The 5th CSIR
CONFERENCE
IDEAS THAT WORK
8-9 October 2015 | CSIR ICC

Development of hydrogen storage technologies

Henrietta Langmi

CSIR
our future through science

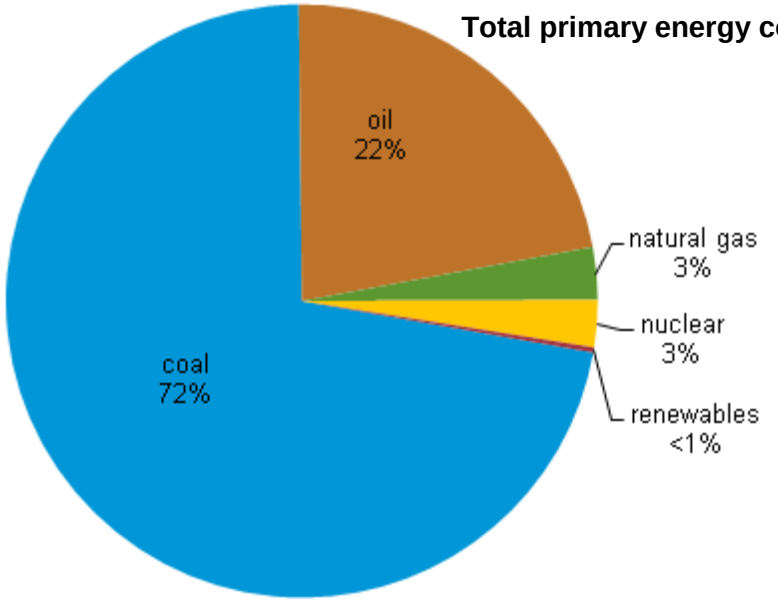
CELEBRATING 70 Years
Ideas that work

Outline

- Context
  - South African energy profile
  - Hydrogen energy
- Hydrogen South Africa (HySA)
  - Brief introduction
- Hydrogen storage
  - Background
  - Research

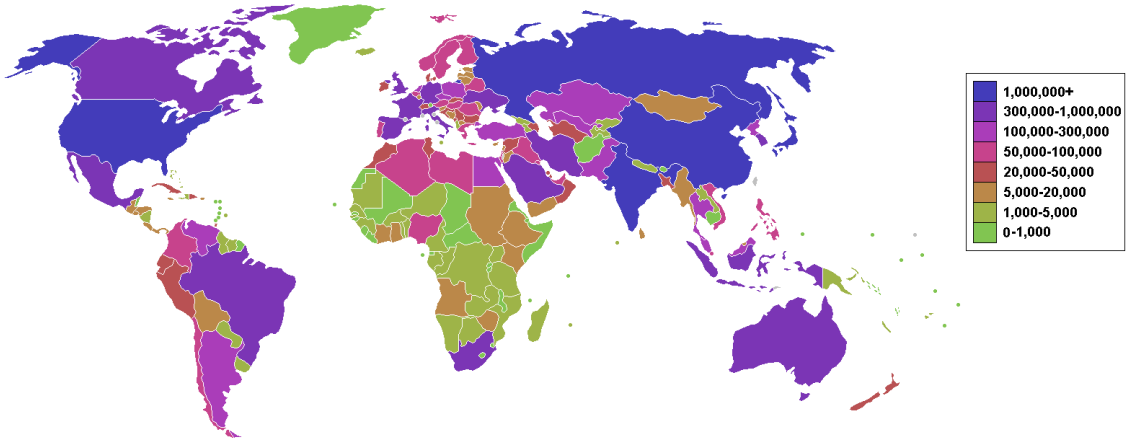
South African energy profile

Total primary energy consumption (2013)



- Coal supplies 72% of South Africa's primary energy and 90% of its electricity requirements

CO_2 emissions in thousands of tonnes per annum, via burning of fossil fuels



- SA 2013 CO_2 emissions:
  - Annual: 330 000 kt
  - Per capita: 6.2 t

Sources:
http://www.eia.gov/
http://www.energytrendsinsider.com

Can hydrogen help?

- High energy content and clean

Hydrogen	+	Oxygen	→	Water	+	Energy
$H_{2(g)}$	+	½ $O_{2(g)}$	→	H_2O	+	E

E = 120 – 142 MJ kg^{-1} heat (combustion) 

= 1.23 V electrical potential + 24 MJ kg^{-1} heat (fuel cell)  + 

(40 – 55 MJ kg^{-1} for combustion of hydrocarbons; CO_2 emitted)

- Abundant
  - 3rd most common element on earth's surface
  - Water (H_2O), fossil fuels ($–CH_x$), biomass ($–CH_yO_z$)

CSIR our future through science | CELEBRATING 70 Years Ideas that work

Source: T. Mays, h2fcsupergen

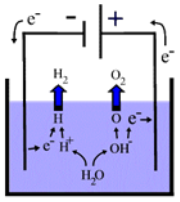
Hydrogen energy chain

Production

Fossil fuels

Biomass

Water splitting



Delivery

Cylinders

Cryogenic tanks

Pipelines

Chemical compounds

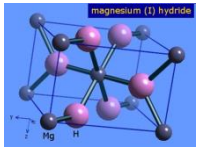
Storage

Compressed

Liquefied

Materials

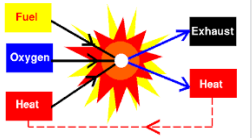
Liquid carriers

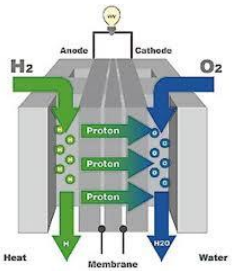


Conversion

Combustion

Fuel cells



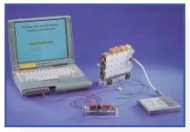


Application

Transport

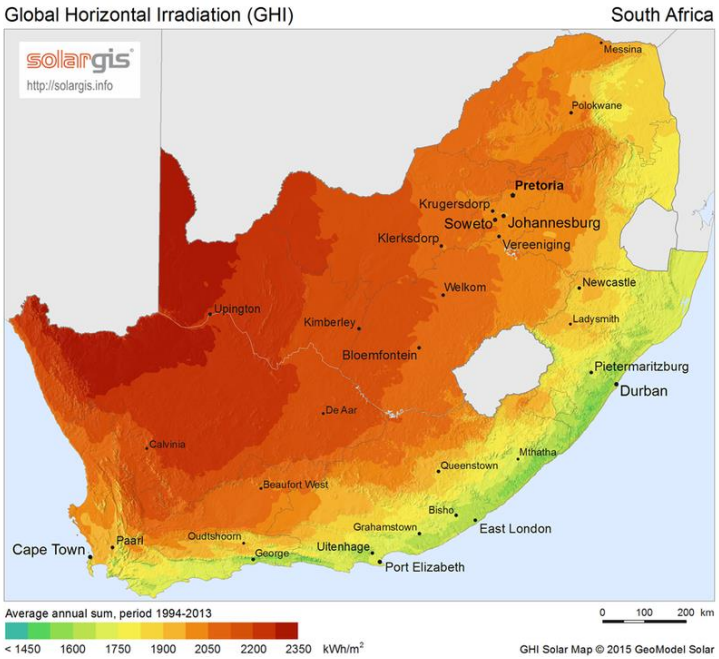
Stationary

Portable

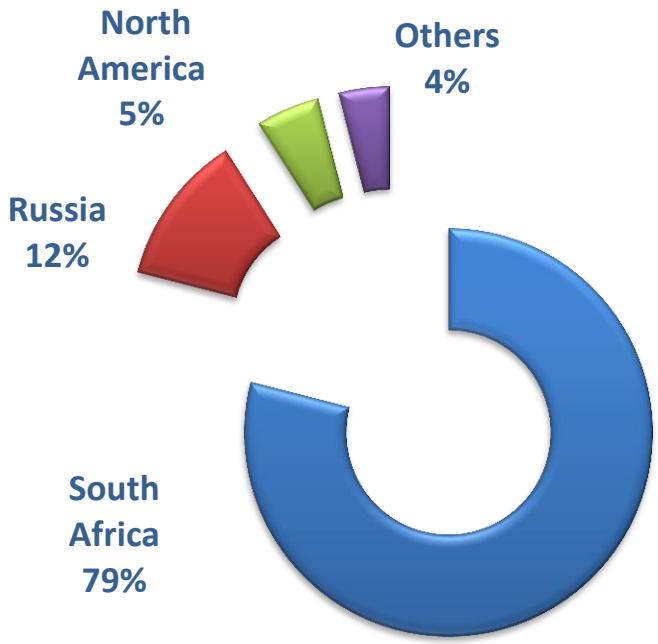


Natural resources in South Africa

South Africa's solar potential



PGM supply by region

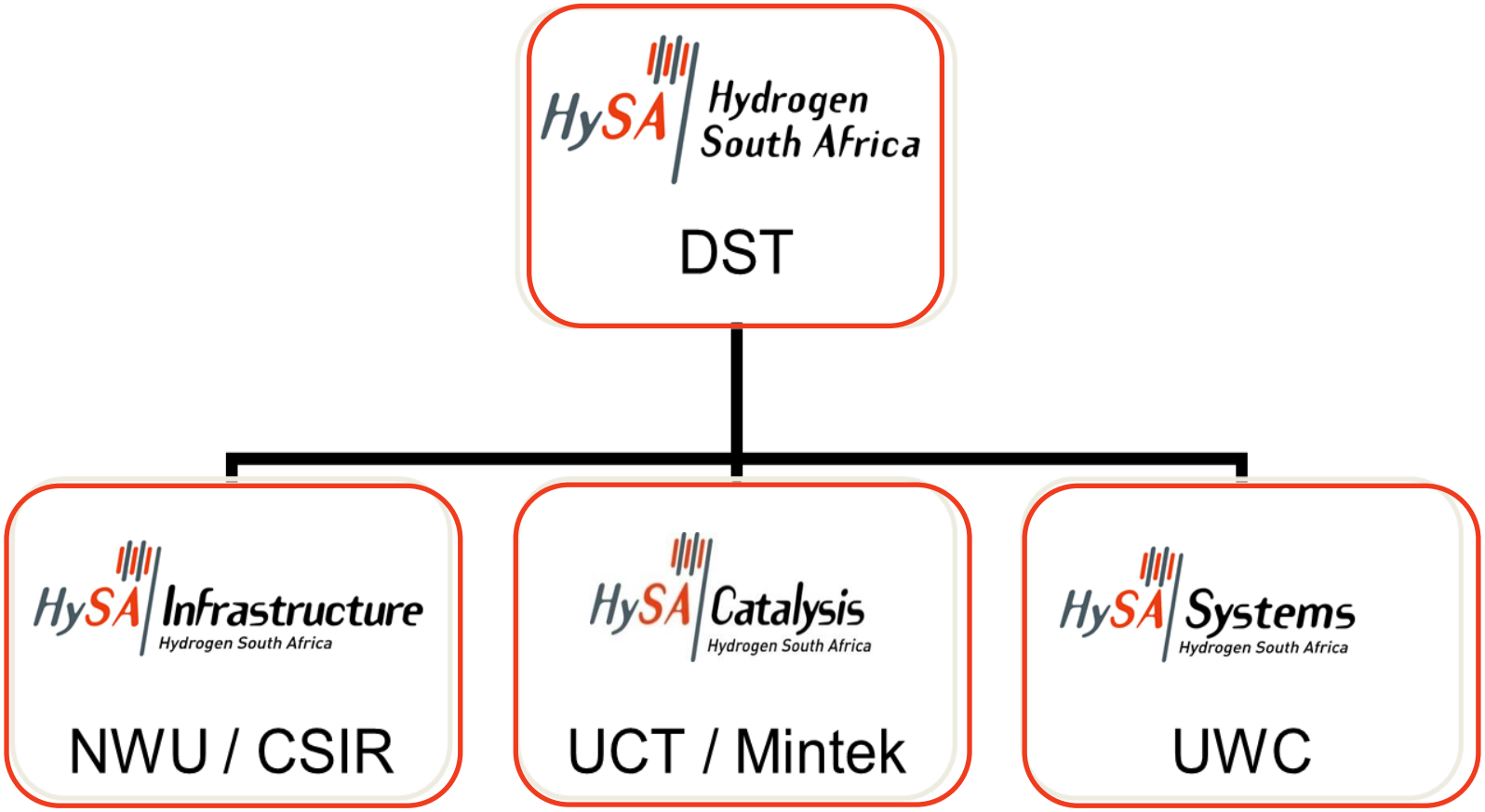


- Annual 24 h global solar irradiation average exceeds values in Europe, Russia, and most of North America

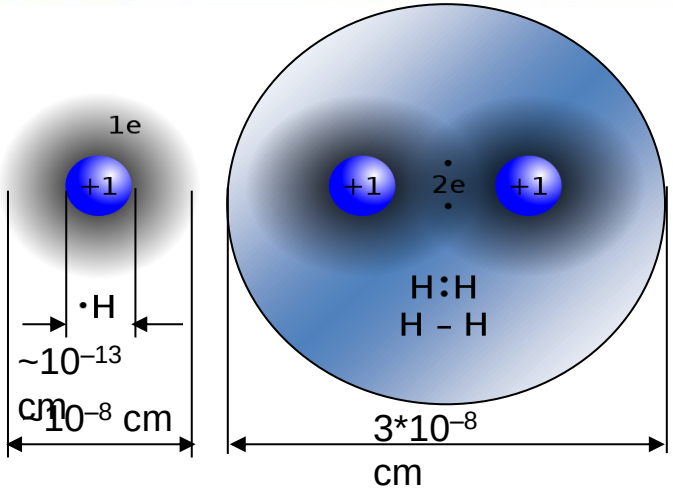
- South Africa has nearly 80% of the world's platinum group metals (PGMs)

Hydrogen South Africa (HySA)

"To create knowledge and human resource capacity that will develop high-value commercial activities in H&FC technologies utilising local resources and existing know-how"



The hydrogen storage challenge



Hydrogen:

- Lightest element, lowest density
- Strong covalent bond
- Low polarisation ability

→ Weak interaction between H_2 molecules

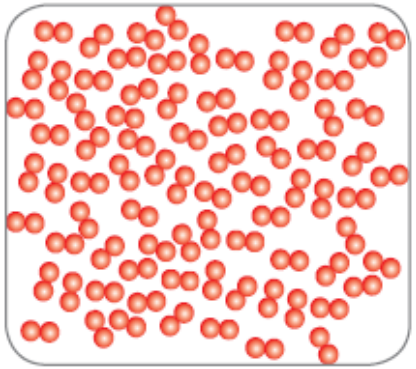
- At room temp and atm pressure:

5 kg H_2 occupies vessel of ≈ 5 m diameter

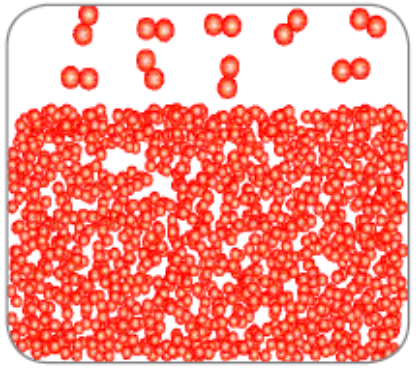
(5 kg H_2 gives 500 km driving range)

Hydrogen storage options

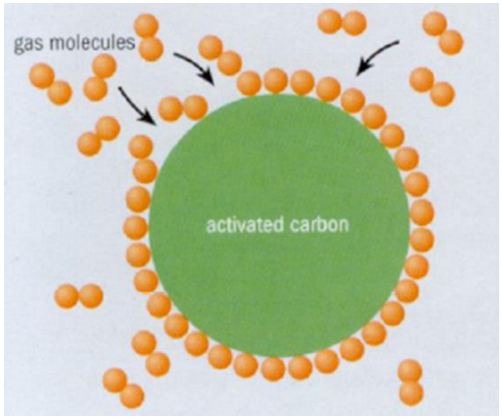
Compressed Gas

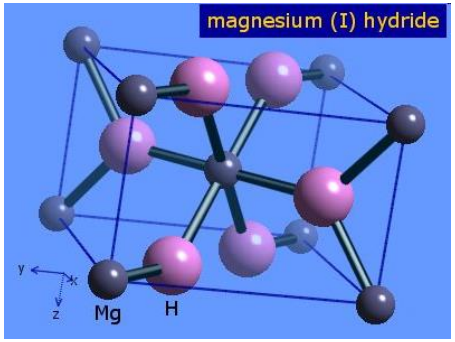


Cryogenic Liquid



Materials-based storage





$LaNi_5H_6$ MgH_2

$NaAlH_4$ $LiNH_2$

$LiBH_4$

NH_3BH_3

Liquid chemical carriers

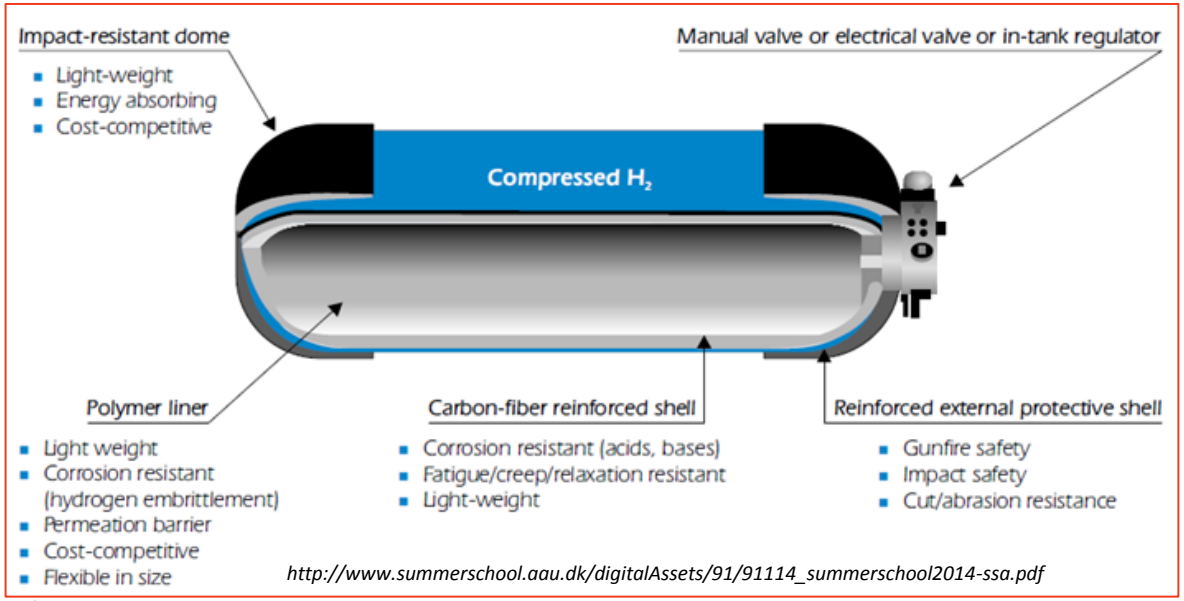
LOHC NH_3 HCOOH

Hydrogen storage research @ CSIR

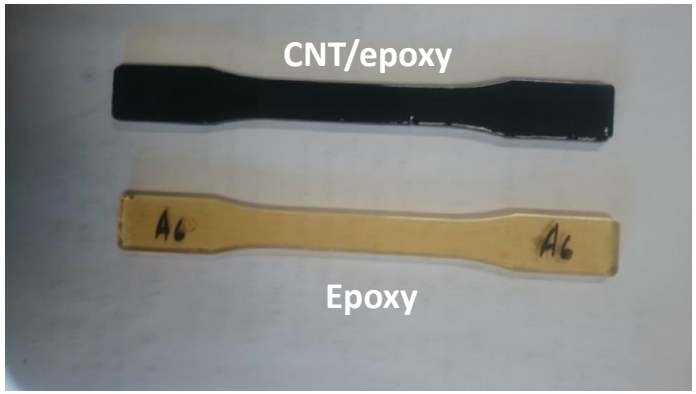
- High pressure composite cylinders
- Chemical carriers (formic acid)
- Porous materials (MOFs, Carbon)

High pressure composite cylinders

- To develop enhanced materials and manufacturing methods to improve the characteristics of hydrogen storage tanks
  - Composite = Carbon fibre + resin + fillers
    - Resin modification (improve mechanical properties)
    - Finite element modelling (design capabilities)



http://www.summerschool.aau.dk/digitalAssets/91/91114_summerschool2014-ssa.pdf

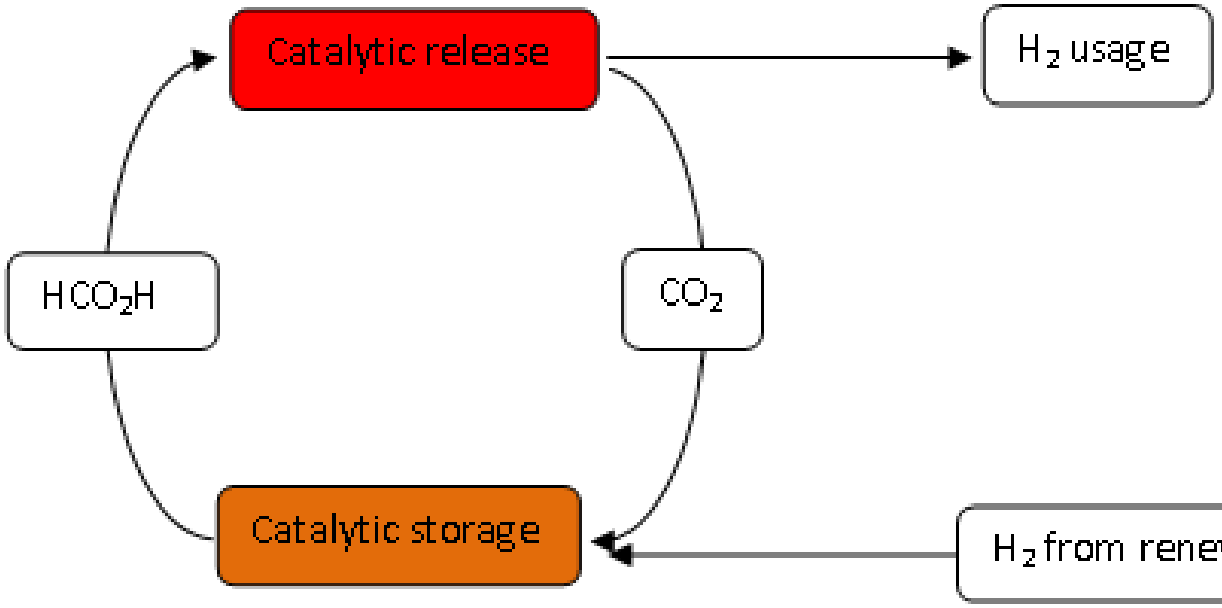


Chemical carriers – formic acid

- Decomposition of formic acid

$HCO_2H(l) \rightarrow CO_{2(g)} + H_{2(g)}$ $\Delta H^0 = 31.2\ kJ/mol$ (Dehydrogenation)

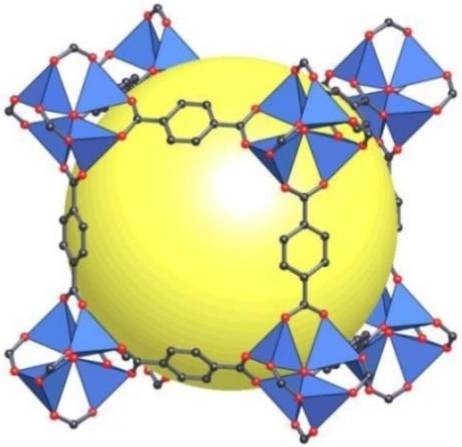
$HCO_2H(l) \rightarrow CO_{(g)} + H_2O_{(g)}$ $\Delta H^0 = 28.7\ kJ/mol$ (Dehydration)



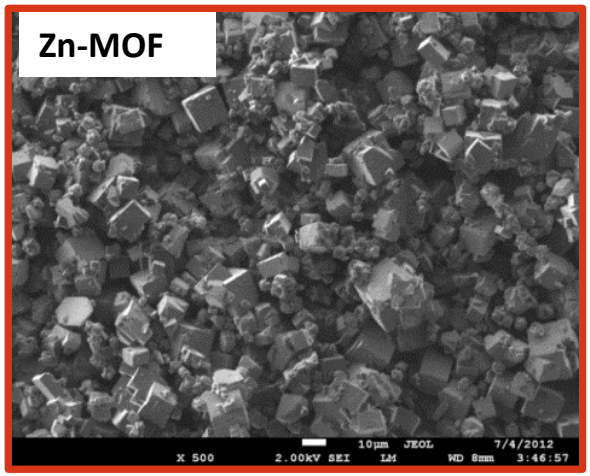
- **Technology gaps**
  - Catalyst
  - Reactor

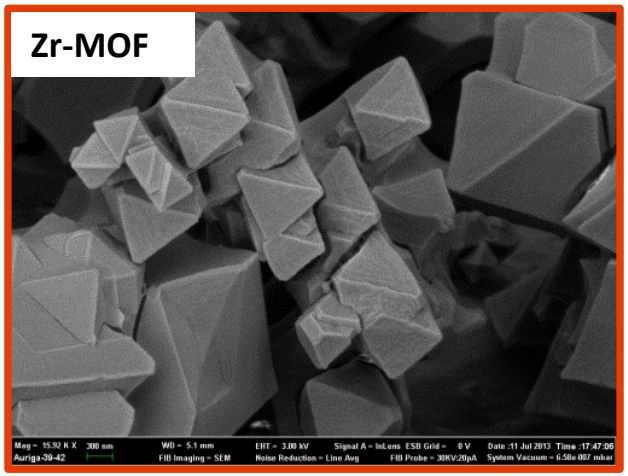
Metal-organic frameworks (MOFs)

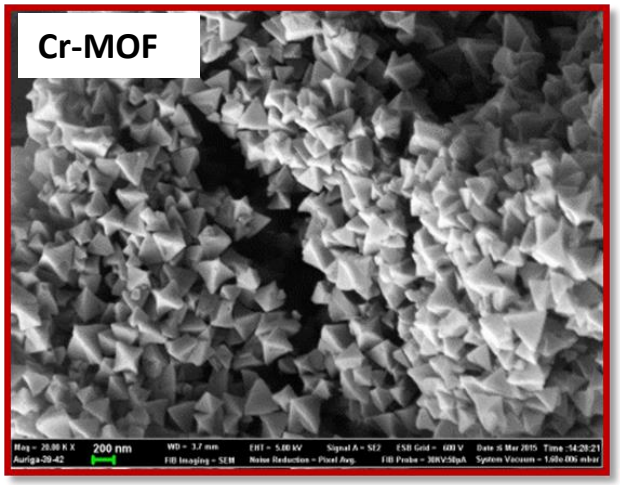
- Several MOFs are being developed



- Beneficiation (Cr, Zr, PGMs)
- Cost saving (cheaper solvents/reagents)
- Environmentally friendly (water as solvent)
- High stability (thermal, air, moisture)







Metal-organic frameworks (MOFs)

Some MOF materials developed in our laboratory

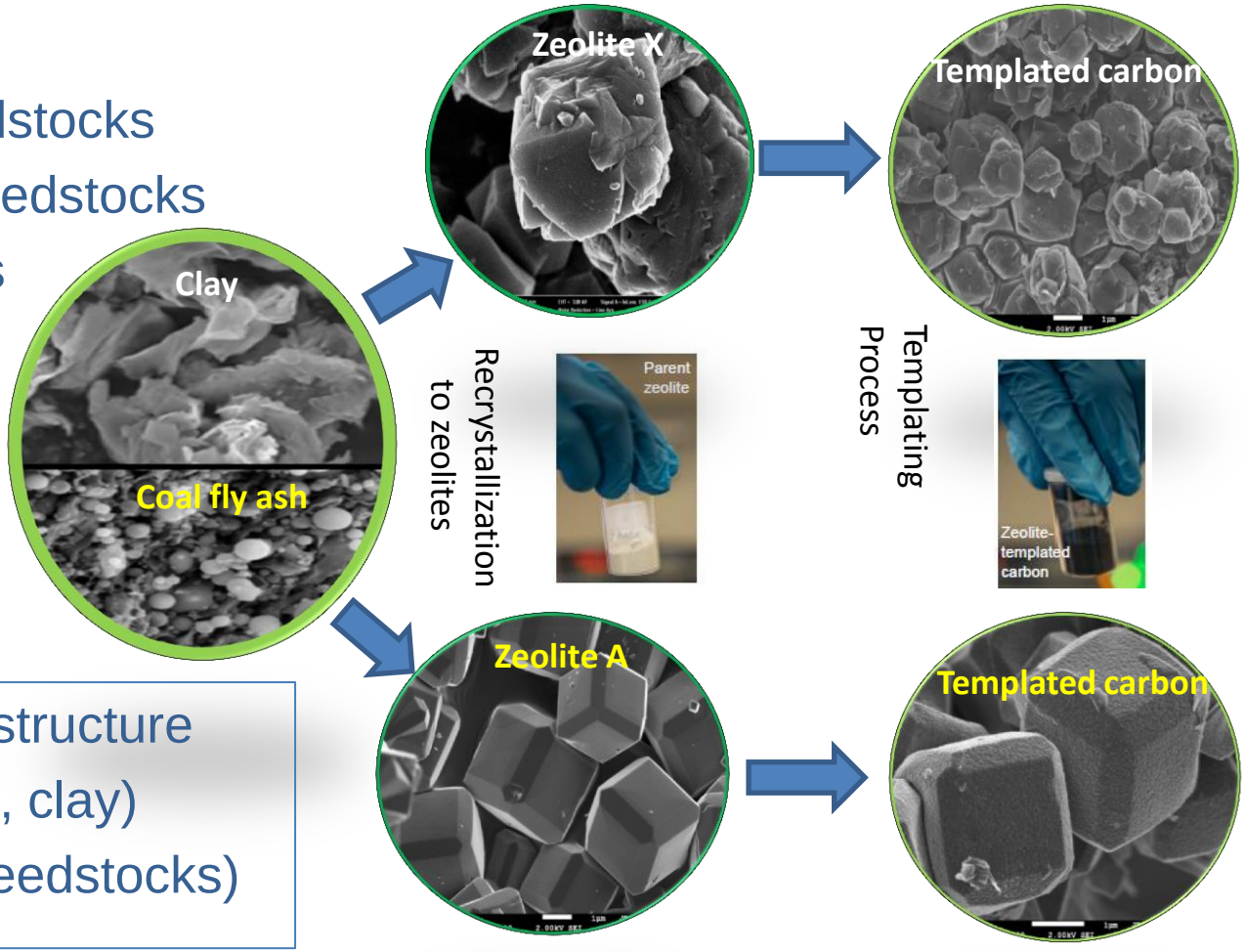
MOF sample (solvent)	Size of crystals	S_{BET} ($m^2 \cdot g^{-1}$)	Pore vol. ($cm^3 \cdot g^{-1}$)	Thermal stability (°C)	Moisture stability	H_2 uptake (wt.%) 77 K, 1 bar
Zr-fum MOF (H_2O)	200 nm	948	0.43	350	good	1.4
MOF-5 (DMF)	5-100 µm	860	0.41	350	poor	1.4
MOF-69c (DMF)	5-100 µm	1086	0.44	--	poor	1.9
Zr-MOF (DMF)	300-500 nm	1186	0.56	500	good	1.5
Cr-MOF (H_2O)	200-300 nm	1716	0.71	350	good	1.9
Cr-MOF@Zr-MOF (DMF)	350-500 nm	2772	1.08	400	good	2.4

- High thermal stability
- Good moisture stability
- Comparable H_2 storage capacity

Int. J. Hydrogen Energy 39, **2014**, 890;
Int. J. Mat. Res. 105, **2014**, 516;
Int. J. Hydrogen Energy 39, **2014**,12018;
Int. J. Hydrogen Energy 39, **2014**, 14912;
Int. J. Hydrogen Energy, 40, **2015**, 10542;
Materials Today: Proceedings, 2, **2015**, 3964.

Carbon nanostructures (CNS)

- Several CNS are being developed
- Templated carbons
  - Conventional feedstocks
  - Unconventional feedstocks
- MOF derived carbons
- Graphene
- Activated carbon

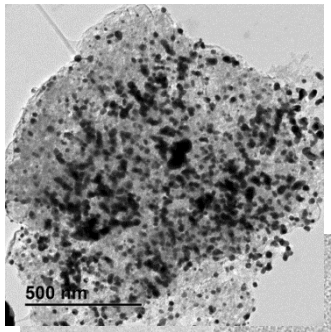


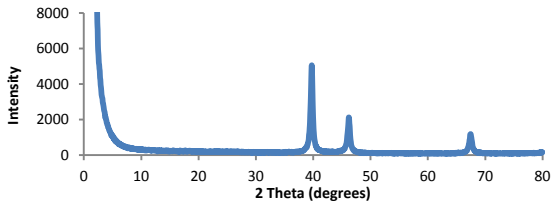
- Highly ordered pore structure
- Beneficiation (fly ash, clay)
- Cost saving (waste feedstocks)

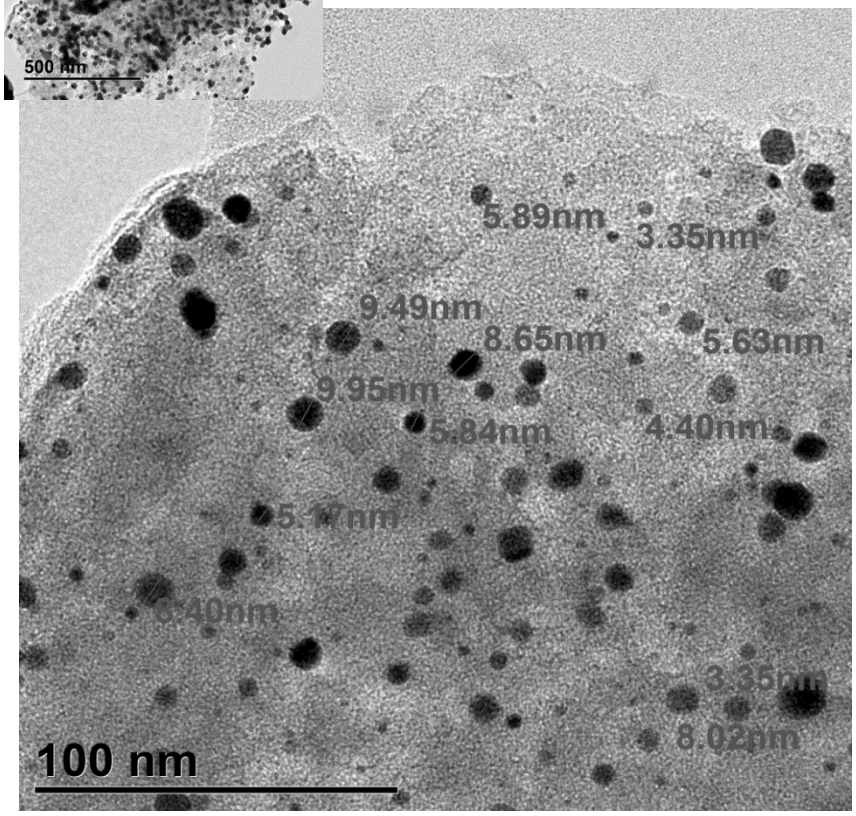
Int. J. Hydrogen Energy 40, **2015**, 9382

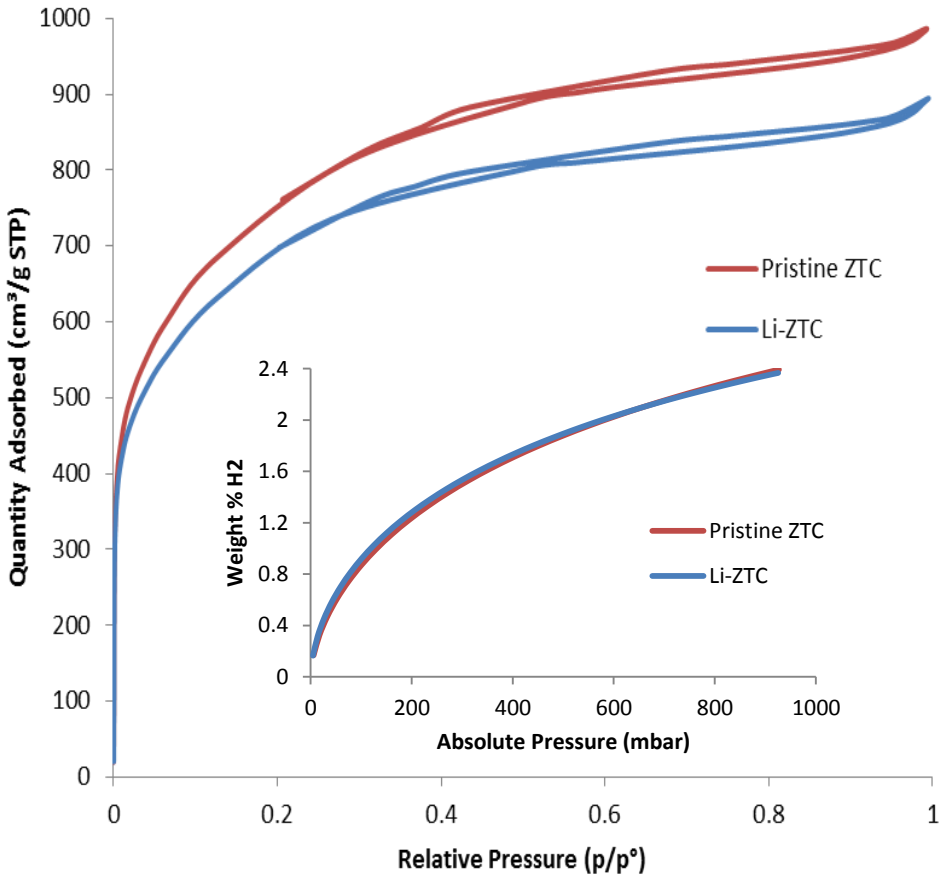
Int. J. Energy Res. 39 **2015**, 494.

Carbon nanostructures: modifications



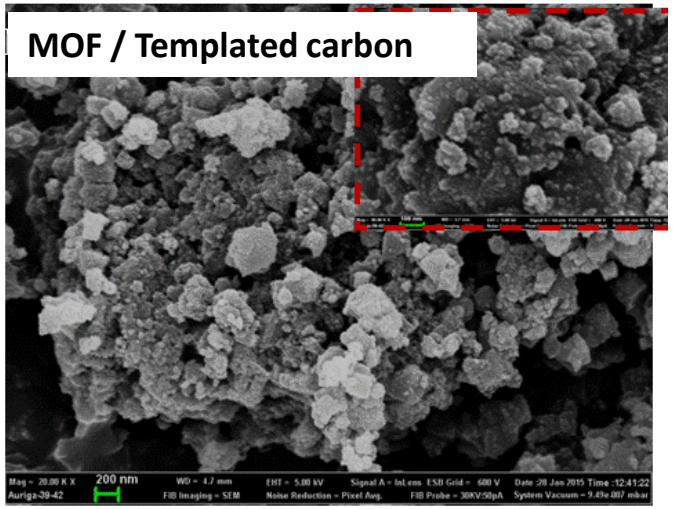


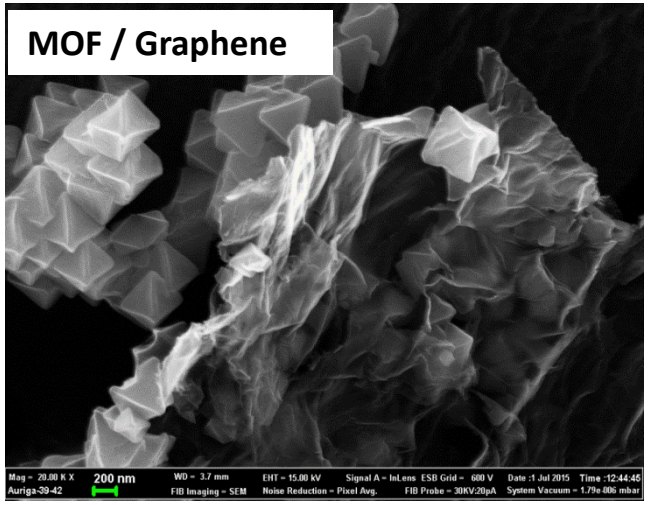


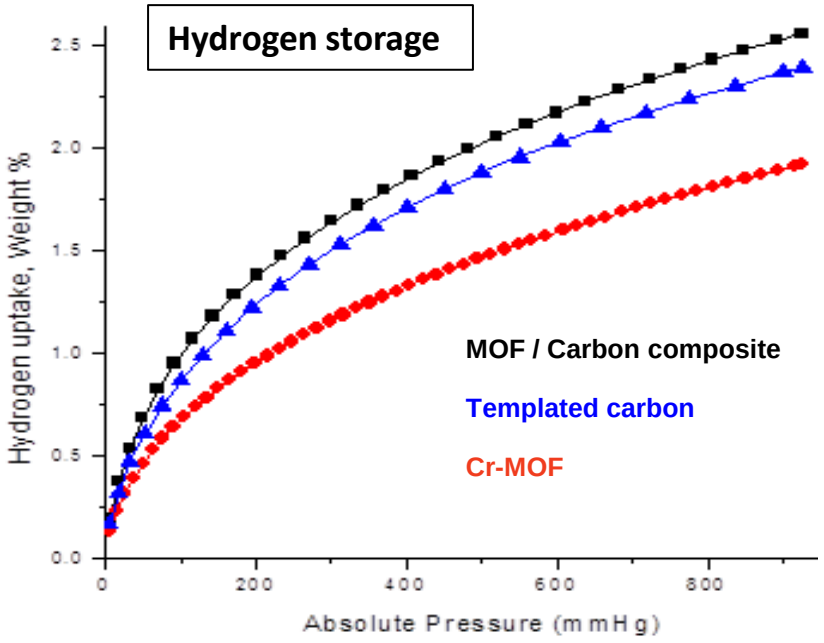


- Modifications – PGMs and Li-doping

MOF / Carbon composites





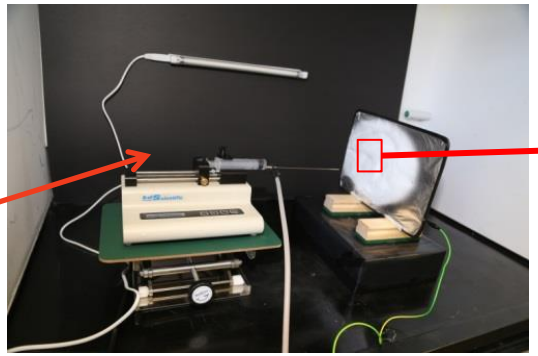


- Beneficial towards practical applications
  - Enhanced H_2 storage capacity
  - Enhanced thermal conductivity
  - Enhanced bulk density

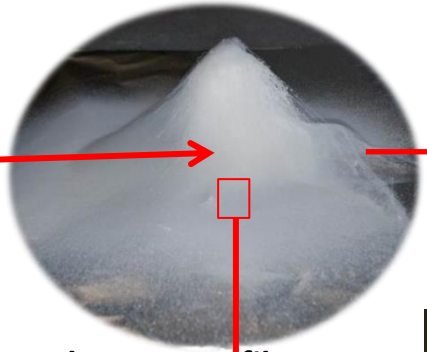
Res. Chem. Intermed. **2015**, In press

Powder shaping: electrospinning

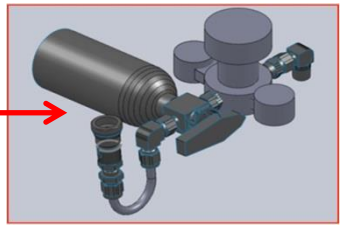
MOF/polymer solution

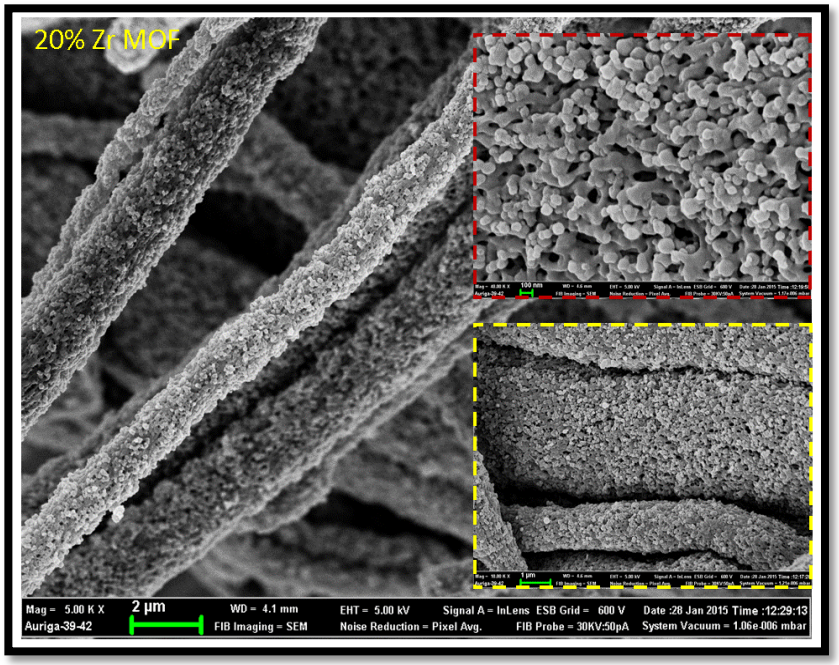


Electrospinning set-up



MOF electrospun fibres



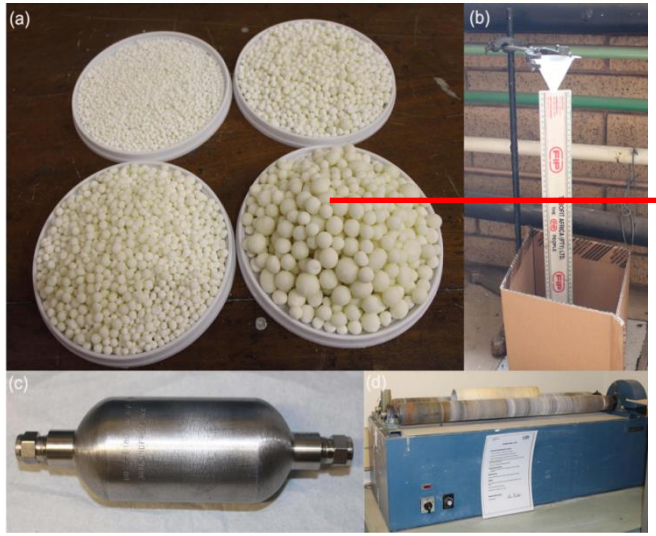


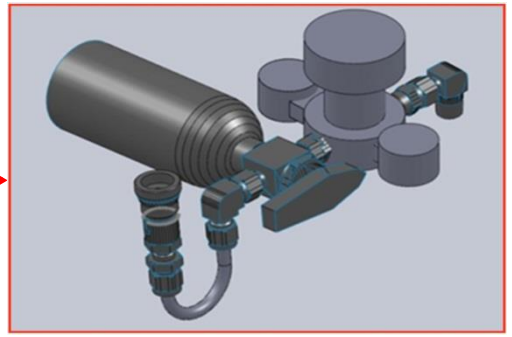
- **Transition from lab to applications**
  - Application-oriented shapes
- **Other attractive properties**
  - High surface areas
  - Hierarchical pores

Int. J. Hydrogen Energy 40, **2015**, 9382

Powder shaping: granulation

MOF powder

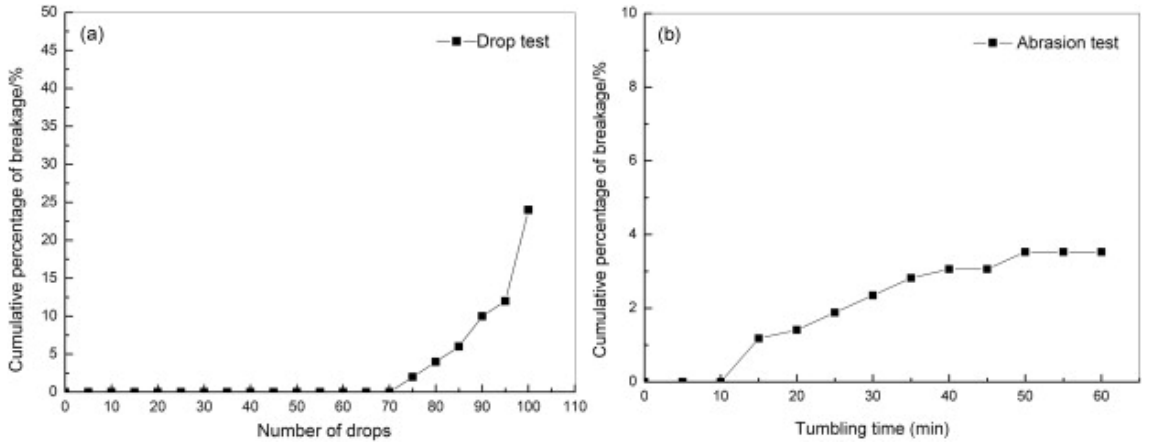




From lab to applications

- Application-oriented shapes

- Compact durability



Int. J. Hydrogen Energy 40, **2015**, 4617

Summary

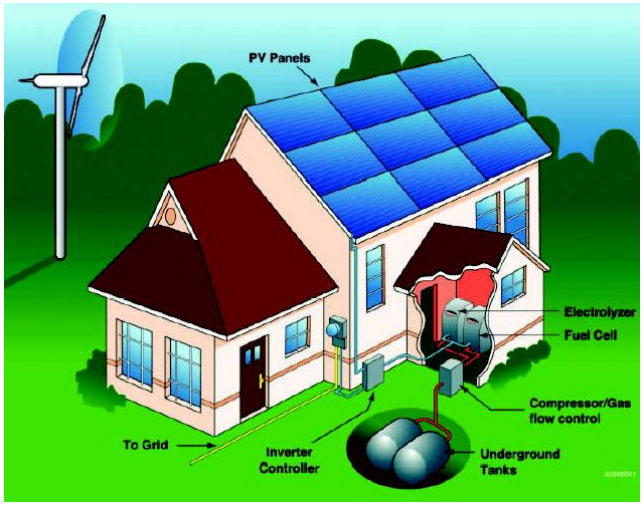
- Hydrogen is potentially a good alternative to fossil-based fuels
- Hydrogen storage presents a major challenge
- HySA Infrastructure is developing attractive and competitive hydrogen storage options for practical applications
- Key considerations are hydrogen storage properties, beneficiation, cost, environment

Dream? Vision? Reality?

*"…I believe that **water** will one day be employed as fuel, that **hydrogen** and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of **heat** and **light** … Water will be the coal of the future...."*

Jules Verne, The Mysterious Island, 1874

Water + Energy → Hydrogen + Oxygen → Water + Energy



J.A. Turner et al., Electrochem. Soc. Interface 13, **2004**, 24.

http://www.Hyweb.de

Acknowledgements

The 5th CSIR CONFERENCE
IDEAS THAT WORK
8-9 October 2015 | CSIR ICC

HySA Infrastructure Team (CSIR, NWU, DST)

Financial Support

science & technology
Department:
Science and Technology
REPUBLIC OF SOUTH AFRICA

NRF National Research Foundation

Newton Fund

ROYAL SOCIETY OF CHEMISTRY

BRITISH COUNCIL

Host Institutions

NORTH-WEST UNIVERSITY
YUNIBESITI YA BOKONE-BOPHIRIMA
NOORDWES-UNIVERSITEIT

CSIR
our future through science

CSIR
our future through science

CELEBRATING 70 Years
Ideas that work

The 5th CSIR
CONFERENCE
IDEAS THAT WORK
8-9 October 2015 | CSIR ICC

Thank you

CSIR
our future through science

CELEBRATING 70 Years
Ideas that work