Hawaii Energy and Environmental Technologies Initiative

Presented to ONR Undersea Energy & Propulsion Workshop
March 29, 2012
Fuel Cell Systems

Objective: Develop proton exchange membrane fuel cell energy systems for use in harsh environments
- Unmanned undersea vehicles (O₂ recirculation in closed environment)
- Ground or air operation in presence of contaminants

Activities
- Characterization of contaminant impacts
- Stack testing for UUV and UAV use
- Dynamic performance of fuel cells and fuel cell systems
- Control of battery-fuel cell hybrid systems
Past Year Accomplishments

• Completed characterization of 5 kW fuel cell stack supporting NRL UUV system components design
• Designed and implemented a compact, custom made tool for the impedance measurement of fuel cell stacks and battery packs
• Designed and tested system controller optimizing energy management for fuel cell-battery hybrid power systems
• Continued contaminant studies including establishing new diagnostic capabilities
Hawaii Fuel Cell Test Facility

- Performance and durability testing of single cells and fuel cell stacks from 15 W to 5 kW
- Wide range of oxidant and fuel streams composition including contaminant injection
- High resolution diagnostic tools for reactant stream composition and flow analysis
- High speed hardware-in-the-loop (HiL) test station to characterize fuel cell and system response
- Fuel cell stack and battery pack performance monitoring with custom designed impedance spectroscopy analyzer
- Ex-situ analysis capability for contaminant studies (new)
New Fuel Cell and Materials Diagnostic Capabilities

- Prior work on contamination focused on the effects of fuel and air contaminants based on fuel cell performance and diagnostics of gas composition.
- Established complementary ex-situ measurements of materials properties to assist interpretation of contaminant effects:
  - Rotating ring/disc electrode (RRDE) for the catalyst
  - Conductivity cell for the membrane
- Acquired an in-situ measurement tracer system to assess commercially relevant issues:
  - Scavenging effect of liquid water on contaminants
  - Reactant flow uniformity in flow field channels (energy efficiency maximization)
  - Intrusion of gas diffusion media into flow field channels (reactant flow blockage)
NRL Hydranox UUV Program Support

• HNEI/GM/NRL team developed stack testing protocols simulating NRL system operation to evaluate performance variability
• Fuel cell performance analyzed at oxygen partial pressures, relative humidities and temperatures relevant to UUV propulsion system design range
• Conducted detailed stack water balances to support design of balance of plant components
• Conducted tests with pure oxygen operation to provide performance data and support oxygen safety risk/reward assessments
• Test results reported to NRL.
New Diagnostic Tool for Fuel Cell Stacks and Battery Packs

- Impedance spectroscopy provides detailed mechanistic information on fuel cell performance losses because measurements are performed over a wide range of frequencies.
- Designed and tested a compact impedance spectroscopy analyzer (ISA) for in-situ testing of fuel cell stacks and battery packs:
  - ISA only 8 inches wide, 5 inches high, 4 inches deep
  - 0.05 Hz to 50 kHz frequency range
  - Simultaneous measurements for 36 channels upgradable to 96 channels

Figure shows changes in both ohmic and kinetic resistances for cell 27 (of a 36 cell stack). Voltage scan only indicates loss of performance. Scan taken at 0.2 A/cm², 55 °C, H₂ in dead end mode with intermittent purging, air at ~2.5 stoichiometry and ~75% relative humidity.
ISA applicable to Battery Pack Energy Management

- Demonstrated use of the compact impedance spectroscopy analyzer to characterize battery health at different state of charges
- Analyzer will be used to investigate impact of alternative battery management strategies on battery life and energy supply

Figures below show variability of cell performance in a 4-cell battery pack. Variations attributed to manufacturing tolerances
New UAV Hybrid System Controller

• Designed and tested a new controller to optimize energy management in fuel cell/battery hybrid systems
  – “Zero volt diodes” minimize power switching losses (patent application being prepared)
  – Optimized battery-fuel cell hybrid allows high power bursts for short durations with minimal loss of mission duration enabling use of a high resolution camera or other energy intensive payload
  – Longer FC system life expected owing to a 33 % decrease in fuel cell power range, controlled cycling, and better control at low power levels
Future Activities

• Characterize the effect of contaminant accumulation in gas recirculation loops for different UUV relevant configurations
  – Contaminants to include those introduced from reactant gases or released from system materials (e.g. seals, gaskets, lines)
  – Coordinate in-situ gas analysis and ex-situ studies to facilitate better understanding of contamination mechanisms

• Coordinate laboratory studies with pending operation of fuel cell buses in Hawaii Volcanoes National Park to assess effectiveness of contaminant mitigation measures and demonstrate practical solutions for operation of fuel cells in very harsh environments

• Complete and analyze long duration fuel cell-battery hybrid system tests under dynamic conditions (duty cycle) for UAV applications to address leading system degradation mechanisms

• Support NRL fuel cell systems testing as requested
Energy From Seafloor Methane Hydrates

- **Motivation:** Potential future energy resource; fuel for subsea power systems.

- **Project objectives:** understand the mechanisms of hydrate formation and dissociation in seafloor sediments to guide development of methane recovery.

- **Past accomplishments:** quantified the effectiveness of conventional reagents used by industry to dissolve methane hydrates; assessed feasibility of seafloor power generation from methane hydrate outcropping and methane seeps.

- **Current research activities:** experimental investigations of hydrate stability and kinetics in sand matrices and investigation of hydrate dissociation using non-conventional reagents.
Methane Hydrates - Potential Future Energy Resource and Fuel for Undersea Power Systems

• Project objective: understand the mechanisms of hydrate formation and dissociation in seafloor sediments to guide development of methane recovery

• Past accomplishments
  – Quantified the effectiveness of conventional reagents used by industry to dissolve methane hydrates
  – Assessed feasibility of seafloor power generation from methane hydrate outcropping and methane seeps

• Current research activities
  – Experimental investigations of hydrate stability and kinetics in sand matrices and investigation of hydrate dissociation using non-conventional reagents

<table>
<thead>
<tr>
<th>Inhibitor Used</th>
<th>Moles Hydrate Decomposed/Moles</th>
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<tbody>
<tr>
<td>Ethylene Glycol</td>
<td>1.00</td>
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<tr>
<td>Methanol</td>
<td>0.80</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.60</td>
</tr>
<tr>
<td>2-Propanol</td>
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</table>

Effectiveness of various reagents to decompose methane hydrates

Burning methane hydrate
Hydrates for H\textsubscript{2} Storage and Transport

- Hydrates may have potential as a medium to store and transport hydrogen fuel for certain applications.
- Pure H\textsubscript{2} hydrates require either extremely high pressures or low temperatures.
- “Semi-clathrate” hydrates where H\textsubscript{2} shares cavities in the water crystal with other molecules may be an option for practicable storage at modest pressures.

<table>
<thead>
<tr>
<th>Hydrate</th>
<th>Formation temperature [K]</th>
<th>Formation pressure [psi]</th>
<th>wt% H\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure H\textsubscript{2}</td>
<td>273</td>
<td>29,000</td>
<td>5</td>
</tr>
<tr>
<td>H\textsubscript{2}+TBAF</td>
<td>298</td>
<td>410</td>
<td>1.5</td>
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<tr>
<td>H\textsubscript{2}+THF</td>
<td>280</td>
<td>870</td>
<td>0.43</td>
</tr>
<tr>
<td>H\textsubscript{2}+TBAB</td>
<td>279</td>
<td>2000</td>
<td>2</td>
</tr>
</tbody>
</table>

Comparison of properties of H\textsubscript{2} hydrates; THF = tetrahydrofuran; TBAB = tetra-\textit{n}-butyl ammonium bromide; TBAF = tetra-\textit{n}-butyl ammonium fluoride

Project objectives:
Explore the use of different reagents, formation protocols, and matrices (e.g., porous ceramics) to identify best candidate semi-clathrates for H\textsubscript{2} storage.
Hydrate Dissociation & Methane Recovery
Recent Results: Unconventional Reagents

Calorimeter thermograms (heat flow vs. T) comparing performance of 5.5 mol% solutions of different hydrate inhibitors. The light blue trace is for water with no added inhibitor. The first endothermic (downward) peak corresponds to melting of the ice phase; the second (between 0 and 10 deg. C) to hydrate dissociation. No hydrate forms in the presence of ferric chloride, FeCl₃ (dark blue).
**Hydrate H₂ Storage**

**Status:** Testing different hydrate formation protocols with the calorimeters to optimize storage characteristics of semi-clathrate hydrates (i.e., maximize H₂ storage capacity & storage temperature; reduce storage pressure)

**Future:** Select best candidate protocols, scale-up (from ~1 g hydrate to >500 g), and quantify H₂ storage capacity.

Calorimeter thermogram showing heat flow (blue) and sample temperature (red) vs. time for 1 g 40% solution of TBAB in water. The exothermic peak at ~8°C corresponds to decomposition of the H₂ semi-clathrate hydrate. The area under the peak can be related to the amount of hydrate.

H₂ hydrate synthesis scale-up facility
Fuel Processing- Vortex Plasma Reformer

- Project objective: support use of logistical fuels for fuel cell power generation
- Past accomplishments
  - Built and tested experimental vortex flow, non-thermal plasma reforming system capable of producing H₂ rich gas and operating at moderate temperatures (~300 °C)
  - Optimized system performance using methane as fuel and established experimental methods to characterize system performance (H₂ yield and selectivity, fuel conversion, efficiency, specific energy ratio)
- Current research activities
  - Modify fuel delivery system and product recovery/conditioning system to permit evaluation of liquid logistic fuels
  - Conduct experiments using dodecane as model compound
Current Activities

– Modify fuel delivery system and product recovery/conditioning system to permit evaluation of liquid logistic fuels (completed)
– Shakedown testing using dodecane as model compound for diesel (currently underway)
  – analysis of permanent gas species
  – recovery of condensable fraction and analysis for dodecane and breakdown products via GC/MS & FID
– Conduct parametric testing of system to establish operating range
– Optimize operating conditions using dodecane, compare results with F76
  – Performance parameters: H₂ yield & selectivity, efficiency, specific energy ratio, fuel conversion, etc.