Thermally Integrated High Power Density SOFC Generator

By
FuelCell Energy, Inc.
Versa Power Systems, Inc.

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Acknowledgements

• Contributors
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  GTI: Robert Remick, Kevin Krist
  MSRI/UU: Tad Armstrong, Anil Virkar
  PNNL: Prabhabkar Singh

• Funding Support
  • DOE-NETL: SECA Program
  • California Energy Commission
  • GTI, VPS, FCE
Overview

- Program Objectives
- Technology Progress
  - Cell
  - Stack
  - System
- Summary
SECA Program Objectives

• Develop a kW-class SOFC power plant per SECA goals

• Natural gas as baseline fuel

• Thermal integration for higher efficiency

• Manufacturing cost reduction

• 9-year, 3-phase program
Cell Technology

- Long Term Testing (VPS)
- Modeling (PNNL)
- Cathode Development (MSRI-UU)
- Sulfur Tolerance (MSRI, GTI)
- Redox Tolerance (MSRI, VPS)
Trend Data

Test #10545; (Long Term Test: TSC1, 10 x 10 cm²)
Test Stand #6, January 9, 2002 - January 10, 2005

SS Cross Flow Interconnects

Test Conditions:
750°C, 556 mA/cm²  389 mA/cm²
54% fuel utilization:
  630  439 mlpm H₂, 630  439 mlpm N₂, 3% H₂O
27% air utilization:
  3000  2092 mlpm air

Degradation rate:
1.3% per 1000 h
(11 mV per 1000 h)

26,000 hours of Operation
Single Cell Data

- **H2/N2Data**
- **Model, Mole Frac. H2=0.485**
- **3-D STAR MODEL: Dsurf,0=0.549**
- **85%DIR-data**
- **3-D STAR MODEL: 85%DIR**

Cell Voltage, V

Current Density, A/cm²

Distributed Energy Generation

FuelCell Energy
Sulfur Tolerance of Anodes

- Anode tested with 1, 5, 10, and 100 ppm H₂S in fuel
- Performance degradation of ~6% with 10 ppm H₂S
- Degradation rate decreases with time until equilibrium is established
- Complete recovery with sulfur free fuel
- No permanent degradation or failure of anode observed

- Tested at 800 °C
- Cycled between H₂ and H₂ with 10ppm H₂S
Effect of $\text{H}_2\text{S}$ Poisoning on Cell Performance

Start Injection of 2.6 ppm H2S

Performance Decay due to H2S Poisoning

Cell On OCV

Performance Recovery

Fuel: 76.3% H2, 19.5% CO2, 4.2% CH4
Oxidant: 100% Air
Single Cell Active Area: 96cm²
Fuel Utilization: 45% @ 300mA/cm²
Oxidant Utilization: 30% @ 300mA/cm²
Anode Dew Point: 73°C (S/C Ratio: 2.3)
Cathode: Dry
Operating Temperature: 800°C
Operating Pressure: 1 atm

% Methane Conversion

Distributed Energy Generation

300mA/cm²

Potential (mV) @ 300mA/cm²

Time (Hours)

Performance Recovery

Performance Decay due to H2S Poisoning

Stop H2S

Start Injection of 2.6 ppm H2S

Cell On OCV

Performance Recovery

Effect of H2S Poisoning on Cell Performance
Stack Technology

• Stack Design for Greater Output (VPS)
• Triple Mode Cooling (VPS-FCE)
• Radiative Cooling (CEC Program)
• Thermal Cycling (MSRI, VPS)
• Gasket Development (MSRI, FCE, VPS)
## Stack Design For Greater Power Output

<table>
<thead>
<tr>
<th>Aurora Stack</th>
<th>3-1 Stack</th>
</tr>
</thead>
<tbody>
<tr>
<td>84-cell single tower with 4 stack modules</td>
<td>112-cell single tower with 4 stack modules</td>
</tr>
<tr>
<td>21-cell stack module</td>
<td>28-cell stack module</td>
</tr>
<tr>
<td>0.33 A/cm²</td>
<td>0.36 A/cm²</td>
</tr>
<tr>
<td>2600 W DC (_{\text{gross BOL}})</td>
<td>3800 W DC (_{\text{gross BOL}})</td>
</tr>
</tbody>
</table>

### 50% Increase In Stack Power
Benefits of Triple Mode Cooling: 2 kW Aurora System

- Higher Efficiency
- Reduced BOP Cost

<table>
<thead>
<tr>
<th>Cooling Mode</th>
<th>Net Electrical Efficiency, %</th>
<th>Air Flow, SLPM</th>
<th>Blower Power, W</th>
<th>Regen. Air HEX Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>30</td>
<td>400</td>
<td>200</td>
<td>12</td>
</tr>
<tr>
<td>Air + DIR</td>
<td>35</td>
<td>500</td>
<td>300</td>
<td>8</td>
</tr>
<tr>
<td>Air + DIR + Radiative</td>
<td>30</td>
<td>600</td>
<td>400</td>
<td>8</td>
</tr>
</tbody>
</table>
Impact Of DIR On Cell Temperatures

Temperature mapping performed on middle cell of a 5-cell, 121 cm² active area stack with city natural gas:

- 0-25% DIR has high DT: hot spot at AO/FI corner
- 75%-100% DIR has high DT: cold spot at Al/FI
- 50% DIR has lowest DT: optimal voltage vs. degradation balance
Stack Operation With 100% Methane DIR

- 10-cell stack, 92 cm² active area per cell
- Tested at 800°C
- Steam to carbon ratio of 2:1
- 60%Uf / 50% Uo

Current density (A/cm²)
Voltage per cell (V)
Power density (W/cm²)
CEC Project: Radiative Cooling

- Goals: Prove concept of radiant air pre-heaters at multi-kilowatt sizes (Higher power density, Lower operating temperature, Lower costs)
- Design 10 kW power module
- RAP/Stack module Tests at GTI and MSRI
- Kevin Krist of GTI will Present CEC Progress on Wednesday at 4:30 pm
Radiative Cooling For Stack

- Preheat Air With Radiation From Stack (RAP)
- Decreased Thermal Stresses
- Reduced Cooling Air Flow
Thermal Cycling of Stacks

- 5-cell stack
- Tested at 800 °C
- Newly developed metal seal
- 98% sealing efficiency of hydrogen gas

![Graph showing voltage (V) vs. number of thermal cycles]

- OCV
- Voltage @ 0.375 A/cm²
Stack Repeat Unit Testing – 50 Thermal Cycles over 5000 hours

Glob 101196
Oven #18, (September 23, 2003 - April 26, 2004)

Degradation Rate: 2.5 mV/Thermal Cycle

T = 750°C
I = 500mAcm-2
Uf = 50%
Ua = 25%
Gasket Test Facility

Compression System (Active, Pneumatic)

Set Up for Controlled Test Conditions
Normalized Gas Leak Rates of PH-2 Gasket

An Order of Magnitude Better Than Mica Gasket
Composite Gasket: Performance on Helium

Gasket inner size: 10x10 cm.

For cell with 10x10 cm active area, given:
- 500mA/cm²
- Fuel Uf: 75%
- Helium flow rate: 500 ml/min

99% seal efficiency: leak rate 5 ml/min

Goal: 99% seal efficiency

Stable Seals for the 3000-hour Test
Single Cell Longevity Testing of Glass-Ceramic Seal - 750ºC

Trend Data, Glob 10920

(Glass Seal: 50% Fuel Utilization, 25% Air Utilization, 0.5 A/cm², 10 x 10 cell)

Oven #3, (October 2, 2002 - January 3, 2004)

Degradation rate is approximately 1% per 1000 h (11 mV per 1000 h)

Advantage of Glass Seals = Hermetic fuel cavity
System Development

- Basis: Natural Gas Fuel, Grid Parallel Operation
- Aurora System with Radiative HEX (2 kW-net AC)
- Baseline System (3 kW-net AC)
- Advance System (10 kW-net AC)
Aurora & 3-1 Hot Power Module & T/C Layout

Aurora hot power module without RadHEX
Aurora hot power module with RadHEX

Black ‘dots’ denote thermocouple locations
Aurora System Operation On Natural Gas

Grid Parallel Operation for 1600 + hours
02-Feb-05 to 05-Apr-05

Stack Tower Voltage, Volts

Elapsed Time, hours

AC Load Interrupts & Facility Safety System Interrupts

2.2 kW_{net} AC Output

1.5 kW_{net} AC Output

1.8 kW_{net} AC Output

2.0 kW_{net} AC Output
Scale-up to 3 kW

2 kW\textsubscript{net} System
“Aurora”

3 kW\textsubscript{net} System
“3-1”

3 kW\textsubscript{net} system commissioning underway
10 kW Advance System

Integrated Module

FROM PROCESS AIR #1
FROM PROCESS AIR #2
FROM PROCESS FUEL

To Recycle Cooler

Radiative Air Exchanger
Solid Oxide Fuel Cell Stack
Radiative Fuel Heat Exchanger

Cathode In
Anode In
Cathode Out
Anode Out

Stack Zone

Warm Fuel Recycle Blower
Recycle Cooler
Regenerative Fuel Heat Exchanger

PreOx
HDS
ZnO

HDS Subsystem

10 kW Concept Design

SYSTEM EXHAUST
Parker Blower to be Used as a Baseline

Developed for use with PEM Fuel Cells
Maximum Temperature Rating of 120°C
Regenerative Fuel HX

• Current Specifications call for a working range of 750°C inlet to 200°C outlet.

• Four vendors have been identified
  – Small size is a problem – not a typical product
  – Temperature range limits manufacturing methods to welding – not brazing
  – Small initial sales volume is a problem for cost reduction
## Hydrocarbon Variability

<table>
<thead>
<tr>
<th>Composition</th>
<th>Full Range</th>
<th>80% Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>73 to 99%</td>
<td>89 to 97%</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.5 to 13%</td>
<td>1 to 5%</td>
</tr>
<tr>
<td>Propane</td>
<td>0 to 8%</td>
<td>0.2 to 2%</td>
</tr>
<tr>
<td>C₄ and above</td>
<td>0 to 13%</td>
<td>0.1 to 2%</td>
</tr>
<tr>
<td>Unsaturated</td>
<td>0 to 7%</td>
<td>Trace</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0 to 4%</td>
<td>&lt;0.01%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0 to 10%</td>
<td>0 to 3%</td>
</tr>
<tr>
<td>CO₂</td>
<td>0 to 2%</td>
<td>0 to 2%</td>
</tr>
<tr>
<td>HHV Btu/SCF</td>
<td>970 to 1200</td>
<td>1000 to 1050</td>
</tr>
<tr>
<td>Component Name</td>
<td>PPMV</td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Ethyl Mercaptan</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>T-Butyl Mercaptan</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Dimethyl Sulfide (DMS)</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>Methyl Ethyl Sulfide</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>Diethyl Sulfide</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>Dimethyl Disulfide</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>Thiophene</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Thiophane</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4.64</strong></td>
<td></td>
</tr>
</tbody>
</table>
# Impurities

<table>
<thead>
<tr>
<th>Composition</th>
<th>Full Range</th>
<th>80% Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odorants</td>
<td>2 to 12 ppmv</td>
<td>2 to 10 ppmv</td>
</tr>
<tr>
<td>Total Sulfur</td>
<td>2 to 17 ppmv</td>
<td>2 to 12 ppmv</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$, lb/MMSCF</td>
<td>0.5 to 10</td>
<td>0 to 8</td>
</tr>
</tbody>
</table>
• Copper impregnated adsorbents work well but have a low capacity for DMS.

• Mole sieve adsorbents for DMS are expensive.

• Hydrodesulfurization (HDS) could be a universal odorant removal system but it requires hydrogen, doesn’t handle unsaturated hydrocarbons well, and will overheat if propane-air is injected.
Summary

• Single Cell Operation using SS Interconnects Demonstrated for 26,000 hours (Degradation Rate: 1.3% per 1000 hr)

• Performed 50 Thermal Cycles in a Stack Repeat Unit During 5000 hours of Operation

• Work Initiated in Improving Redox and Sulfur Tolerance of the Anode Verified

• The 112 cell Stack Tower Showed a 50% Increase in Power Output (3.8 kW/Stack Tower)

• Aurora System Operated for 1600 + hours on Natural Gas Fuel and in Grid Parallel Mode
Approach to Advanced Cathodes

- Novel materials.
- Transport and adsorption properties; focus on materials with strong tendency for oxygen adsorption.
- Particle size and morphology; inter-particle contact.
- Microstructure stability at elevated temperatures.
- Introduction of electro-active species by infiltration.
- Identification of electro-active materials using patterned electrodes.

Performance of a button cell (2 cm$^2$ cathode) at 800°C

$\sim 1.7 \text{W/cm}^2$ @ 0.7V
Patterned Electrodes – Impedance Spectroscopy – Charge Transfer Resistivity

Patterned Electrodes

Impedance spectra at various pO2

Charge transfer resistivity as a function of temperature and pO2

Collaborative work: University of Utah and PNNL

Distributed Energy Generation
Development of Redox Tolerant Anodes

- Standard Ni-YSZ anodes tested for redox tolerance
- Tested at 600-800 °C
- Cells mechanically fail
  - Electrolyte microcracks
  - Anode support weakened
  - Some delamination
- Mechanism: expansion of Ni during oxidation microcracks YSZ in anode
Development of Redox Tolerant Anodes

- New anode compositions have been developed
- Exhibit better redox tolerance
  - Anode support mechanically intact after redox cycling
  - No microcracking of electrolyte
  - Delamination has been suppressed
- Future work
  - Improve anode strength after deep redox cycles
  - Optimize compositions and microstructure

As-sintered | Reduced | Reoxidized
<table>
<thead>
<tr>
<th>Thermal Cycle Number</th>
<th>Open Circuit</th>
<th>0.74A/cm², low Uf</th>
<th>0.5A/cm², 50% Uf, 25% Ua</th>
<th>0.5A/cm², 70% Uf, 35% Ua</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.078</td>
<td>788</td>
<td>795</td>
<td>748</td>
</tr>
<tr>
<td>1</td>
<td>1.078</td>
<td>799</td>
<td>803</td>
<td>759</td>
</tr>
<tr>
<td>5</td>
<td>1.072</td>
<td>794</td>
<td>801</td>
<td>759</td>
</tr>
<tr>
<td>15</td>
<td>1.073</td>
<td>783</td>
<td>793</td>
<td>753</td>
</tr>
<tr>
<td>25</td>
<td>1.080</td>
<td>780</td>
<td>792</td>
<td>759</td>
</tr>
</tbody>
</table>
Sealing Requirements in SOFC

- Within designed leakage tolerance over the life of the stack at both steady state and transient operating conditions
- More than 10^5 ohm·cm to avoid possible current leakage and cell shortening
- More than 30% to allow deformation for stack assembly requirements
- Thermal, chemical and mechanical stability to stack components and conditions

Development of a high temperature seal requires integrated solutions to these requirements
Composite Seal Test

Green tape of MSRI composite seal

- Thermally and mechanically robust
- Flexible configuration
- Tape cast, easy manufacturing, and low cost

800°C, H₂ gas maintained at 4 kPa

[Graph showing H₂ leak rate vs. spring load for Composite A and Composite B]