



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



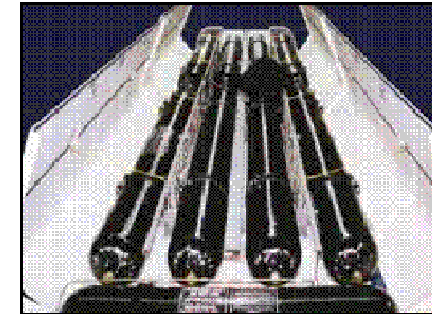
Outline

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



Canadian Interests

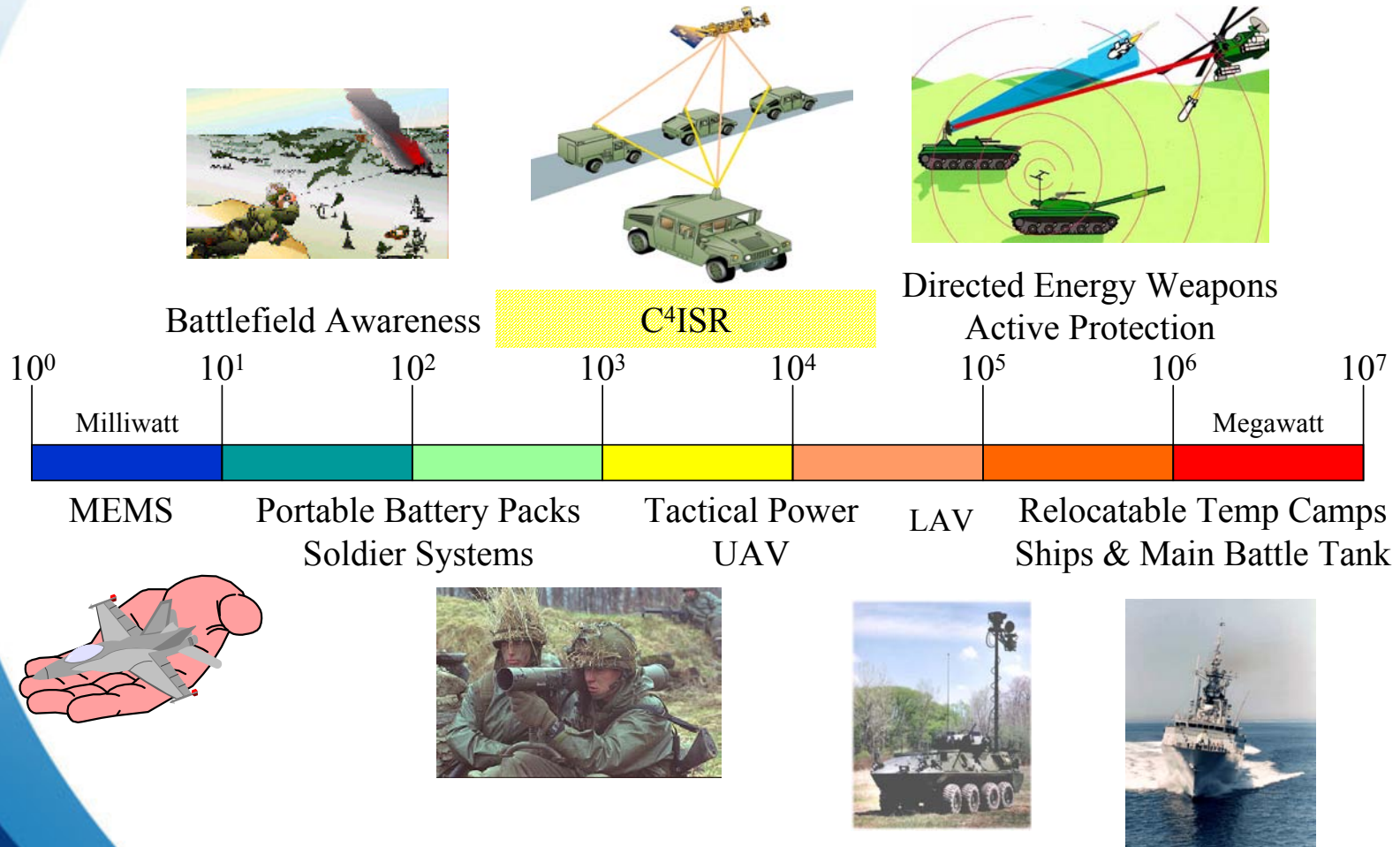
- **H₂ Production, Delivery, and Utilization**
 - Electrolysis, gasification (biomass, carbon (CO₂ neutral)), novel methods (process by-product, etc)
 - H₂ ICE
- **Fuel Cells**
 - PEM, DMFC, SOFC, Alkaline
 - Stack and system development
 - Manufacturing
 - Transportation, stationary, portable, and mobile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





Range of Power Source Applications

Forces Need Wide Range of Power Systems





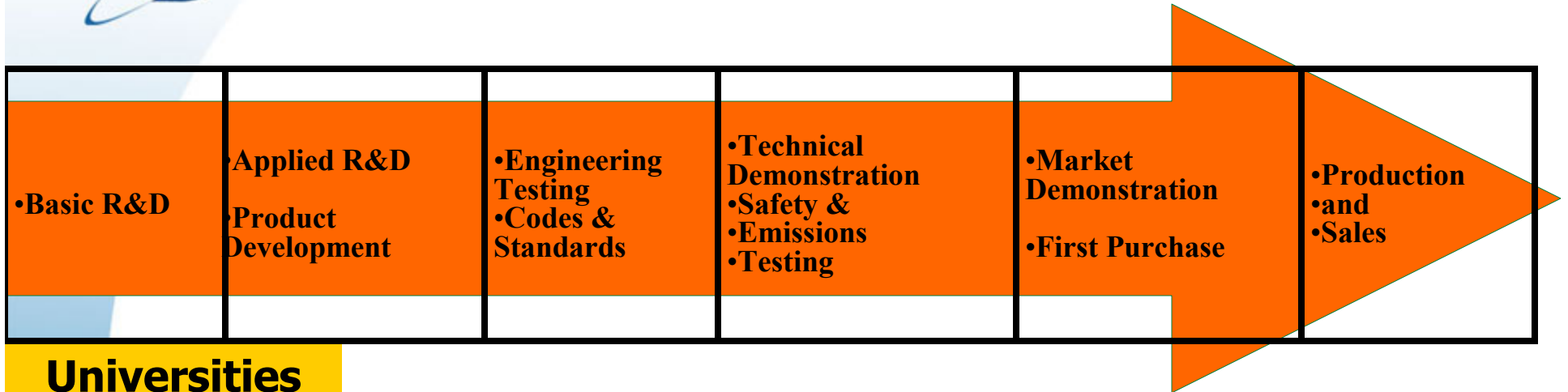
Canada H₂ & FC History

- 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

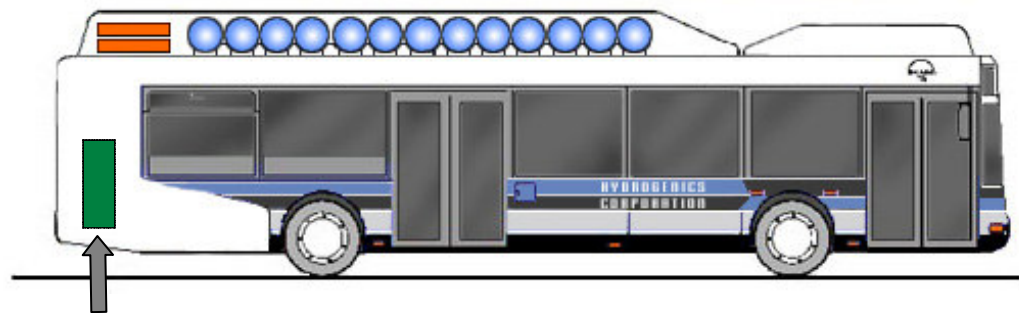
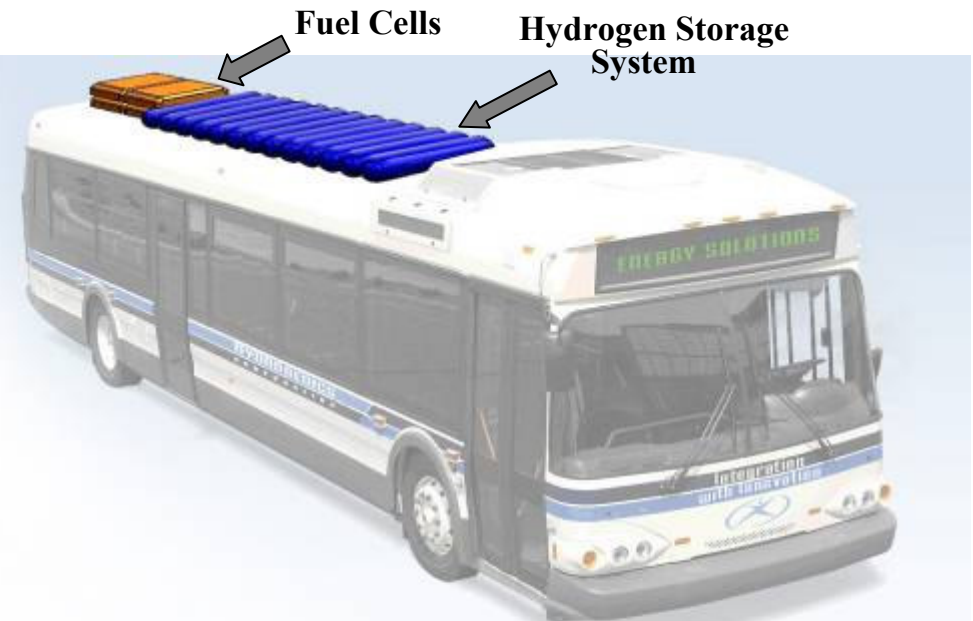
Industry Canada



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



Ultra-Capacitors

R & D pour la défense Canada • Defence R&D Canada



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

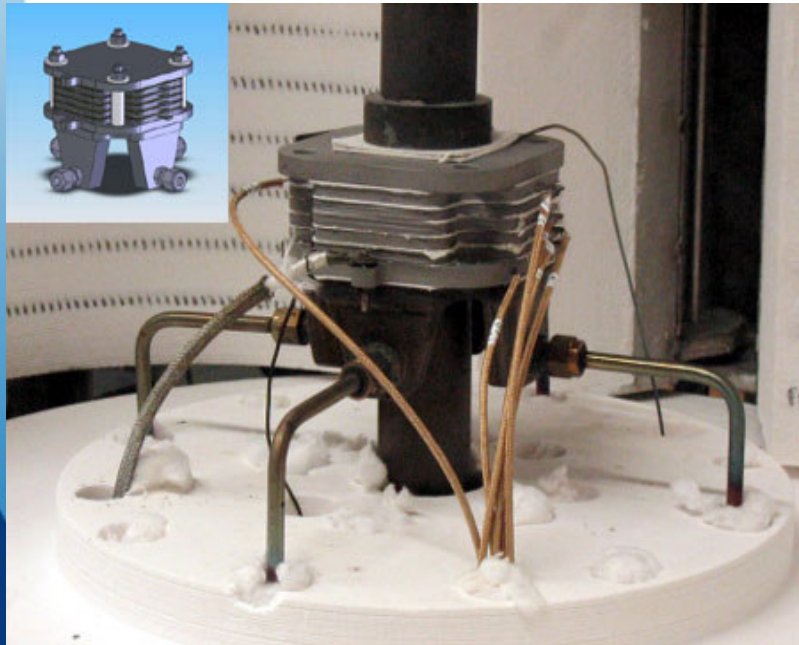
- **FCRC- OFCRIN**

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

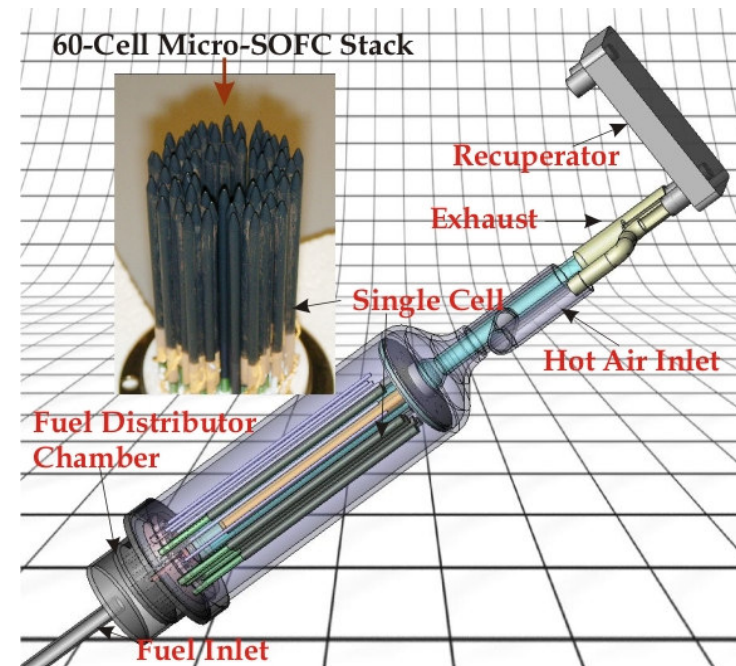


SOFC Canada

Metal-supported Planar SOFC



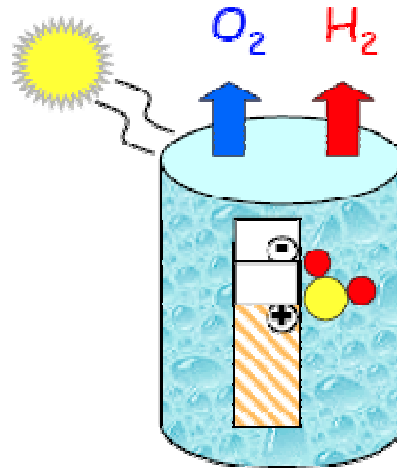
Porous electrolyte support Micro-tubular SOFC)





Hydrogen Production Materials Issues

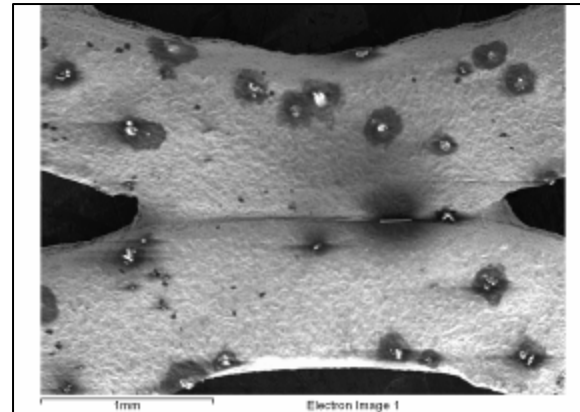
- **Splitting H₂O**



Solar electrolysis
Nano structured high surface
Band gap
Dye sensitized

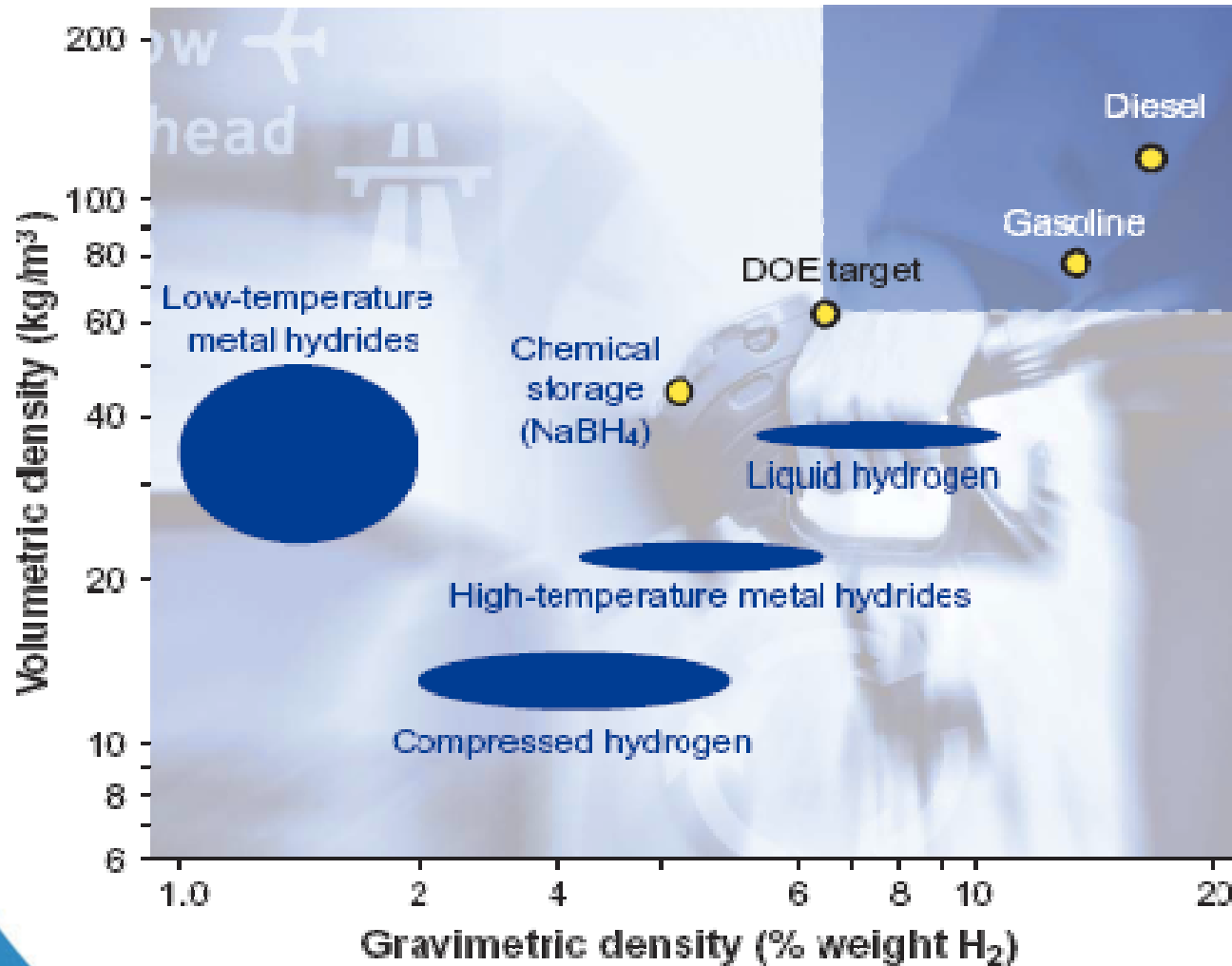
- **Electrolysis**

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





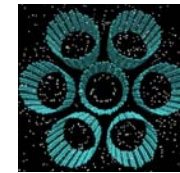
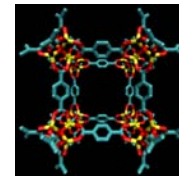
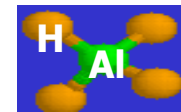
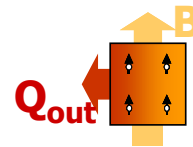
Hydrogen Storage Today: Gas and Liquid





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**

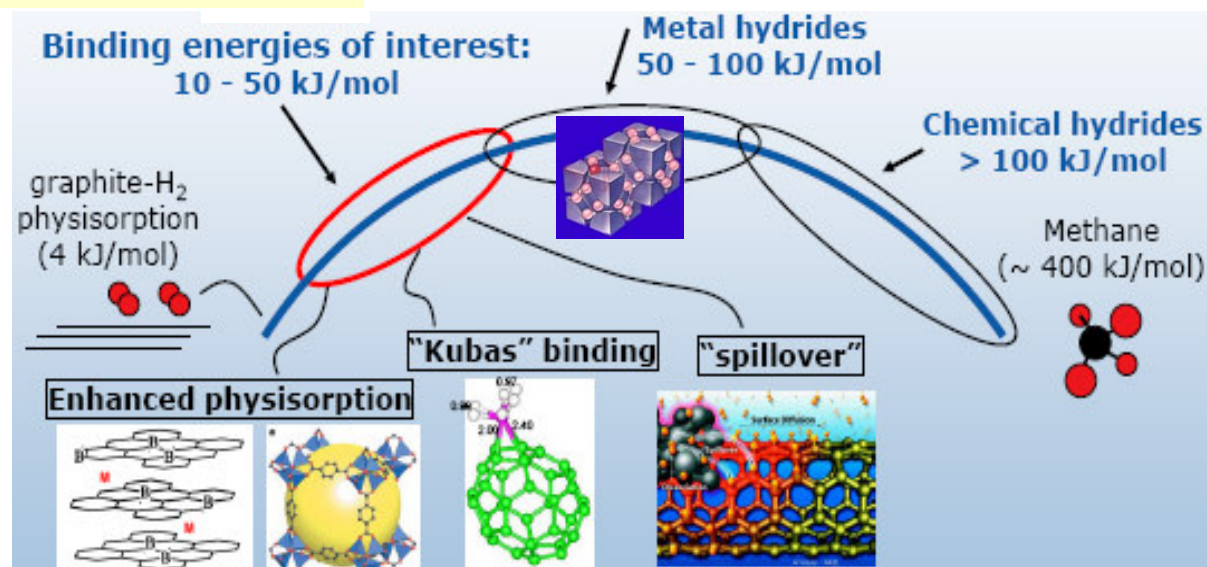




Continuum of Hydrogen Binding Energies

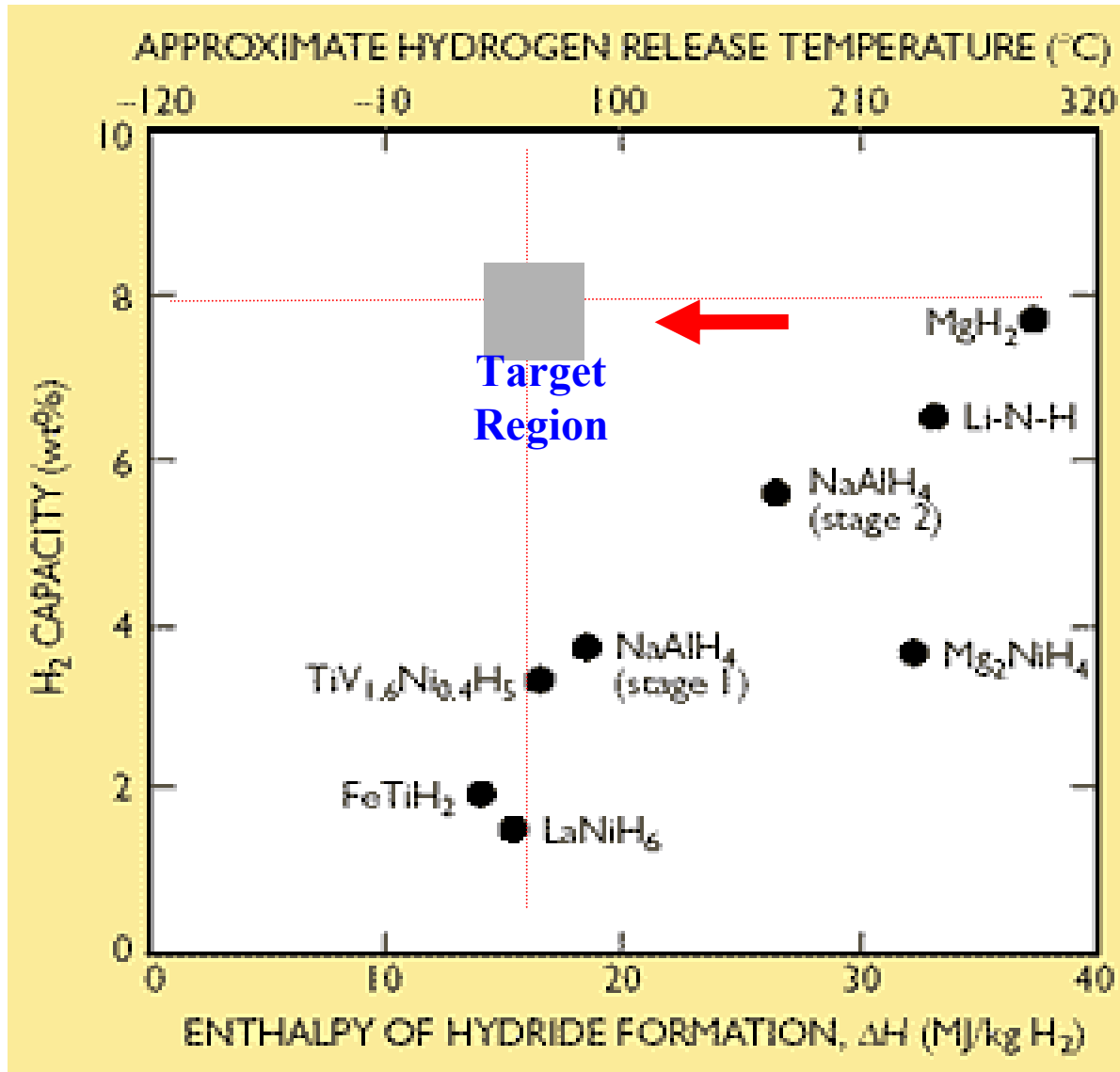
For reversible systems, equilibrium between gas and solid is given by:

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



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

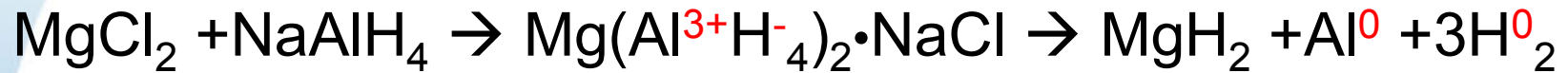
Issues with hydride storage



- Materials investigated do not meet goals
 - Lower enthalpy by destabilization
 - Use nano-catalysts to increase rates of H_2 release
 - MgH_2 nanocomposites with $LiAlH_4$

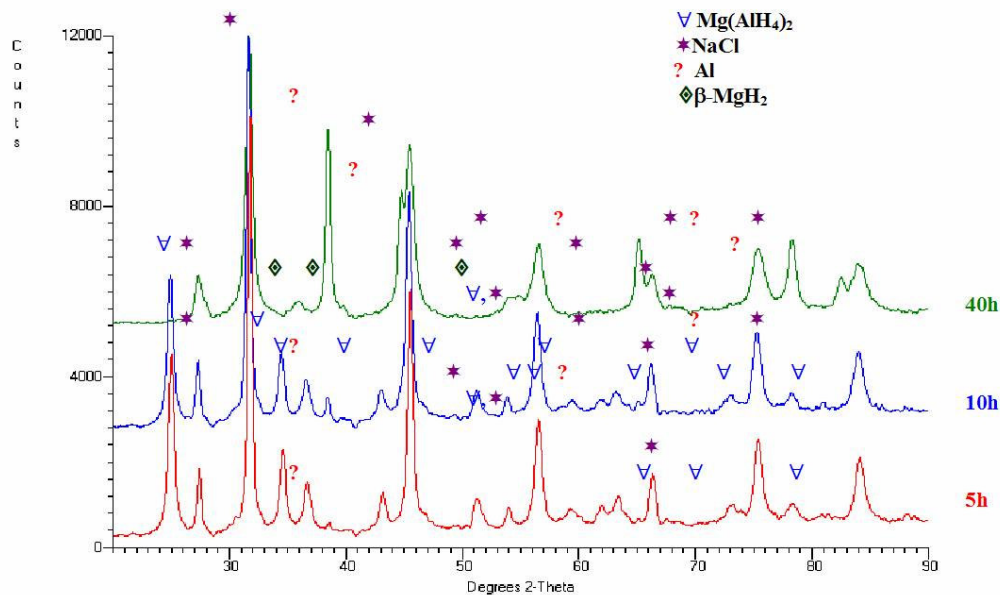


Mechanosynthesis of $\text{Mg}(\text{AlH}_4)_2$



1

2



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

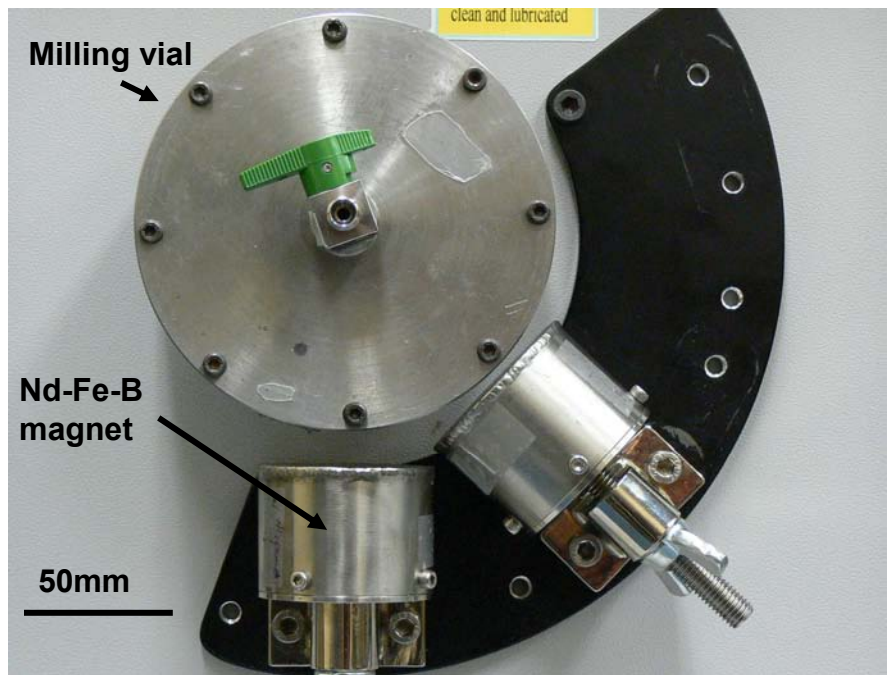
stage 1: **synthesis** via
metathesis reaction

Stage 2: **decomposition**
via redox
disproportionation



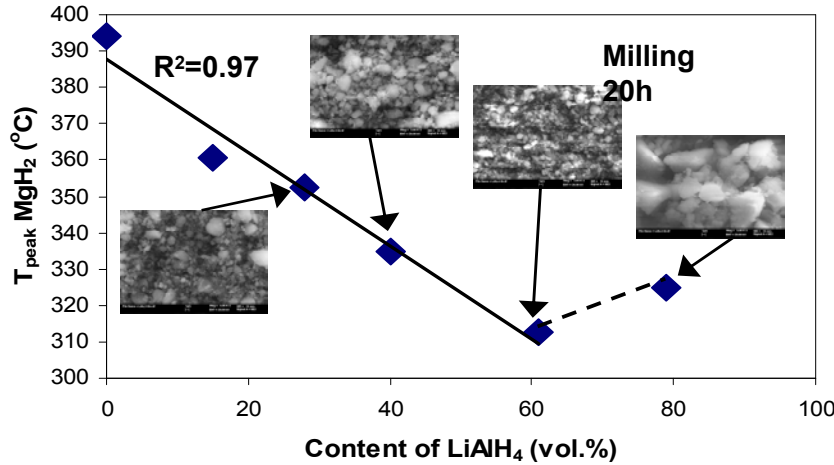
Hydrogen Ball Milling

- 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.

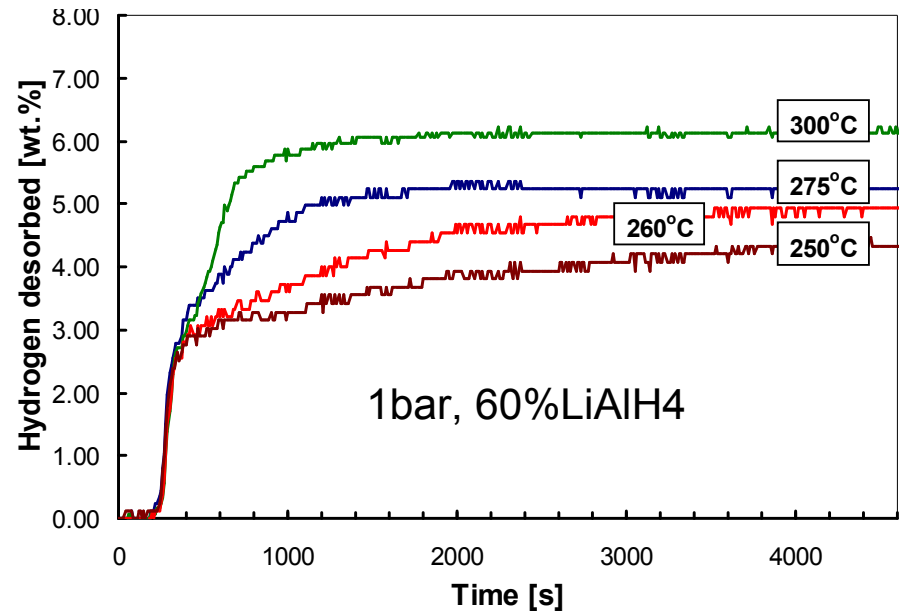




MgH₂/LiAlH₄ nanocomposite



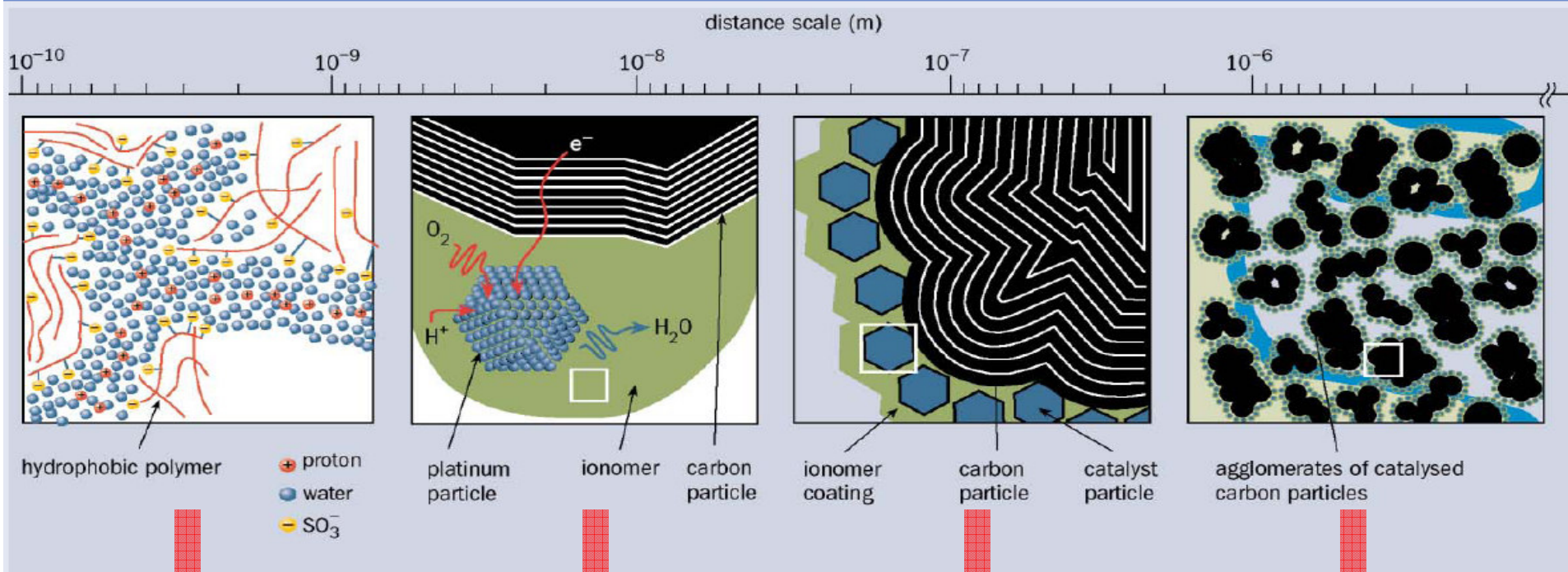
MgH₂ destabilization by chemical hydride





Challenges for Materials and Operation PEMFC

2 A problem of scales



Molecular scale, nanoscale

**proton conductors:
Higher Temperature**

**electrocatalysis:
Pt dissolution**

Mesoscale

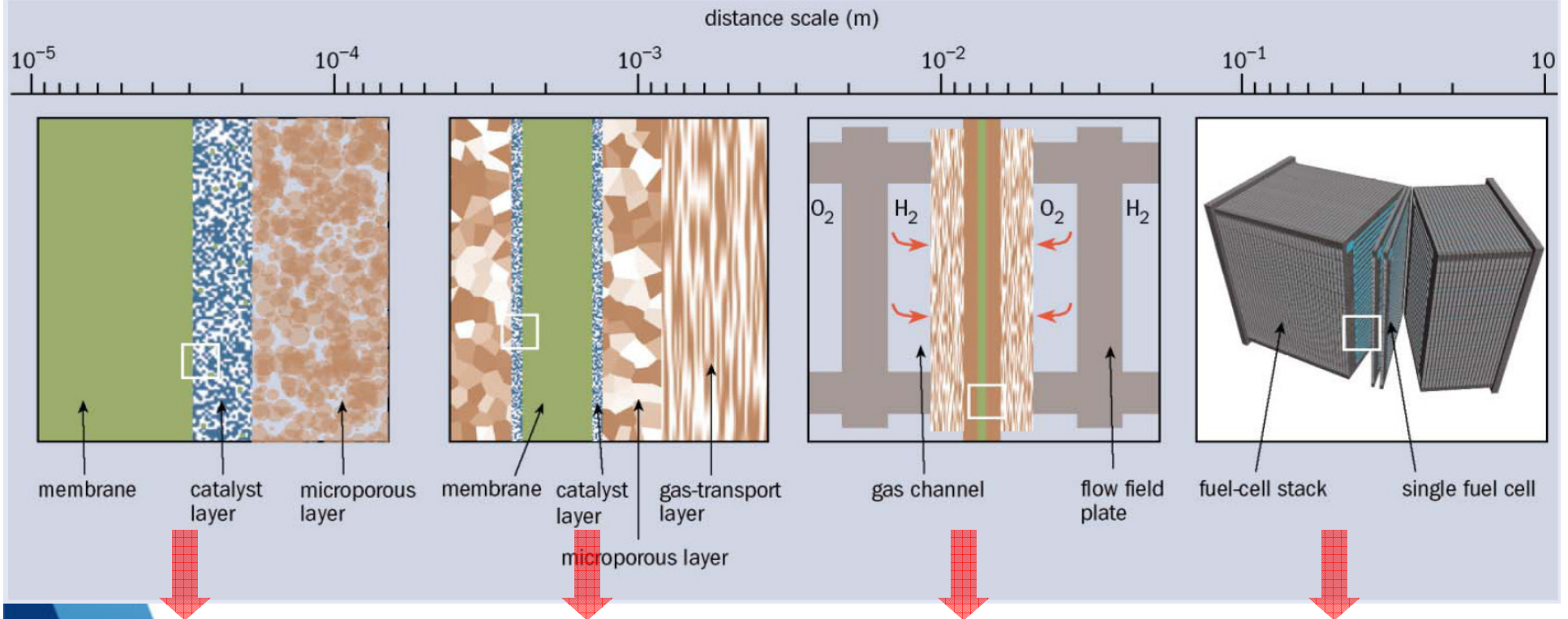
**Carbon support:
stability**

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

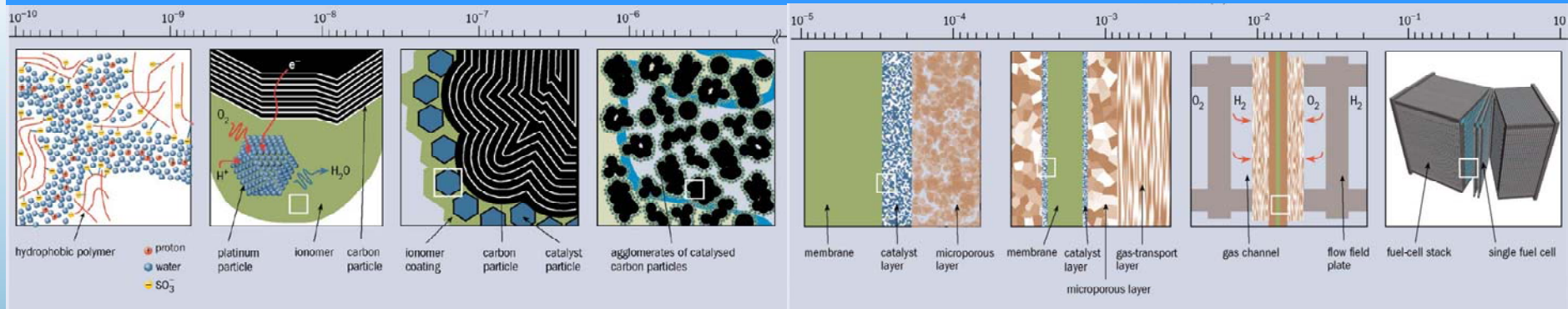
Carbon felt
stability

Water
management

Fuel: gasification
purification



Design Challenge: Multiple Scales



> 10 orders of magnitude,



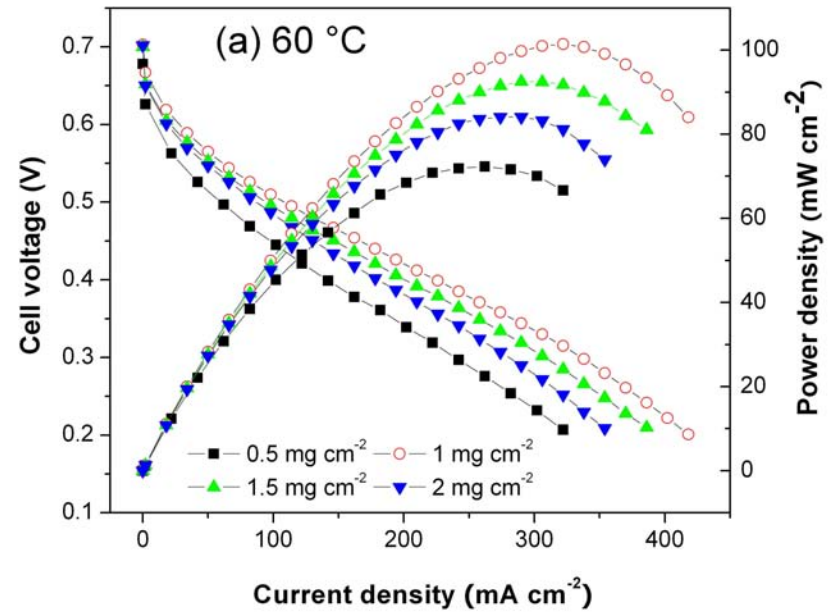
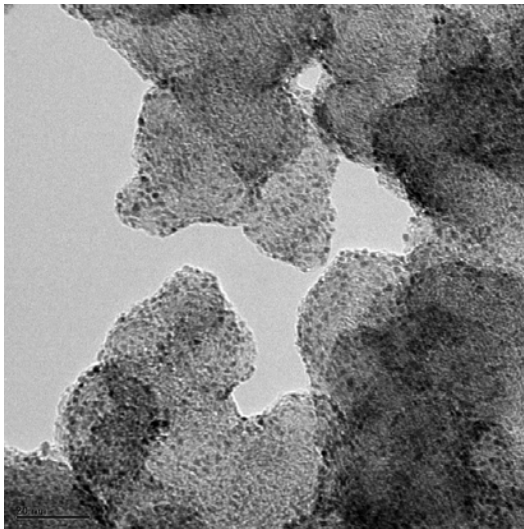
Multidisciplinary materials approach

- 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



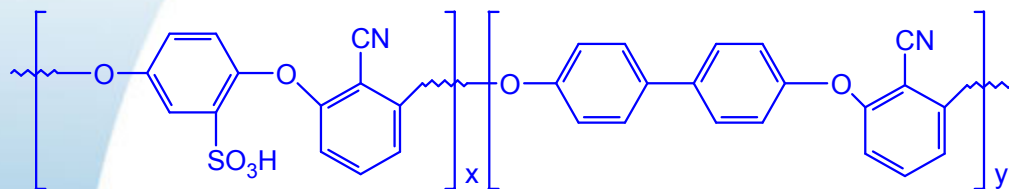
- Relative high performance for “low” noble metal catalyst loadings for DMFCs (<3mg cm⁻²)

Max. 100 mW cm⁻²,

- ~6 times less catalyst than reported

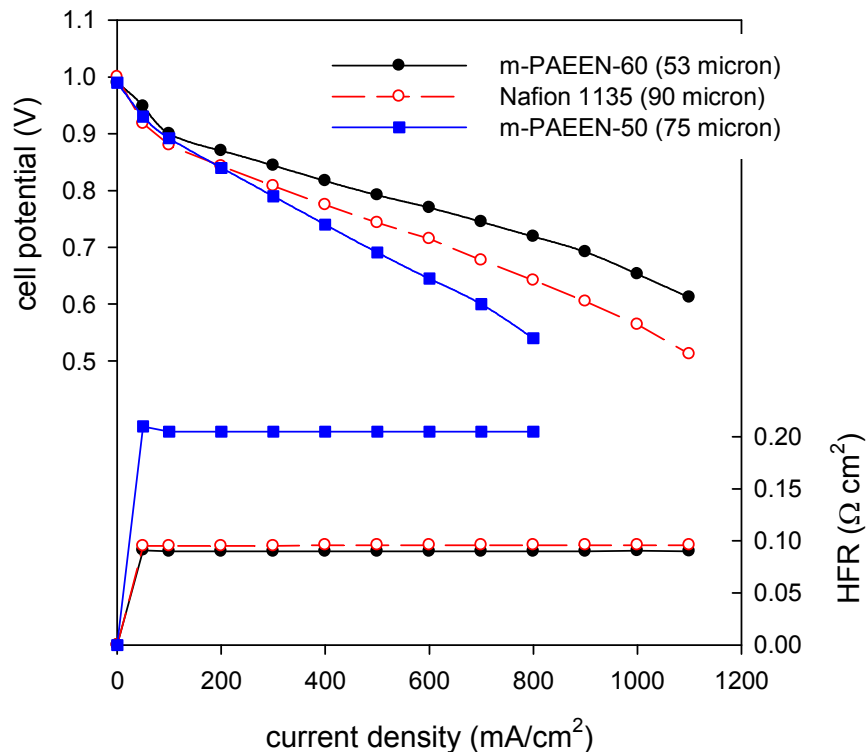
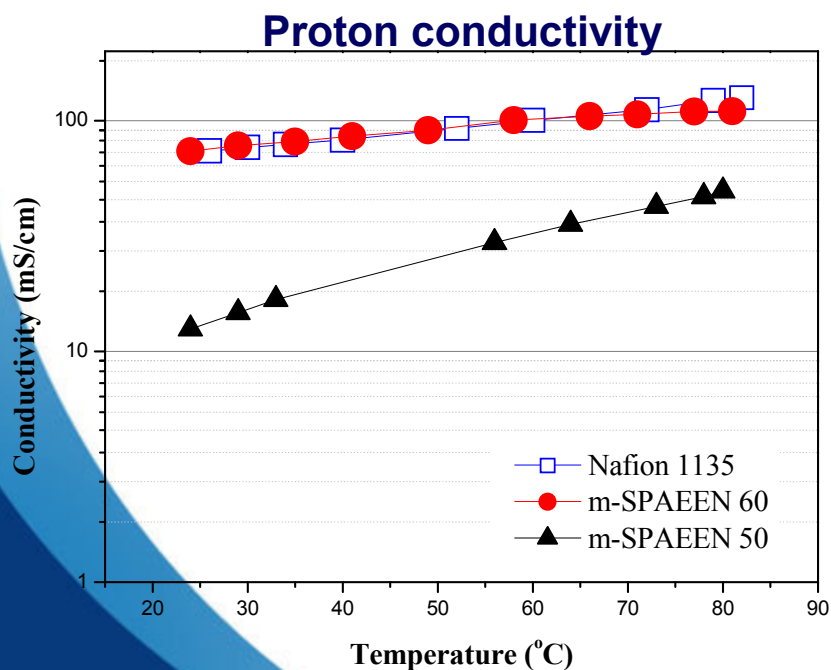


Polynitrile PEM Materials from Commercial Monomers



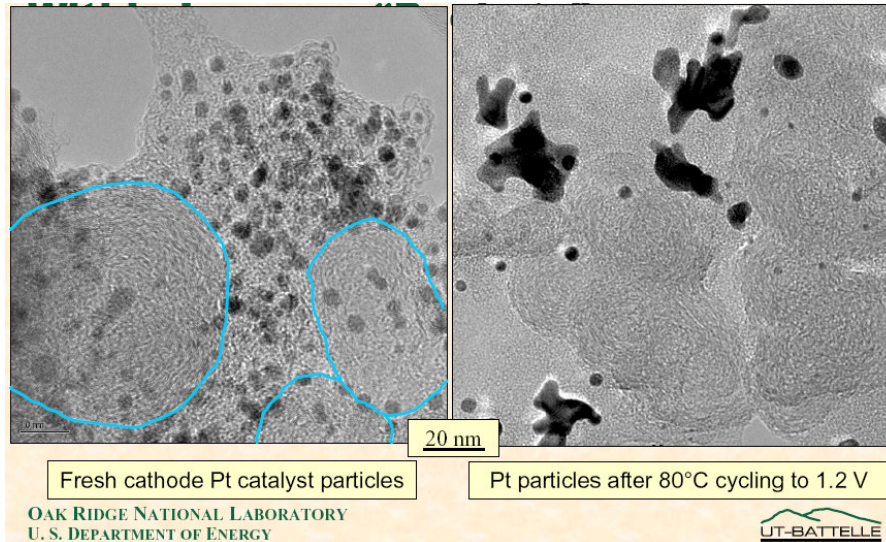
□ m-SPAEEN-60. ● Nafion. Swelling
 Swelling 17% @ 80°C 16-20% @ 80°C

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





PEMFC Cathode Degradation

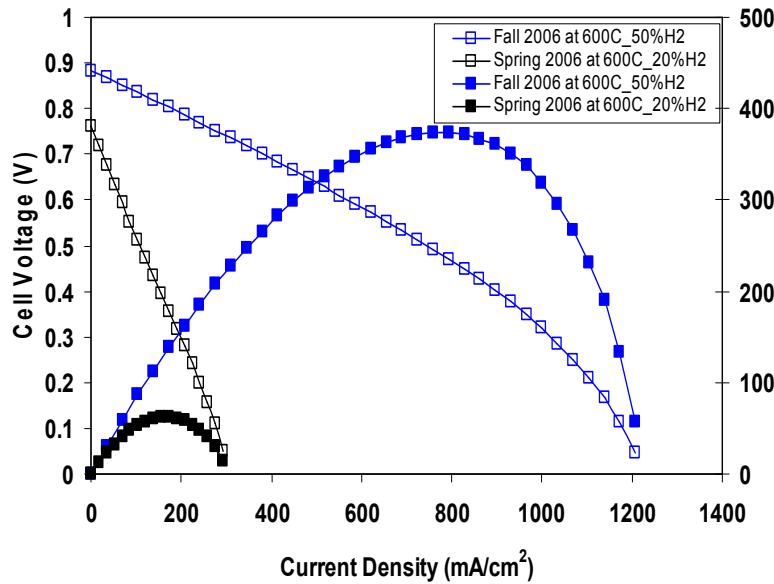


- High cathode voltage cycling causing Pt dissolution and recrystallization

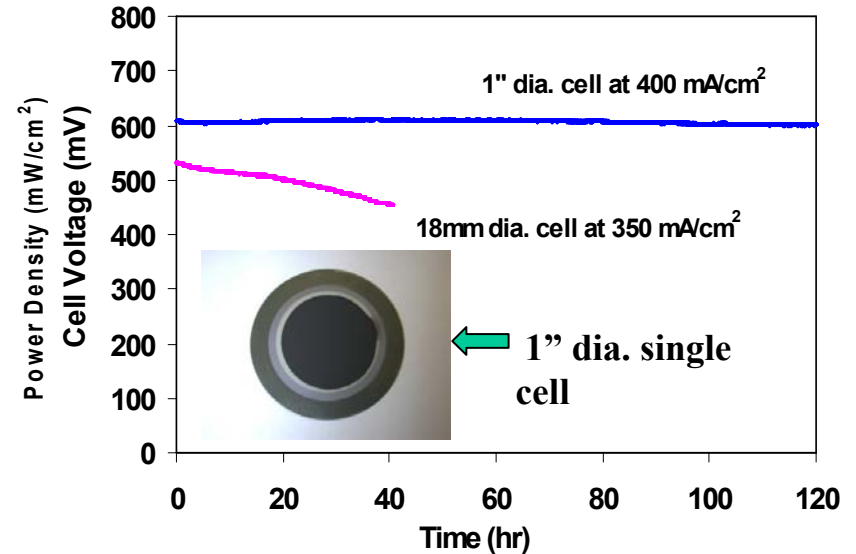


Reduced Temperature SOFC

- 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