LG Fuel Cell Systems SOFC Technology and SECA Program Update

2014 SECA Workshop, 22 July 2014
Richard Goettler

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Outline

- LGFCS Business Activities - 220 kW test
- Degradation Mechanisms and Mitigation
  - Cathode
  - Anode
  - Primary Interconnect
- Cell-Stack changes for lower cost
- Strip Reliability
  - Probability of failure predictions
  - Residual strength of substrates
- Block Testing Update
Phases of the business supported by SECA

**IST 1) Phase**
- Design, Build and Demonstrate a SOFC power system from fuel in to AC power out (1MW Design)
- Further development of key components / subsystems
- Accelerate EIS activities in parallel with development
- North America Market Assessment (VOC Meetings) 2)

**EIS 3) Phase**
- Adjustments to key components / subsystems from IST results
- Deploy up to five field test systems at “friendly” locations in North America
- Build initial manufacturing facility
- Active supply-chain management
- Secure first order for a commercially available fuel cell power system

**Commercial Phase**
- Facility expansion (all types)
- Supply-chain expansion
- Sales / Installation / Service capability
- Product scaling
- Market expansion

**500kW – 1MW Field Tests**
SECA supported lower ASR, in-block reforming and degradation improvements

~220 kW grid connected test
Cell/stack technology for IST reduced to practice under SECA (19 kW testing)

1) IST : Integrated String Test  2) VOC : Voice of the Customer  3) EIS : Entry Into Service
2014 Key Program Milestones Update

- Fuel Cell Vessel 1 (FCV-1): emulator blocks plus 1 active block for systems commissioning
- Fuel Cell Vessel 2 (FCV-2): fully loaded with active block for 220 kW
Commissioning of IST Subsystems is Progressing

- Fuel Processor commissioning completed
- FCV1 turbogenerator assembly under test, controls system completed
- FCV2 turbogenerator under test
- Block assembly for FCV1 in progress
- All substrates printed for FCV2, strip build underway
- Power electronics installed, grid connected, commissioning starting

Cell Print Line

2014 System Integration Outdoor IST Test Pad

2013 CAD rendering
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**Product Durability Strategy**

- End of Life ASR = 0.42 ohm-cm$^2$ to meet efficiency requirement

- Assumes constant power over service life

- Degradation rate target based on starting ASR and required stack life to meet cost

- Lifetime improved by reducing degradation mechanisms and/or lowering initial ASR
Ongoing durability testing at pentacell scale used to understand degradation contributions

- Impedance measured at ~ 1000 hour intervals
- Resistance, capacitance, and Warburg elements to represent behavior
- Estimates of degradation contributions can then be charted over the life of the test
- Cathodic mechanisms dominate

### Graphs:

**800°C**
- ASR & Rs vs. Time
- Cell ASR
- Cathode Activation
- Ohmic
- Anode Activation & Concentration

**925°C**
- ASR & Rs vs. Time
- Cell ASR
- Cathode Activation
- Ohmic
- Anode Activation & Concentration

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LG data
Cathode Degradation Mechanisms

- Localized densification near electrolyte interface
- $\text{MnO}_x$ segregation and/or migration
- $\text{MnO}_x$ valence changes
- Moisture effect
- Cr effect
- Ionic phase degradation
- Material diffusion
Cathode Densification vs. Testing Conditions

- Kinetics is a key factor for baseline LSM cathode densification

**Graph:**

- **Densification**
  - PCT150 7,000 hrs (925C)
  - PCT63A 8,000 hrs (860C)
  - PCT89 16,000 hrs (800C)
  - PCT150 7,000 hrs (925C)

**Temperature and Time:**

- Temp, C: 800, 850, 900
- Time, hrs: 8,000, 16,000

**Cell ASR change during operation:**

- PCT89 (800C)
- PCT63 (860C)
- PCT65 (925C)
MnO$_x$ Segregation/Migration Observed Across Temp. Range

As-fab  2,000hrs  8,000hrs  16,000hrs

800C

860C

900 - 925C

LG data
Minor amount of Mn exsolves from LSM near interface

- Data from baseline LSM cathode
- Tested at 800°C for 16,000 hours under simulated system conditions

![TEM image](image-url)

**Graph:**

- Mn, La, Sr cation percentages against distance from cathode/electrolyte interface (µm)

**Diagram:**

- TEM image of cathode/CCC interface
MnOₓ accumulation at interface not observed under OCV

Reference cell w/o current load
- MnOₓ at cathode/CCC interface

Active cell with current load
- MnOₓ at electrolyte
- MnOₓ elimination from bulk cathode

- Tested ~5000 hrs at 925°C and 4 bar
Accelerated Testing of Densification Mechanism

- Symmetric button cell tested under selected conditions to accelerate densification
- 860C, 16000 hr densification at NOC matched in 1200 hours accelerated
Long-term cathode material studies ongoing at different temperatures

- Candidate EIS cathodes show benefit at low temperature, similar degradation rates at high temperature
- Still seeking understanding of major degradation mechanisms across temperature ranges
  - Densification not a major contributor at low temp.
  - Further documenting the variation of $\text{MnO}_x$ as function of temp. and LSM cathode composition

![Cathode Rp Comparison (800°C)](image1)

![Cathode Rp Comparison (900°C, 925°C)](image2)
Triple bundle test with candidate cathodes showing improved durability trends

- Only change from baseline cell technology was the cathode
- Rates consistent with cathode degradation studies
- Projects to a 2-½ year life across block temp. profile and for block starting ASR
- Further durability extension with anode and interconnect changes

<table>
<thead>
<tr>
<th>Time = 5082 hours</th>
<th>Bundle 1: 3167-5</th>
<th>Bundle 2: 3167-52</th>
<th>Bundle 3: 3168-164</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Temperature</td>
<td>834.5 °C</td>
<td>858.3 °C</td>
<td>882.2 °C</td>
</tr>
<tr>
<td>Bundle Degradation Rate</td>
<td>0.52%</td>
<td>0.43%</td>
<td>0.35%</td>
</tr>
<tr>
<td>Bundle ASR</td>
<td>0.0085</td>
<td>0.0071</td>
<td>0.0065 ohm-cm²/1000 hr</td>
</tr>
</tbody>
</table>

1 Bara

Elapsed Time, hours | Average Temperature, °C | ASR, ohm-cm² | Bundle ASR | Bundle Degradation Rate |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Maintenance Shutdown</td>
<td>Maintenance Shutdown</td>
<td>Maintenance Shutdown</td>
<td>Maintenance Shutdown</td>
<td>Maintenance Shutdown</td>
</tr>
<tr>
<td>Hot Stand-By</td>
<td>Hot Stand-By</td>
<td>Hot Stand-By</td>
<td>Hot Stand-By</td>
<td>Hot Stand-By</td>
</tr>
<tr>
<td>3167-5, Bundle Degradation Rate = 8.5 micro-ohm-cm²/hr</td>
<td>3167-52, Bundle Degradation Rate = 7.1 micro-ohm-cm²/hr</td>
<td>3168-164, Bundle Degradation Rate = 6.5 micro-ohm-cm²/hr</td>
<td>3167-5, Average Temperature = 834.5°C</td>
<td>3167-52, Average Temperature = 858.3°C</td>
</tr>
</tbody>
</table>
Single Layer Anode Selected for EIS Business Phase

- Exhibits more uniform microstructure than baseline bi-layer at similar test times
- Accelerated testing being developed for quicker screening of final anode compositions

H₂: 14%, CO: 7.5%, H₂O: 50%, CO₂: 25.5%, N₂: 3%
Single Layer Anode Showing Improved Durability

- Lower ASR change and degradation rate after accelerated testing
- The results were repeated

<table>
<thead>
<tr>
<th>NOC</th>
<th>Acceleration Testing at 925C/90% Fuel Util.</th>
<th>Return NOC</th>
</tr>
</thead>
</table>

```
<table>
<thead>
<tr>
<th>Time, hours</th>
<th>0</th>
<th>200</th>
<th>400</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
<th>1400</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASR, ohm-cm²</td>
<td>0.20</td>
<td>0.30</td>
<td>0.40</td>
<td>0.50</td>
<td>0.60</td>
<td>0.70</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>770</td>
<td>790</td>
<td>810</td>
<td>830</td>
<td>850</td>
<td>870</td>
<td>890</td>
<td>910</td>
</tr>
</tbody>
</table>

Similar TPB for Accel. vs NOC Test

<table>
<thead>
<tr>
<th>TPB Density, m/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active TPB</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>As-reduced</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>925C, 90% FU, 1000hr</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>925C, 80% FU, 5000hr</td>
</tr>
</tbody>
</table>

TPB was generated from 3D database

PCT 73

ΔASR, ohm-cm² (before/after accel.)

<table>
<thead>
<tr>
<th>Anode Type</th>
<th>ΔASR, ohm-cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline Bi-layer anode</td>
<td>0.018</td>
</tr>
<tr>
<td>Single layer anode</td>
<td>-0.003</td>
</tr>
</tbody>
</table>
Improved Redox Tolerance is Sought for Anode Protection Simplification

- Tolerate low probability of occurrence emergency events
- Anodes tested
  - Baseline single layer anode
  - Modified 1: composition modification
  - Modified 2: microstructure optimization
- Screening tests
  - Pellet test
  - Single cell test

**Pellet test:** 5 redox cycles for different pellets

**Single cell test**
- Redox Cycle: 900°C, 3 hrs oxidation, N₂ purge

![Graph showing Cell ASR vs. # of Redox cycles for different anodes.](image)
Primary Interconnection Modification to Further Reduce Materials Migration

- Barrier layer modification does not increase the ASR
- Longer-term testing at most aggressive bundle conditions to accelerate mechanisms
- Post-test evaluations versus time to confirm benefits
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Lower ASR technology demonstrated at bundle-scale

- ASR reduction at 4 bar of >0.04 ohm-cm$^2$
- Meets ASR targets for initial products
- Optimized LSM compositions (lower $R_p$)
- Modified primary interconnect design
- Single layer anode
- Durability testing at higher current density design point
Print pattern changes to optimize power output

- Smaller primary interconnect dimension has lower ASR contribution
- Decreased cell pitch gives a lower in-plane resistance
- Lower ASR combined with increased active area per tube gives a potential increase in power output up to 26%
- Printing trials with 0.95 mm PIC in process

**Bundle Power for Smaller PIC Dimension**
(Constant Efficiency)

**Repeat Unit ASR Reduction vs PIC Dimension**
(Constant Efficiency)
Increasing In-Block-Reforming (IBR) to increase power density and manage Block $\Delta T$

- Thermal integration enables operation at higher current density while maintaining reasonable stack temperature
- Higher power density means less stack, smaller package, reduced size of BOP components
  - Single turbogenerator serves greater kW
- May also minimize stack temperature extremes at the hot and cold end which may be beneficial for performance and durability considerations.

![Impact of Lower ASR and IBR](chart.png)
IBR development activities addressing Thermal Stresses and Carbon Avoidance

- Multi-physics modeling

- Bundle test at 50% and 100% IBR performed
  - Nearly full conversion of CH₄
  - Lower power at 100% IBR from Nerst potential difference

<table>
<thead>
<tr>
<th>Case</th>
<th>Bundle Power</th>
<th>Bundle ΔT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reformate</td>
<td>322 W</td>
<td>20°C</td>
</tr>
<tr>
<td>50% IBR</td>
<td>320 W</td>
<td>12°C</td>
</tr>
<tr>
<td>100% IBR</td>
<td>316 W</td>
<td>6°C</td>
</tr>
</tbody>
</table>

Lower thermal gradients with incorporation of in-block reforming (inlet substrate shown)
Further Reduction in Cell ASR using Nickelate Cathodes

- Phase instability under operating conditions has been major issues
- Technical approaches to improve nickelate phase stability
  - A-site doped Pr$_2$NiO$_{4+\delta}$
    - $(\text{Pr}_{0.25}\text{Nd}_{0.75})$ A-site ratio is phase stable$^1$, $(\text{Pr}_{0.5}\text{Nd}_{0.5})$ exhibits instability
  - Addition of B-site dopants provides phase stability for A-site $(\text{Pr}_{0.5}\text{Nd}_{0.5})$

Nickelate provides ~0.02 ohm-cm$^2$ lower ASR than most favorable LSM-based cathode

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FEA Validation and CARES Prediction

- **FE Stress Modelling:** Validation at RT

  \[ y = 740.56x^2 - 2200.7x^2 + 2261.4x - 4.9828 \]
  \[ R^2 = 0.9997 \] (non-linear response)

  \[ y = 1872.9x + 9.6794 \]
  \[ R^2 = 0.9991 \] (FE linear elastic analysis)

- **CARES Prediction:** 4pt bend test at RT

<table>
<thead>
<tr>
<th>MMA Substrate Gen 2</th>
<th>Ratios (Exp./FE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Substrate</td>
<td>K(_{\text{max}}) ((\text{N-mm}))</td>
</tr>
<tr>
<td>(avg. strength from 30 test)</td>
<td>1804/1777.6 = 1.01</td>
</tr>
<tr>
<td>Glassed Substrate</td>
<td>1831/2102.5 = 0.87</td>
</tr>
<tr>
<td>(120(\mu)m thick glass layer and avg. strength from 6 test)</td>
<td></td>
</tr>
<tr>
<td>Full Printed Substrate</td>
<td>2504/2726.5 = 0.92</td>
</tr>
<tr>
<td>(avg. strength from 15 test)</td>
<td></td>
</tr>
</tbody>
</table>

- **Input from 4pt bend test on MMA Substrate:**
  \[ \sigma_0 = 57.48, \ m = 16.48 \]

- **CARES Output:**
  \[ P_f, \text{CARES prediction} = 63\% \]

\[ P_f = 1 - e^{-\left(\frac{\sigma_{\text{MAX}}}{\beta}\right)^m} \]

\[ R = \exp(-B) \]

\[ P_f = 1 - R \]

\[ P_f = 1 - \prod_{i=1}^{N}(1 - P_i) \]

\[ P_f, \text{expected} = 63.2\% \] (Good Agreement)
Very Low $P_f$ of Substrate under Operating conditions (Fast fracture)

- Conservative assumptions of Weibull parameters – used RT values under 2 conditions
  - Tube specification (MoR= 29MPa, $m=15$)
  - Actual Tube MOR (MoR= 1.31MPa, $m = 14.98$)
- Bundle thermal boundary conditions mapped in ABAQUS.
- Peak stresses for substrate 2 of top bundle in strip 5 (worst case)

<table>
<thead>
<tr>
<th>MMA Substrate (Tube #)</th>
<th>Max. Stress (MPa)</th>
<th>Pf (%), Actual</th>
<th>Pf (%), Tube Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.40</td>
<td>$0.86e^{-11}$</td>
<td>$0.18e^{-11}$</td>
</tr>
<tr>
<td>2</td>
<td>15.27</td>
<td>$0.51e^{-8}$</td>
<td>$0.107e^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>9.10</td>
<td>$0.13e^{-10}$</td>
<td>$0.27e^{-8}$</td>
</tr>
<tr>
<td>4</td>
<td>7.40</td>
<td>$0.10e^{-9}$</td>
<td>$0.25e^{-7}$</td>
</tr>
<tr>
<td>5</td>
<td>5.95</td>
<td>$0.95e^{-11}$</td>
<td>$0.19e^{-8}$</td>
</tr>
<tr>
<td>6</td>
<td>7.54</td>
<td>$0.16e^{-9}$</td>
<td>$0.33e^{-7}$</td>
</tr>
</tbody>
</table>

Table showing the probability of failure for different substrates under varying conditions.
Low $P_f$ of Substrate under Normal Operating Conditions (Slow fracture)

- Conservative assumptions of Weibull parameters – used RT values under 2 conditions
- Used actual high temperature SGC parameters from ORNL

Future Work:
- FEA for dense parts + CARES prediction for a full strip
- Low risk of failure of dense parts as strength 4X substrate and similar SCG parameters and $> K_{IC}$
- Block transient stress states

SCG parameters used for Analysis

1. Weibull & Fatigue Parameters:
   - $m = 14.98$
   - $\sigma_{90} = 58.92 \text{ MPa mm}^{-3/4}$
   - $N = 35.52$
   - $A = 4e^{-13}$
   - $K_{IC} = 2.08 \text{ MPa m}^{1/2}$
   - $Y = 2.3$
   - $B = \frac{2}{4^{1/2}K_{IC}^{1/2}(N-2)} = 0.615 \text{ MPa}^2 \text{ sec}$

$P_f$ in $10^{-4}$ range for substrate 2

Room Temp. Weibulls

<table>
<thead>
<tr>
<th></th>
<th>MoR (MPa)</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous MMA</td>
<td>41.31</td>
<td>14.98</td>
</tr>
<tr>
<td>Dense MMA</td>
<td>248.61</td>
<td>9.38</td>
</tr>
</tbody>
</table>
Phase 2 Block Test: Post-test Reliability Assessment

Approach: Measure RT 4-pt and compare to bare substrate of identical lot.
- The ratio of Tested Substrate: As-rec’d Bare Substrate is ~1.3-1.5, typical of ratio for as-processed substrates
- This indicates little or no loss in strength over the nominal 3000 hours of operation.

Mechanical Properties
- Fracture can start from surface defect as well as from volume imperfection.
- All the data (~600) from Strip 1, 3 and 5 put together show a good linear fit.

<table>
<thead>
<tr>
<th>Strip No.</th>
<th>Lot No.</th>
<th>No. of Test Specimens</th>
<th>Strength Ratio (± 95% Conf. Int.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22</td>
<td>186</td>
<td>1.32 ± 0.019</td>
</tr>
<tr>
<td>1</td>
<td>32-2</td>
<td>19</td>
<td>1.32 ± 0.048</td>
</tr>
<tr>
<td>3</td>
<td>32-1</td>
<td>196</td>
<td>1.46 ± 0.014</td>
</tr>
<tr>
<td>5</td>
<td>32-2</td>
<td>36</td>
<td>1.39 ± 0.15</td>
</tr>
<tr>
<td>5</td>
<td>24</td>
<td>132</td>
<td>1.40 ± 0.14</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>33</td>
<td>1.53 ± 0.07</td>
</tr>
</tbody>
</table>

(Mix of Gen1 and Gen2 substrates)

<table>
<thead>
<tr>
<th>MoR (MPa)</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Post-test</td>
<td>46.76</td>
</tr>
</tbody>
</table>
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Block Testing Matching Product Cycle, Components and Operating Conditions

- Initial design of block testing rigs
- Representative of cycle and components
- Not packaged for product

- One rig converted to match IST block design
- Allows testing of 3 blocks
- Fully representative of product
3 Block Tests Supported by Current Program

- Two 15 kW tests – original block design
  - Screening of cathode technology
  - 1\textsuperscript{st} test: Chromium mitigation, pipeline nat. gas and SCSO desulfurization (started July 2014)
  - 2\textsuperscript{nd} test: higher Chromium sources, pipeline nat. gas (starting Aug 2014)
    - Similar Cr content as Phase 1 and Phase 2 block tests

- 3\textsuperscript{rd} 4-strip test of combined cell technology for lower ASR and improved durability
  - expected <0.75%/1000 hours
  - Single layer anode, alternate cathode, primary interconnect redesign
Current Phase Block Test #1

- 4 Strip test with EIS cathode candidates
- 15.4 kW target value achieved
- ASR improved over Phase 2 test, especially at lower temp.
- Problems with BOP forced early shutdown
  - NG-SCSO connectivity
  - Air compressor failure
Conclusion

- Cell and stack developments supported by SECA are moving into 220 kW-scale system integration testing
- Degradation rates being reduced, further verification through accelerated and longer-term testing across testing platforms
- Active layer materials in final screening for inclusion in next business phase of system field testing
- In-block reforming coupled with lower ASR cell technology provides significant cost reductions – focus of next Phase.
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