Materials Issues for H₂ R&D in Canada

Defence R&D Canada Atlantic
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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

- Battlefield Awareness
- C\textsuperscript{4}ISR
- Directed Energy Weapons
- Active Protection
- LAV
- Relocatable Temp Camps
- Ships & Main Battle Tank

10\textsuperscript{0} Milliwatt
10\textsuperscript{1} Portable Battery Packs
10\textsuperscript{2} Soldier Systems
10\textsuperscript{3} Tactical Power
10\textsuperscript{4} UAV
10\textsuperscript{5} LAV
10\textsuperscript{6} Relocatable Temp Camps
10\textsuperscript{7} Ships & Main Battle Tank

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• 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

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

• **SOFCC 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

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Hydrogen Production Materials Issues

- Splitting $\text{H}_2\text{O}$
  - Solar electrolysis
  - Nano structured high surface
  - Band gap
  - Dye sensitized

- Electrolysis
  - Increased stability & durability of cathode in alkaline media
  - Increase energy density to 855 mA/cm² at 1.80 V and 70°C
Hydrogen Storage Today: Gas and Liquid
Hydrogen Storage Materials Issues

- 700 Bar Compressed $\text{H}_2$
  - Al carbon fibre reinforced – weight and cost issues – Dynetek
  - 1kg/L, 19,000 fill cycles

- Magnetic Refrigeration

- 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 Mg(AlH$_4$)$_2$

MgCl$_2$ + NaAlH$_4$ $\rightarrow$ Mg(Al$^{3+}$H$_4^-$)$_2$·NaCl $\rightarrow$ MgH$_2$ + Al$^0$ + 3H$_2^0$

1

2

Theoretical 9% except for salt*
Irreversable 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.
MgH$_2$/LiAlH$_4$ nanocomposite

MgH$_2$ destabilization by chemical hydride

R$^2$=0.97

![Graph showing the relationship between peak temperature of MgH$_2$ and content of LiAlH$_4$.]

1 bar, 60% LiAlH$_4$

![Graph showing hydrogen desorption over time at different temperatures.]
### Challenges for Materials and Operation of PEMFC

**2 A problem of scales**

<table>
<thead>
<tr>
<th>Distance Scale (m)</th>
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<td>$10^{-10}$</td>
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**Molecular scale, nanoscale**
- Proton conductors: Higher Temperature
- Electrocatalysis: Pt dissolution

**Mesoscale**
- Carbon support: stability

** Macroscale**
- Effective properties: Active surface area

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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

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

Proton conductivity

Swelling 17% @ 80°C  16-20% @ 80°C
• High cathode voltage cycling causing Pt dissolution and recrystallization
Reduced Temperature SOFC

- intermediate temperature metal supported SOFCs

![Graph showing cell voltage and power density vs. current density](image)

- metal supported cell of SSC//SDC/ScSZ//Ni-SDC//SS substrate (H$_2$ in Ar/air)

![Degradation graph](image)

- Degradation of metal supported cells of LSCF//GDC//Ni-SDC//SS substrate at 600 °C (H$_2$ in Ar/air)

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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