Recent Developments at the UD Center for Fuel Cell Research

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What is a Fuel Cell?

- A fuel cell combines fuel and oxidant electrochemically to produce electricity
- Two to three times more efficient than an internal combustion engine
- Fuel cell stack is quiet, has no moving parts, produces zero emissions
**Voltage** = 1.23 V

**Anode Reaction**

\[ 2H_2 \rightarrow 4H^+ + 4e^- \]

**Cathode Reaction**

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]
Fuel Cell Applications

Honda Clarity

Portable Power
- Recreational use (RV, boats, camping)
- Vehicle-based defense applications
- Soldier power

Toyota Mirai

Stationary Power
- Bloom energy
UD Center for Fuel Cell Research

• About 20 affiliated faculty in Mechanical Engineering, Chemical Engineering, Electrical Engineering, and Chemistry.

• Close proximity to DuPont, WL Gore, Ion Power, Bloom Energy, Air Liquide. Also close to Arkema, Johnson Matthey, BASF, Air Products.

• Research topics:
  • Polymer Electrolyte Membrane fuel cells (PEM) - automotive
  • Hydroxide Exchange Membrane (HEM) Fuel Cells
  • Direct Methanol Fuel Cells (DMFC) - portable electronics
  • Solid Oxide Fuel Cells (SOFC) - stationary power

• UD Fuel Cell Bus Program is a high-visibility demonstration project. A fleet of three buses and a hydrogen refueling station are in operation.
1. PEM fuel cells
2. Hydroxide exchange membrane fuel cells
3. DMFC
4. SOFC

Hydrogen storage

System-level

Batteries

Operational experience

Solar Hydrogen Generation
List of Current Projects

- **Catalysts and Membranes**
  - Mechanically-reinforced composite membranes
  - Self-healing membranes
  - Membranes with ceria/zirconia free-radical scavengers
  - Numerical investigation of membrane mechanics
  - Low-cost Tungsten-Carbide catalysts
  - Improved catalyst layer agglomerate model
  - Bidirectional optimization of Pt, Nafion, and carbon loading in the catalyst layer
  - Low-cost SPEEK and SPPSU membranes
  - Accelerated mechanical and chemical stress testing of membranes

- **Balance of Plant**
  - Cell voltage monitoring and diagnostics
  - Hydrogen recirculation ejector
  - Fuel cell manifolds
  - Freeze protection

- **Battery Studies**
  - Air-cooling of Li-ion batteries

- **Flow Field Design**
  - Numerical and experimental investigation of convective bypass
  - Flow field geometry optimization

- **Gas Diffusion Layer**
  - Ultra-low thickness metallic GDL

- **Hydrogen Production & Storage**
  - Solar fuels by thermochemical cycles
  - Metal hydride storage

- **System Level Analysis**
  - Fuel cell/battery hybrid vehicle simulation
  - Real-time data acquisition/user interface
  - Fuel Cell Bus operations analysis
  - Hydrogen refueling station operation and analysis
1. Freeze/Thaw Cycling of Nafion/MWCNT Membrane

Temperature vs. Time

- Temperature: 70 °C, 25 °C, -20 °C
- Time: 40 min, 90 min

One Cycle

Reinforced membrane has better tensile strength and durability.
Better dimensional stability delays delamination during freeze/thaw cycling.

Hydrogen Crossover

- Nafion 112
- MWCNT/Nafion

Delamination at membrane/electrode interface

- Reinforced membrane has better tensile strength and durability
- Better dimensional stability delays delamination during freeze/thaw cycling.
2. Self-Healing Membranes for PEM Fuel Cells

Pinholes in used membrane imaged by SEM/FIB

Pinholes interacting with microcapsules carrying self-healing agent

Fuel cell performance at 70° C and 100% RH with H2 and O2

Durability test at OCV and 90° C with RH cycling

Microcapsules by in-situ polymerization of urea and formaldehyde by stirring Nafion polymer dispersion in tributyl phosphate

FIB cross-section of microcapsule showing hollow structure
3. Ceria Migration in PEM Membrane Electrode Assemblies

Cerium improves PEM durability by neutralizing free radicals, but Cerium migrates in the MEA!

- Dry operation and wet/dry cycling moves cerium from the PEM to the CLs
- Cerium concentration in the PEM and/or CL will diminish ionic conductivity
- Cerium depletion will reduce local radical scavenging efficacy

Fatigue Crack Characterization

Experimental Results (Lai, et al. 2009)

Numerical in-situ model Results

(a) Nafion® NR111
(b) Nafion® NR111
(d) Gore-Select® 57
(e) Gore-Select® 57

non-reinforced

reinforced
### UD Fuel Cell Hybrid Bus Program (2005-present)

<table>
<thead>
<tr>
<th>Bus #</th>
<th>Size</th>
<th>Stack</th>
<th>Batteries</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22-ft</td>
<td>20 kW</td>
<td>Ni-Cad</td>
<td>2007</td>
</tr>
<tr>
<td>2</td>
<td>22-ft</td>
<td>40 kW</td>
<td>Ni-Cad</td>
<td>2009</td>
</tr>
<tr>
<td>3</td>
<td>40-ft</td>
<td>60 kW</td>
<td>Li-Ti</td>
<td>2015</td>
</tr>
</tbody>
</table>

- Bus maintenance building at STAR campus

- H2 Refueling station at Air Liquide
Matlab/Simulink simulator for fuel cell hybrid vehicles

- Simulation tools are a cost-effective way to model the design and performance optimization of power systems before committing to hardware implementation.
- Our simulator is a drive cycle-based, forward-facing model. Drive cycle-based means that the simulation is “driven” entirely by an input drive cycle.
- The simulator has been validated by on-board vehicle measurements and is now a reliable design tool.
A robust and low-cost CVM system employing a single isolated ADC and relays to multiplex signals with low pass filtering to reduce electrical noise.

Cell voltage monitoring is an important diagnostic tool for fuel cell stacks and battery systems:

- Patterns in cell voltage vs. cell number
- Patterns in cell voltages as reactant flows change
- Patterns in cell voltages as stack current changes
Variable-area Ejector for Hydrogen Recirculation

- Employs a stepper motor-lead screw based linear actuator for ease of control.
- Simple PI pressure feedback control system on a custom-designed circuit board.
- Working well on both UD fuel cell buses and a patent application has been filed.

Customers: Toyota, Nissan, VW, Intelligent Energy, Bosch, Tata Motors
Solar Hydrogen from Thermochemical Cycles

Net inputs: sunlight, water

Net outputs: \( \text{H}_2, \text{O}_2 \)
1. Water-Cooled Quartz Window
2. Water-Cooled Aperture
3. Data Acquisition Ports
4. Pure Alumina Reaction Tiles
5. Solids Outlet
6. High Temperature Insulation
7. Gas Outlet
Hydrolysis Step: Quartz Tube Furnace

Constant T: Max efficiency = 28.5%
Temp gradient: Max efficiency = 33.8%
1. Component materials- membranes, catalysts, GDL, flow fields
2. Durability studies of reinforced membranes
3. Demonstration projects: UD Fuel Cell Bus Program
4. Matlab/Simulink studies of fuel cell hybrid systems
5. Balance-of-plant improvements
6. Hydrogen storage
7. Solar hydrogen from thermochemical cycles
H2 storage systems employing solid-state materials

Effect of pitch

- Mass of H2 stored per unit volume of tank (g/cm³)
- Non-dimensional pitch
- Effect of heat transfer coefficient

- Convection heat transfer coefficient $h$ (W/m²-K)
- 0% Al foam
- 10% Al foam

3 min charge

Contours of H2 storage

2. Composite Membrane Based On SiO₂/MWCNTs

- CNTs can increase electronic conductivity in the through-plane direction.
- SiO₂ coating on CNT can insulate CNTs so higher loadings of CNTs can be applied.
- Also, SiO₂ absorbs water which can be released under dry operating conditions.

Electrical resistance of membranes

![Graph showing electrical resistance of membranes]
• Materials: membranes, catalysts, GDL, cell architecture
• Operating protocols and strategies: cell temperature, reactant stream flow rates, and humidity
• Performance and durability testing
• Accelerated stress testing: wet/dry cycling; freeze/thaw cycling; characterize degradation and failure modes
The future?

Solar simulator at PSI, Zurich

Power-Tower and Heliostat Field

www.brightsourceenergy.com