Rolls-Royce Coal-Based SECA Program Update
26 July 2011
Ted Ohrn and Zhien Liu
Outline

- RRFCS SECA Program and IP-SOFC Technology
- IGFC Systems Analysis
- Block-scale Test Rigs
- IP-SOFC Durability
- IP-SOFC Optimization
RRFCS SECA Program

- Phase 1
  - Extended to Sept 2011
    - 11 kW Metric Test to commence in Q3
  - Partners:
    - UCONN: BOP alloys/coating, Cr release rates
    - CWRU: detailed analytical analysis (TEM, XPS)
    - ORNL: substrate mechanical properties
    - PNNL: glass-ceramic seal
**RRFCS Integrated Planar SOFC**

- **RRFCS IP-SOFC operates at high voltage, low current**
- **Narrow cell pitch reduces ohmic losses**
- **Extruded MgO+MgAl$_2$O$_4$ substrate with screen printed layers**

**Bundle assembly (~350W):**
Serial fuel and current flow

**Block assembly (~20kW):**
5 strips of 12 fuel-parallel bundles

**Initial 1MW distributed power system will consist of ~250kW generator modules with larger blocks**

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**Via-based interconnect design**

- Porous substrate
- YSZ
- Anode current collector
- Primary Interconnect
- Air
- Cathode current collector
- Cathode

**RRFCS SOFC** operates at high voltage, low current

**Narrow cell pitch reduces ohmic losses**

**Extruded MgO+MgAl$_2$O$_4$ substrate with screen printed layers**
Market Entry is a 1MW Distributed Energy System

- Natural gas fired
- Potential net-AC electrical efficiencies of 60%
- Very low environmental impact, quick wins on air quality
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Rolls-Royce data

Plant Configuration

RRFCS NG “Dry Cycle” Configuration

- Uses “Cold Gas Clean-up” providing:
  - anode recycle to achieve,
  - sufficient steam in feed for reforming
- IGFC cycle similar to current RRFCS natural gas cycle

Current IGFC Plant Configuration

- Heat Source for Cathode Loop:
  - Partially-Spun Anode Gas,
  - Heated Cathode Loop Air,
  - Hot Recycle
  - Dried Coal-Derived Syngas

### Anode Exit Composition

<table>
<thead>
<tr>
<th>Cycle</th>
<th>NG, dry</th>
<th>IFGC</th>
<th>IGFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uf (HHV)</td>
<td>80</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>Anode Exit Composition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>16.2</td>
<td>8.0</td>
<td>4.1</td>
</tr>
<tr>
<td>CO</td>
<td>8.9</td>
<td>7.7</td>
<td>3.9</td>
</tr>
<tr>
<td>Total Flammables</td>
<td>25.1</td>
<td>15.7</td>
<td>8.0</td>
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<tr>
<td>H₂O</td>
<td>47.5</td>
<td>44.6</td>
<td>48.7</td>
</tr>
<tr>
<td>CO₂</td>
<td>23.8</td>
<td>39.2</td>
<td>43.0</td>
</tr>
</tbody>
</table>
60% overall efficiency requires:
- Inter-cooling of all gas compression
- 90% coal gasifier efficiency
- ~90% fuel utilization (challenging)
- Improved ASR (~30% relative to current technology), demonstrated with advanced cathodes

Increased pressure did not show performance improvement because:
- Improved reactivity at elevated pressure was offset by
- Less air and therefore, increased reaction resistance due to oxygen depletion
Porous Inert Substrate Controls Reforming Endotherm

- Reforming occurs as CH$_4$ diffuses to reaction site at anode-electrolyte interface
  - Rapid reforming yields equilibrium concentration at anode
  - Rate of bulk reforming controlled by diffusion of CH$_4$ to anode
- Small-scale cell experiments support this mechanism.

![Diagram showing electrolyte layer, anode layer, CH$_4$, H$_2$, H$_2$O, CO, and CH$_4$ at equilibrium at reaction site.](image)

![Graph showing CH$_4$ mole fraction as a function of cell number from fuel inlet for low and high permeability tubes.](image)
On-Cell Reforming Provides no Efficiency Improvement in a Pressurized System

- Heat absorption via reforming at constant cathode recycle ratio,
  - required less air, and enabled
  - a contracted temperature profile (i.e. increasing inlet temperature, higher average temperature)
- Higher average temperature did not yield improved performance because;
  - Decrease in average ASR was offset by
  - Increase in reversible voltage

<table>
<thead>
<tr>
<th>On-Cell Reforming Results for Repeat Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>% On-Cell Reforming</td>
</tr>
<tr>
<td>Constant Fuel Feed (HHV) kWe</td>
</tr>
<tr>
<td>Constant Uf (HHV) %</td>
</tr>
<tr>
<td>Constant Current Density mW/cm²</td>
</tr>
<tr>
<td>Fuel Cell Anode In</td>
</tr>
<tr>
<td>H₂ mole %</td>
</tr>
<tr>
<td>CO mole %</td>
</tr>
<tr>
<td>CH₄ mole %</td>
</tr>
<tr>
<td>Fuel Cell Operation</td>
</tr>
<tr>
<td>Model Calculated ASR ohm-cm²</td>
</tr>
<tr>
<td>Vreversible volts</td>
</tr>
<tr>
<td>Air-Side Operation</td>
</tr>
<tr>
<td>Air Inlet Temperature deg. C</td>
</tr>
<tr>
<td>Air Outlet Temperature deg. C</td>
</tr>
<tr>
<td>Air Inlet Flow g/s</td>
</tr>
<tr>
<td>Cathode Recycle Ratio</td>
</tr>
<tr>
<td>Predicted Power Output KW</td>
</tr>
<tr>
<td>Predicted Efficiency %</td>
</tr>
</tbody>
</table>

But, on-cell reforming provides opportunities for stack delta-T management, influencing long-term durability
Distribution of RRFCS IGFC System Costs

- Estimates for 2 stages of technology
  - Current technology (Ph. 1 block): 0.29 ohm-cm$^2$
  - Next generation (Ph. 2 candidate): 0.24 ohm-cm$^2$, precious metal cost savings
- Monte Carlo simulations with variables having greatest cost uncertainty
- Cost estimates
  - Current technology: $673/kW
  - Next generation: $621/kW

Monte Carlo Simulation
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Block-scale Test Rigs

- Rigs closely represent product
  - Anode and cathode recycle
  - Heat exchanger
  - Reformer
  - OGB
  - Ejectors
  - Insulation system, thermal self-sustaining
  - Control system/methodology
  - Safety systems

- These rigs are providing the foundational precommercial durability database
  - 3 rigs in Derby, UK
  - 1 rig in Canton, OH
Block Rigs Representative of Heat Balance within Generator Modules and Considered Thermal Self-Sustaining

Phase 1 metric test meets the TSS requirement in Phase 2

- **Generator Module (GM)**
  - Exhaust gas expanded through TG
  - Provides heat of compression for incoming air
  - OGB heat transfer to air by HX

- **Pressurized Block Rig**
  - No TG, air compressors used
  - TG compressor heat simulated with electric heaters upstream of main test vehicle
  - 2kW extra heat to offset greater heat loss for block vs GM (surf. area:volume)

Rolls-Royce data

July 26, 2011
Schedule for Pressurized Metric Tests

- Completing manufacture of the latest technology 10 kW class metric block
- UK rig has completed recent 1000 and 500 hour block tests of pre-SECA technology that:
  - Confirmed performance expectation with new dry cycle versus original cycle with combustion products in cathode stream
  - Confirmed reliable operation of rig to be used for metric test
- Commence test in 3rd Quarter
- Timing of test influenced by substrate qualification cycle
  - Conservative path taken for substrate selection for strip build
- Additional metric testing through Sept 2012 (~20 kW)
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Degradation and Life in Operation

- Degrade efficiency to meet constant power

Anode Loop Efficiency

- 0.037 ohm-cm²/1000 hrs (1.5% Power/1000 hrs CC)
- 0.003 ohm-cm²/1000 hrs (0.12% Power/1000 hrs CC)

Power Output, % Rating

- 0.12% - Efficiency
- 1.5% - Efficiency
- 0.12% - Power
- 1.5% - Power

Assumes:
- System Avg Vrev = 0.936 V
- Power = 0.8 W/cell

0.003 ohm-cm²/1000 hrs
(0.12% Power/1000 hrs CC)
0.037 ohm-cm²/1000 hrs
(1.5% Power/1000 hrs CC)
Durability Testing Program

- Map long-term performance over operating envelope
  - Anode Inlet: 67% flammables, 25% H₂O
  - Anode Outlet: 25% flammables, 50% H₂O
  - Cathode Inlet: 800°C, 12% O₂
  - Cathode Outlet: 920°C, 10% O₂ (extreme envelope)

- 5-cell Scale Tests
  - Full system conditions
  - Minimum 2000 hours
  - Current longest test ~ 9500 hrs

- Pressurized Bundle Tests
  - Complete anode flow path
  - Single cathode strip condition
5-cell Power Durability Trends

- Current IP-SOFC technology meets SECA Phase 1 degradation targets

- Cathode: ~10% O\(_2\), 1.2% H\(_2\)O, bal N\(_2\)
- 6.4 Bara

- PCT65: 925°C, 0.49%/1000 hrs
- PCT63: 860°C, 0.33%/1000 hrs
- PCT67: 800°C, 0.72%/1000 hrs

Shutdown for Post-test Analysis
Durability Data Summary

- Current IP-SOFC technology is projected to meet power and efficiency targets over a 2-year service life

**Targeted Operating Range**

- Useful Stack Life: 2866 hrs
- ASR @ 16K hrs = 0.42 ohm-cm²

**Temperature, °C**

**Useful Stack Life**

- 2000 hrs
- 4000 hrs
- 2866 hrs
- 1150 hrs
- 9028 hrs
- 1590 hrs
- 7845 hrs
- 3606 hrs

**ASR, ohm-cm²**

- Model: BOL
- Model: EOL
- PCT48 Inlet
- PCT59 Inlet
- PCT63 Mid-Block
- PCT65 Outlet
- PCT67 Outlet
- Bundle PBT3
- Bundle T1200
- PCT87
- PCT89

**ASR @ 16K hrs = 0.42 ohm-cm²**
Bundle Scale Performance

- Bundle performance matches models based on subscale performance
  - Bundle and subscale: 0.28 ohm-cm$^2$ at block average temperature
- Performance to > 90% $U_F$ (system) behaves as predicted

![Graph showing tube voltage vs. current density with models and experimental data points for different tube and model configurations at specified reformate and temperature conditions.](image-url)
Bundle Peak Power Consistent with Cost Model

- Achieved at 75% $U_F$ and 0.75 volts/cell
Bundle vs 5-cell Durability Comparison

- Bundle tests (360 cells per bundle) show similar durability trends as 5-cell test (PCT63) at same conditions

![Graph showing Power Density per RU, mW/cm² over time on test, hours. The graph compares PCT63: 860°C, Bundle T1200: 860°C, and Bundle PBT-3: 860°C in terms of bundle power, Watts. The cathode is described as ~10% O₂, 1.2% H₂O, bal N₂ at 6.4 Bara.](image-url)
Optimization of bundle-to-bundle fuel distribution

- Bundle geometry simplified to achieve equal pressure drop then stacked into a strip. This results in a simpler and quicker CFD model.
- Redesigned strips achieve improved bundle-to-bundle fuel distribution
- Block-to-block fuel flows are also well balanced
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  - Understand Sources of Degradation
  - Active Layers Improvement
Using Impedance Analysis to Track Degradation Sources

Referenced cathode symmetric cell test

Regular fuel cell with LSM cathode
Cathodic Peak Changes with Time

- Primary degradation mechanism appearing to be associated with the cathode at 860°C

Parametric cathode testing
- EIS to verify cathode processes

EIS data versus time

- 1.2% Steam, Varying O₂
- Anode: 26%H₂/37%H₂O
- Pressure = 6.4 Bara
- Temperature = 860°C

- 5% O₂
- 11.3% O₂
- 20.6% O₂

- 75 Hz
- 190 Hz
- 300 Hz

- 150 Hz @8000 h
- 300 Hz @1300 h

- PCT63B
- Cathode: 12%O₂
- Anode: Anode
- Midpoint
- Temperature = 860°C
- Pressure = 6.4 Bara

- 1313 hrs
- 2000 hrs
- 6000 hrs
- 7000 hrs
- 8000 hrs
Cathode Analysis after Long-Term Testing

- Mn-rich at cathode/electrolyte interface
- 3D reconstruction in process. Preliminary results may indicate possible microstructure change (CWRU)

860°C for 8000 hrs

Cathode pillar by CWRU
Degradation Increases with Temperature

Tests run at different conditions (800°C, 860°C, 925°C), but taken to identical conditions for EIS comparison

- Degradation rate greater at higher temperatures
- Increases in both anodic and cathodic peaks
- Cathodic peak change is dominant

![Graph showing degradation increases with temperature](image-url)
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  - Understand Sources of Degradation
  - Active Layers Improvement
Modification of LSM-Based Cathode

- Modification to the cathode composition has resulted in less free MnOx
- Minor MnOx observed at interface upon testing

Modified cathode: 925°C for 2000 hrs
Durability of Modified LSM-based Cathode

- RRFCS has observed an initial degradation when testing in moist (3%) air, accentuated at low temperatures (<800°C)
- Improvement shown for a modified LSM-based cathode
- Long term degradation at high temperature is under evaluation
Reversibility of Moisture-Induced Degradation
May be a Clue to Origin

- ASR change at low temperature is reversible at high temperatures

Effect of unstable fuel supply

Add 3% H$_2$O on cathode

Cathode: 12%O$_2$, anode: anode inlet fuel

775°C
Cell ASR Breakdown

- Full instrumentation to separate ASRs from different components
- EIS plus RC circuit fitting to separate cathode and anode
- Cathode dominates ASR at low temperature
- Cathode development to achieve lower ASR and lower temperature operation.

![Cell ASR Breakdown Graph]

- ASR Contribution, ohm-cm²
- Temperature: 800°C, 860°C, 920°C
- Components: Interconnect, CCC ohmic, ACC ohmic, Electrolyte, Cathode activation, Cathode concentration, Anode activation, Anode concentration
Alternate Cathode for Lower-ASR

- Lower overall cell ASR can allow reduced stack operation for improved durability and/or improved efficiency or cost
- LSCF, a well-accepted cathode, has CTE mismatch with RRFCS substrate
- Ruddlesden-Popper nickelate cathodes are under evaluation (Ln_{n+1}Ni_nO_{3n+1})
  - Nickelates, with lower $E_a$, can significantly reduce cathode ASR, especially at lower operation temperatures.
  - This is a long term development activity

![Graph showing cathode symmetric cell testing at various temperatures and pressures, with data points for 6.4 bara, 12% $O_2$.]
Initial Evaluation of Pr$_2$NiO$_4$

- Shows phase instability under testing conditions

Pr$_2$NiO$_4$ is unstable

As-fired Pr$_2$NiO$_4$

200 hr/900C

Higher order Pr$_{n+1}$Ni$_n$O$_{3n+1}$

PrO$_x$

(PrNi)O$_x$

PrO$_x$

NiO

Interlayer
Improved Nickelate Cathodes Show Less Decomposition

- XRD did not identify phase decomposition after short term aging
- TEM shows only minor decomposed phase, further optimization underway

Improved nickelate is more stable

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**As-fired**

**200 hrs/900C**

Single phase

Improved nickelate is more stable
Anode Degradation Mechanisms Identified

- Noticeable microstructure change after testing, especially at higher temperature, limited impact on performance to 9000 hours
- Early evidence of materials migration
- Peak block temperature and fuel utilization conditions pose greatest risk to anode long-term durability
- Developing even more stable anode side materials for 5-year service life

Anode 3D reconstruction by CWRU under separate program

Microstructure state after 8000 hours (860°C, anode midpoint)
Anode Optimization for 5-year Service

- More stable microstructure
- Maintain reliability: interfacial strength/cell adhesion to substrate
- Promising initial results for screening under aggressive system conditions (925°C, low flammables)

![Graph showing power degradation rates and cell power density]

- Anode A: 0.4%/1000 h
- Anode B: 0.1%/1000 h

Single-layer

12%O₂-dry

1 bar

Cell Power Density, mW/cm²

Elapsed Time, hours

Anode inlet

Anode outlet
Microstructure of Single Layer Anode Tested at Aggressive System Conditions

- Single layer performs as anode and in-plane current collector, engineered conductance
- Candidates show stable uniform microstructures
- Improved interfacial, cell attachment characteristics

Uniform microstructure after testing under aggressive system conditions

2300 hrs at 925°C at anode outlet
Durability of the Primary, cell-to-cell, Interconnect (PIC)

- Mitigated a major degradation mechanism in 2010, further validation in 2011
- Interconnect shows no degradation trend in 8000 hrs required for SECA metric test
Ceramic Interconnect: Long Term Objective

- **Modeling Results:**
  - Low conductivity requirement
  - Many material options

- **Materials and design:**
  - Single chromite layer
  - Bilayer structure*: p-type conductor on air side, n-type conductor on fuel side

*Srikanth Gopalan:

- **Challenge:** achieve gas-tight under constrained sintering conditions
- **Collaborating with Core Technology team PNNL**

![Graph](image-url)
Historical Cell Development Trend

- Single cell performance data for anode inlet fuel composition
- Factor of 2 improvement in ASR from pre-SECA
- Pressurized operation ASR benefit is ~0.05 ohm-cm²

The graph shows the development trend of cell ASR (Cell ASR, Ohm-cm²) with varying temperature (Temperature, °C) and pressure (1 bara, 6 bara). Key milestones include:

- 60-Cell with optimized LSM cathode
- ScSZ cathode
- Nickelate cathode

Technology frozen for near term block metric testing.
Conclusions

- Durability testing of IP-SOFC technology to >9000 hours exhibits average degradation rates <0.5%/1000 hours
- RRFCS hierarchic design shows scaling from subscale to full-scale bundle test articles
  - Similar performance expected at block-scale
- Current cell technology is on-track for initial commercialization
  - Also meets SECA defined cost targets
- Optimized anode and cathode approaches are being screened to achieve lower degradation rates
  - RRFCS views anode durability as top challenge for efficient IGFC systems operating at high $U_F$
  - Modified cathodes exhibit improved low-temperature moisture tolerance
- Thermal self-sustaining block test rigs prepared for metric test to commence later this quarter
Acknowledgements

- This material is based on work supported by the Dept. of Energy National Energy Technology Laboratory under Award Number DE-FE0000303
- RRFCS project manager Patcharin Burke and the entire SECA program management team
- UK and US based RRFCS team
- RRFCS SECA partners

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