Korea-South Africa H_2 Fuel Cell Collaboration Workshop,15-18 July 2013, Hyundai Hotel, Gyeongju, Rep. of Korea

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

HYDROGEN STORAGE FOR FUEL CELL APPLICATIONS:

CHALLENGES, OPPORTUNITIES AND PROSPECTS FOR METAL-ORGANIC FRAMEWORKS

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HySA Infrastructure
Hydrogen South Africa

CSIR
our future through science

crb
CHEMICAL RESOURCE BENEFICIATION

NORTH-WEST UNIVERSITY
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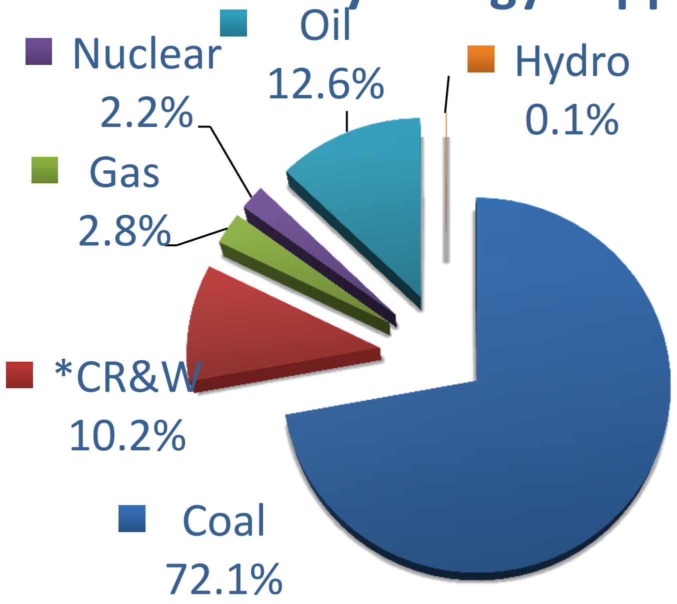
Presentation Outline

- ❑ **Hydrogen and Fuel Cells in South Africa**
    - ❑ Strategic drivers
    - ❑ R&D and Innovation Strategy
    - ❑ Scope of HySA Infrastructure Centre of Competence
    - ❑ HySA Infrastructure Project Portfolio (Selected)
- ❑ **Hydrogen Storage**
    - ❑ Challenge
    - ❑ Storage options
    - ❑ Technical targets
    - ❑ Metal-Organic Frameworks

South African Energy Profile

Current South Africa Total Primary Energy Supply



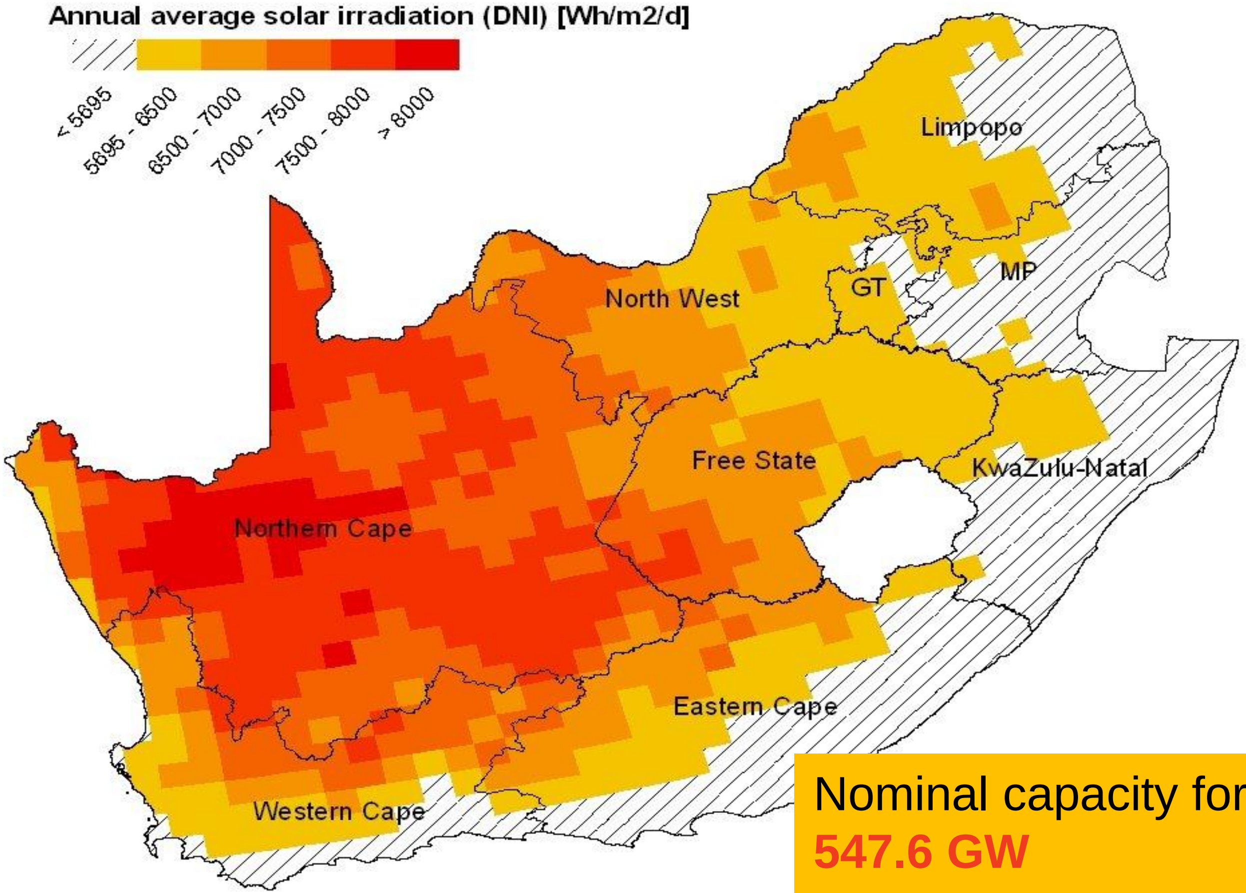
- Coal supplies ~75 % of South Africa's primary energy and 90 % of its electricity requirements

*CR&W: Combustible Renewable and Waste

Source: International Energy Agency (IEA)

- RSA has energy intensive economy
- RSA has a large SO_2/CO_2 footprint
- RSA's **CO_2** footprint per capita ranks among the **top 12 in the world**

Solar Energy Potential in South Africa



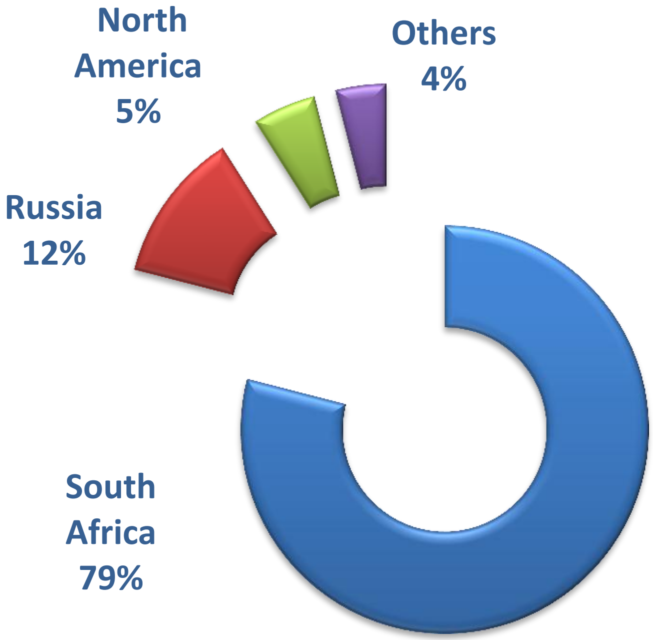
Nominal capacity for CSP in South Africa is **547.6 GW**

Thomas P. Fluri, *Energy Policy, v 37, Issue 12, December 2009, 5075–5080*

Mineral Resources in South Africa

Rank in the World	SA Mineral Resource
1	**Gold**
1	**Platinum**
1	**Titanium**
1	**Chromium**
1	**Manganese**
1	**Vanadium**
2	**Zirconium**

PGM Supply by region



- ☐ South Africa produces about **59 different minerals** from 1115 mines and quarries
- ☐ South Africa has nearly **80% of the world's PGMs**.
- ☐ These metals contribute US$2,200 billion of the country's total resource value of US$2,494 billion.

H&FC R&D Technology and Innovation Strategy

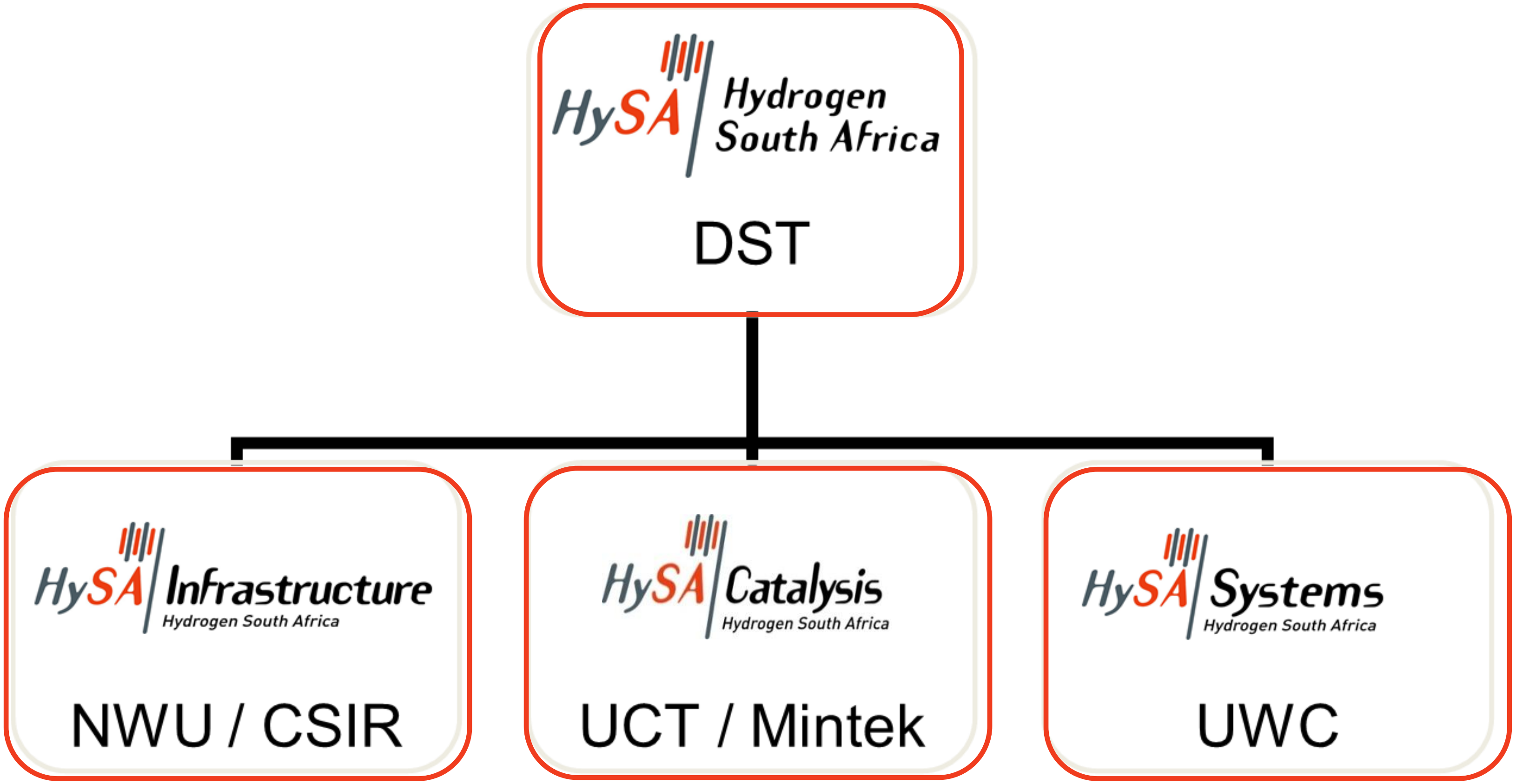
Strategic Goals

- Establish a base for hydrogen production, storage technologies and processes

- Establish a base for developing catalysts based on PGMs; supply 25% of PGM catalysts demand by 2020

- Build on existing global knowledge to develop know-how to leap-frog existing fuel cell technologies for niche applications to address regional developmental challenges

Centres of Competence



HySA Hydrogen South Africa

DST

HySA Infrastructure Hydrogen South Africa

NWU / CSIR

HySA Catalysis Hydrogen South Africa

UCT / Mintek

HySA Systems Hydrogen South Africa

UWC

HySA Infrastructure Centre of Competence

Dr. Dmitri Bessarabov
Centre of Competence Director

Key Programme 4 (CSIR)

Hydrogen Storage/Distribution/Safety

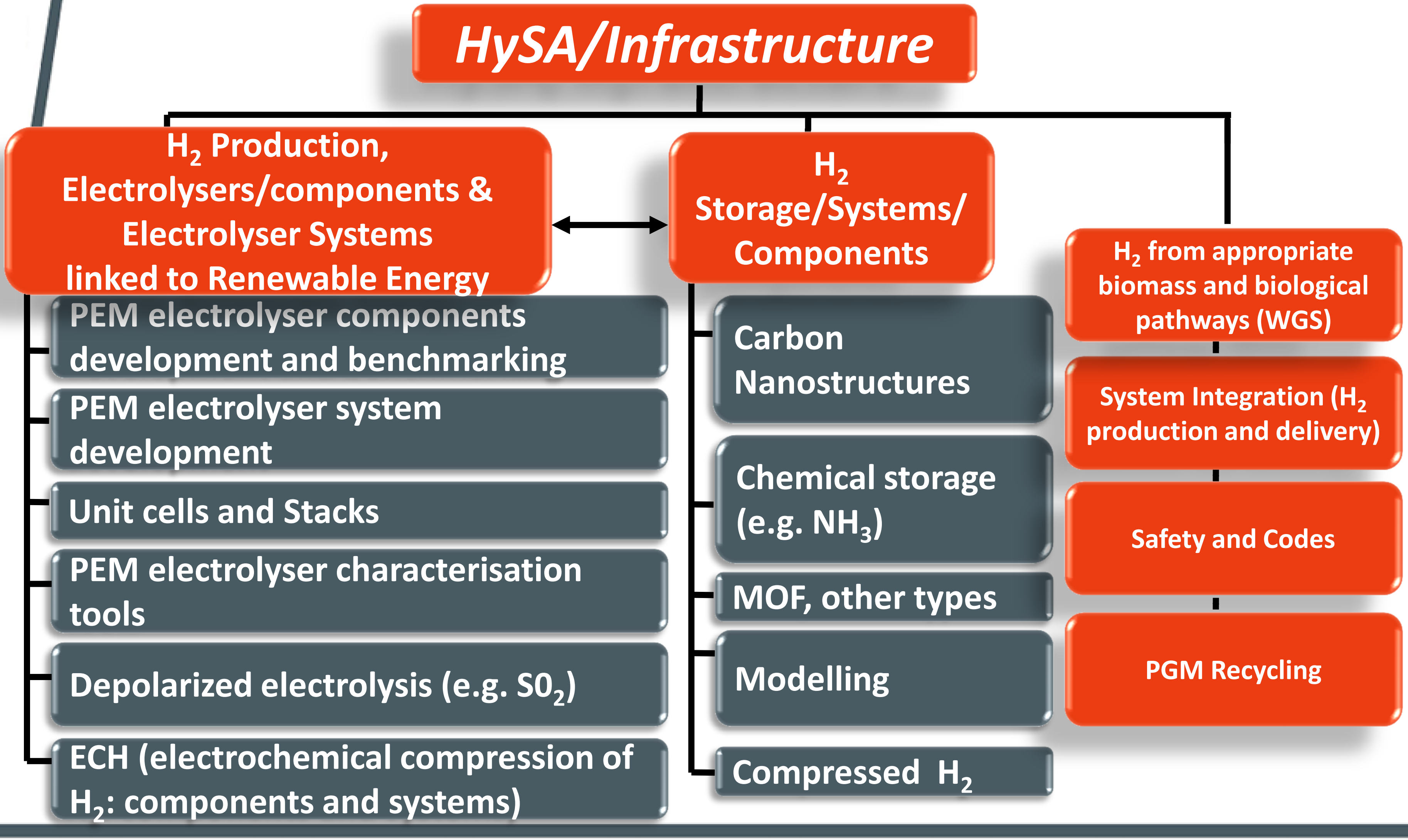
Key Programme 5 (NWU)

Hydrogen Production/ Electrolysers/components & Electrolyser Systems linked to Renewable Energy

HySA Infrastructure: Mission

To deliver **technologies** for **H_2 Production, Storage** and **Distribution Infrastructure** that meet set cost targets and provide best balance of safety, reliability, robustness, quality and functionality

HySA Infrastructure: Programme Scope



HySA/Infrastructure

- **H_2 Production, Electrolysers/components & Electrolyser Systems linked to Renewable Energy** ↔ **H_2 Storage/Systems/ Components**

- **H_2 Production, Electrolysers/components & Electrolyser Systems linked to Renewable Energy**
  - PEM electrolyser components development and benchmarking
  - PEM electrolyser system development
  - Unit cells and Stacks
  - PEM electrolyser characterisation tools
  - Depolarized electrolysis (e.g. SO_2)
  - ECH (electrochemical compression of H_2: components and systems)
- **H_2 Storage/Systems/ Components**
  - Carbon Nanostructures
  - Chemical storage (e.g. NH_3)
  - MOF, other types
  - Modelling
  - Compressed H_2
- **H_2 from appropriate biomass and biological pathways (WGS)**
- **System Integration (H_2 production and delivery)**
- **Safety and Codes**
- **PGM Recycling**

Characterization Tools Development for PEM Water Electrolysis

☐ Electrochemical Impedance Spectroscopy (EIS)

Technique

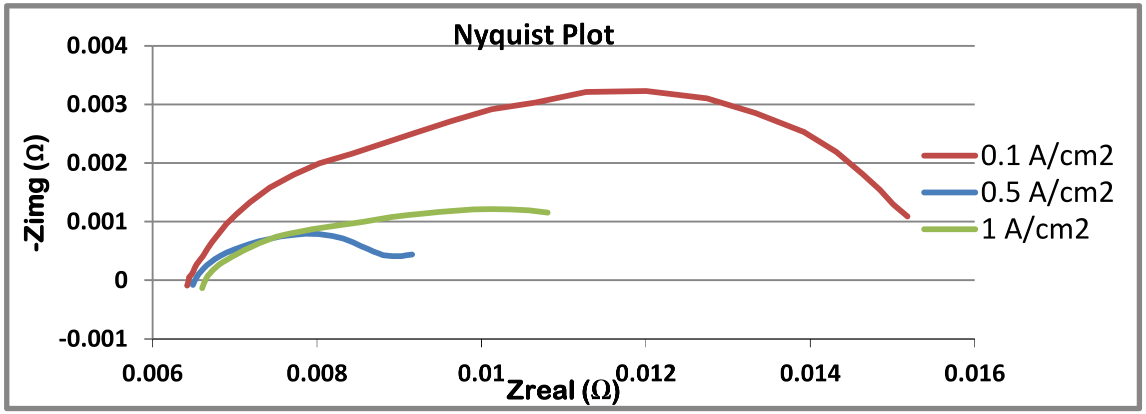
- Steady State
- AC disturbance signal

Equipment

- Gamry
- Solartron

Advantages

- Individual loss contributions
  - Ohmic, Activation, Mass transfer



Characterization Tools Development for PEM Water Electrolysis

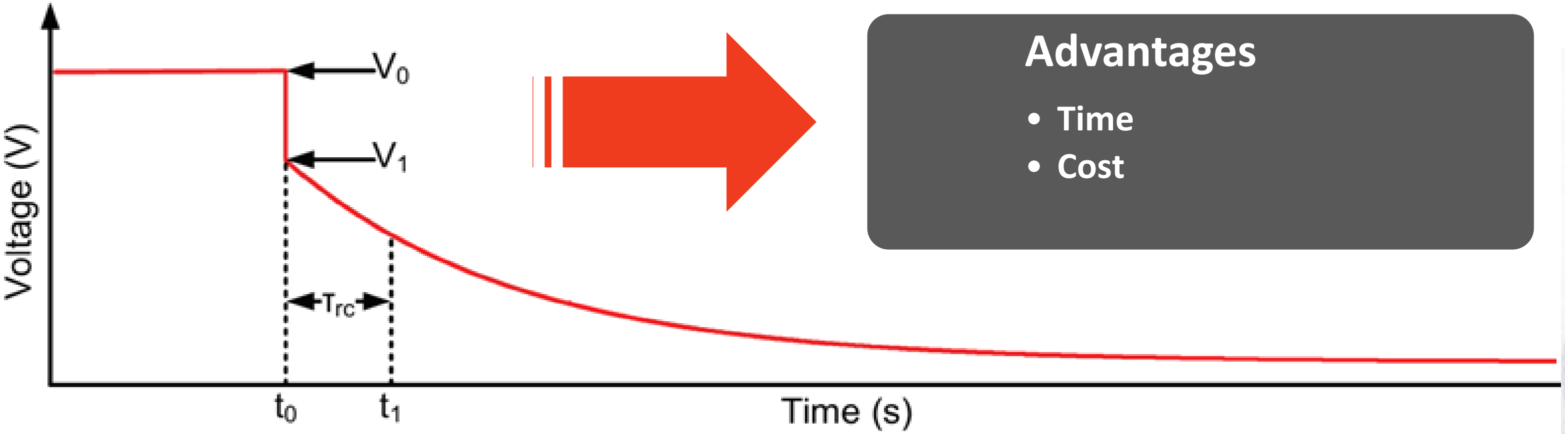
❑ Current Interrupt (CI)

Technique

- Current Interrupt
- Voltage drop

Equipment

- In-house developed switch
- LeCroy Oscilloscope



Advantages

- Time
- Cost

Characterization Tools Development for PEM Water Electrolysis

❑ Current Mapping (CM)

Technique

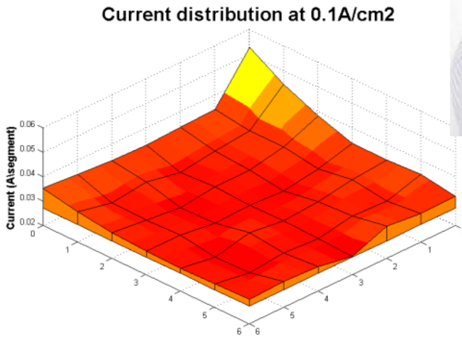
- Steady State
- Current measurements

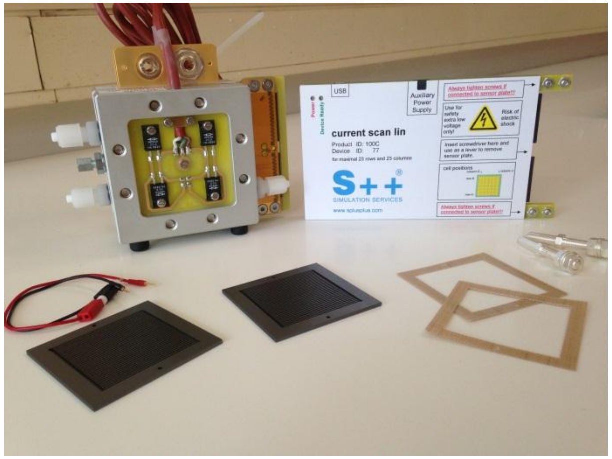
Equipment

- S++

Advantages

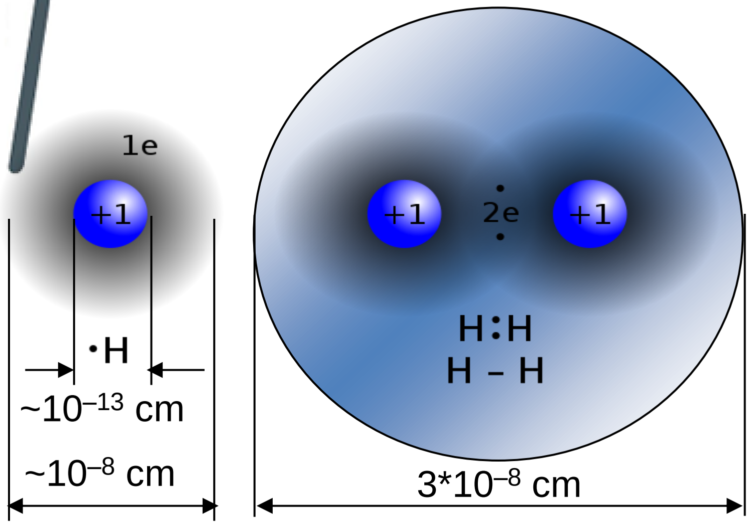
- Identify irregular current distributions
- Investigate the effects of: temperature, water management, flow-field patterns, start up / shut down, operating pressure





Hydrogen Storage

The Hydrogen Storage Challenge



- **HYDROGEN:**
  - One proton, one electron
  - Lightest element, lowest density
  - Stong covalent bond
  - Non-polar bond
  - Low polarisation ability

→ Weak interaction between H_2 molecules

- At 298 K and 1 atm:

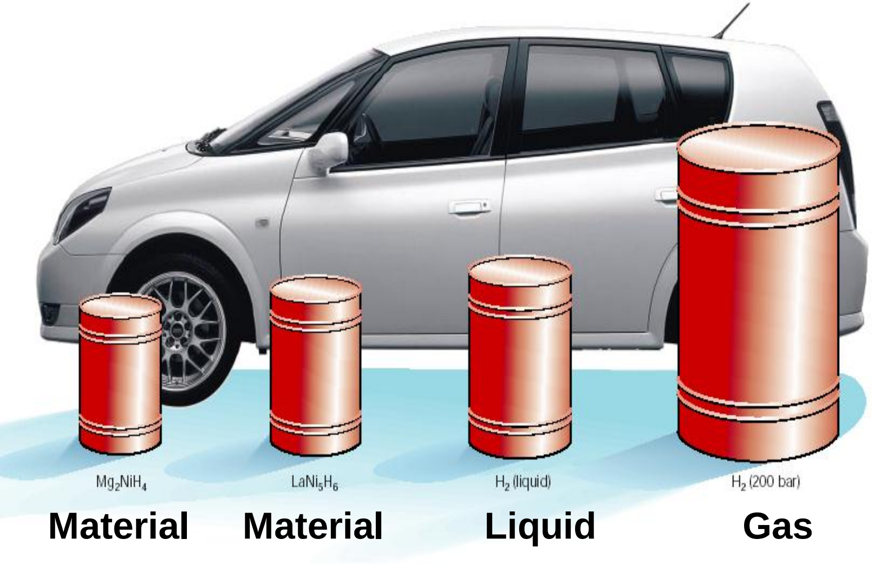
4 kg H_2 = 45,000 L ≡ balloon of 5 m diameter

(4 kg H_2 gives 500 km driving range)

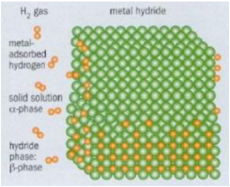
http://www.imageproduction.nl

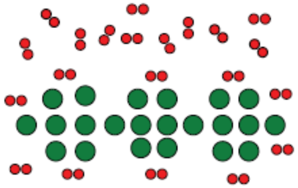
Hydrogen Storage Options

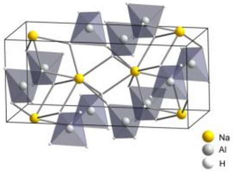
- Hydrogen can be stored in various ways



- Compressed gas
- Liquid hydrogen
- Materials-based storage
  - *Metal hydrides*
  - *Complex hydrides*
  - *Chemical hydrides*
  - *Porous materials*







L. Schlapbach, A. Züttel, *Nature* **414** (2001) 353; R. Harris et al., *Fuel Cell Rev.* **1** (2004) 17.

US DOE On-board Technical Targets

Storage Parameter	Unit	2010	2017	Ultimate
System gravimetric capacity	wt.% (kWh/kg)	4.5 (1.5)	5.5 (1.8)	7.5 (2.5)
System volumetric capacity	kg H_2/m^3 (kWh/L)	28 (0.9)	40 (1.3)	70 (2.3)
Fuelling time (5 kg)	min	4.2	3.3	2.5
Fuel system cost	\$/kg H_2	TBD	TBD	TBD
Durability	cycles	1000	1500	1500
H_2 loss rate	(g/h)/kg	0.1	0.05	0.05

☐ Targets are less stringent for stationary / portable power applications

Analysis from US DOE

Current status	Gravimetric (kWh/kg sys)	Volumetric (kWh/L sys)	Costs ($/kWh)
700 bar compressed (Type IV)	1.7	0.9	18.9
350 bar compressed (Type IV)	1.8	0.6	15.5
Cryo-compressed (276 bar)	1.9	1.4	12.0
Metal Hydride ($NaAlH_4$)	0.4	0.4	11.3
Sorbent (MOF-5, 200 bar)	1.7	0.9	18.0
Off-board regenerable (AB)	1.4	1.3	N/A
2017 targets	**1.8**	**1.3**	**TBD**

Source: N.T. Stetson, US DOE 2012 Annual Merit Review and Peer Evaluation Meeting

Metal–Organic Frameworks (MOFs)

☐ Inorganic-organic hybrid crystalline materials

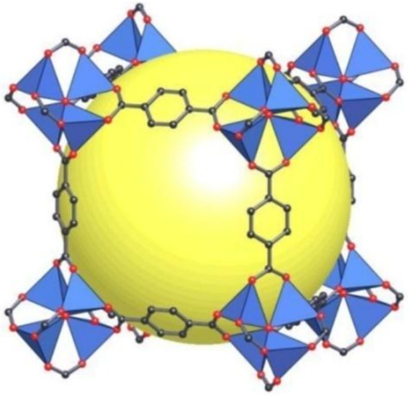
☐ Metal ions + organic linkers

☐ Structural diversity

☐ High surface area (up to 7140 m^2/g)

☐ Ultrahigh porosity (up to 90% free volume)

☐ Tunable pore sizes and functionalities



MOF-5:
$Zn_4O(BDC)_3$

Rosi N.L., Eckert J., Eddaoud M., Vodak D.T., Kim J., O'Keeffe M., Yaghi O.M.. Science, 2003, **300**, 1127-1129.

Metal—Organic Frameworks (MOFs)

❑ **Highlights**

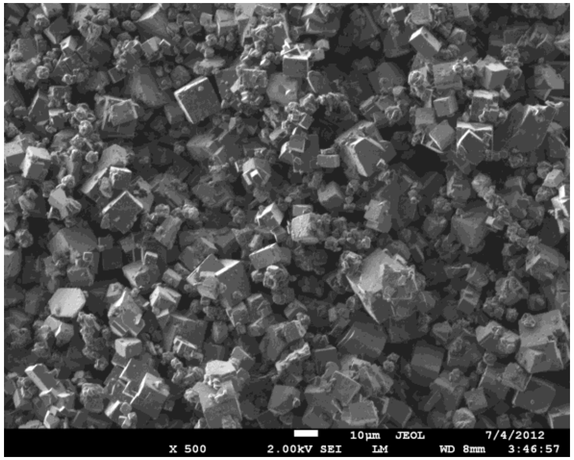
❑ MOF synthesis and scale-up

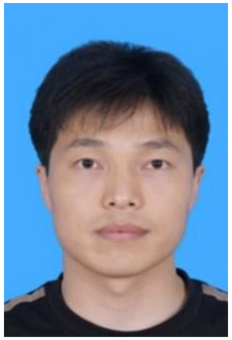
❑ MOFs characterization

❑ Effect of variables

❑ Preliminary modifications

❑ H_2 storage behaviour





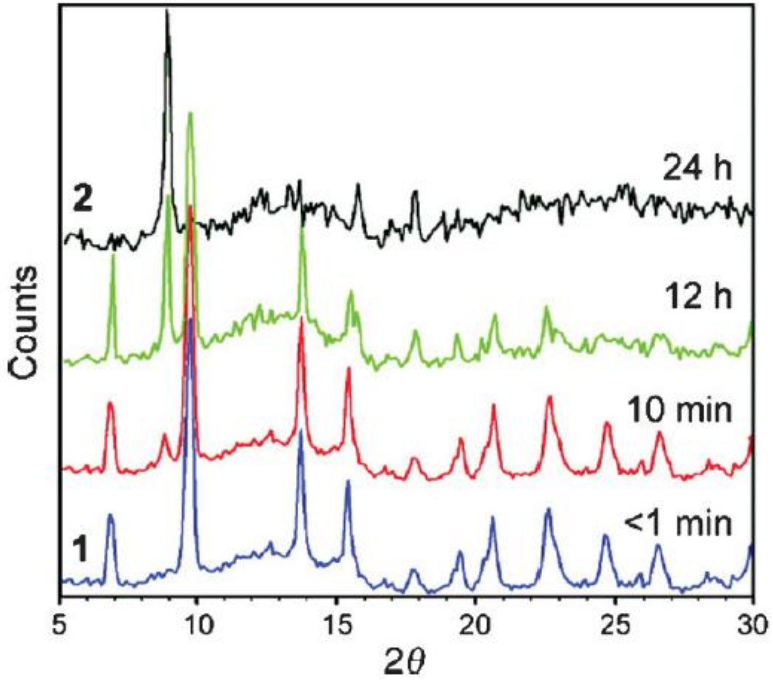
Metal–Organic Frameworks (MOFs)

❑ **Technology gaps:**

❑ Cryogenic storage of H_2 (77 K)
  ❑ Low heat of ads 4–12 kJ/mol
  ❑ Need 15–25 kJ/mol

❑ Cost

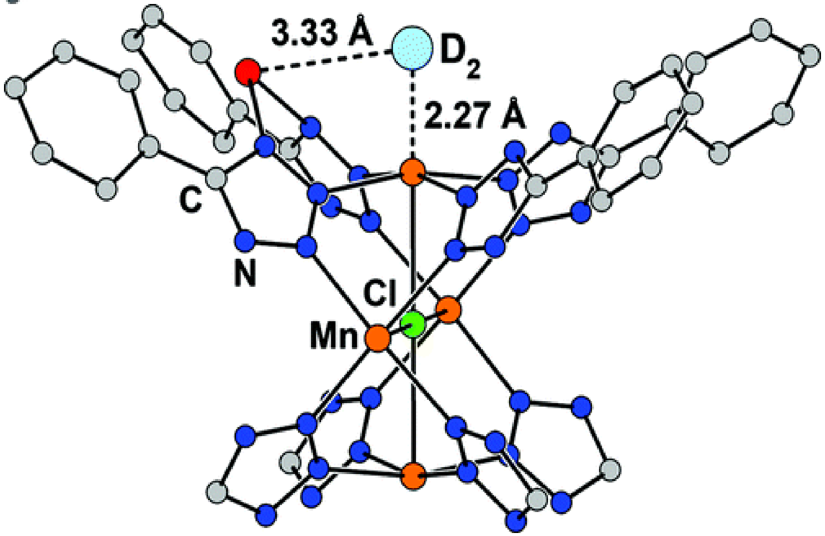
❑ Moisture sensitivity

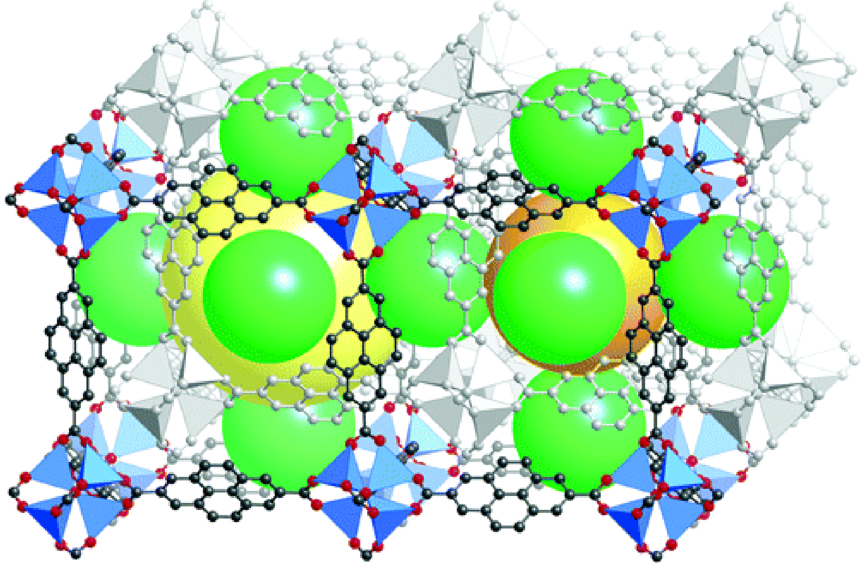


S. S. Kaye, A. Dailly, O. M. Yaghi, J. R. Long, J. Am. Chem. Soc. 2007, 129, 14176.

Metal–Organic Frameworks (MOFs)

☐ Strategies for enhancing H_2 storage





☐ Control of pore size

☐ Unsaturated metal sites

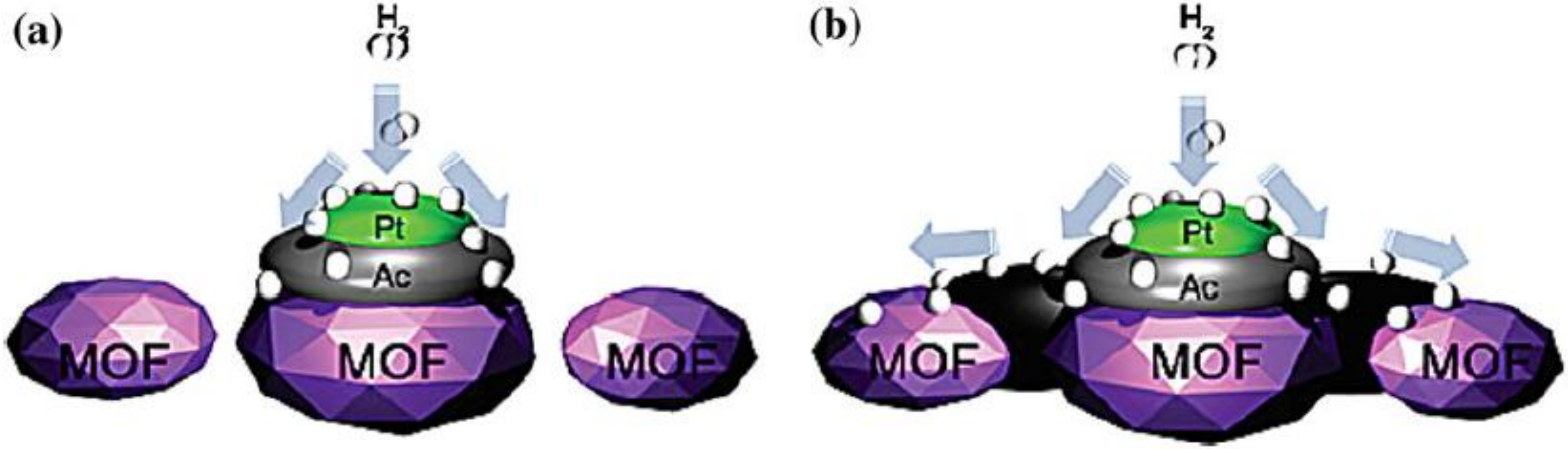
☐ Ligand functionalisation

M. Dinca, J.R. Long, J. Am. Chem. Soc. 129 (2007) 11172-11176.

J.L.C. Rowsell, O.M. Yaghi, J. Am. Chem. Soc. 128 (2006) 1304-1315.

Enhancing Hydrogen Storage in MOFs

- **Strategies for enhancing H_2 storage**



- Incorporate Pd or Pt nanoparticles

Li, Y.; Yang, R. T. J. Am. Chem. Soc. 2006, 128, 8136

Conclusion

- Hydrogen storage is still a serious challenge

- MOFs are promising with potential to meet US DOE targets

- Breakthrough for MOFs:
    - *Low cost*
    - *High heat of H_2 adsorption*
    - *Large surface area and pore volume*
    - *High hydrostability and thermal stability*

Acknowledgements

☐ Financial Support

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Thank You