HYDROGEN STORAGE FOR FUEL CELL APPLICATIONS: CHALLENGES, OPPORTUNITIES AND PROSPECTS FOR METAL-ORGANIC FRAMEWORKS

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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: 72.1%
- Gas: 2.8%
- Nuclear: 2.2%
- Oil: 12.6%
- *CR&W: 10.2%
- Hydro: 0.1%

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

- RSA has energy intensive economy
- RSA has a large SO₂/CO₂ footprint
- RSA’s CO₂ footprint per capita ranks among the **top 12 in the world**

*CR&W: Combustible Renewable and Waste
Source: International Energy Agency (IEA)
Nominal capacity for CSP in South Africa is 547.6 GW

### 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

<table>
<thead>
<tr>
<th>Region</th>
<th>PGM Supply by region</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Africa</td>
<td>79%</td>
</tr>
<tr>
<td>Russia</td>
<td>12%</td>
</tr>
<tr>
<td>North America</td>
<td>5%</td>
</tr>
<tr>
<td>Others</td>
<td>4%</td>
</tr>
</tbody>
</table>

- 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

- NWU / CSIR
- UCT / Mintek
- 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 H₂ 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

H₂ 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. S0₂)
- ECH (electrochemical compression of H₂: components and systems)

H₂ Storage/Systems/Components
- Carbon Nanostructures
- Chemical storage (e.g. NH₃)
- MOF, other types
- Modelling
- Compressed H₂

H₂ from appropriate biomass and biological pathways (WGS)
- System Integration (H₂ production and delivery)
- Safety and Codes
- PGM Recycling

HySA Infrastructure: Hydrogen South Africa
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

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Nyquist Plot

- Zreal (Ω)
- Zimag (Ω)

- 0.1 A/cm²
- 0.5 A/cm²
- 1 A/cm²
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

- At 298 K and 1 atm:

  4 kg $\text{H}_2 = 45,000 \text{ L} \equiv \text{balloon of 5 m diameter}$

(4 kg $\text{H}_2$ gives 500 km driving range)

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

$\rightarrow$ Weak interaction between $\text{H}_2$ molecules
Hydrogen can be stored in various ways:

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

### US DOE On-board Technical Targets

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Unit</th>
<th>2010</th>
<th>2017</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>System gravimetric capacity</td>
<td>wt.%</td>
<td>4.5 (1.5)</td>
<td>5.5 (1.8)</td>
<td>7.5 (2.5)</td>
</tr>
<tr>
<td></td>
<td>(kWh/kg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System volumetric capacity</td>
<td>kg H₂/m³</td>
<td>28 (0.9)</td>
<td>40 (1.3)</td>
<td>70 (2.3)</td>
</tr>
<tr>
<td></td>
<td>(kWh/L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuelling time (5 kg)</td>
<td>min</td>
<td>4.2</td>
<td>3.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Fuel system cost</td>
<td>$/kg H₂</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
</tr>
<tr>
<td>Durability</td>
<td>cycles</td>
<td>1000</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>H₂ loss rate</td>
<td>(g/h)/kg</td>
<td>0.1</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

- Targets are less stringent for stationary / portable power applications
## Analysis from US DOE

<table>
<thead>
<tr>
<th>Current status</th>
<th>Gravimetric (kWh/kg sys)</th>
<th>Volumetric (kWh/L sys)</th>
<th>Costs ($/kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 bar compressed (Type IV)</td>
<td>1.7</td>
<td>0.9</td>
<td>18.9</td>
</tr>
<tr>
<td>350 bar compressed (Type IV)</td>
<td>1.8</td>
<td>0.6</td>
<td>15.5</td>
</tr>
<tr>
<td>Cryo-compressed (276 bar)</td>
<td>1.9</td>
<td>1.4</td>
<td>12.0</td>
</tr>
<tr>
<td>Metal Hydride (NaAlH₄)</td>
<td>0.4</td>
<td>0.4</td>
<td>11.3</td>
</tr>
<tr>
<td>Sorbent (MOF-5, 200 bar)</td>
<td>1.7</td>
<td>0.9</td>
<td>18.0</td>
</tr>
<tr>
<td>Off-board regenerable (AB)</td>
<td>1.4</td>
<td>1.3</td>
<td>N/A</td>
</tr>
</tbody>
</table>

### 2017 targets

|                      | 1.8 | 1.3 | TBD |

Metal–Organic Frameworks (MOFs)

- Inorganic-organic hybrid crystalline materials
- Metal ions + organic linkers
- Structural diversity
- High surface area (up to 7140 m²/g)
- Ultrahigh porosity (up to 90% free volume)
- Tunable pore sizes and functionalities

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 H₂ (77 K)
    - Low heat of ads 4–12 kJ/mol
    - Need 15–25 kJ/mol
  - Cost
  - Moisture sensitivity

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Metal–Organic Frameworks (MOFs)

- Strategies for enhancing H$_2$ storage
- Unsaturated metal sites
- Ligand functionalisation

Enhancing Hydrogen Storage in MOFs

- Strategies for enhancing H₂ 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

- Host Institutions
Thank You