# LG Fuel Cell Systems SOFC Technology and SECA Program Update

2014 SECA Workshop, 22 July 2014

Richard Goettler

# 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

**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)

## 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

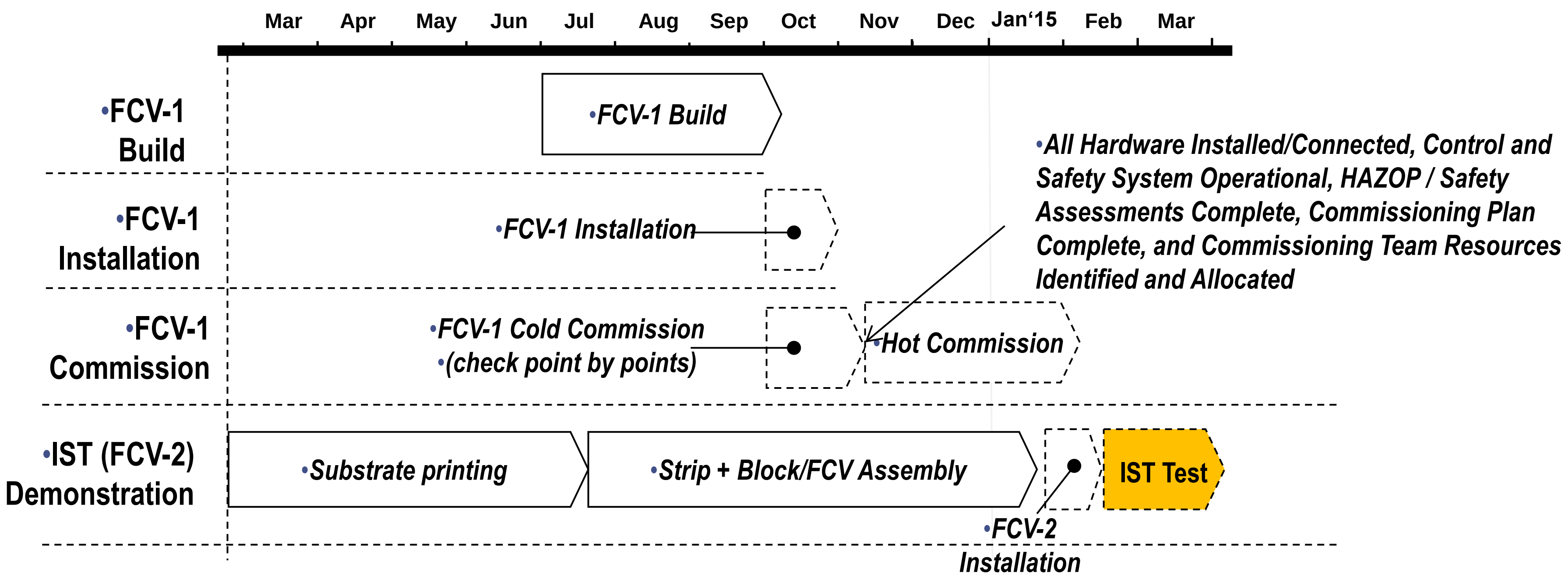
## Commercial Phase

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

•1) IST : Integrated String Test 2) VOC : Voice of the Customer 3) EIS : Entry Into Service

# LGFCS Integrated String Test Schedule

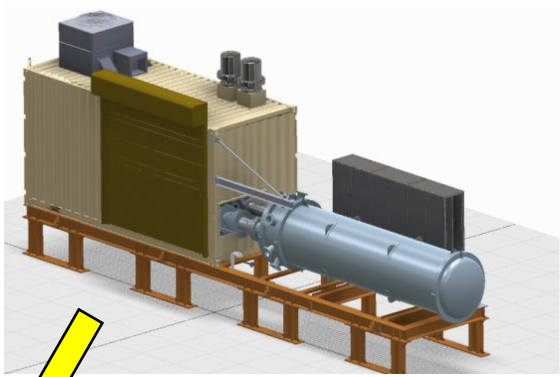
- **2014 Key Program Milestones Update**
  - **Fuel Cell Vessel 1 (FCV-1): emulator blocks plus 1 active block for systems commissioning**
  - **Fuel Cell Vessel 2 (FCV-2): fully loaded with active block for 220 kW**



# 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


2014 System Integration
Outdoor IST Test Pad



2013 CAD rendering

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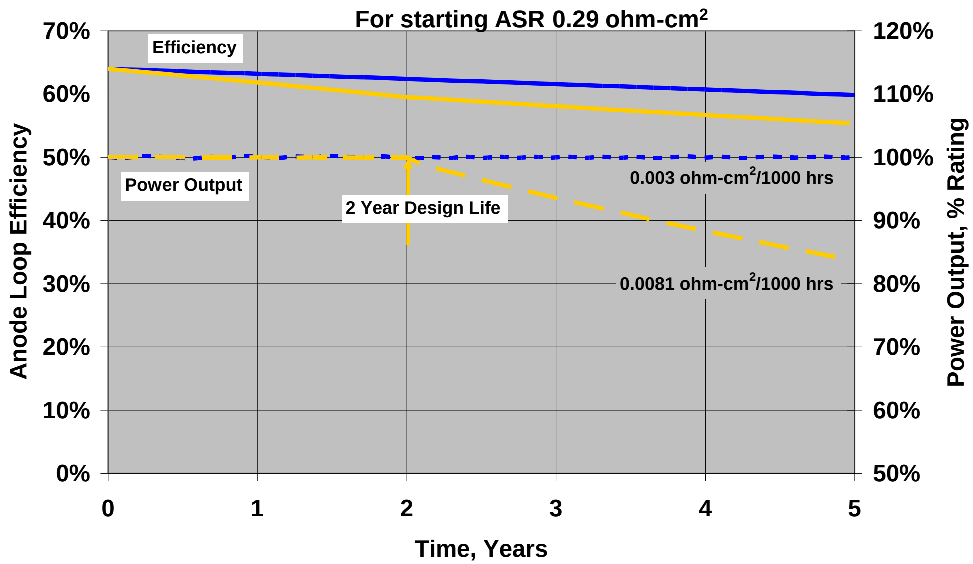
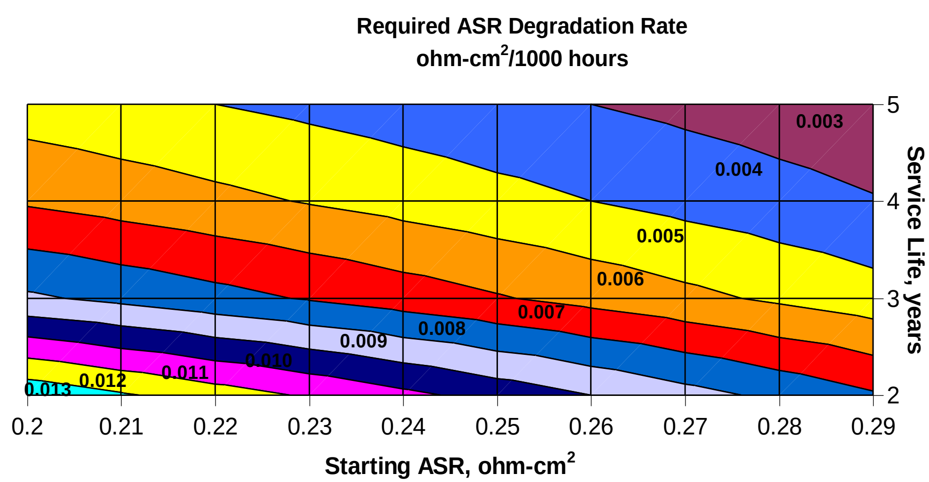
# Product Durability Strategy

- End of Life ASR = 0.42 ohm-cm² to meet efficiency requirement
- Assumes constant power over service life

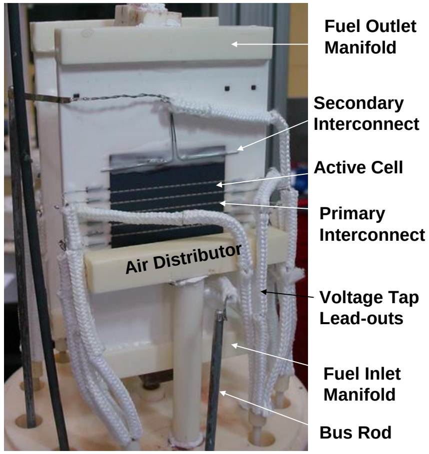



- Degradation rate target based on starting ASR and required stack life to meet cost
- Lifetime improved by reducing degradation mechanisms and/or lowering initial ASR

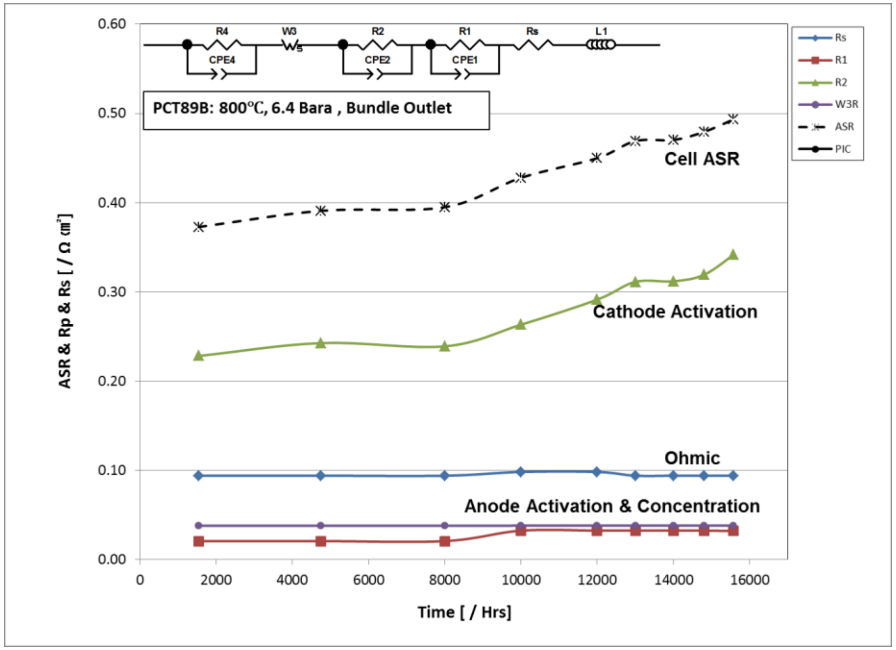


# Ongoing durability testing at pentacell scale used to understand degradation contributions

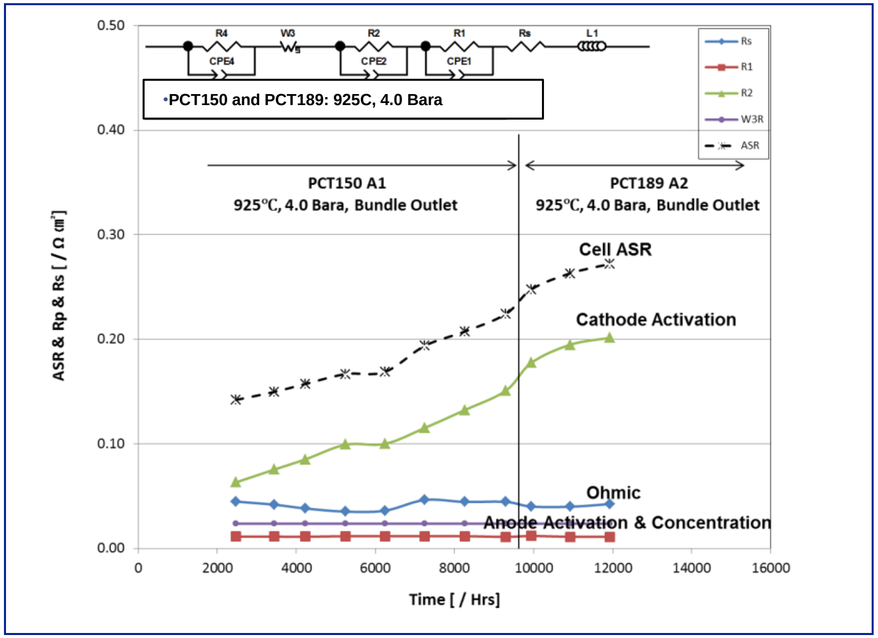
- Impedance measured at ~ 1000 hour intervals
- Resistance, capacitance, and Warburg elements to represent behavior
- Estimates of degradation contributions can then be charted over the life of the test
- Cathodic mechanisms dominate




**800C**




**925C**

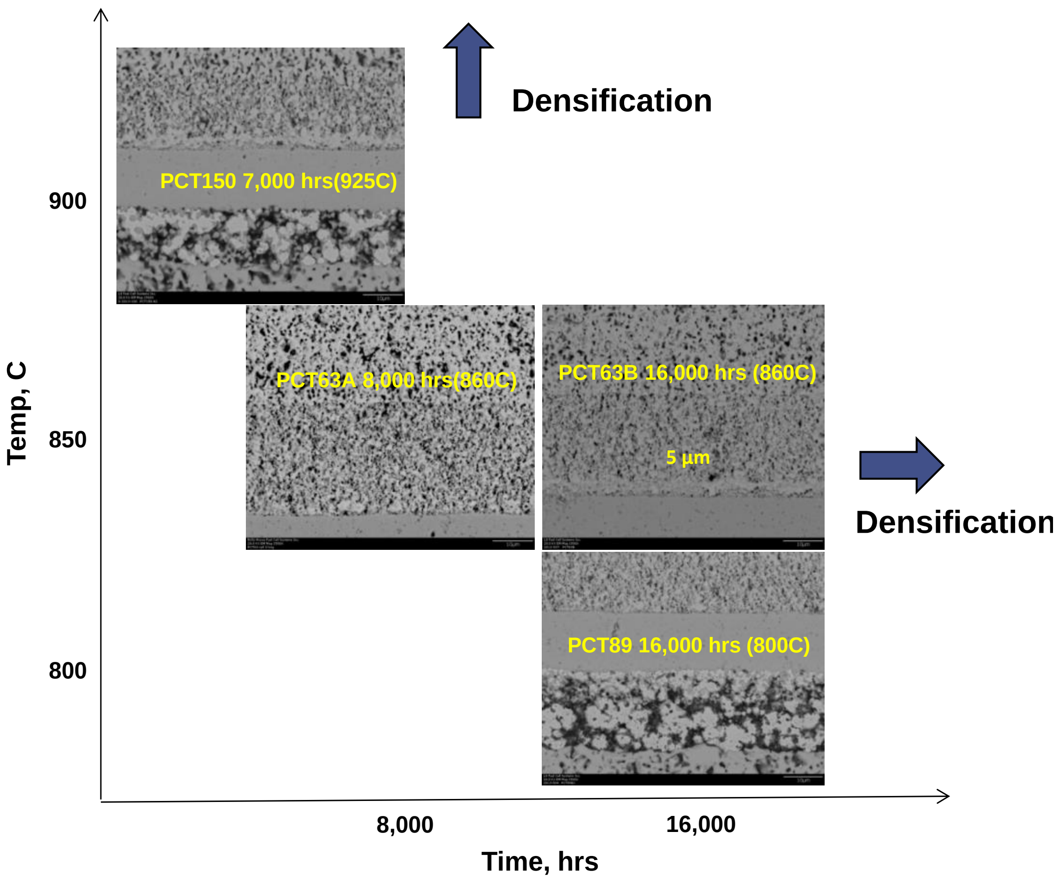


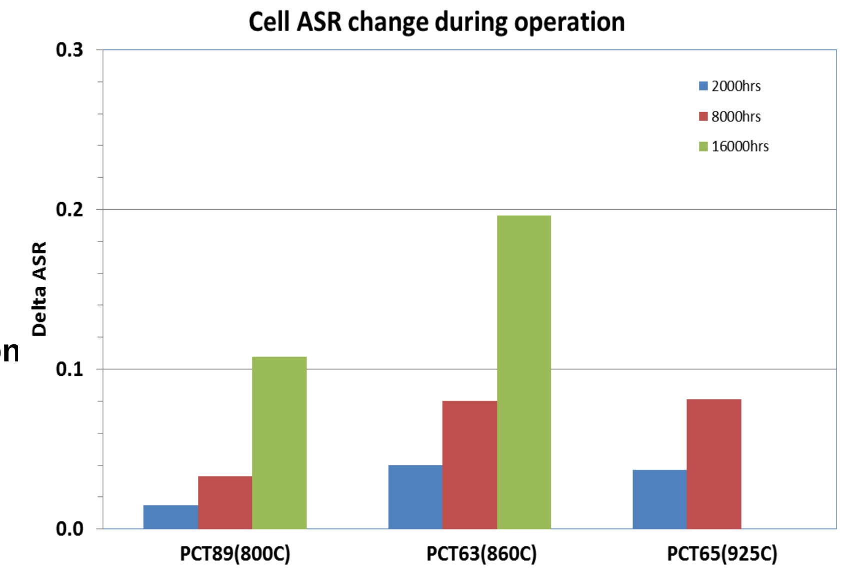
# Cathode Degradation Mechanisms

- Localized densification near electrolyte interface
- $MnO_x$ segregation and/or migration
- $MnO_x$ valence changes
- Moisture effect
- Cr effect
- Ionic phase degradation
- Material diffusion

# Cathode Densification vs. Testing Conditions

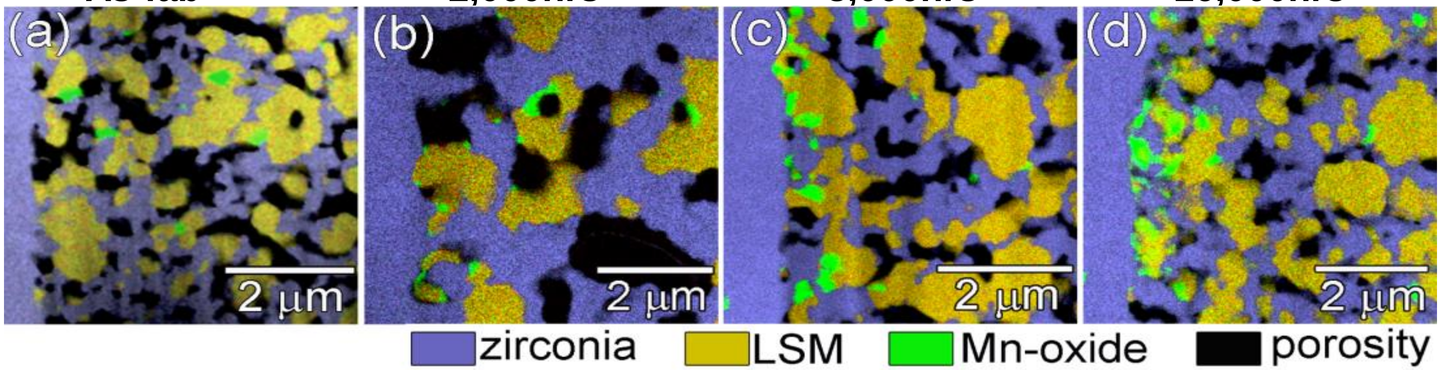
- Kinetics is a key factor for baseline LSM cathode densification



# $MnO_x$ Segregation/Migration Observed Across Temp. Range

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

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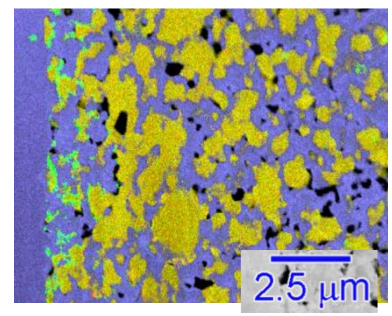
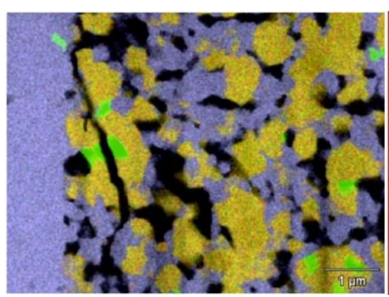
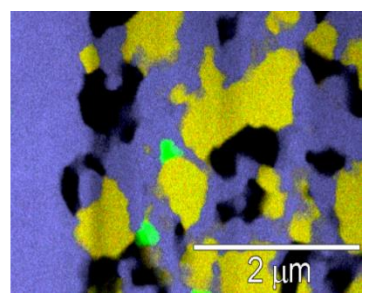


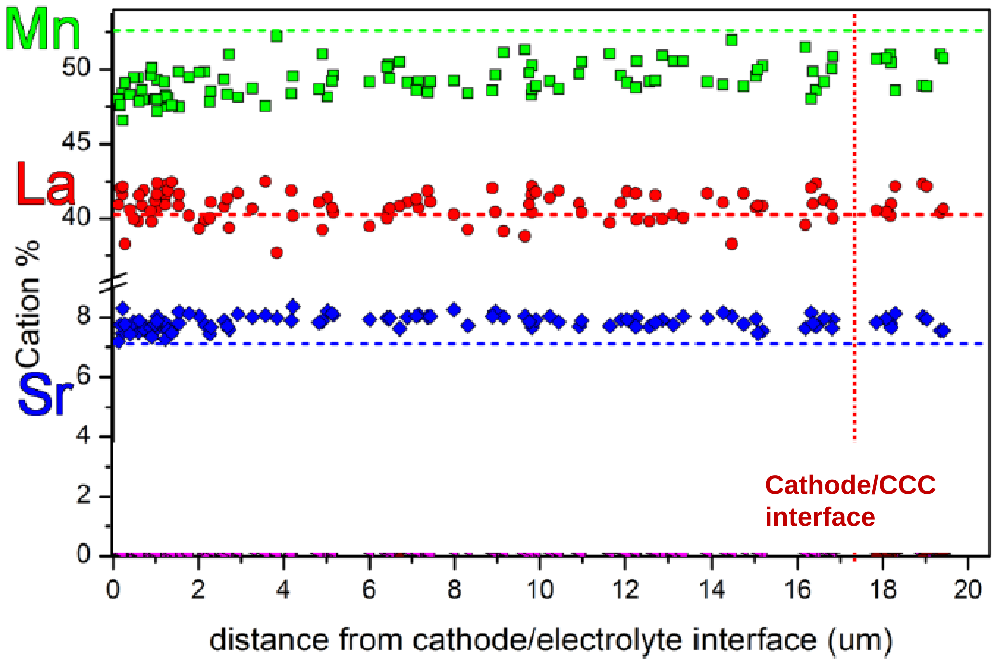

860C

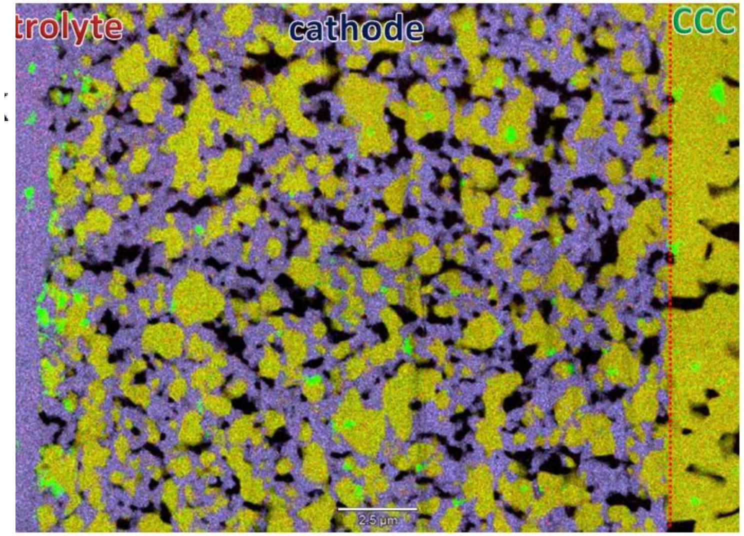




900 -
925C

# Minor amount of Mn exsolutes from LSM near interface

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




**TEM image**

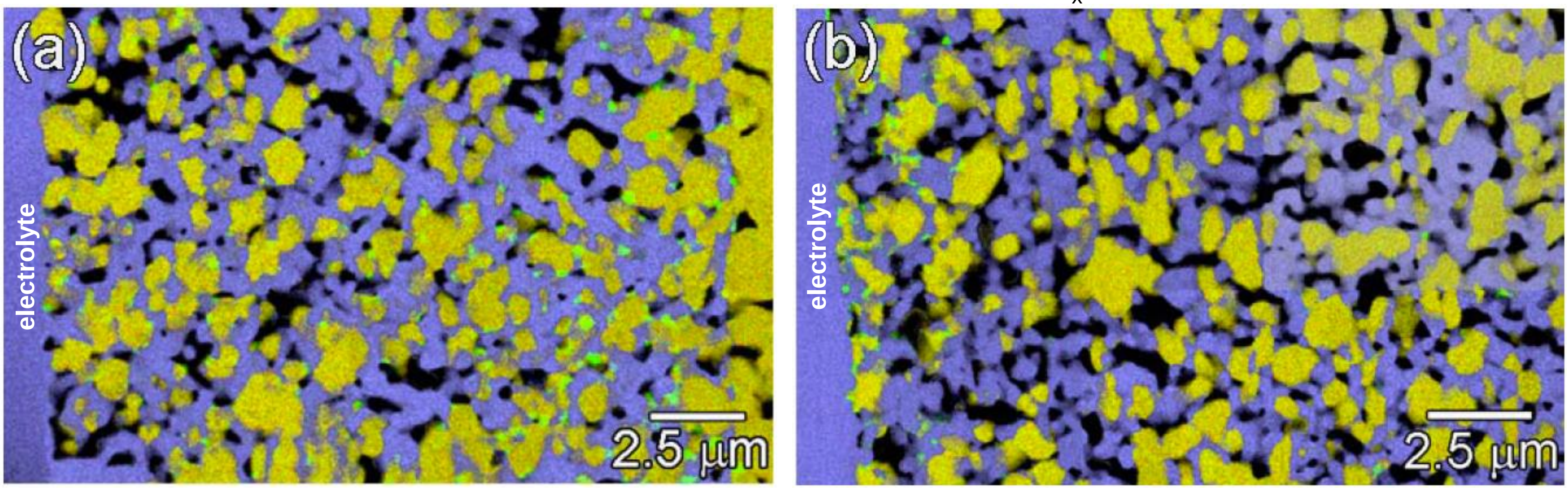
# $MnO_x$ accumulation at interface not observed under OCV

**Reference cell w/o current load**

**-** $MnO_x$ at cathode/CCC interface

**Active cell with current load**

- $MnO_x$ at electrolyte
- $MnO_x$ elimination from bulk cathode



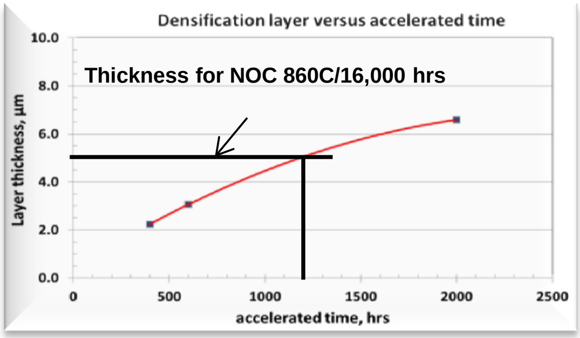

- **Tested ~5000 hrs at 925$^oC$ and 4 bar**

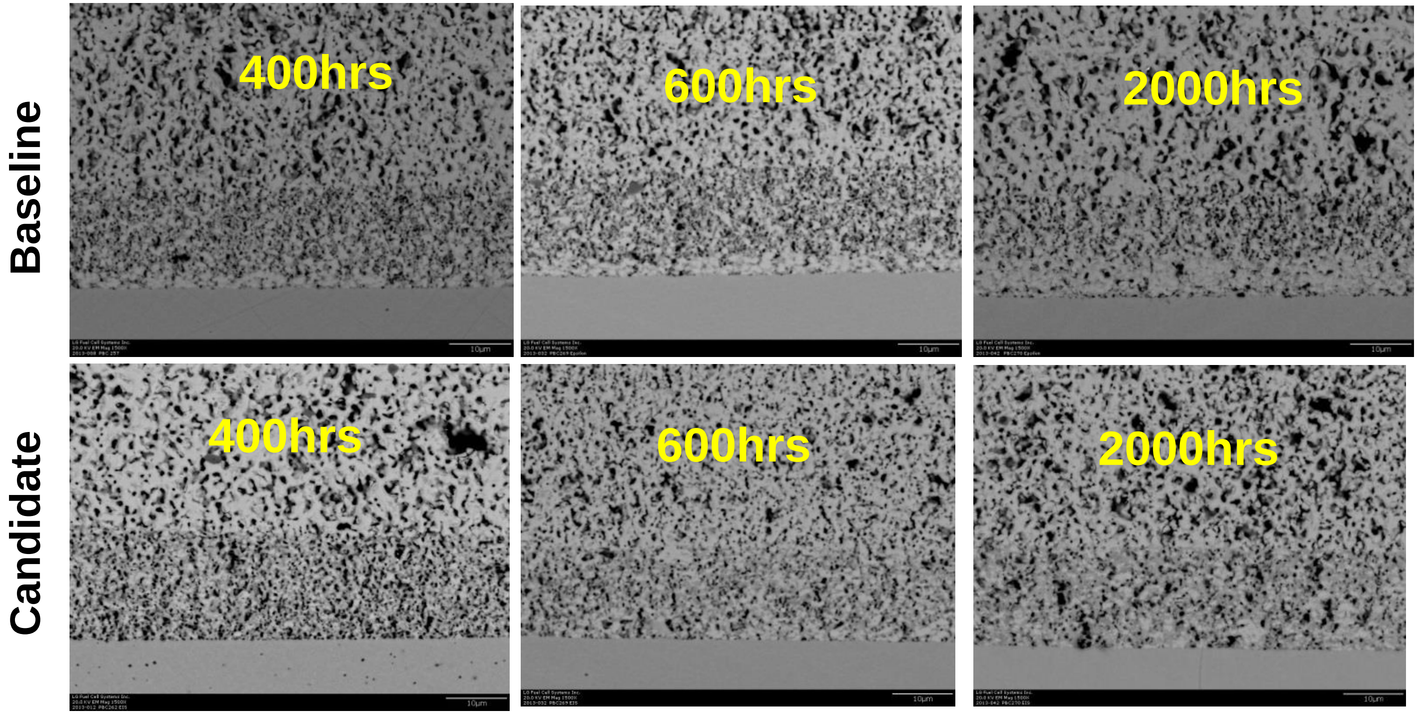
**Mn**

**LSM**

# Accelerated Testing of Densification Mechanism

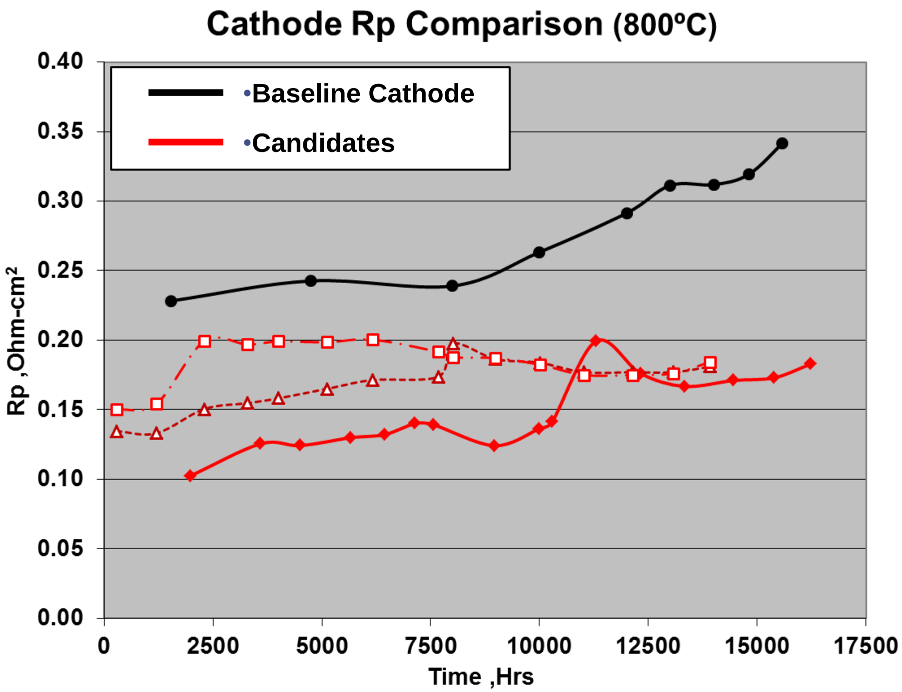
- Symmetric button cell tested under selected conditions to accelerate densification
- 860C, 16000 hr densification at NOC matched in 1200 hours accelerated

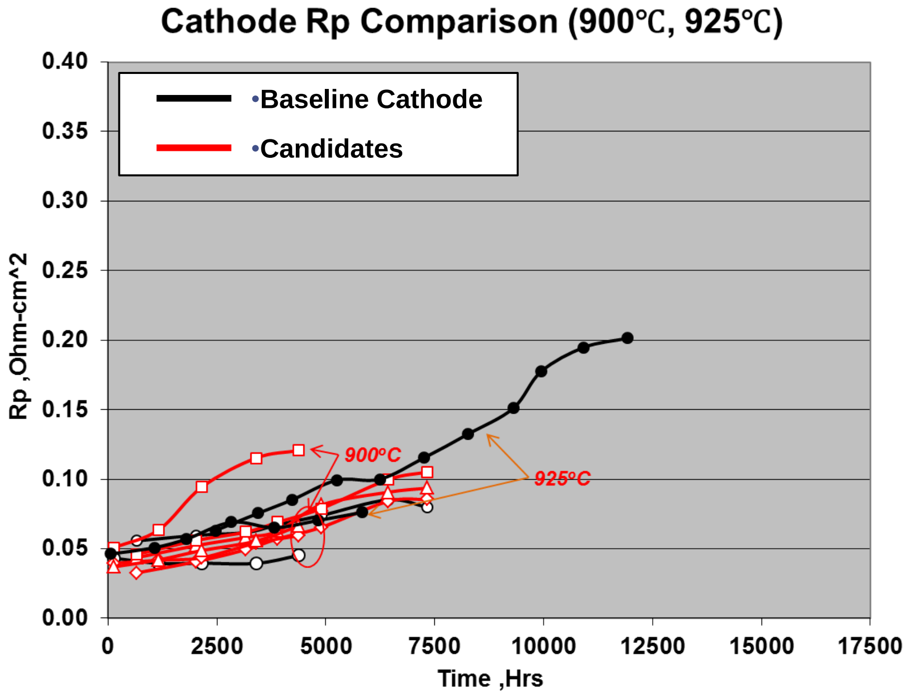


# Long-term cathode material studies ongoing at different temperatures

- **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 $MnO_x$ as function of temp. and LSM cathode composition**

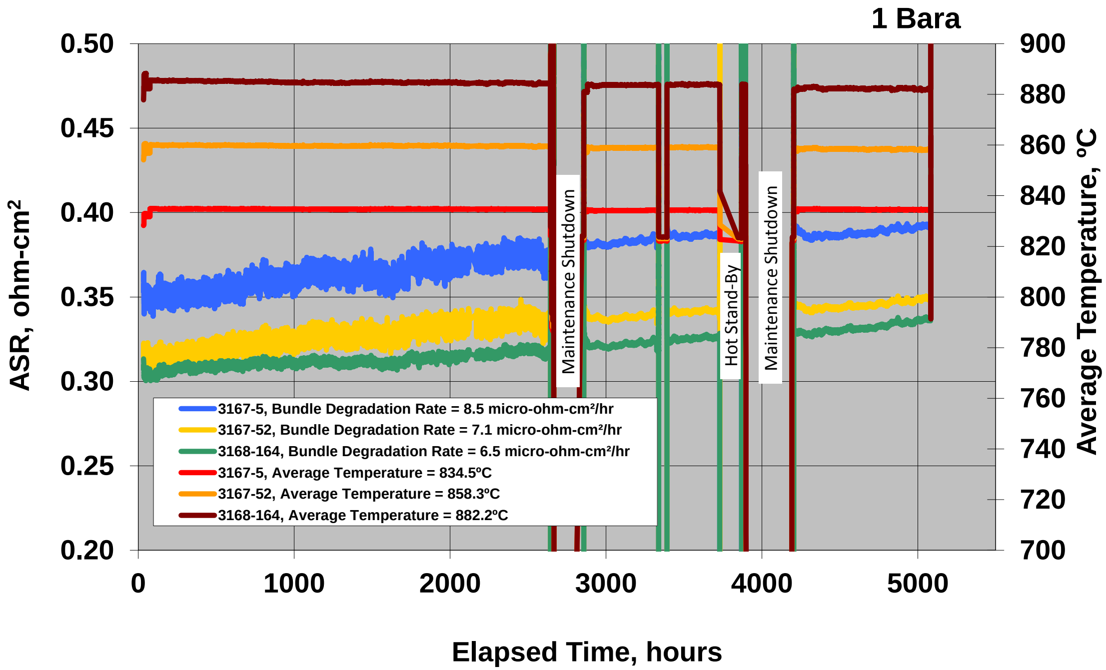


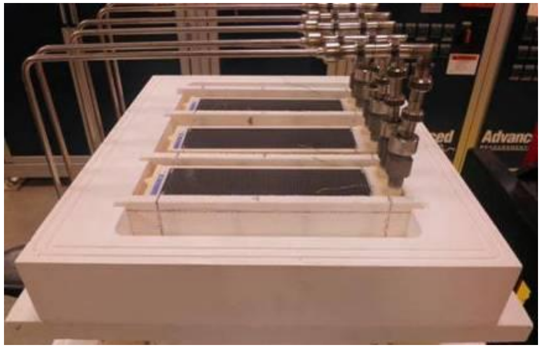



# Triple bundle test with candidate cathodes showing improved durability trends

- 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

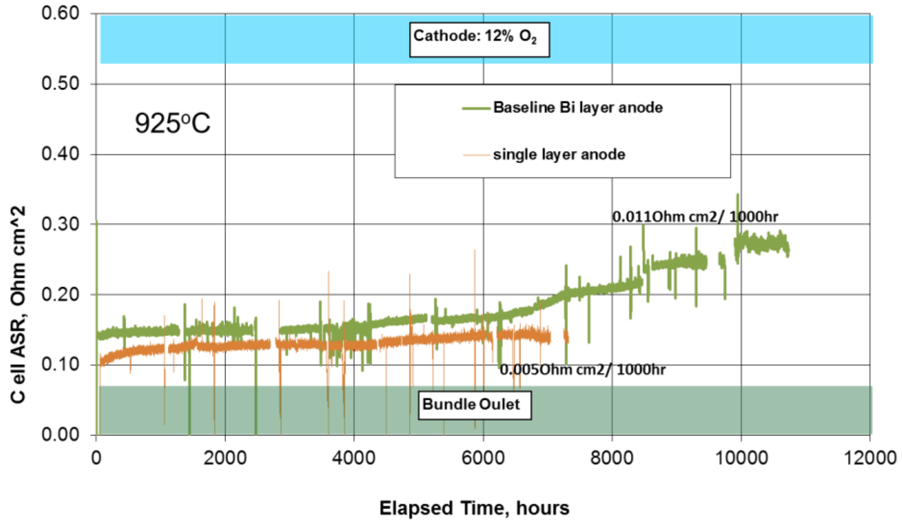
| Time = 5082 hours | Bundle 1: 3167-5 | Bundle 2: 3167-52 | Bundle 3: 3168-164 | |
|---|---|---|---|---|
| **Average Temperature** | 834.5 | 858.3 | 882.2 | ºC |
| **Bundle Degradation Rate** | 0.52% | 0.43% | 0.35% | %Power/1000 hrs |
| Bundle ASR | 0.0085 | 0.0071 | 0.0065 | ohm-cm²/1000 hr |

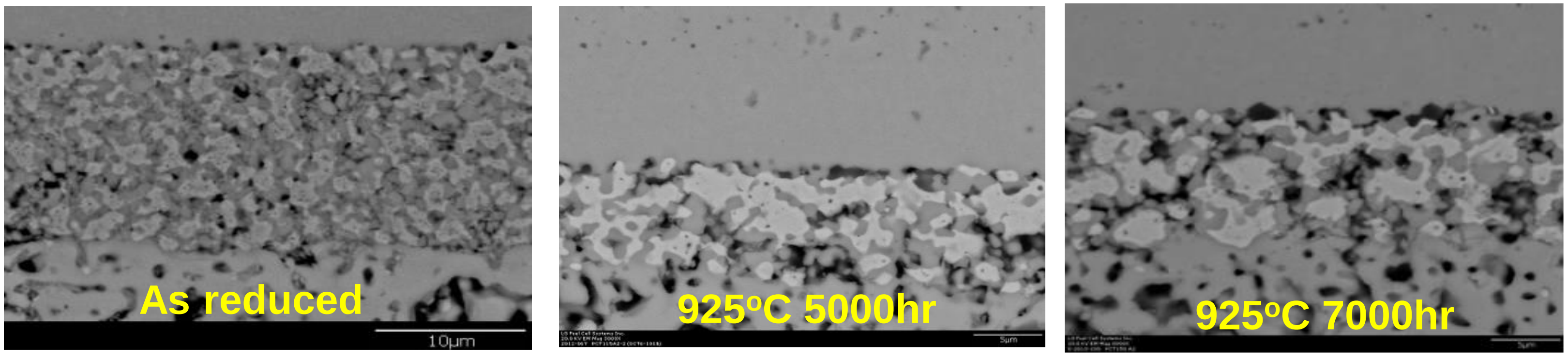


# Single Layer Anode Selected for EIS Business Phase

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

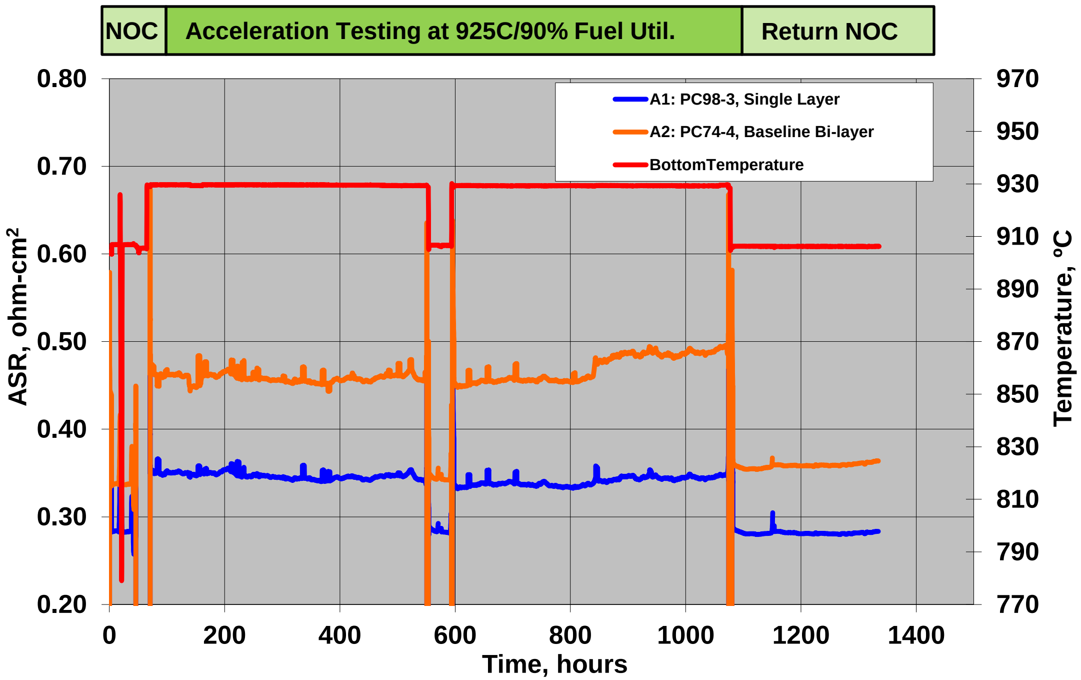



$H_2$: 14%, CO:7.5%, $H_2O$: 50%, $CO_2$: 25.5%, $N_2$: 3%

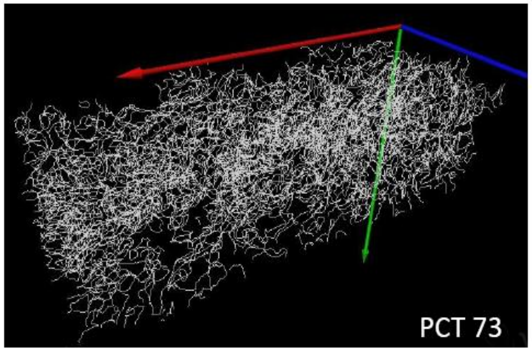
# Single Layer Anode Showing Improved Durability

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

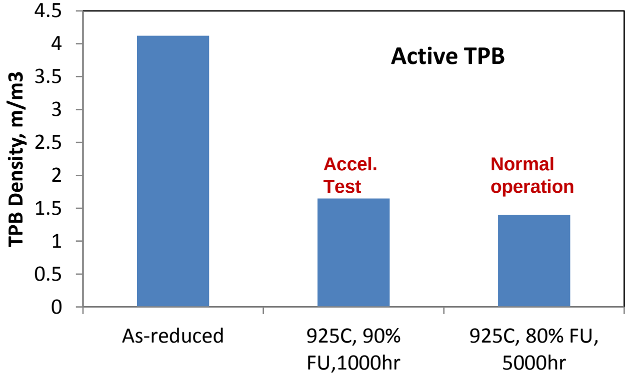



| | $\Delta$ASR, ohm-cm$^2$ (before/after accel.) |
|---|---|
| Baseline Bi-layer anode | 0.018 |
| Single layer anode | -0.003 |

**TPB was generated from 3D database**



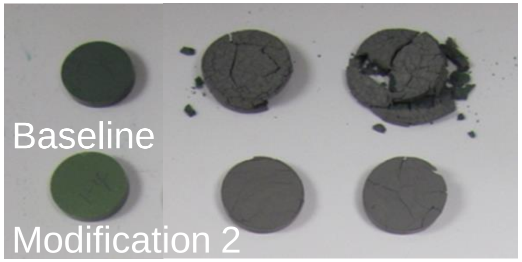

**Similar TPB for Accel. vs NOC Test**



# Improved Redox Tolerance is Sought for Anode Protection Simplification

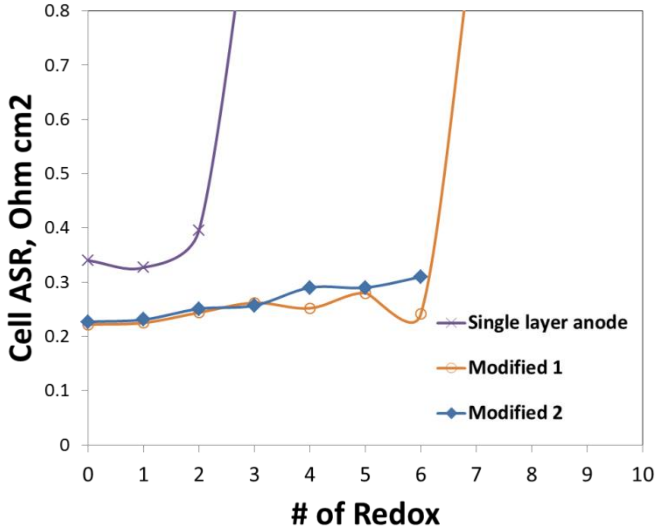
- **Tolerate low probability of occurrence emergency events**
- **Anodes tested**
  - **Baseline single layer anode**
  - **Modified 1: composition modification**
  - **Modified 2: microstructure optimization**
- **Screening tests**
  - **Pellet test**
  - **Single cell test**

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



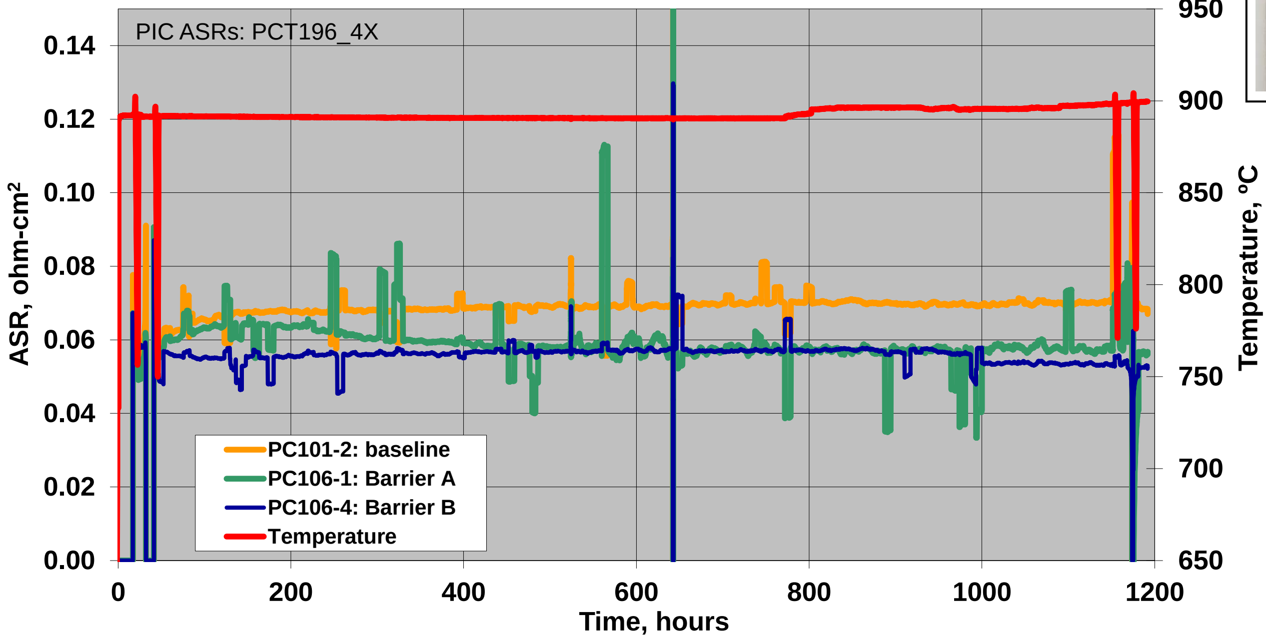

**•Single cell test**

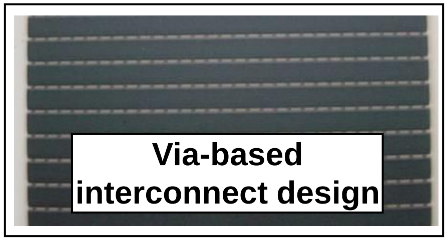
**•Redox Cycle: 900C, 3 hrs oxidation, $N_2$ purge**



# 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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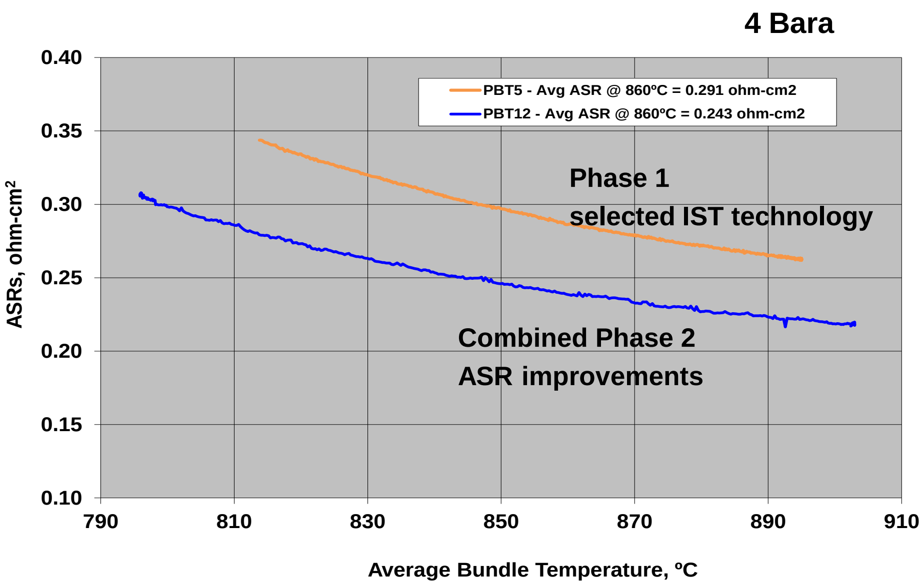
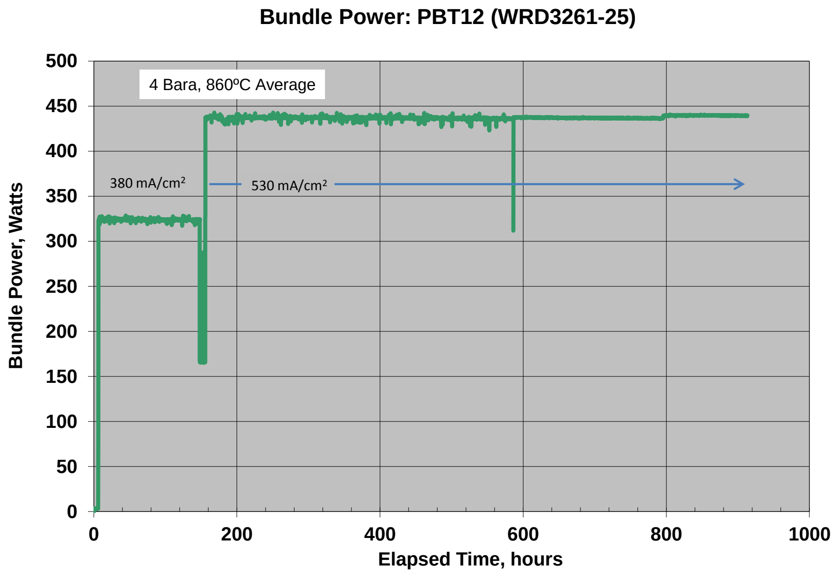
# Lower ASR technology demonstrated at bundle-scale

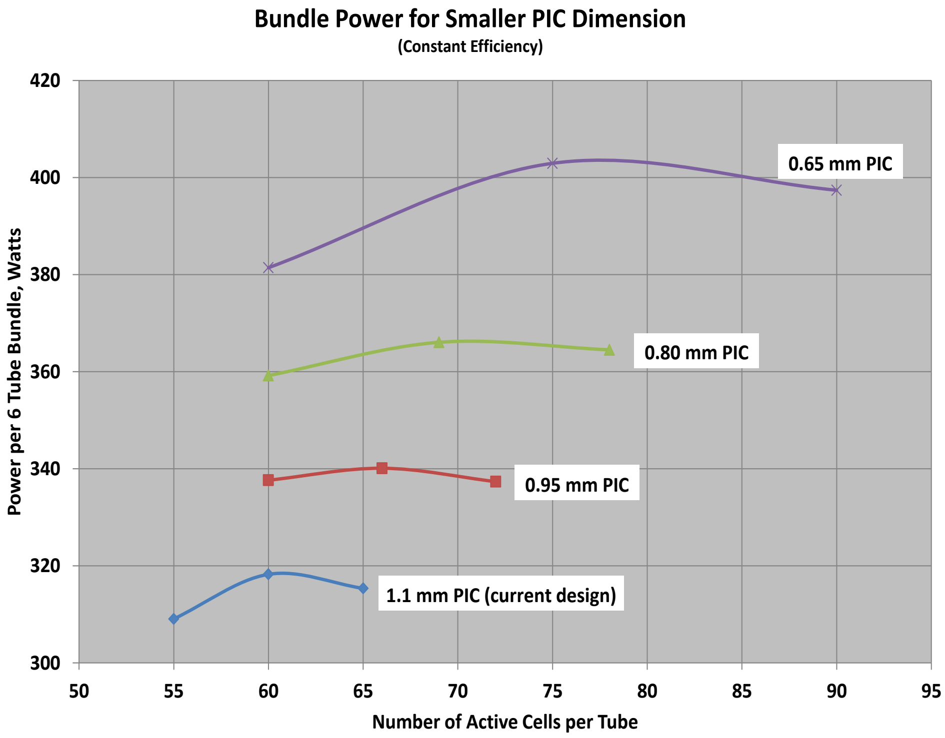
- ASR reduction at 4 bar of >0.04 ohm-cm$^2$
- Meets ASR targets for initial products
- Optimized LSM compositions (lower $R_p$)
- Modified primary interconnect design
- Single layer anode
- Durability testing at higher current density design point

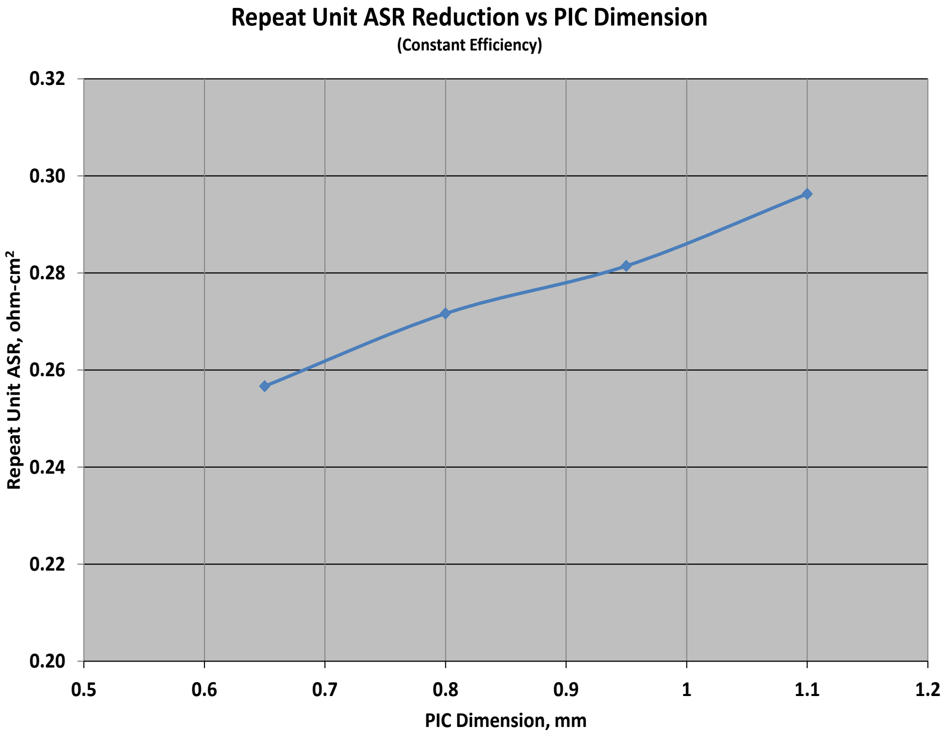


# Print pattern changes to optimize power output

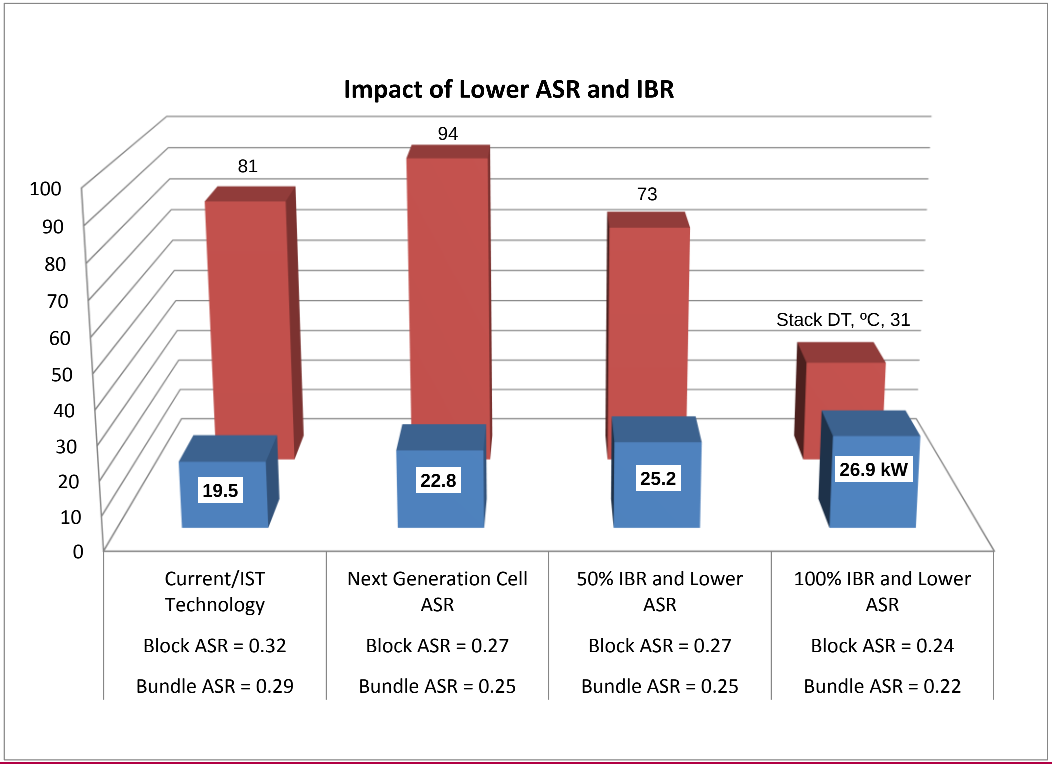
- Smaller primary interconnect dimension has lower ASR contribution
- Decreased cell pitch gives a lower in-plane resistance
- Lower ASR combined with increased active area per tube gives a *potential* increase in power output up to 26%
- Printing trials with 0.95 mm PIC in process



# Increasing In-Block-Reforming (IBR) to increase power density and manage Block ΔT

- 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.

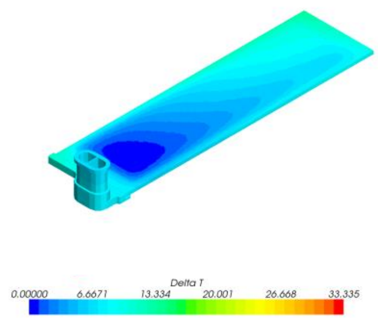



Block ΔT

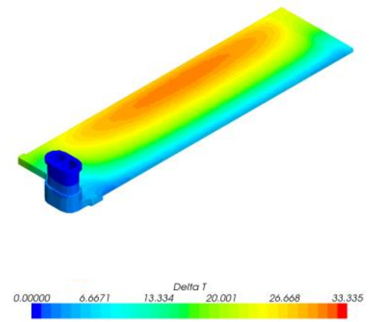
Block Power (5 strips)

# IBR development activities addressing Thermal Stresses and Carbon Avoidance

- **Multi-physics modeling**




**All reforming within bundle**

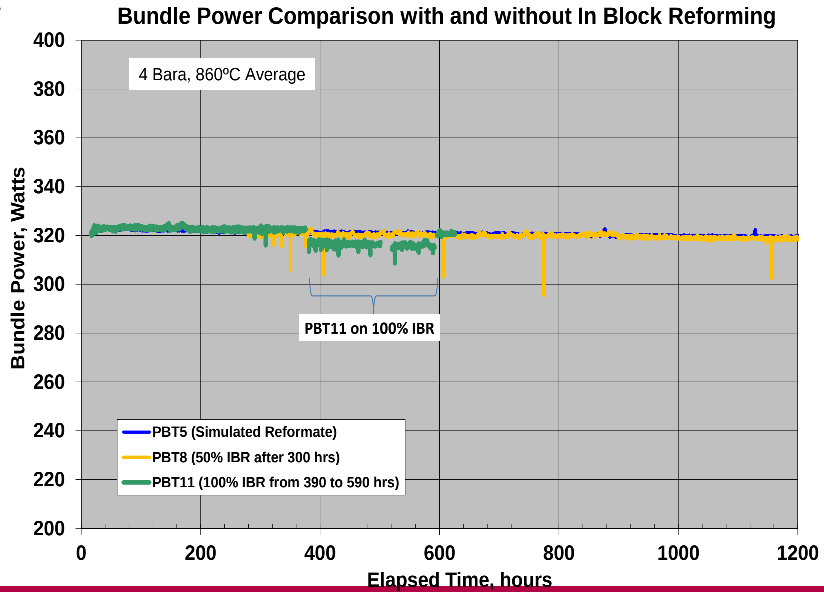



**Current approach: reforming external to bundle**

**Lower thermal gradients with incorporation of in-block reforming**
(inlet substrate shown)

- **Bundle test at 50% and 100% IBR performed**
  - **Nearly full conversion of $CH_4$**
  - **Lower power at 100% IBR from Nerst potential difference**

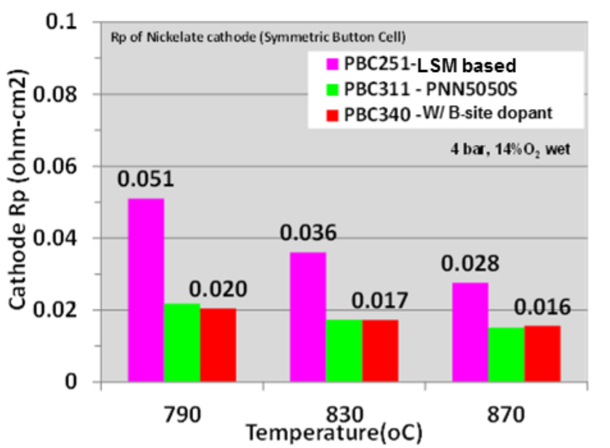
| Case | Bundle Power | Bundle ΔT |
|---|---|---|
| Reformate | 322 W | 20ºC |
| 50% IBR | 320 W | 12ºC |
| 100% IBR | 316 W | 6ºC |

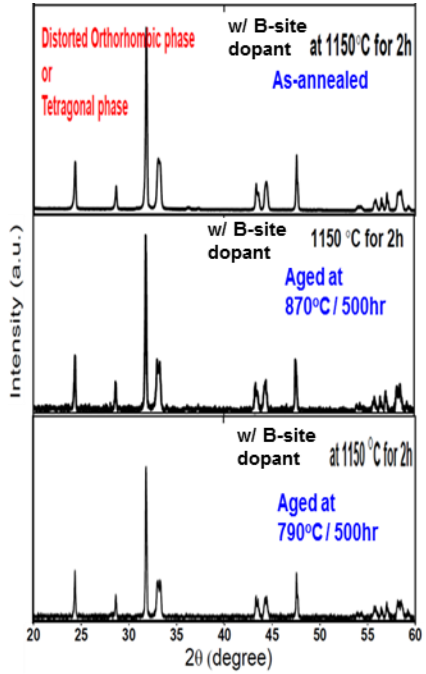


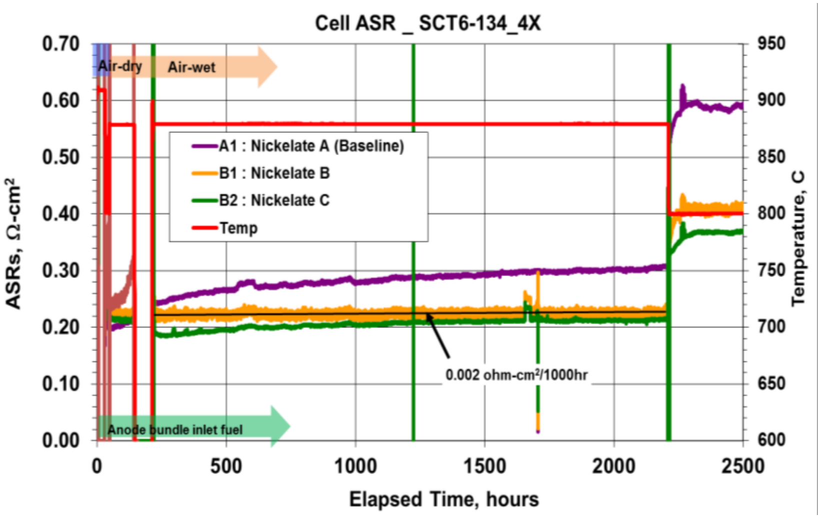
# Further Reduction in Cell ASR using Nickelate Cathodes

- Phase instability under operating conditions has been major issues
- Technical approaches to improve nickelate phase stability
  - A-site doped $Pr_2NiO_{4+\delta}$
    - $(Pr_{0.25}Nd_{0.75})$ A-site ratio is phase stable[1], $(Pr_{0.5}Nd_{0.5})$ exhibits instability
  - Addition of B-site dopants provides phase stability for A-site $(Pr_{0.5}Nd_{0.5})$

Nickelate provides ~0.02 ohm-cm² lower ASR than most favorable LSM-based cathode





1. Advances in Solid Oxide Fuel Cells III, Ceramic Eng. and Sci. Proc., 28(4) 2008.

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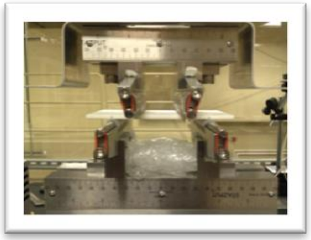
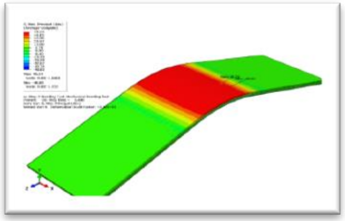
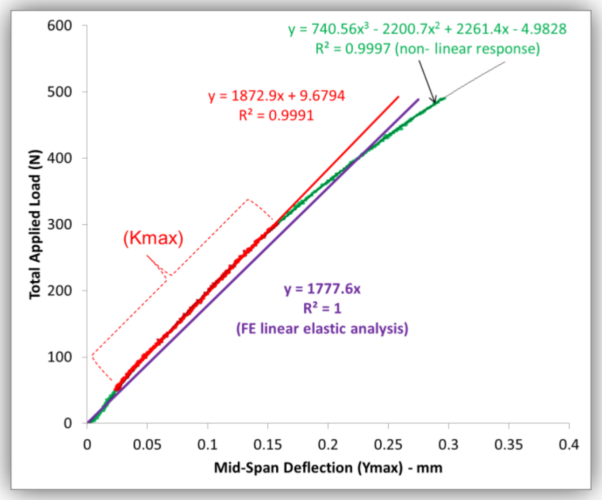
# FEA Validation and CARES Prediction

## • FE Stress Modelling: Validation at RT








| MMA Substrate Gen 2 | Ratios (Exp./FE) $K_{max}$ (N-mm) |
|---|---|
| Bare Substrate<br>*(avg. strength from 30 test)* | 1804/1777.6 =**1.01** |
| Glassed Substrate<br>*(120µm thick glass layer and avg. strength from 6 test)* | 1831/2102.5 = **0.87** |
| Full Printed Substrate<br>*(avg. strength from 15 test)* | 2504/2726.5 = **0.92** |

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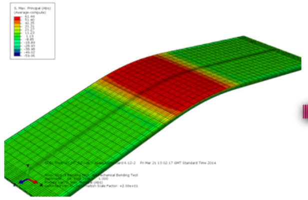
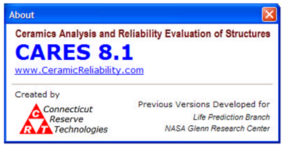
## • CARES Prediction: 4pt bend test at RT



$$B = \left[\left(\frac{\sigma_1}{\sigma_0}\right)^m V_1\right] + \left[\left(\frac{\sigma_2}{\sigma_0}\right)^m V_2\right] + \left[\left(\frac{\sigma_3}{\sigma_0}\right)^m V_3\right] + \cdots$$

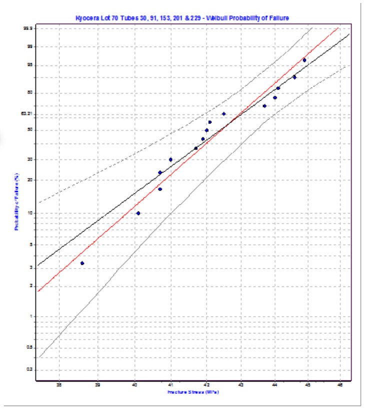
$$R = \exp(-B)$$

$$P_f = 1 - R$$




$$P_i = 1 - e^{-V\left(\frac{\sigma_{max}}{\beta}\right)^m}$$

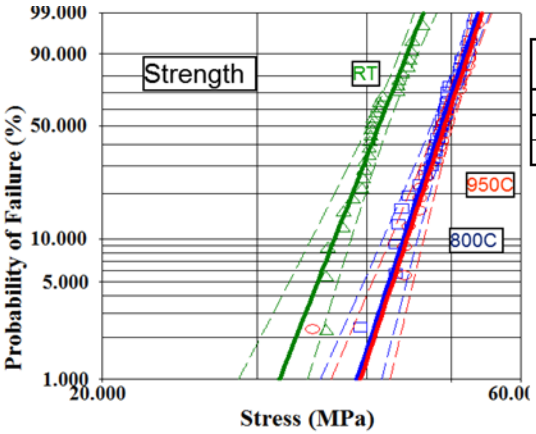
$$P_f = 1 - \prod_{i=1}^{N}(1 - P_i)$$



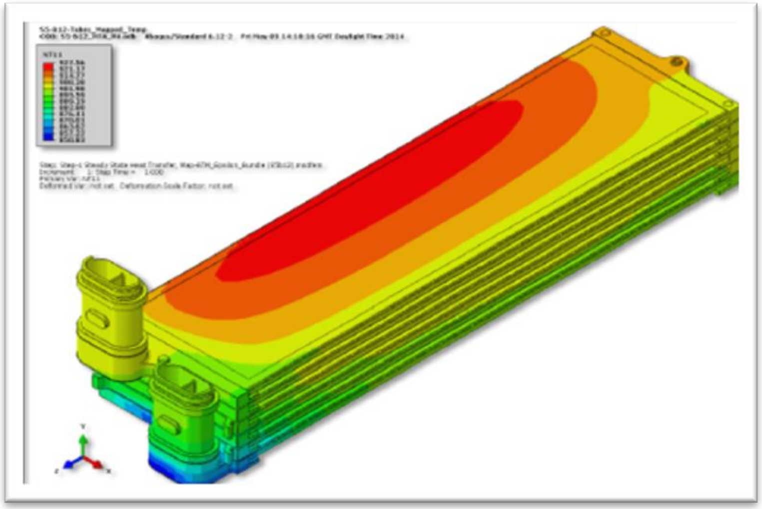
- ***Input from 4pt bend test on MMA Substrate :***
- ***$\sigma_0 = 57.48$, $m = 16.48$***
- ***CARES Output:***
- ***$P_{f,\ CARES\ prediction} = 63\%$***
- ***$P_{f,\ expected} = 63.2\%$ (Good Agreement)***

# 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)




| Temperature | Strength, MPa (Pf=63.2%) | Weibull Modulus |
|---|---|---|
| room temp. | 42.3 | 16.2 |
| 800C | 49.5 | 19.3 |
| 950C | 50 | 19.2 |



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

# 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:

$m = 14.98$

$\sigma_{0V} = 58.92$ MPa mm$^{3/m}$

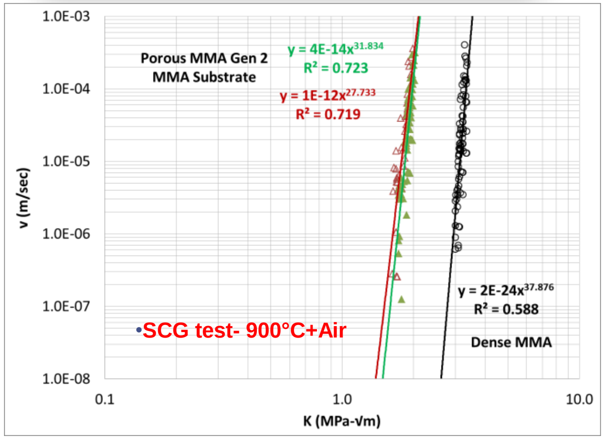
$N = 35.52$

$A = 4e^{-13}$

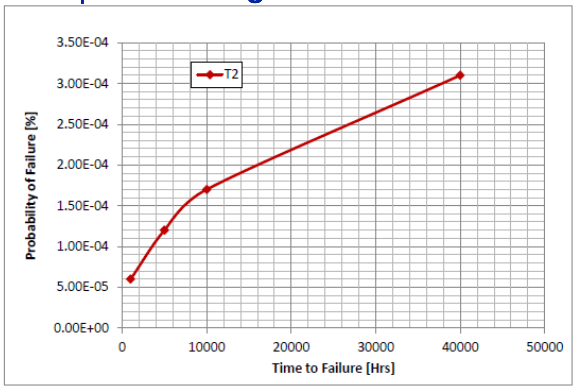
$K_{IC} = 2.08$ MPa m$^{1/2}$

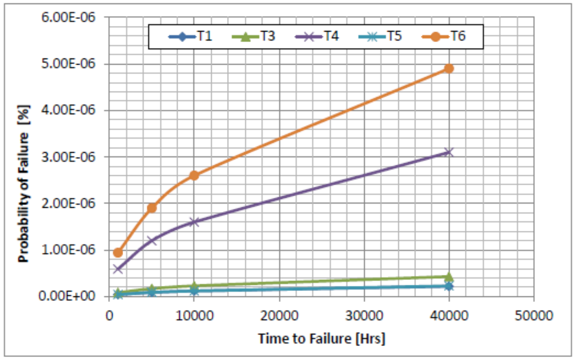
$Y = 2.3$

$$B = \frac{2}{AY^2 K_{IC}^{N-2}(N-2)} = 0.615 \text{ MPa}^2 \text{ sec}$$

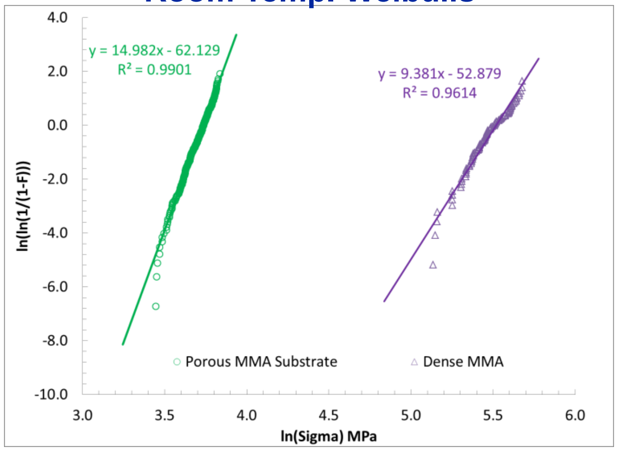



## $P_f$ in $10^{-4}$ range for substrate 2




## Room Temp. Weibulls




| | MoR (MPa) | m |
|---|---|---|
| Porous MMA | 41.31 | 14.98 |
| Dense MMA | 248.61 | 9.38 |

# 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.

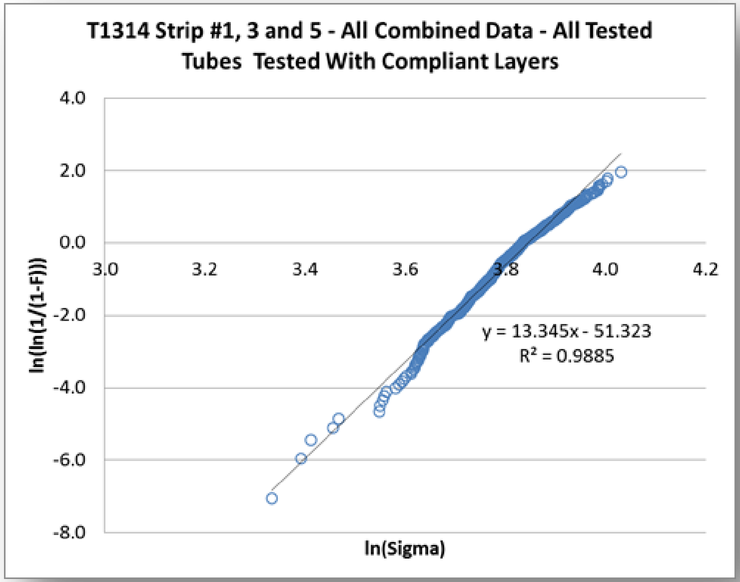
| Strip No. | Lot No. | No. of Test Specimens | Strength Ratio (± 95% Conf. Int.) |
|---|---|---|---|
| 1 | 22 | 186 | 1.32 ± 0.019 |
| 1 | 32-2 | 19 | 1.32 ± 0.048 |
| 3 | 32-1 | 196 | 1.46 ± 0.014 |
| 5 | 32-2 | 36 | 1.39±0.15 |
| 5 | 24 | 132 | 1.40±0.14 |
| 5 | 25 | 33 | 1.53±0.07 |

(Mix of Gen1 and Gen2 substrates)

## 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.

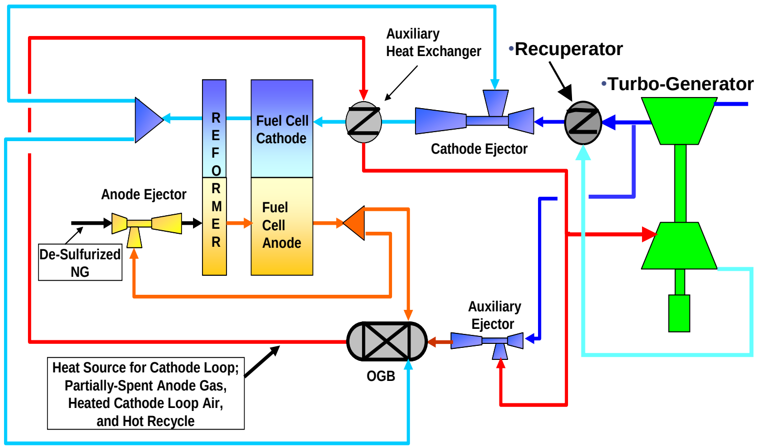
| | MoR (MPa) | m |
|---|---|---|
| Post-test | 46.76 | 13.43 |



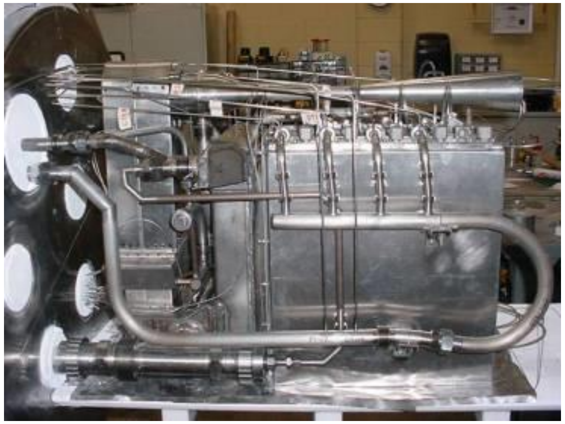
# Outline

- 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**

# Block Testing Matching Product Cycle, Components and Operating Conditions





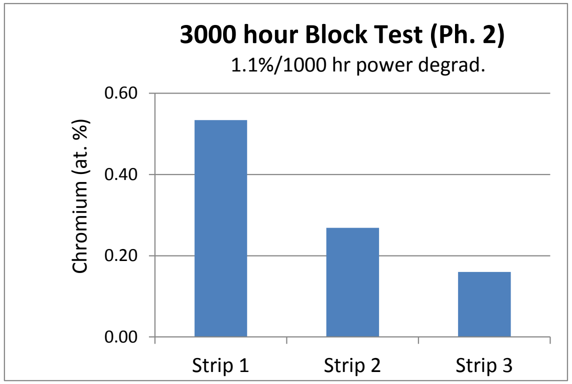


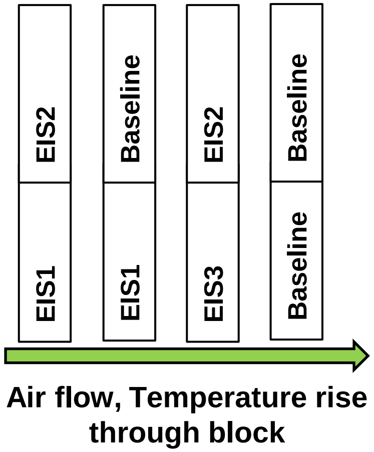
- Initial design of block testing rigs
- Representative of cycle and components
- Not packaged for product

- 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**
  - **1st test: Chromium mitigation, pipeline nat. gas and SCSO desulfurization (started July 2014)**
  - **2nd test: higher Chromium sources, pipeline nat. gas (starting Aug 2014)**
    - **Similar Cr content as Phase 1 and Phase 2 block tests**

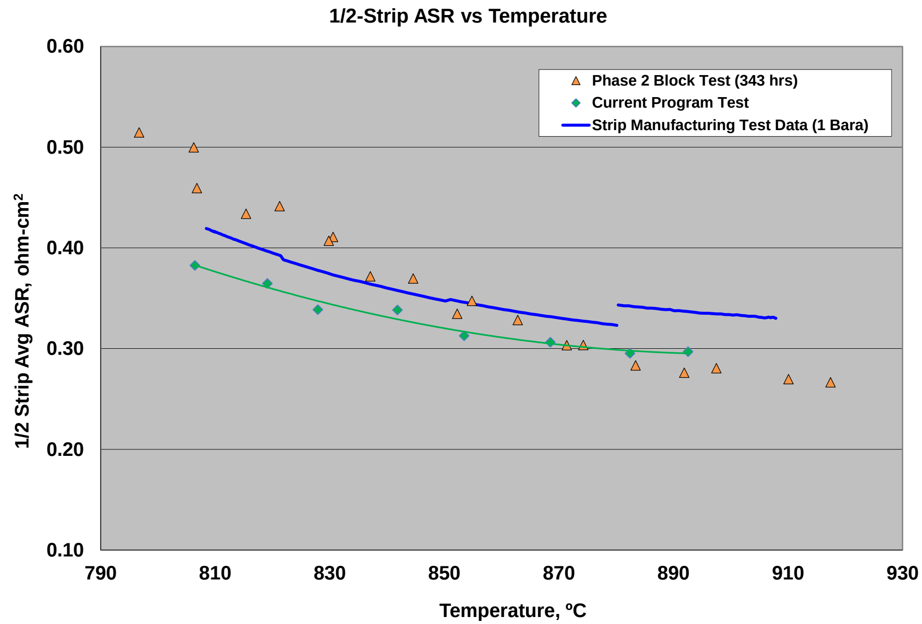


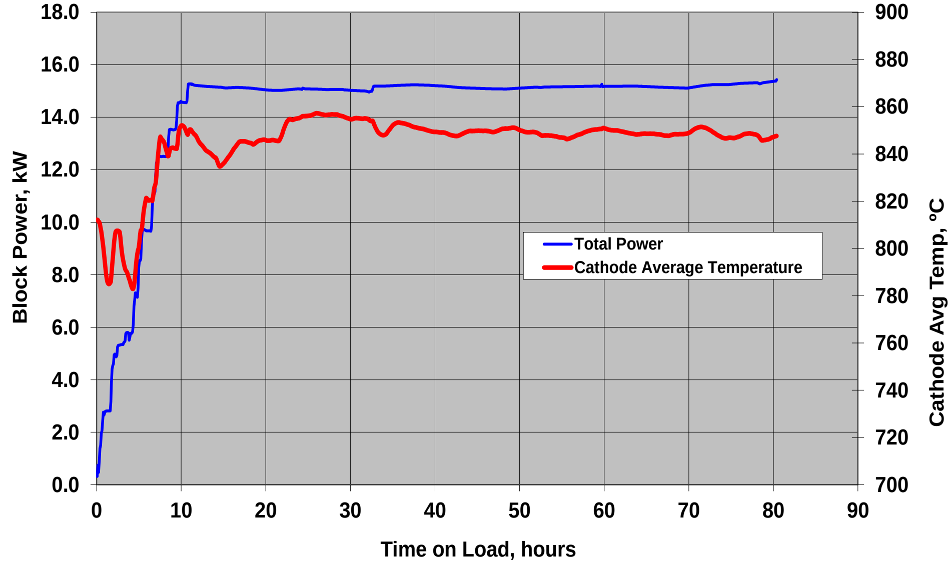




- **3rd 4-strip test of combined cell technology for lower ASR and improved durability**
  - **expected <0.75%/1000 hours**
  - **Single layer anode, alternate cathode, primary interconnect redesign**

# 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.

# Acknowledgements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