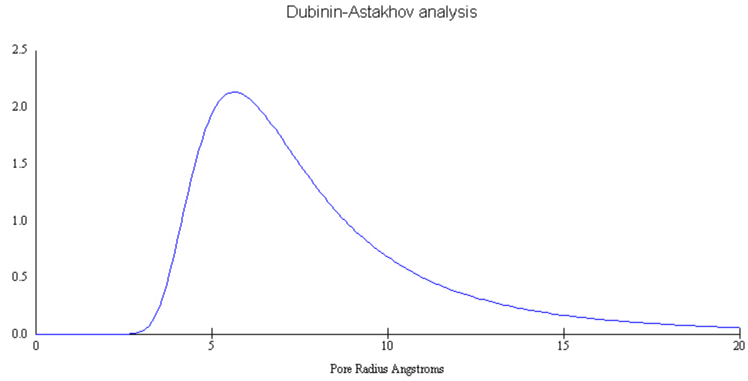
1st Objective Results

Novel Polymer-based Material:

Modal average pore size = 5.6 Angstroms (0.56nm)



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2nd Objective Research

Introduction of Light Metal Hydrides (e.g. Lithium)

According to literature reports* Li_3N / $LiNH_2$ offers ability to absorb in excess of 10 wt.% hydrogen into a solid state.

$$Li_2NH + H_2 \rightleftarrows LiNH_2 + LiH$$

Imide/Amide phase reactions offer around 6 wt.% storage which is readily reversible at reasonable temperatures.

Inclusion of lithium into carbon system will create novel hybrid physisorption / chemisorption materials.

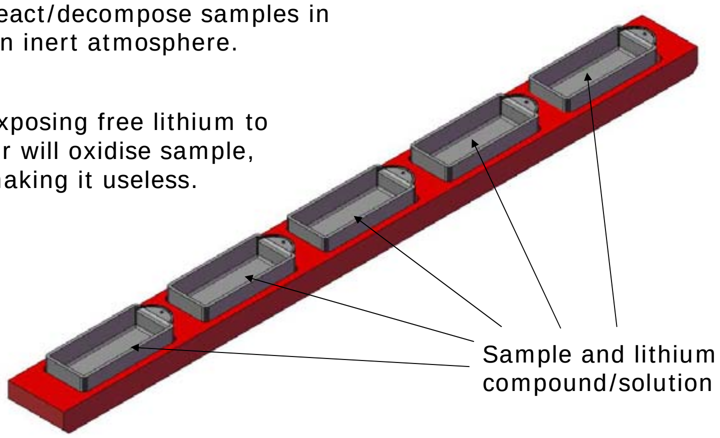
Our 2nd objective aims to deposit lithium (nitride/imide/amide) onto carbon surfaces or into pores.

* P. Chen *et al.*, Nature, **2002**, *420*, 302

2nd Objective Design

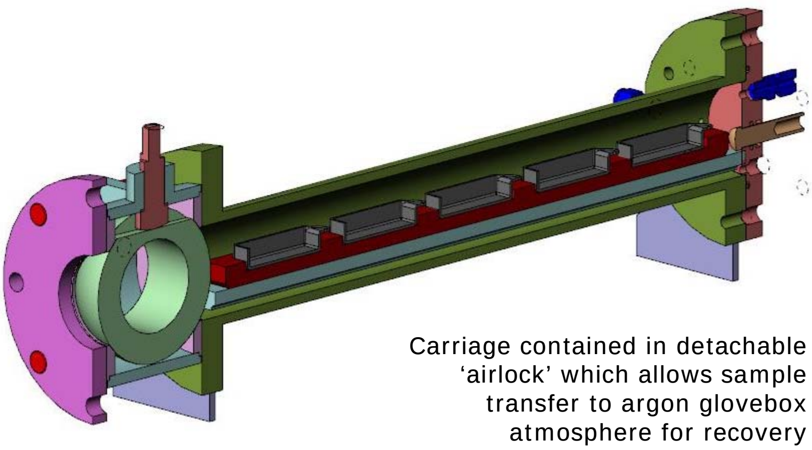
A special reactor is needed to react/decompose samples in an inert atmosphere.

Exposing free lithium to air will oxidise sample, making it useless.



2nd Objective Design

Airlock design



Carriage contained in detachable 'airlock' which allows sample transfer to argon glovebox atmosphere for recovery

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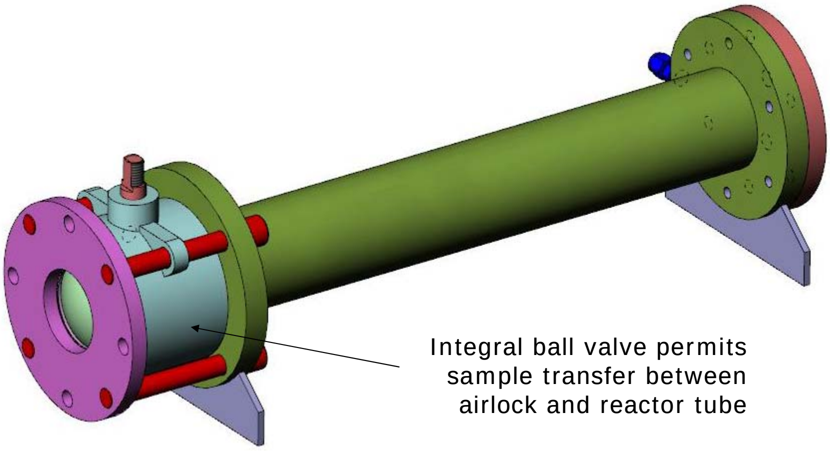
2nd Objective Design

Airlock design



Integral ball valve permits
sample transfer between
airlock and reactor tube

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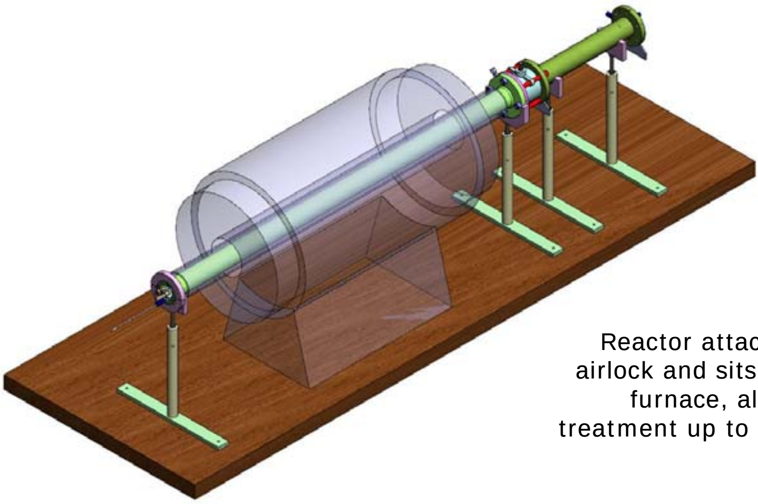
2nd Objective Design

Reactor design



Reactor attaches to
airlock and sits inside
furnace, allowing
treatment up to 1200C

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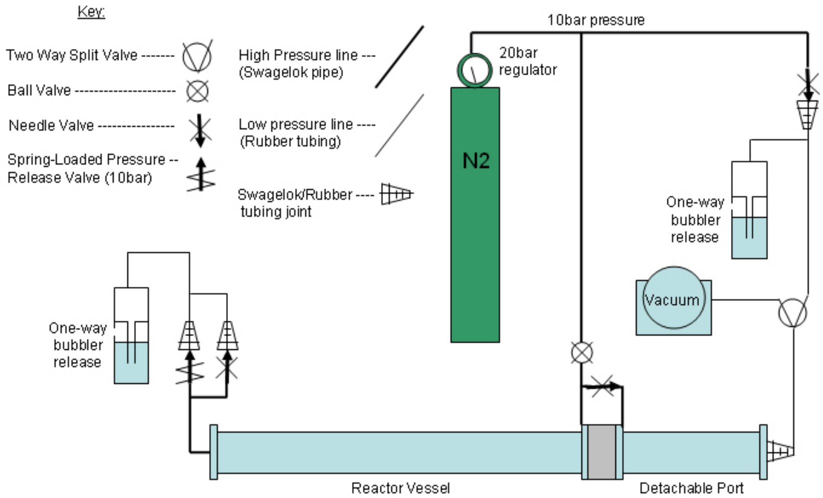
2nd Objective Design

Reactor design



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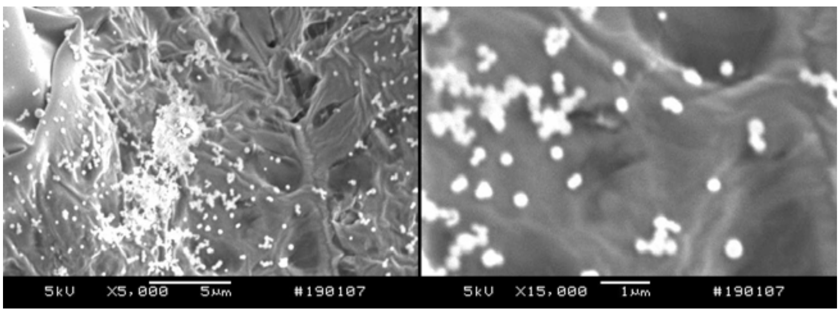
2nd Objective Design

Similar methods have deposited nano-scale titanium onto carbon surfaces in Salford (unpublished to date)



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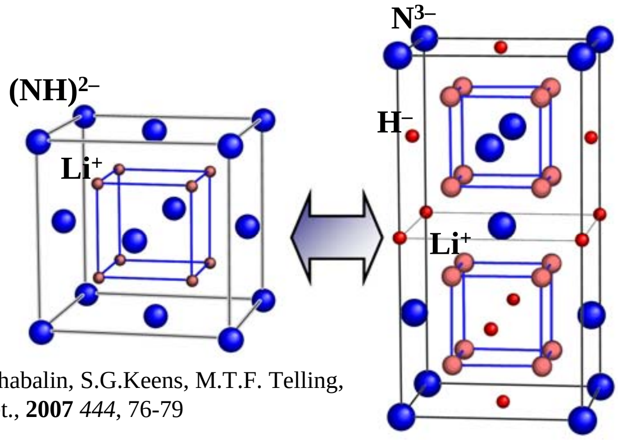
Optimising Hydrogenation Mechanism

Nano-scale deposition of lithium imide/amide is desirable as previous research shows that intermediate phases place larger crystals under internal stress, grinding them to dust.

Creation of nano-particles with materials is assumed to prevent stresses destroying the imide/amide



E.Weidner, D.J.Bull, I.L.Shabalin, S.G.Keens, M.T.F. Telling, D.K.Ross, Chem. Phys. Let., **2007** *444*, 76-79

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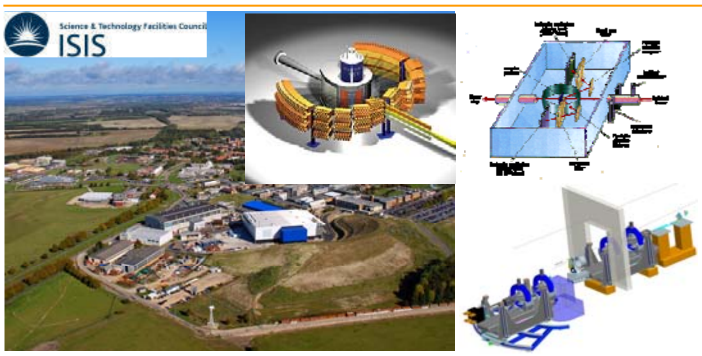
Investigating Hydrogenation Mechanism



http://www.isis.rl.ac.uk

Following the creation of novel samples, our partnership with world-class research facilities, such as ISIS, will allow use of neutron scattering techniques to fully understand the hydrogen storage mechanisms occurring within our materials, and development of technology with a view to commercial production

Key Outcomes Benefiting the North West Region

- Development and patenting of nano-structured hybrid hydrogen storage material
- Commercialisation of production process in conjunction with North-West industrial partners – Chemviron Carbon
- Development of market for existing hydrogen production in the North West.
- Expanded market for hydrogen sorption instrumentation, benefiting Hiden Analytical.
- International investment in renewable energy within the North-West.

For more information

For any additional enquiries please contact us:

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Thank you for

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