



Materials Issues for H₂ R&D in Canada

Defence R&D Canada Atlantic

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Recherche et développement
pour la défense Canada

Defence Research and
Development Canada

Canada¹



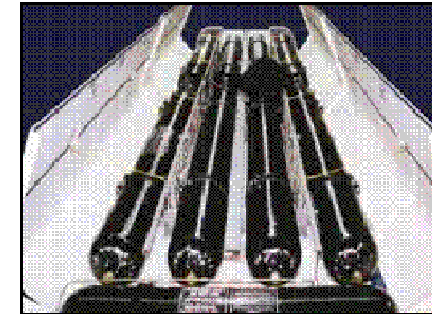
Outline

- Canadian Interests
- History
- R&D&D Programs
- Research Networks
- Materials Research Projects



Canadian Interests

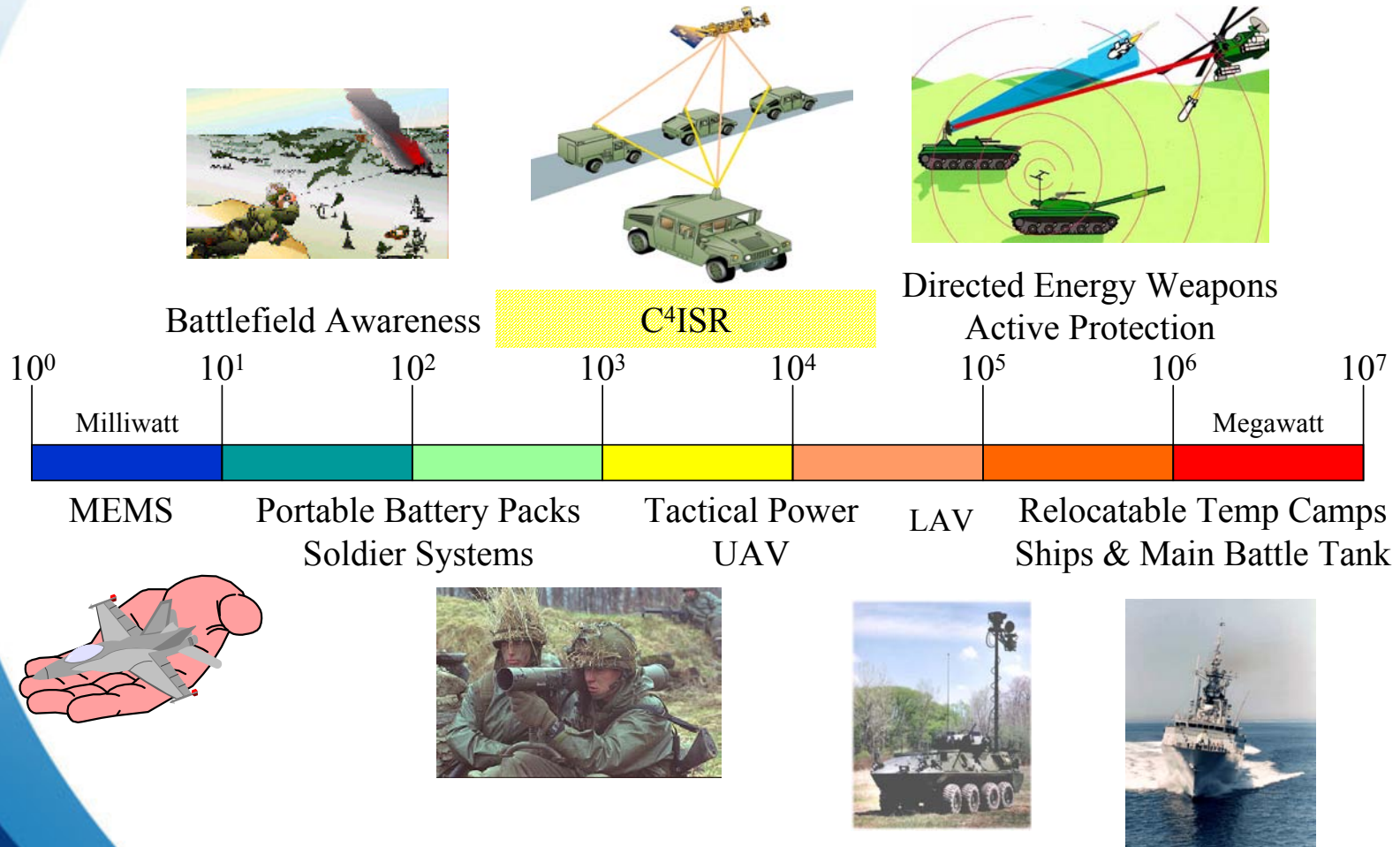
- **H₂ Production, Delivery, and Utilization**
 - Electrolysis, gasification (biomass, carbon (CO₂ neutral)), novel methods (process by-product, etc)
 - H₂ ICE
- **Fuel Cells**
 - PEM, DMFC, SOFC, Alkaline
 - Stack and system development
 - Manufacturing
 - Transportation, stationary, portable, and mobile
- **Codes and Standards**





Range of Power Source Applications

Forces Need Wide Range of Power Systems





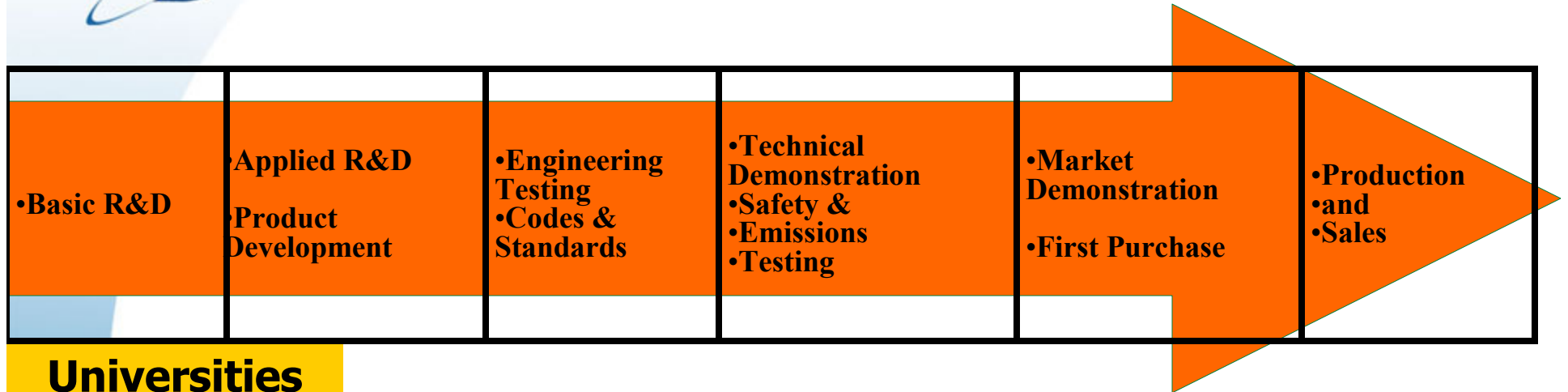
Canada H₂ & FC History

- 1982 first contract for Ballard Power Systems
- Through Government-industry partnerships
- fuel cell transit bus 1997
- Ford P2000 engine, the first prototype fuel cell engine for the Ford Motor Company
- Vancouver Fuel Cell Vehicle Project - demonstration of fuel cell cars in real-world fleet applications 2005- 2008
- 10,000 psi (700-bar) H₂ fuelling station
- 250 kw pre-commercial SOFC CHP system





Canadian Programs



Universities

National Research Council

Natural Resources Canada

National Defence

National Defence

Environment Canada

Transport Canada

Industry Canada

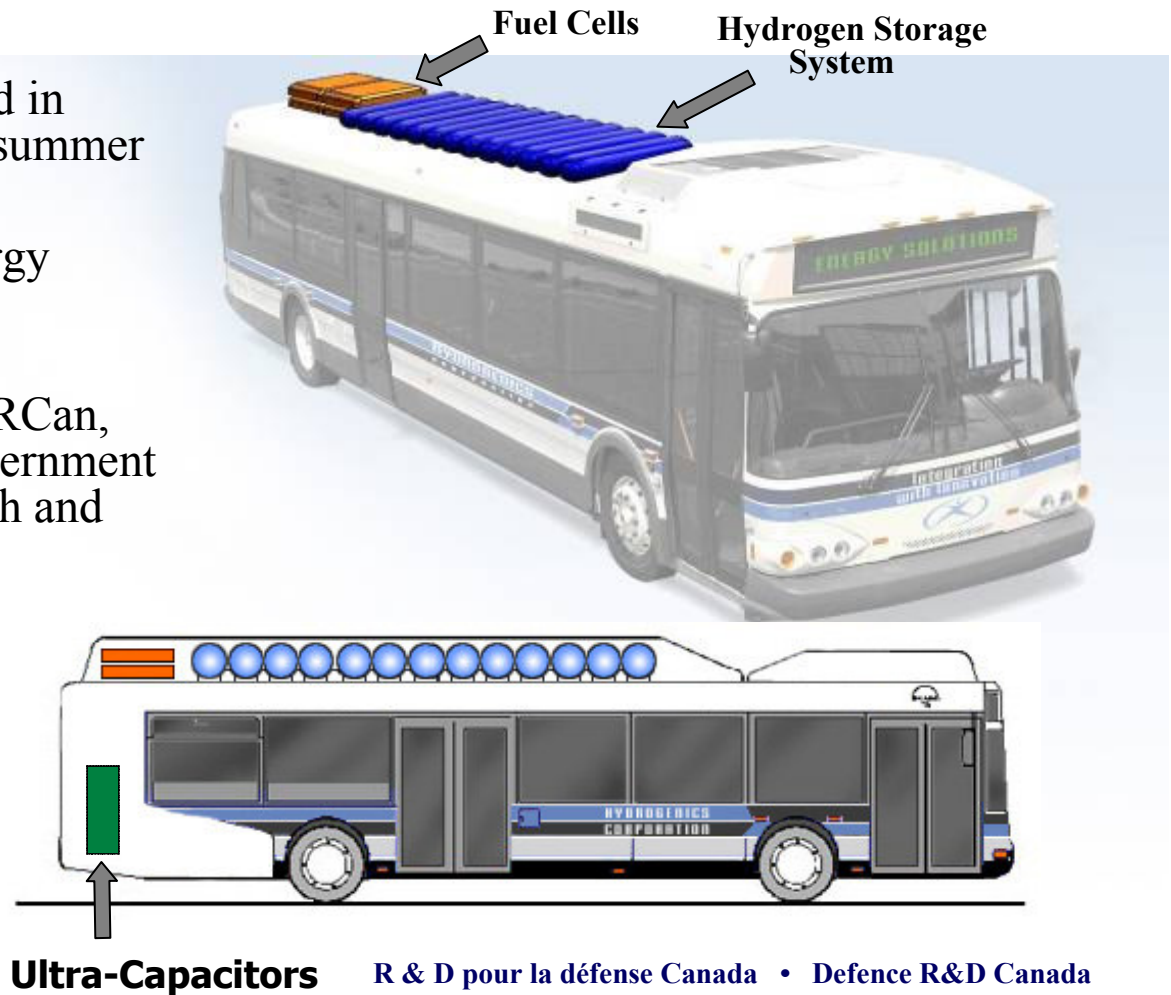
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Hydrogen and Fuel Cell Demonstration

Hybrid Fuel Cell / Ultra-capacitor Transit Bus

- Successfully demonstrated in Winnipeg, Manitoba last summer
- 25% improvement in energy efficiency
- Partners: Hydrogenics, NRCan, Dynetek, New Flyer, Government of Manitoba, ISE Research and Maxwell Technologies





Canadian Networks

- **International Networks**

- Government (NRC, NRCan), industry, and university participation
- IPHE, IEA, HIA, AFCIA, BSIA

- **Academic Networks**

- Funded by NSERC
- Hydrogen, PEMFC, SOFC,
- FCRC, OFCRIN, SOFC Canada, WCFCI. PEMFC Network, CANH2

- **SOFC Canada**

- Four themes: Fuel processing, C/S tolerant anodes, system integration, cell substrates

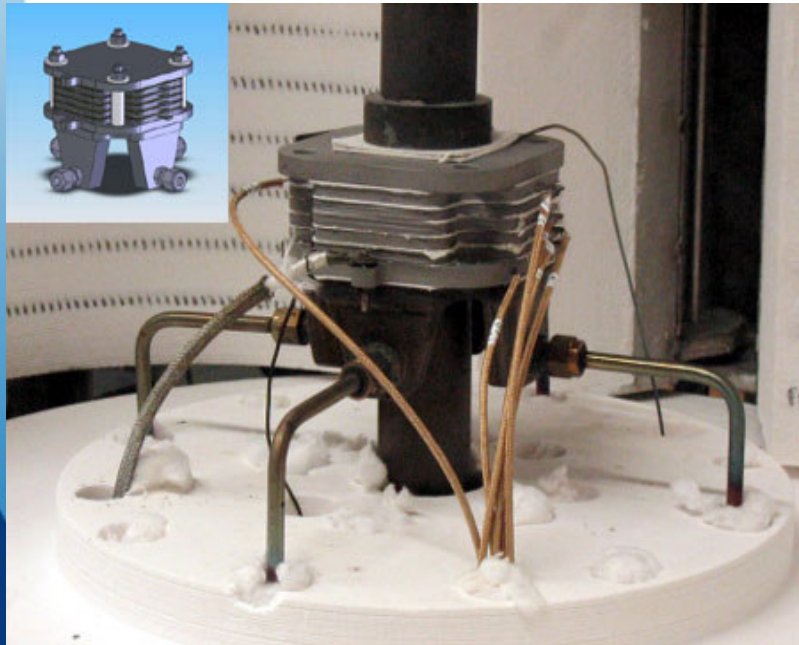
- **FCRC- OFCRIN**

- Performance, reliability, & durability, reduced costs through material design
- Five Themes: Fuel Storage & supply, reliability & durability, system modelling, materials development, systems analysis

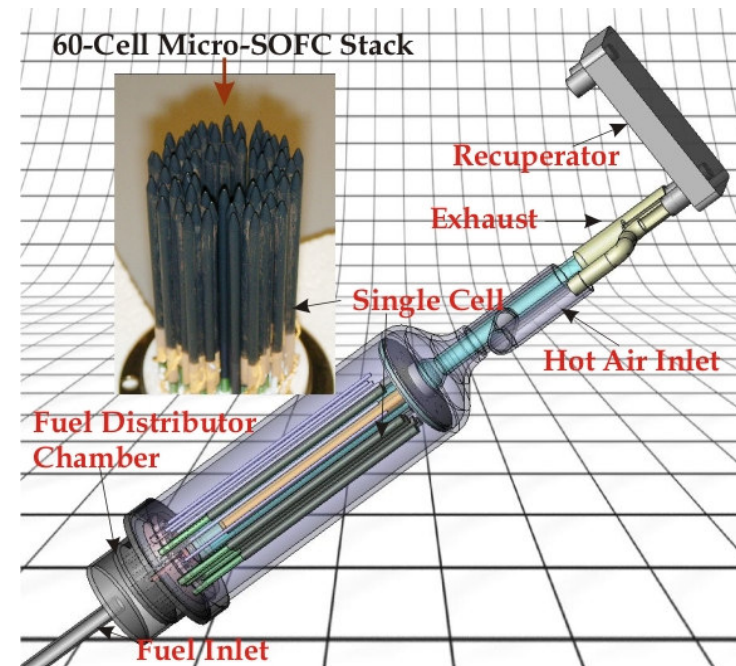


SOFC Canada

Metal-supported Planar SOFC



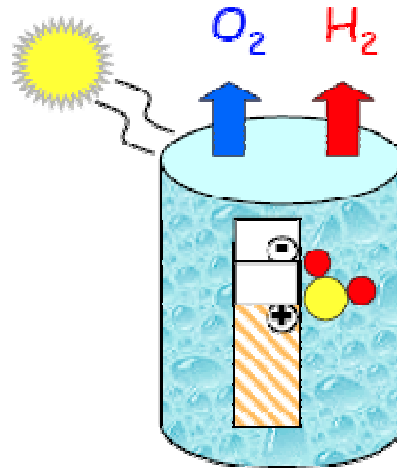
Porous electrolyte support Micro-tubular SOFC)





Hydrogen Production Materials Issues

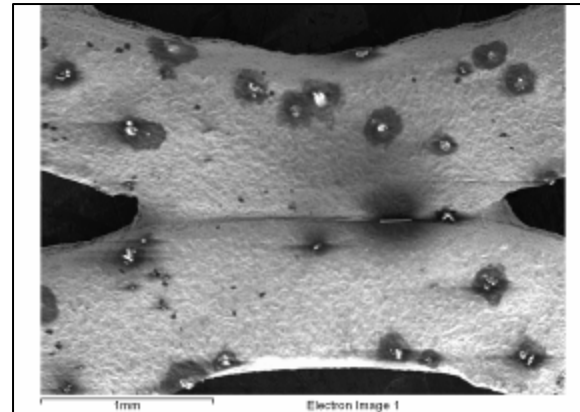
- **Splitting H₂O**



Solar electrolysis
Nano structured high surface
Band gap
Dye sensitized

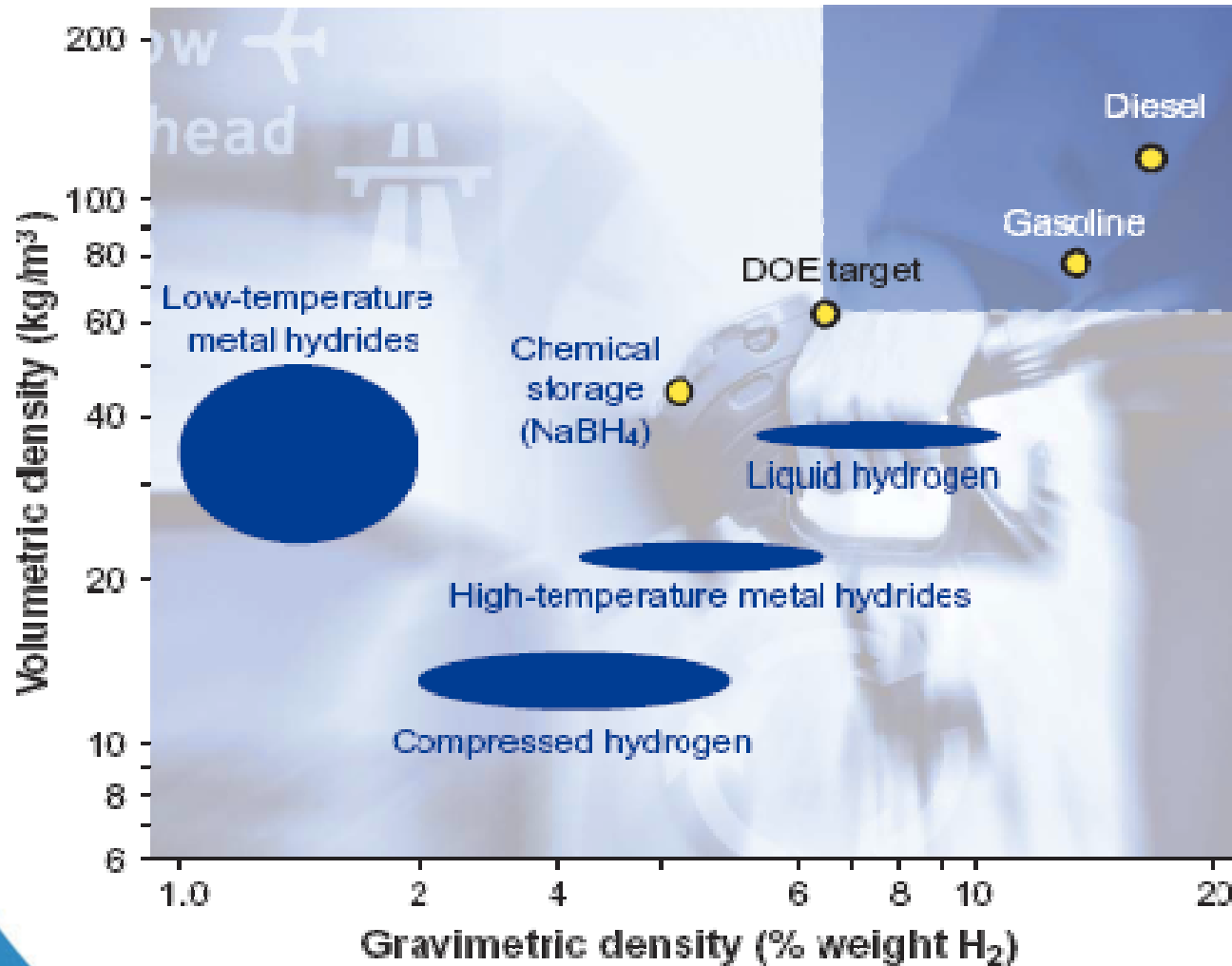
- **Electrolysis**

- Increased stability & durability of cathode in alkaline media
- Increase energy density to 855ma/cm² at 1.80 v and 70 C





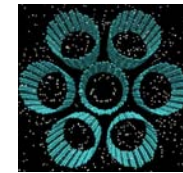
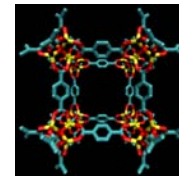
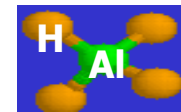
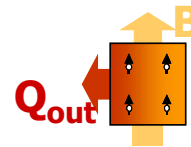
Hydrogen Storage Today: Gas and Liquid





Hydrogen Storage Materials Issues

- **700 Bar Compressed H₂**
 - Al carbon fibre re-inforced – weight and cost issues – Dynetek
 - 1kg/L, 19,000 fill cycles
- **Magnetic Refridgerization**
- **Complex Hydrides & metal Hydrides**
- **Nanostructured Materials**

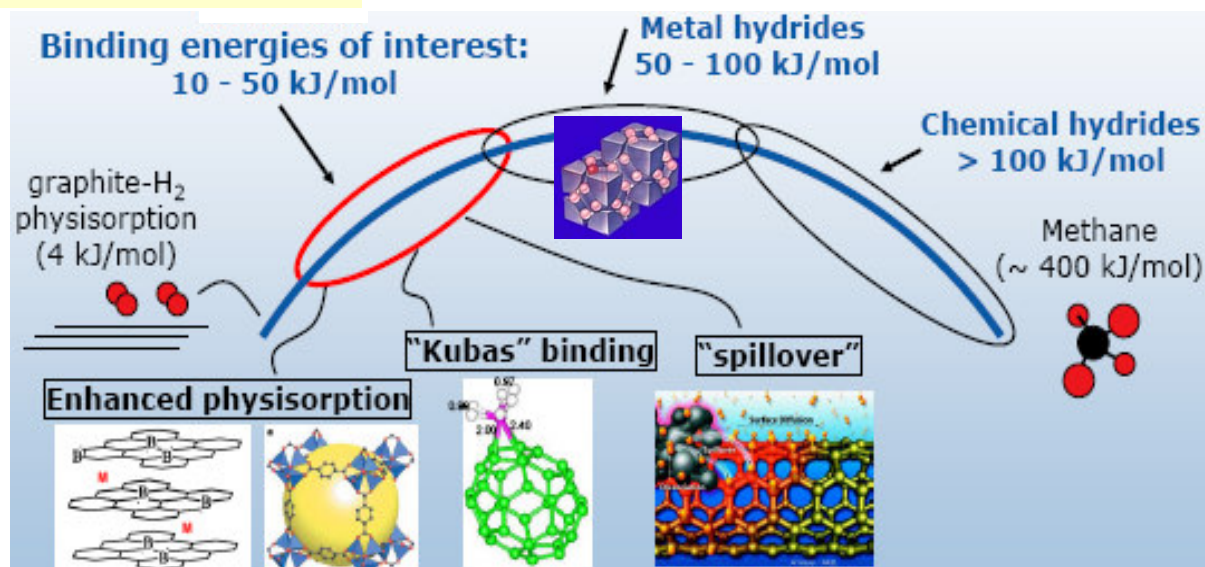




Continuum of Hydrogen Binding Energies

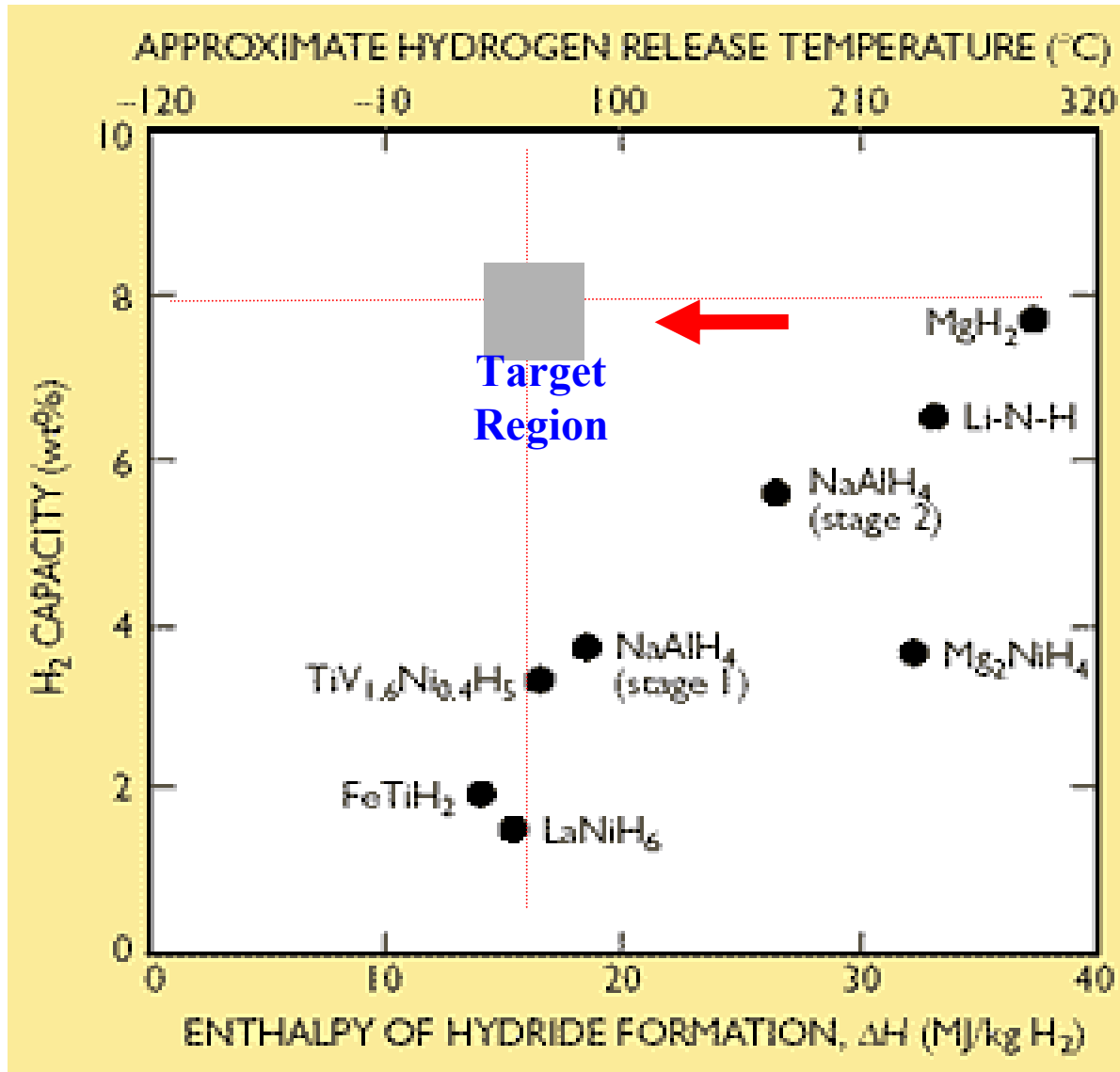
For reversible systems, equilibrium between gas and solid is given by:

$$P = \exp(-\Delta H/RT + \Delta S/R)$$



- Want lower enthalpy or higher temperature
- Increase rate of desorption

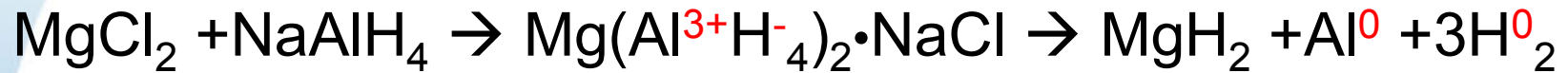
Issues with hydride storage



- Materials investigated do not meet goals
 - Lower enthalpy by destabilization
 - Use nano-catalysts to increase rates of H₂ release
 - MgH₂ nanocomposites with LiAlH₄

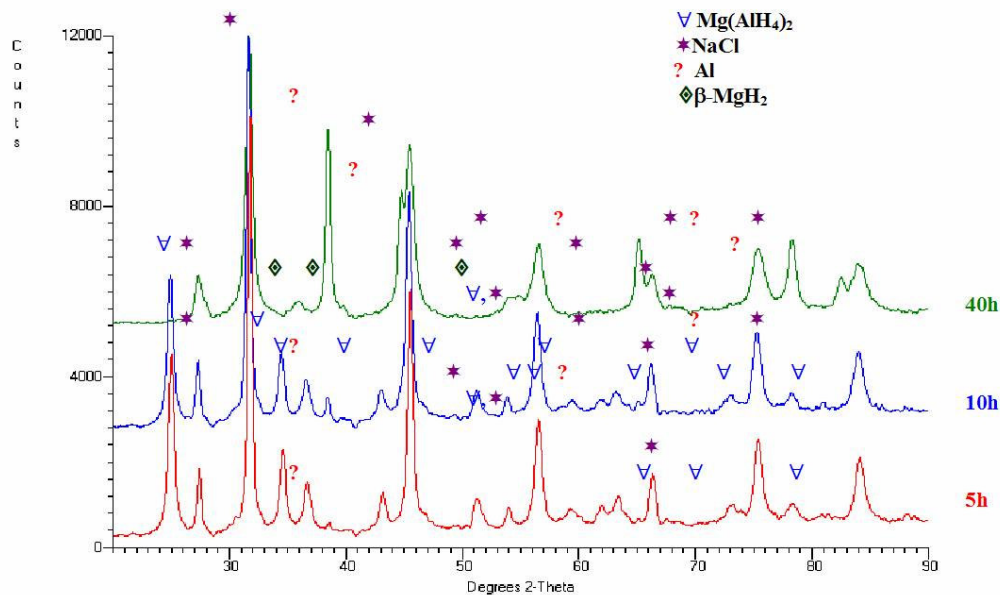


Mechanosynthesis of $\text{Mg}(\text{AlH}_4)_2$



1

2



Theoretical 9% except for salt*
Irreversible ca. 3 wt% H @ 150 C

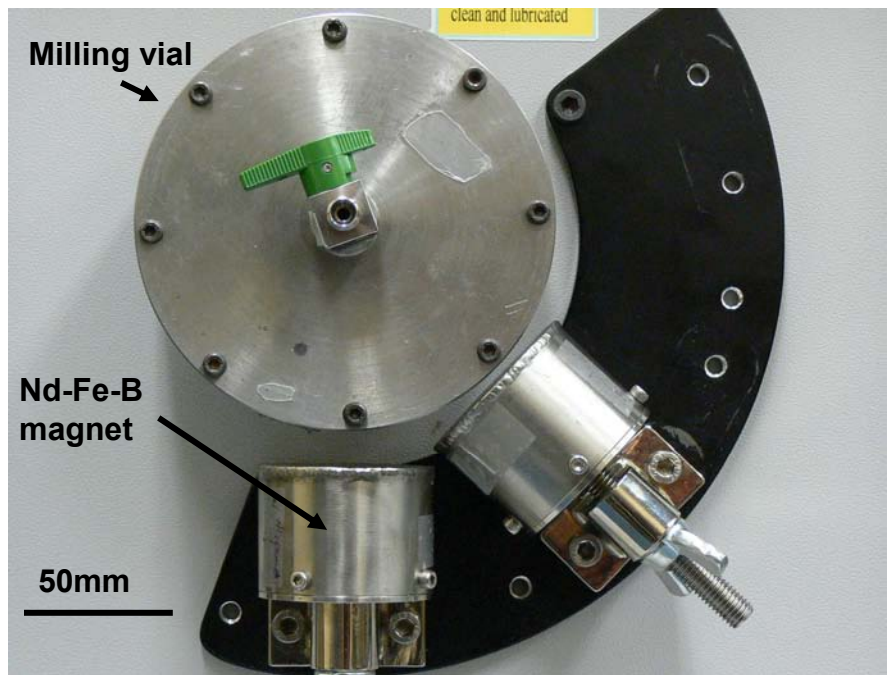
stage 1: **synthesis** via
metathesis reaction

Stage 2: **decomposition**
via redox
disproportionation



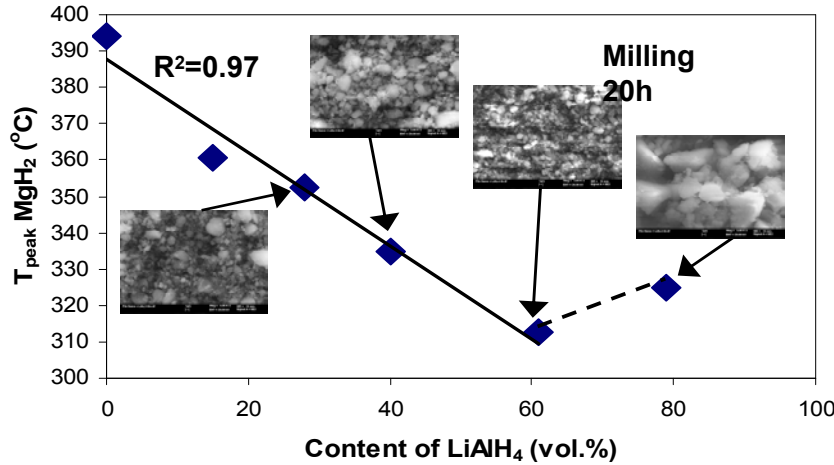
Hydrogen Ball Milling

- Controlled mechanical modes of milling : Impact or Shear Mode
- Sequential supply of hydrogen gas
- Angular positions of Nd-Fe-B supermagnets under shear mode. The angular positions of external magnets can be changed for each of the controlled modes of milling.

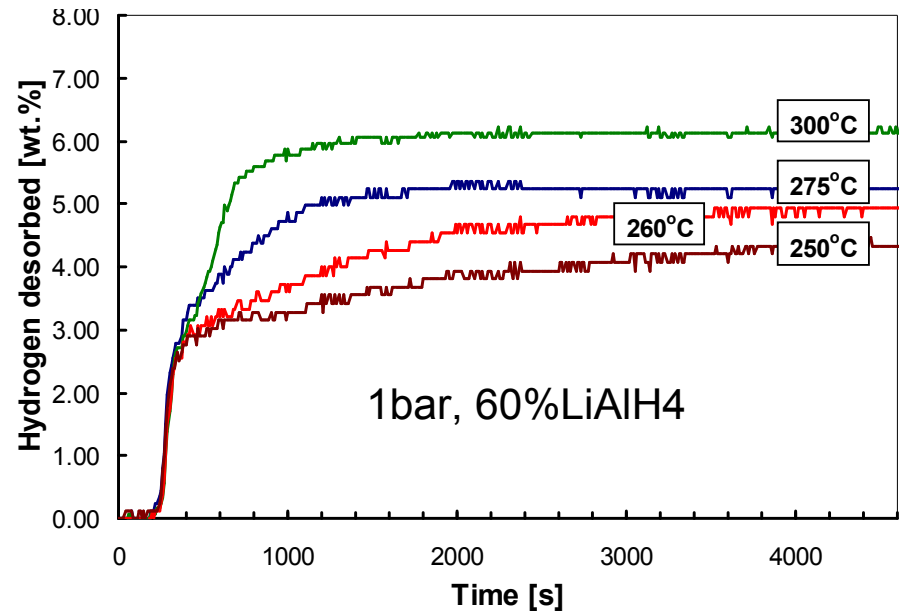




MgH₂/LiAlH₄ nanocomposite



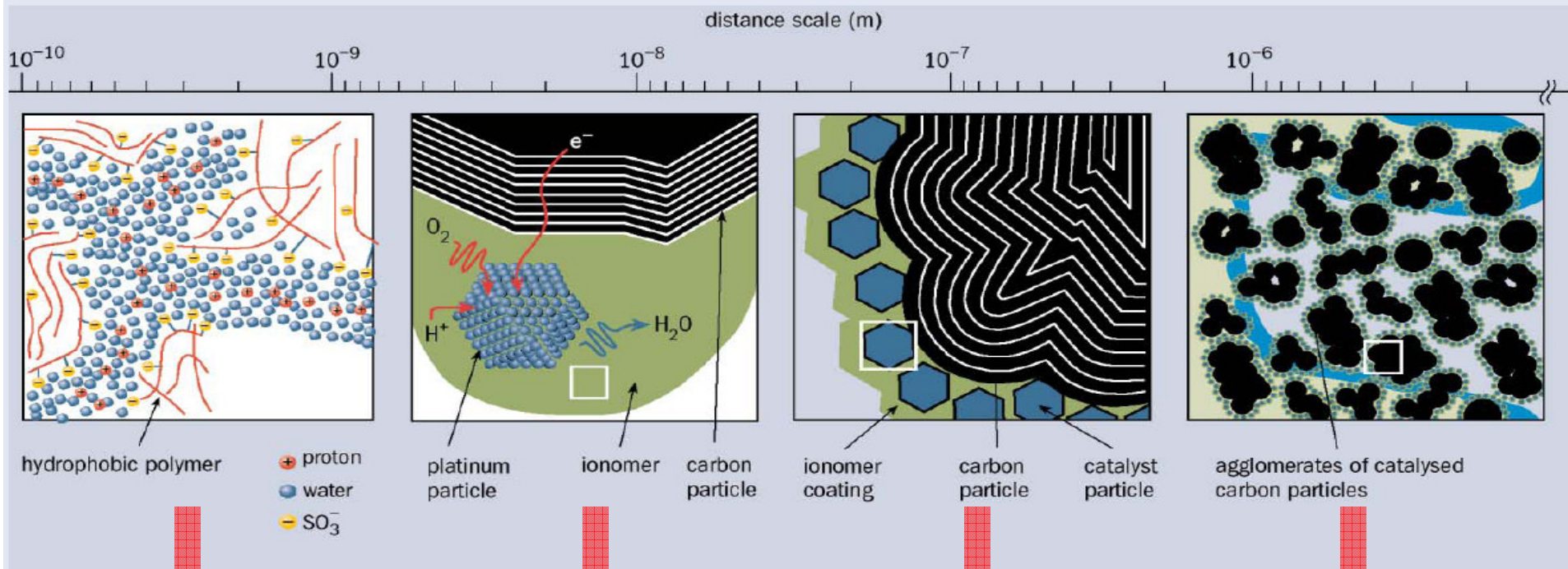
MgH₂ destabilization by chemical hydride





Challenges for Materials and Operation PEMFC

2 A problem of scales



Molecular scale, nanoscale

**proton conductors:
Higher Temperature**

**electrocatalysis:
Pt dissolution**

Mesoscale

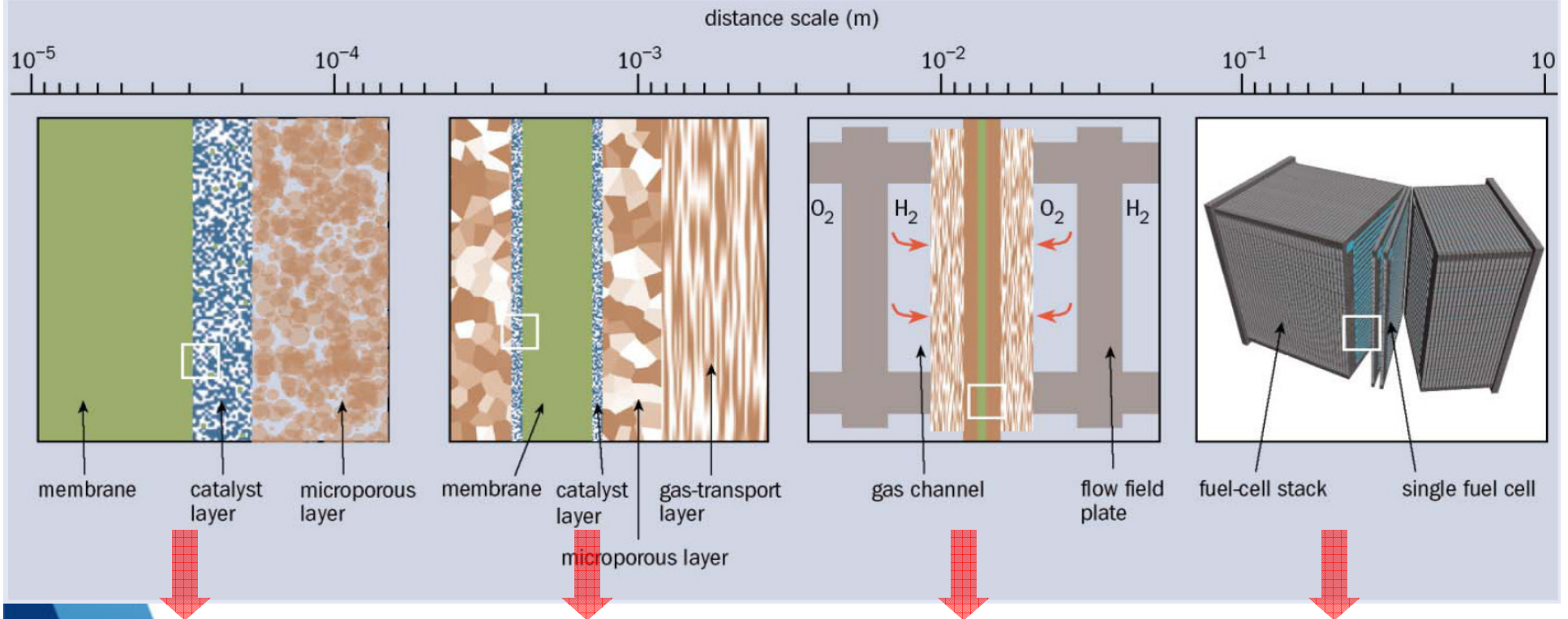
**Carbon support:
stability**

Macroscale

**effective properties:
Active surface area**



Challenges for Materials and Operation PEMFC



Fabrication and optimization of MEAs. Engineering of Cells & Stacks

MEAs:
High temp membrane

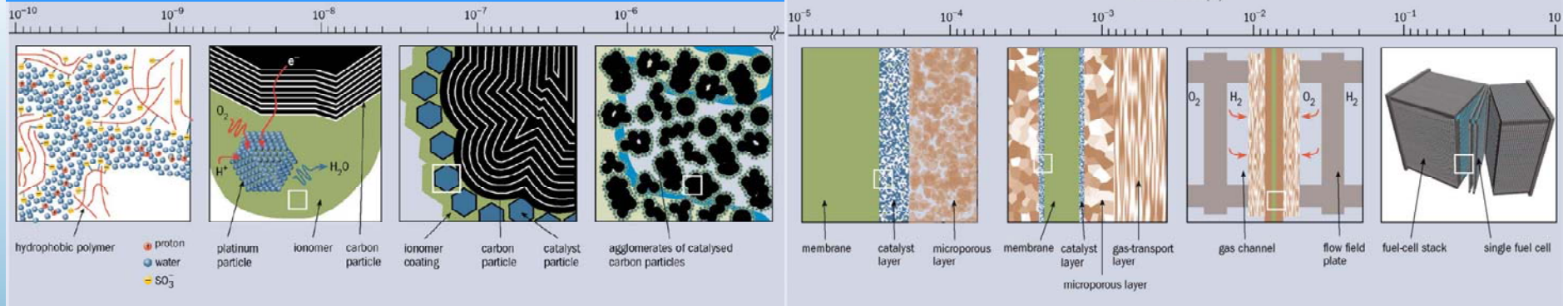
Carbon felt
stability

Water
management

Fuel: gasification
purification



Design Challenge: Multiple Scales



> 10 orders of magnitude,



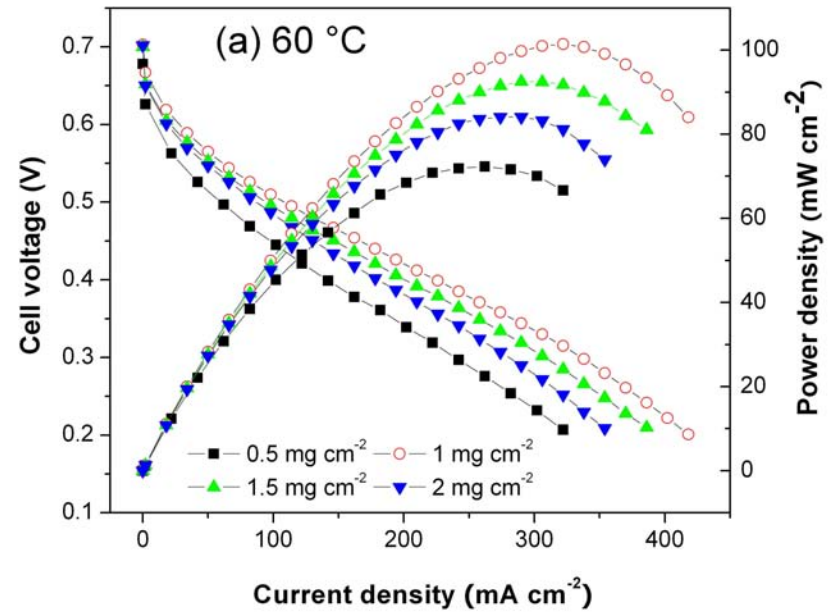
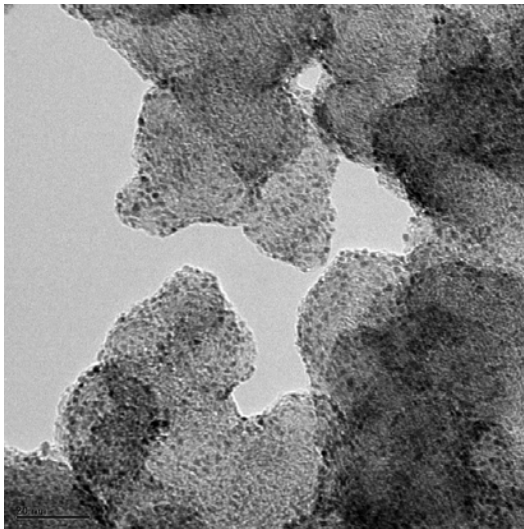
Multidisciplinary materials approach

- High temperature PEMFC for Transportation (>100 C)
 - Durable, Low cost materials
 - Membrane, low-humidity proton conductors
 - Less Pt, CO tolerance, non Pt
 - Low cost bipolar plates



Controlled Synthesis of Bimetallic Nanoparticles for DMFC

Modified polyol method using small stabilizers



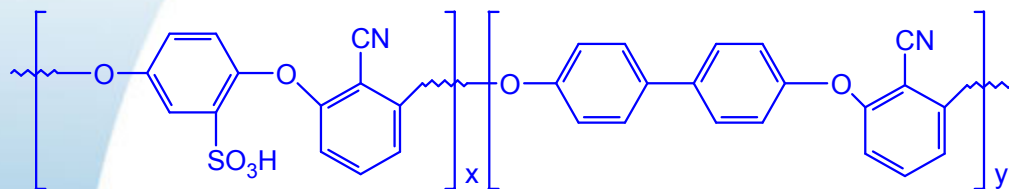
- Relative high performance for “low” noble metal catalyst loadings for DMFCs (<3mg cm⁻²)

Max. 100 mW cm⁻²,

- ~6 times less catalyst than reported

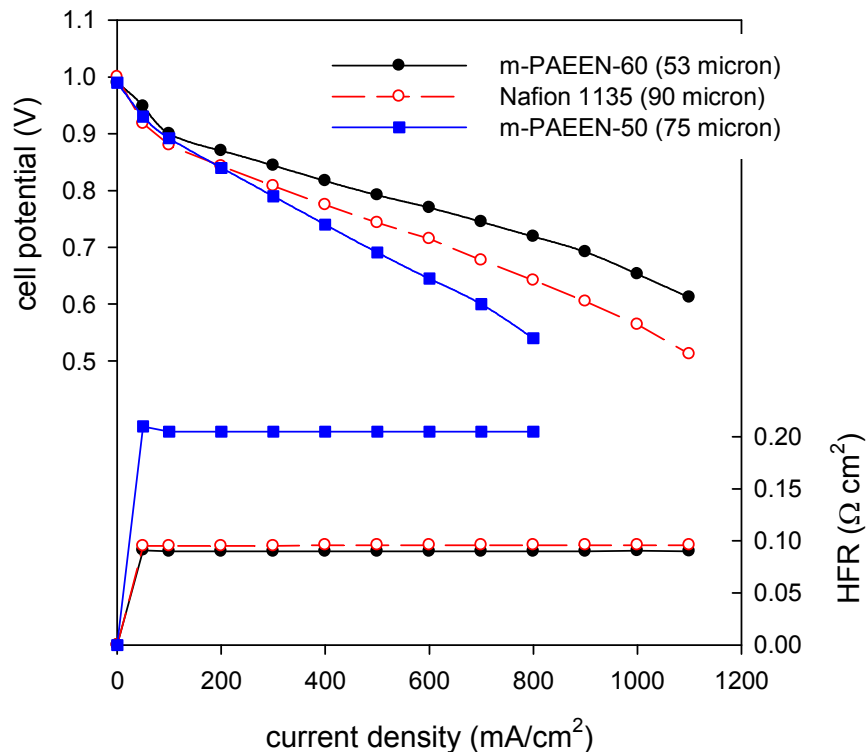
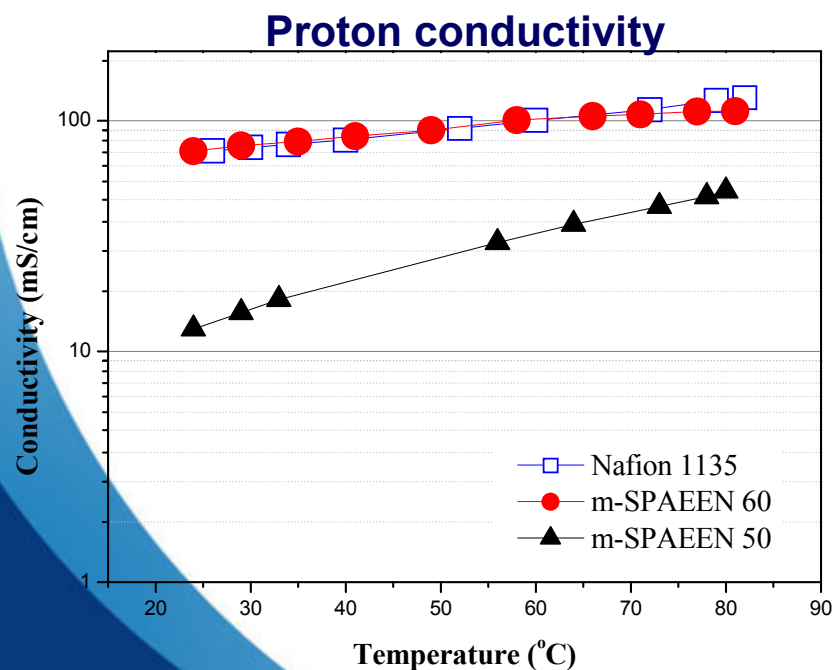


Polynitrile PEM Materials from Commercial Monomers



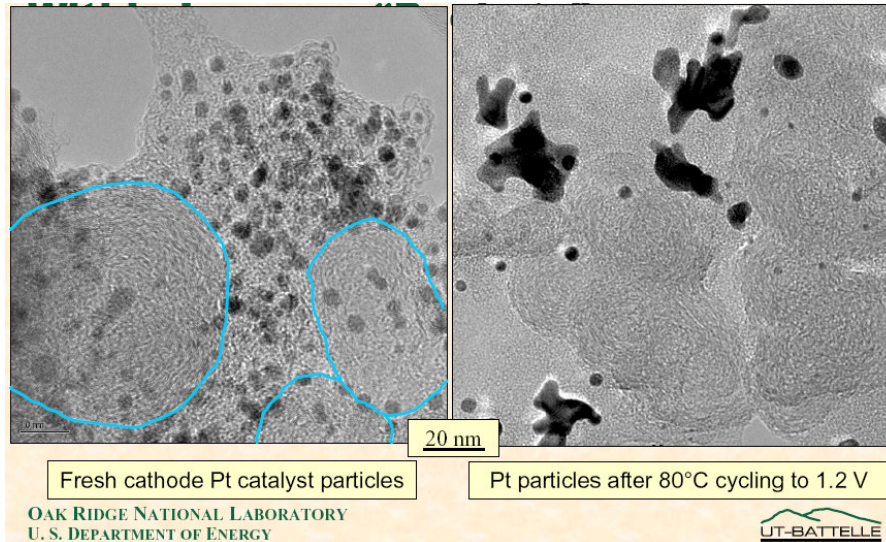
□ m-SPAEEN-60. ● Nafion. Swelling
 Swelling 17% @ 80°C 16-20% @ 80°C

- Inexpensive
- High proton conductivity
- Low dimensional swelling
- Good catalyst adhesion
- Excellent cell performance
- Stable under MEA conditions





PEMFC Cathode Degradation

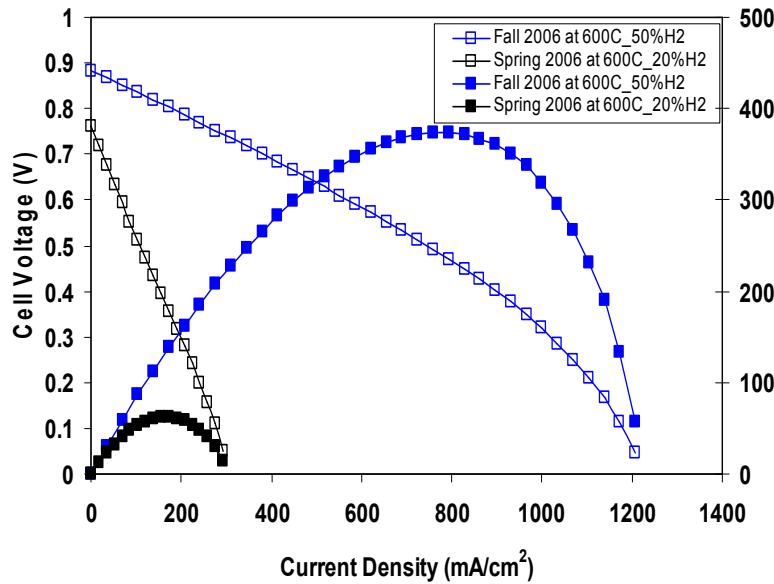


- High cathode voltage cycling causing Pt dissolution and recrystallization

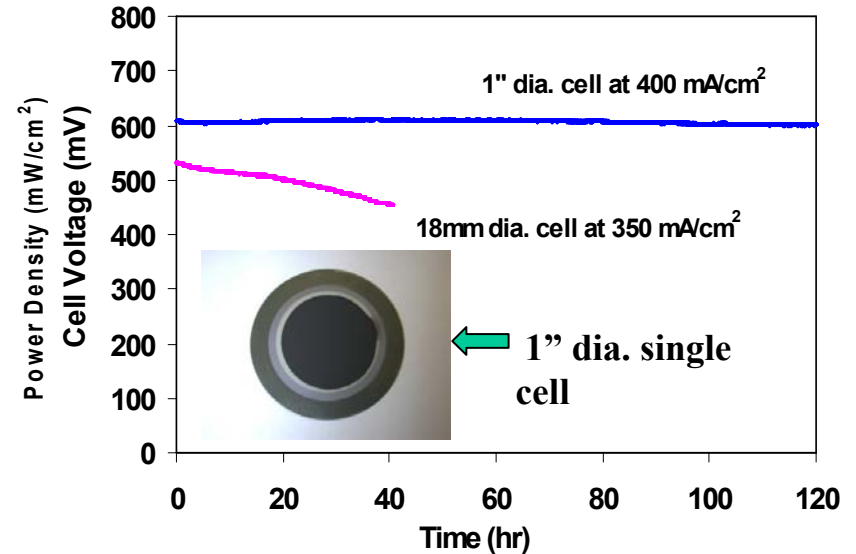


Reduced Temperature SOFC

- intermediate temperature metal supported SOFCs



metal supported cell of
SSC//SDC/ScSZ//Ni-
SDC//SS substrate (H₂ in
Ar/air)



Degradation of metal supported cells
of LSCF//GDC//Ni-SDC//SS substrate
at 600 °C (H₂ in Ar/air)



Canadian Interests

- **H₂ Production, Storage, and Delivery**
 - Electrolysis- more efficient electrocatalysts
 - Gasification- gasifier materials, carbon capture materials
 - Materials for thermo-nuclear water splitting cycles
 - Materials that provide sufficient storage for automobiles
- **Fuel Cells**
 - PEM, DMFC- Hybrids – electrocatalysts (low Pt, & non-noble), proton conducting membrane materials. battery materials
 - SOFC- materials for low temperature operation
 - DCFC (MCFC)- stable cathode materials