Solid Oxide Fuel Cells in Unmanned Undersea Vehicle Applications

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Mission Statement

The Naval Undersea Warfare Center is the United States Navy's full-spectrum research, development, test and evaluation, engineering, and fleet support center for submarines, autonomous underwater systems, and offensive and defensive weapon systems associated with Undersea Warfare. (SECNAVINST)

A Navy Core Equity – A National Asset
“Swimlanes”- Fuel Cell Programs

CRANE
- Aerospace packaging and construction
- Air breathing
- Man-Portable Power
- Expeditionary Power
- Team w/ NUWC on air independent applications

NEWPORT
- Aerospace packaging and construction
- Air independent
- Specialty fuels
- Seawater activated
- $O_2$ and $H_2$ sources
- Team w/ NSWCCD on Logistic Fuels

CARDEROCK
- Heavy duty packaging and construction
- Shore / Reformer Power
- Predominately air breathing for ships
- Submarine power application in the future
- Team w/ NUWC on air independent applications

Average Power (KW)
- <<100 kW
- >>100 kW
Autonomous Undersea Vehicles
Ragone Plot

Challenges to meeting UUV power requirements include:

- Air-independent operation
- Refuelability
- Multi-mission capability
- Stealth
- Safety
- Environmentally benign
- Endurance (high energy density)
- Weight/volume constraints
- Buoyancy
- Start-up

Existing Commercial Sector and Conventional Energy Sources will **NOT** meet the Navy UUV Future Requirements

* David Linden Handbook of Batteries, 2nd ed, 1995
Why SOFCs for UUVs?

• Fuel Flexibility
  - Pure H₂ not required for operation
  - Hydrocarbon fuels (diesel-type) can be utilized & rapidly refueled
  - Internal reforming of light hydrocarbons within fuel cell stack
  - Tolerates impurities such as carbon monoxide and sulfur (ppm level)

• High Efficiency, 55-65%
  (based on LHV of fuel conversion to electricity)

• Noble metal catalysts not required for electrodes
  and fast reaction kinetics at electrodes

• Combined heat and power (CHP) - heat utilized for reforming
### PEM System, Reactants ONLY

<table>
<thead>
<tr>
<th>Material</th>
<th>kg</th>
<th>L</th>
<th>2015 capability?</th>
</tr>
</thead>
<tbody>
<tr>
<td>9wt% H₂</td>
<td>10</td>
<td>15</td>
<td>1300 W-hr/L</td>
</tr>
<tr>
<td>LOX</td>
<td>7.2</td>
<td>8</td>
<td>1750 W-hr/kg</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>kg</th>
<th>L</th>
<th>Current capability</th>
</tr>
</thead>
<tbody>
<tr>
<td>4wt% H₂</td>
<td>10</td>
<td>15</td>
<td>720 W-hr/L</td>
</tr>
<tr>
<td>LOX</td>
<td>3.2</td>
<td>3.6</td>
<td>1010 W-hr/kg</td>
</tr>
</tbody>
</table>
## SOFC System, Reactants ONLY

<table>
<thead>
<tr>
<th>Material</th>
<th>kg</th>
<th>L</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-8</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>LOX</td>
<td>26</td>
<td>29</td>
</tr>
<tr>
<td>CO$_2$ Sorbent</td>
<td>64</td>
<td>80</td>
</tr>
</tbody>
</table>

### Current Capability
- 1070 W-hr/L
- 1300 W-hr/kg

Sorbent w/ ~50% mass gain,
# Broad Fuel Comparisons

## Energy Content (LHV)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Flashpoint, °C</th>
<th>MP, °C</th>
<th>MJ/L</th>
<th>MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>12</td>
<td>-98</td>
<td>15-18</td>
<td>19-22</td>
</tr>
<tr>
<td>Ethanol</td>
<td>13</td>
<td>-114</td>
<td>18</td>
<td>23</td>
</tr>
<tr>
<td>Gasoline</td>
<td>-7.2</td>
<td>-58 (aviation)</td>
<td>31-34</td>
<td>42-46</td>
</tr>
<tr>
<td><strong>Diesel</strong></td>
<td><strong>40-50</strong></td>
<td><strong>-20 to 5 (cloud)</strong></td>
<td>~36-40</td>
<td><strong>42-47</strong></td>
</tr>
<tr>
<td>Liquid H₂ (no tank)</td>
<td></td>
<td>-252 (BP)</td>
<td>8</td>
<td>121</td>
</tr>
<tr>
<td>LNG (no tank)</td>
<td></td>
<td>-164(BP)</td>
<td>21</td>
<td>51</td>
</tr>
<tr>
<td><strong>2015 H₂ Storage Goal (9wt% systems basis)</strong></td>
<td></td>
<td></td>
<td>10-15</td>
<td>10</td>
</tr>
<tr>
<td>Glycerin</td>
<td>176</td>
<td>~ 17</td>
<td>22</td>
<td>18</td>
</tr>
<tr>
<td>Coal</td>
<td></td>
<td></td>
<td>13-25</td>
<td>15-30</td>
</tr>
</tbody>
</table>
## Appropriate Fuel Selection

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Sulfur? Aromatics?</th>
<th>Flash &amp; Cloud Pt.</th>
<th>Energy Density, MJ/L</th>
<th>Shelf life</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT-diesel (S-8)</td>
<td>&lt; 5 ppm &lt; 1%</td>
<td>40 - 50°C, -47°C</td>
<td>~37</td>
<td>8 yrs *</td>
</tr>
<tr>
<td>JP-8</td>
<td>~ 500 ppm ~ 20%</td>
<td>&gt; 38°C, -47°C</td>
<td>34</td>
<td>1 yr</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>~ 10 ppm ~ none</td>
<td>&gt; 130°C, ~ 0°C</td>
<td>33</td>
<td>6 months</td>
</tr>
<tr>
<td>Diesel</td>
<td>10-500 ppm 10-25%</td>
<td>40 - 50°C, -20 - 5°C</td>
<td>35-40</td>
<td>2 yrs Max</td>
</tr>
</tbody>
</table>

Fuel Processing (Reformers)

Catalytic Partial Oxidation (CPOX)

\[ C_m H_n + \frac{m}{2} O_2 \rightarrow \frac{n}{2} H_2 + mCO + \text{heat} \]

- Exothermic reaction - no additional heating required for heating inlet
- Fast kinetics - reformer starts and achieves operating temperature quickly
- **Air-dependent** operation; further studies needed to consider pure O\textsubscript{2} feed

Steam Reforming

\[ C_m H_n + mH_2O + \text{heat} \rightarrow (m+n/2) H_2 + mCO \]

- Endothermic reaction - requires heat for reaction and fuel/water evaporation
  - Heat is supplied from fuel cell exhaust gases and CO\textsubscript{2} scrubber
  - Steam can be supplied by SOFC product gases (anode recycle)
- More hydrogen produced per mole of fuel than in CPOX
  - **Air-independent operation & 15\% reduction in O\textsubscript{2} consumption vs. combustion**
Proposed System Design with Anode Recycle

- Fuel
- Water (for start-up only)

Steam Reformer

Heat to Reformer

CO2 Scrubber

Scrubber Cooler

Recycle Stream

Condenser

Cooled Exhaust

Water Recovery

Cathode

Cathode Cooler

Oxygen Utilization ~100% for this application!
SECA Coal Based Systems

Air → Air Separation → Gasifier → Gas Cleaning → Solvent CO₂ Separation → SOFC → Heat Recovery e.g., Turbine

Coal → CO₂, CO, H₂, H₂O

O₂ → H₂O

Marketable Ash/Slag By-product

Sulfur Recovery → Marketable Sulfur By-product

Sequestration

Enhanced Oil Recovery

Unminable Coal Bed

Depotted Oil & Gas Reservoirs

Deep Sulfate Aquifer

-Graphic courtesy of NETL, SECA Workshop 2007
Basis for SECA Collaboration with NUWCDIVNPT

NUWCDIVNPT serves as honest broker for stack and related-component evaluation as well as testing under unique operating conditions (i.e. pure oxygen).

Although SECA has a coal-based central generation focus, spin-off applications are encouraged. Testing under the demanding UUV conditions provides valuable insight into performance entitlement of current SOFC technology.

Niche military applications like UUVs can pave the way for commercial applications. Cost and operational lifetime not necessarily major concerns for military applications, as long as new technical capability can be delivered (reliably and safely).
Recent Stack Testing at NUWC DIVNPT

Delphi Stack, 10-cell

Delphi Stack, 30-cell
Pure Oxygen vs. Air

Polarization Curves For 10-Cell Delphi Stack
24 July 2007, NUWCDIVNPT
Cathode Air vs Cathode Pure O2
Anode Gas: 4.25 sLPM H₂, 3.5 sLPM N₂, w/ 3% H₂O

10% Power Gain
July 2007, Voltage versus time (at constant load) for Delphi 10-cell stack. Anode Feed: 6.91 sLPM H₂, 0.3 sLPM CH₄, 0.44 g/min S-8, and 2.9 g/min Steam

Steady-State, 100-hour Run

22% Utilization Reformate & ~20% Utilization Pure O₂
0.3 mA/cm²
Stoichiometric Oxygen Control

Comparison of IV plots shows that stoichiometric oxygen control has negligible effect on operating voltage.
IV-Plot with Reformate and Stoichiometric Oxygen

Polarization for Delphi Stack Test, 11-07-2007
Reformer Input - 6.91 SLPM H₂, 0.30 SLPM CH₄, 0.44 g/min. S-8 Fuel, w/ 3.0 g/min. Steam
Cathode Input - Stoichiometric O₂

Stack Voltage (V) vs. Current Density (mA/cm²)
Power Density (mW/cm²) vs. Oxygen Utilization, %

Voltage
Power Density
O₂ Util
Steady state operation at 50 amps for eight hours using S-8 reformate and stoichiometric oxygen feed to the stack. At 50 amps, the single-pass fuel utilization was 35% and the oxygen utilization was 95%.
InnovaTek Steam Reformer

ONR STTR Deliverable:

-A compact, fully integrated steam reformer that operates on hydrocarbon fuels and a design concept for an integrated hot zone.

-Diesel-type fuels are converted to hydrogen and methane-rich reformate gas streams

\[ C_m H_n + m H_2 O(g) + \text{heat} \rightarrow (m+n/2) H_2 + m CO \]
Steam Reformer provided by InnovaTek

Reformer Inlet Streams for Delphi Test:
- Gas stream: 6.93 L/min H₂, 0.33 L/min CO, 3.09 g/min steam
- Liquid stream: 0.45 g/min S-8 fuel from Syntroleum

600 °C
~ 1 atm

Reformer Outlet Stream for Delphi Test:
- Dry Flow: 8.7 L/min (87.4% H₂, 3.4% CO₂, 3.9% CO, 5.3% CH₄)
- ~2.6 mL/min water
- S/C ~ 2.8
Anode Gas Recycle Blower

Blower Attributes:

- Inlet T = 600-850º C
- Inlet P is atmospheric
- $\Delta P \sim$ 4-10” water
- 100 SLPM gas flow
- Nominal composition of 46 slpm $H_2O$, 27 slpm $CO_2$, 20 slpm $H_2$, and 7 slpm CO
- $\eta > 40\%$
- Variable speed control with turn-down ratio of 5 to 2
- 0.5 L, 4.26 kg

R&D Dynamics

**U.S. DOE-sponsored SBIR Phase II prototype matches 21” UUV design goals**
Carbon Dioxide Scrubber

- CaO + CO₂ → CaCO₃ + HEAT (178 kJ/mol)
- CaCO₃ Decomposes ~ 850º C

- Sorbent shows fast kinetics and stability for repeated cycles
- Production methods have been scaled up for this extruded CaO sorbent
- Sorbent provided by TDA Research, Inc.
- Sorbent tested at NUWC

Over 50% mass gain demonstrated
Laboratory System Demonstration

• **30-Cell** Delphi Stack integrated with
  1) InnovaTek’s Steam Reformer
  2) TDA Research’s CO$_2$ Sorbent
  3) R&D Dynamics’ High Temperature Blower

• Benchmarks achieved in first Demo:
  – > 75% S-8 Utilization
  – > 90% Oxygen Utilization
  – > 50% Efficiency ($P_{SOFC} / S-8 LHV$)*
  – > 1 kW

* Furnace power neglected

All achieved simultaneously in initial proof-of-concept study (several hours of operation).
Masses and Volumes of SOFC System Components delivers 2.5 kW net output for 30 hours (75 kW-hrs)

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass, kg</th>
<th>Volume, L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two 30-cell SOFC stack modules</td>
<td>18</td>
<td>5</td>
</tr>
<tr>
<td>Insulation</td>
<td>3</td>
<td>23</td>
</tr>
<tr>
<td>Steam reformer/burner</td>
<td>40</td>
<td>6</td>
</tr>
<tr>
<td>Oxidant storage (LOX)</td>
<td>30</td>
<td>34</td>
</tr>
<tr>
<td><strong>LOX Tank</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>70 (steel)</td>
<td>100 (40 w/hull as vacuum jacket)</td>
</tr>
<tr>
<td><strong>Dodecane/JP-8 Storage</strong></td>
<td>12</td>
<td>16</td>
</tr>
<tr>
<td><strong>Fuel Tank</strong></td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Steam Recuperator/Condensor</td>
<td>2</td>
<td>0.75</td>
</tr>
<tr>
<td>Fuel Pump</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>AOG Recycle Compressor (R&amp;D)</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Bussing</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Trim</td>
<td>??</td>
<td>??</td>
</tr>
<tr>
<td><strong>CO₂ Scrubber (TDA to date)</strong></td>
<td>65</td>
<td>90</td>
</tr>
<tr>
<td><strong>BoP (piping, circuits, etc…)</strong></td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>~230 kg for 325 W-hr/kg</td>
<td>~235 L for 320 W-hr/L</td>
</tr>
</tbody>
</table>

Available mass: 209 kg  
Available volume: 189 L
Conclusions

• SOFC technology has the potential to greatly increase UUV mission time compared with current battery technology.

• SOFC degradation and lifetime need further study using stoichiometric oxygen control

• Main challenges for UUV application:
  - Oxygen Storage
  - SOFC stack reliability for multiple thermal cycles
  - Thermal management of closed system

• NUWCDIVNPT is the Navy lead for testing SOFC stacks, integrating components and designing UUV systems.
Acknowledgements

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