Advanced Materials for RSOFC Dual Operation with Low Degradation

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Annual Merit Review
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Project ID: FC042

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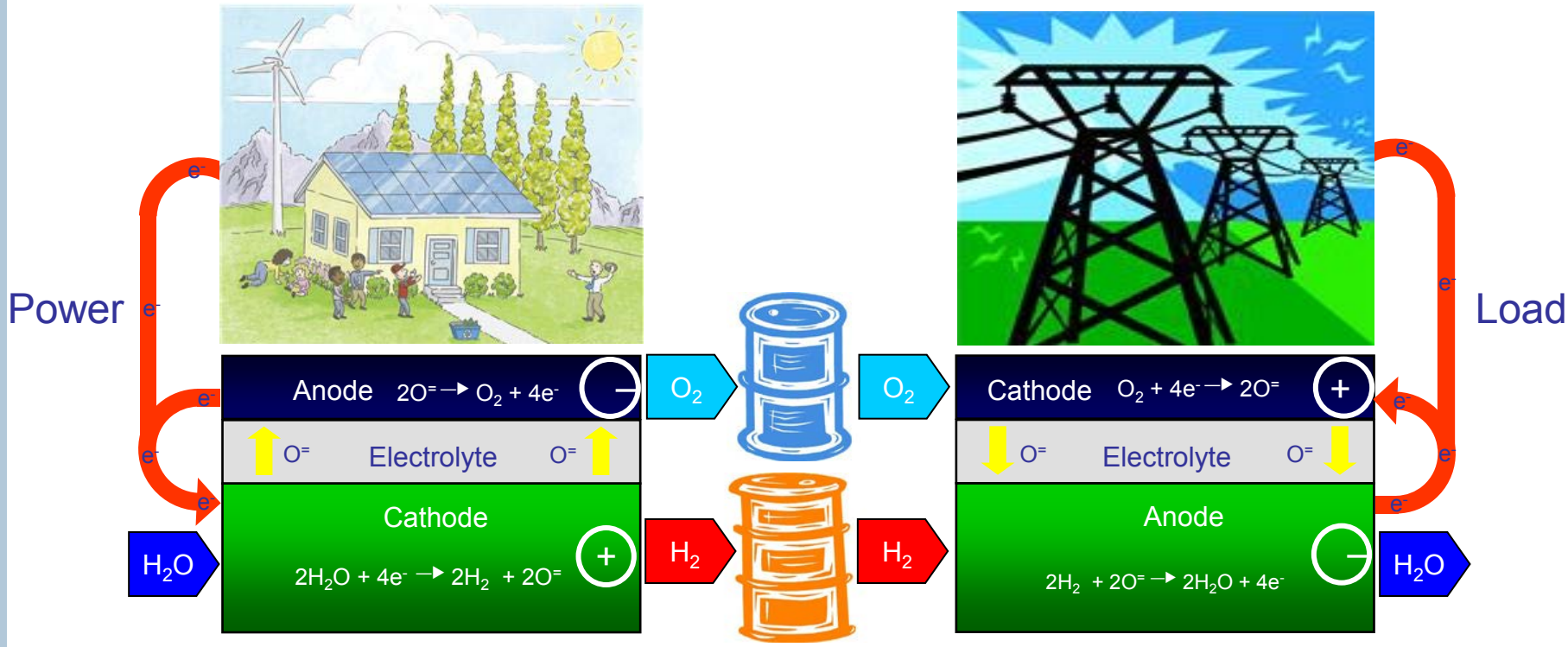
Overview

- Timeline
  - Start: September 2009
  - Original End: September 2011
  - NCTE End: June 2012
- Barriers
  - A. Durability
  - B: Cost
  - C. Performance
- Budget
  - Total project funding: $1,890,630
    - DOE share: $1,512,504
    - VPS share: $ 378,126
  - FY11 DOE Funding: $435,647
  - Planned Funding for FY12: $0
- Partners
  - Boeing
  - NREL
  - Idaho National Laboratory (INL)
  - SECA

Project Background

- Reversible Solid Oxide Fuel Cells (RSOFCs) are energy conversion devices: they are capable of operating in both power generation mode (SOFC) and electrolysis mode (SOEC)
- RSOFC can integrate renewable production of electricity and hydrogen when power generation and steam electrolysis are coupled in a system, which can turn intermittent solar and wind energy into “firm power”



Relevance

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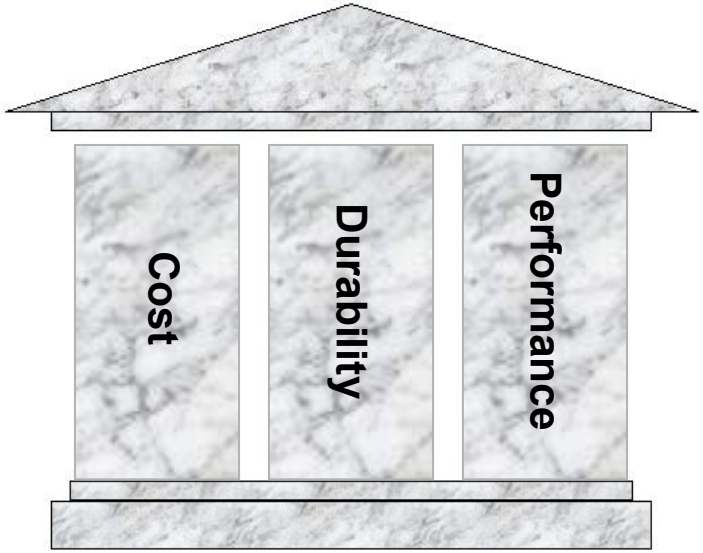
Relevance

Project Objectives

- To advance RSOFC cell stack technology in the areas of endurance and performance through RSOFC materials development and reversible stack design
- To meet the following performance targets in a kW-class RSOFC stack demonstration:
  - RSOFC dual mode operation of 1500 hours with more than ten SOFC/SOEC transitions
    - Performance (C), Durability (A)
  - Operating current density of more than 300 mA/cm^2 in both SOFC and SOEC modes
    - Cost (B), Performance (C)
  - Overall decay rate of less than 4% per 1000 hours of operation
    - Durability (A), Cost (B)



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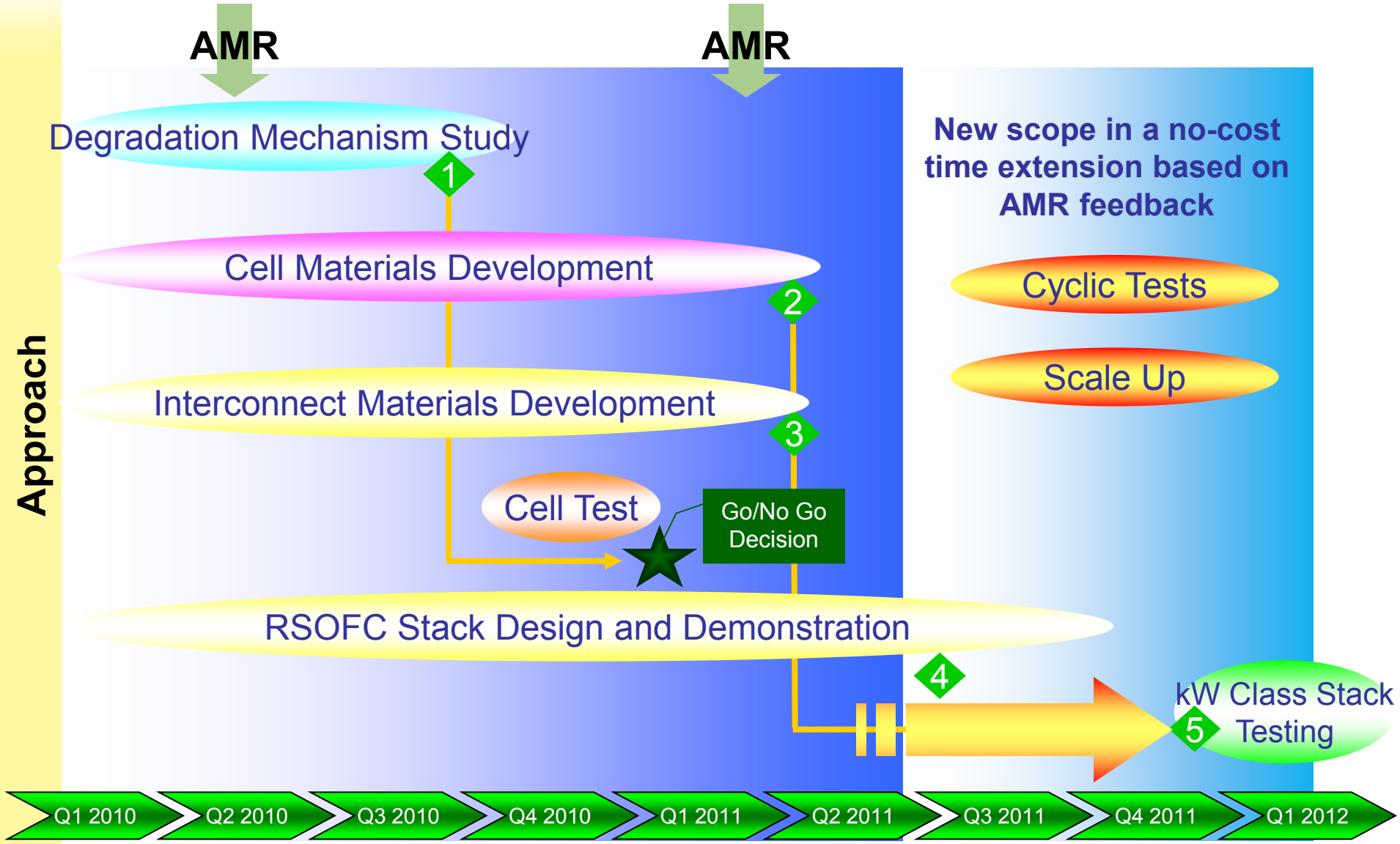
How Objectives Address Barriers

Relevance

	Hurdle	Targets
Endurance	**Performance decay in SOEC mode is too high for RSOFC system development** ▶ Materials system is not stable in the SOEC operating mode; with a decay rate more than 20% per 1000 hours ▶ Performance decay during transient between SOEC and SOFC is high	**Reducing decay to under 4% per 1000 hours for both SOFC and SOEC** ▶ Meet endurance target in a 1000 hour single cell test ▶ Meet endurance target in a 1500 hour, kW-class stack ▶ Demonstrate transient capability with more than 10 FC/EC transients
Performance	**Performance in SOEC mode is not sufficient for viable RSOFC system development** ▶ ASR is more than 1.0 Ω-cm^2 at 750°C and below in SOEC mode	**Improve performance at 750°C in SOEC mode by reducing ASR to less than 0.3 Ω-cm^2** ▶ Meet performance technical target in a single cell test ▶ Operate kW-class RSOFC stack at more than 300 mA/cm^2

Progress from the Last Review Meeting



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Decision Points and Milestones

Approach

- At month 15, a go/no-go gate was passed based on a 1000-hour single-cell test relative to the following performance and endurance metrics:
  - RSOFC area specific resistance of less than 0.3 Ω-cm^2 in both SOFC and SOEC operating modes
  - Operating current density of more than 300 mA/cm^2 in both SOFC and SOEC modes
  - Overall decay rate of less than 4% per 1000 hours of operation
- Five technical milestones have been tracked and measured throughout the project:
  - 1 – Task 1: Completion of degradation mechanisms study of baseline cells (4th quarter)
  - 2 – Task 2: Completion of RSOFC cell materials selection (6th quarter)
  - 3 – Task 3: Completion of RSOFC interconnect materials selection (6th quarter)
  - 4 – Task 4: Completion of RSOFC stack design (7th quarter)
  - 5 – Task 4: Starting end of the project RSOFC stack metrics test (8th quarter)

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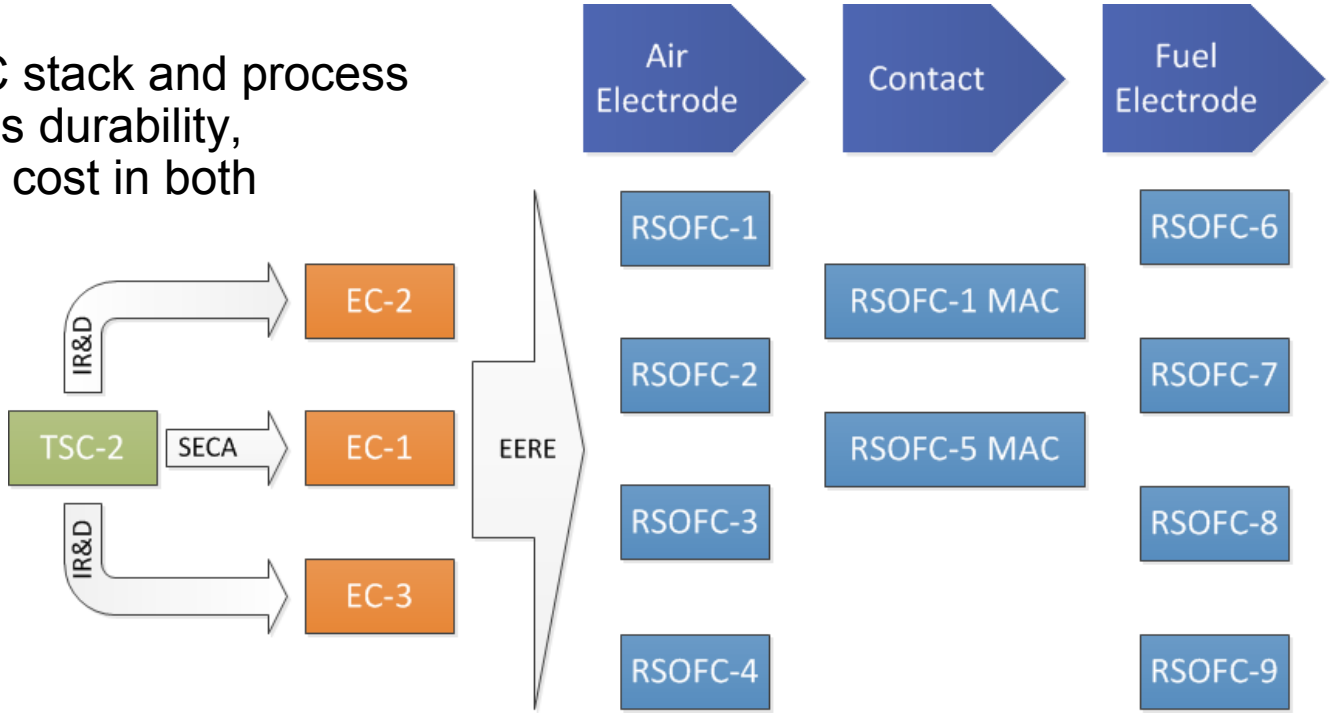
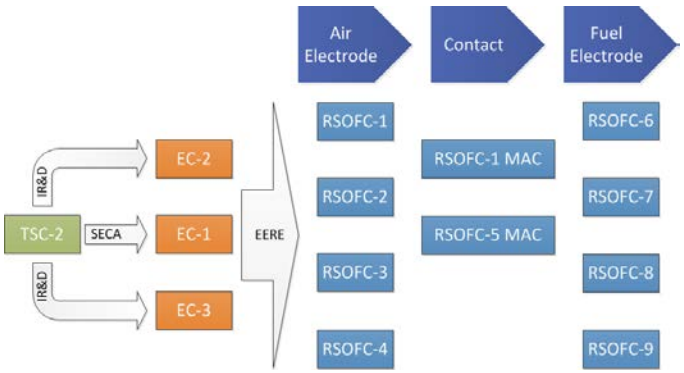
RSOFC Development Path

Approach

- Build on VPS's strong SOFC cell and stack baseline
- Leverage cell and stack advancements from the DOE-SECA SOFC project
- Address RSOFC degradation mechanisms in SOEC mode with innovative cell and stack repeat unit configurations
- Conduct parallel materials development activities and integrating them with cell production technology development
- Complete RSOFC stack and process designs to address durability, performance, and cost in both SOFC and SOEC operating modes



RSOFC Cell Performance Development Status



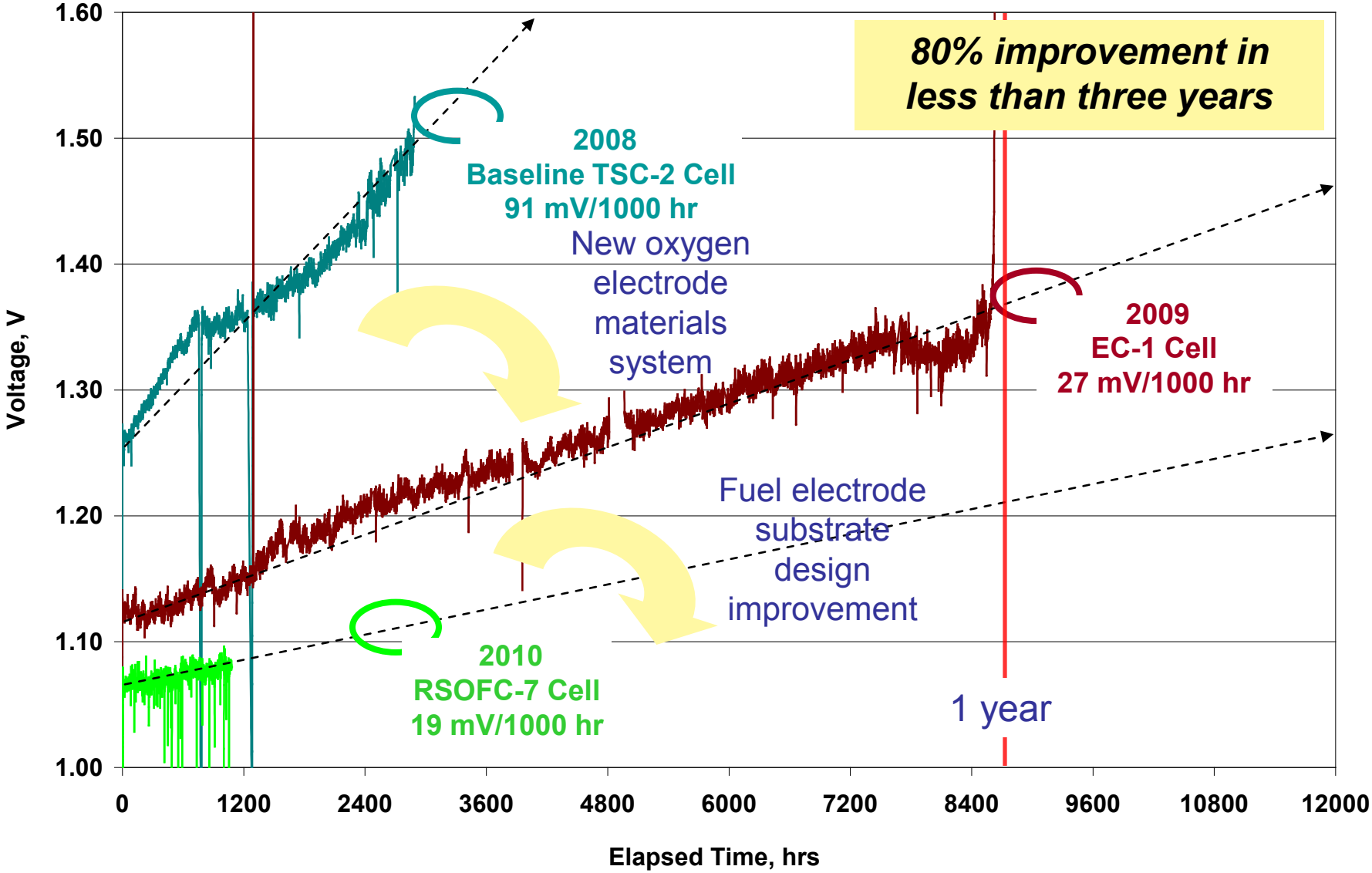
- Initial focus: degradation in electrolysis
  - Cyclic degradation was less than electrolysis
- Addressing three root causes
  - Air electrode materials, morphology, and processing
  - Air electrode contacts
  - Fuel electrode substrate materials, morphology, and processing
- Degradation was reduced to less than 4% per 1000 hours
  - Engineering development focus shifted to cyclic degradation

Eight cell types passed the performance criteria of ASR less than 300 mΩ-cm² in both SOFC and SOEC modes at 750ÁC

Cell Type	SOEC ASR (mΩ-cm²)	SOFC ASR (mΩ-cm²)
TSC-2	375	180
EC-1	366	281
EC-2	362	393
EC-3	278	251
RSOFC-1	308	245
RSOFC-1 MAC	251	245
RSOFC-2	285	295
RSOFC-3	386	283
RSOFC-4	268	238
RSOFC-5	341	253
RSOFC-6	271	242
RSOFC-7	223	224
RSOFC-8	194	223
RSOFC-9	230	219

- Fuel Cell (SOFC) ASR at 3% humidity and 750°C
- Electrolysis (SOEC) ASR at 50% humidity and 750°C

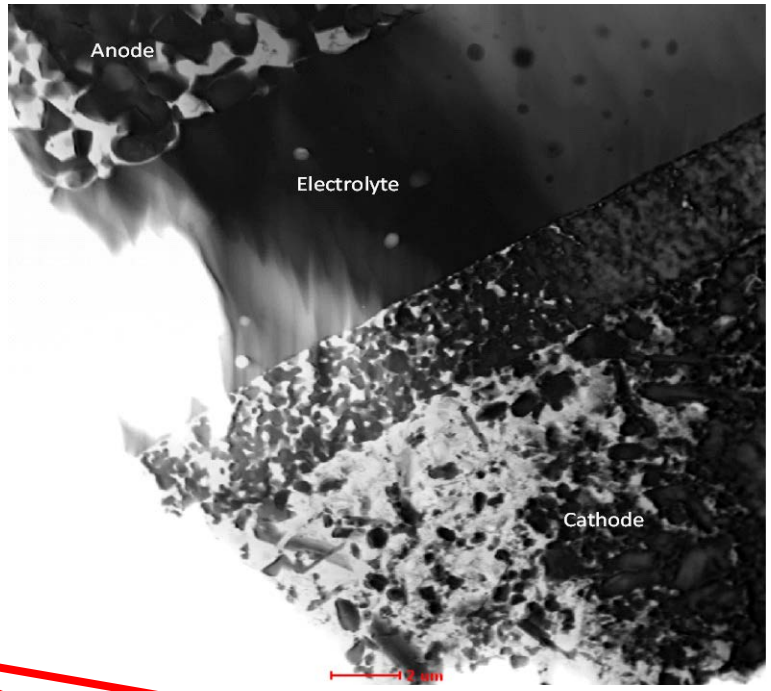
Electrolysis Lifetime



Electrolysis Degradation Status

- Six cell types have passed the degradation criteria of less than 4%/1000 hours in SOEC mode
- RSOFC-4 and RSOFC-7 passed both performance and degradation criteria

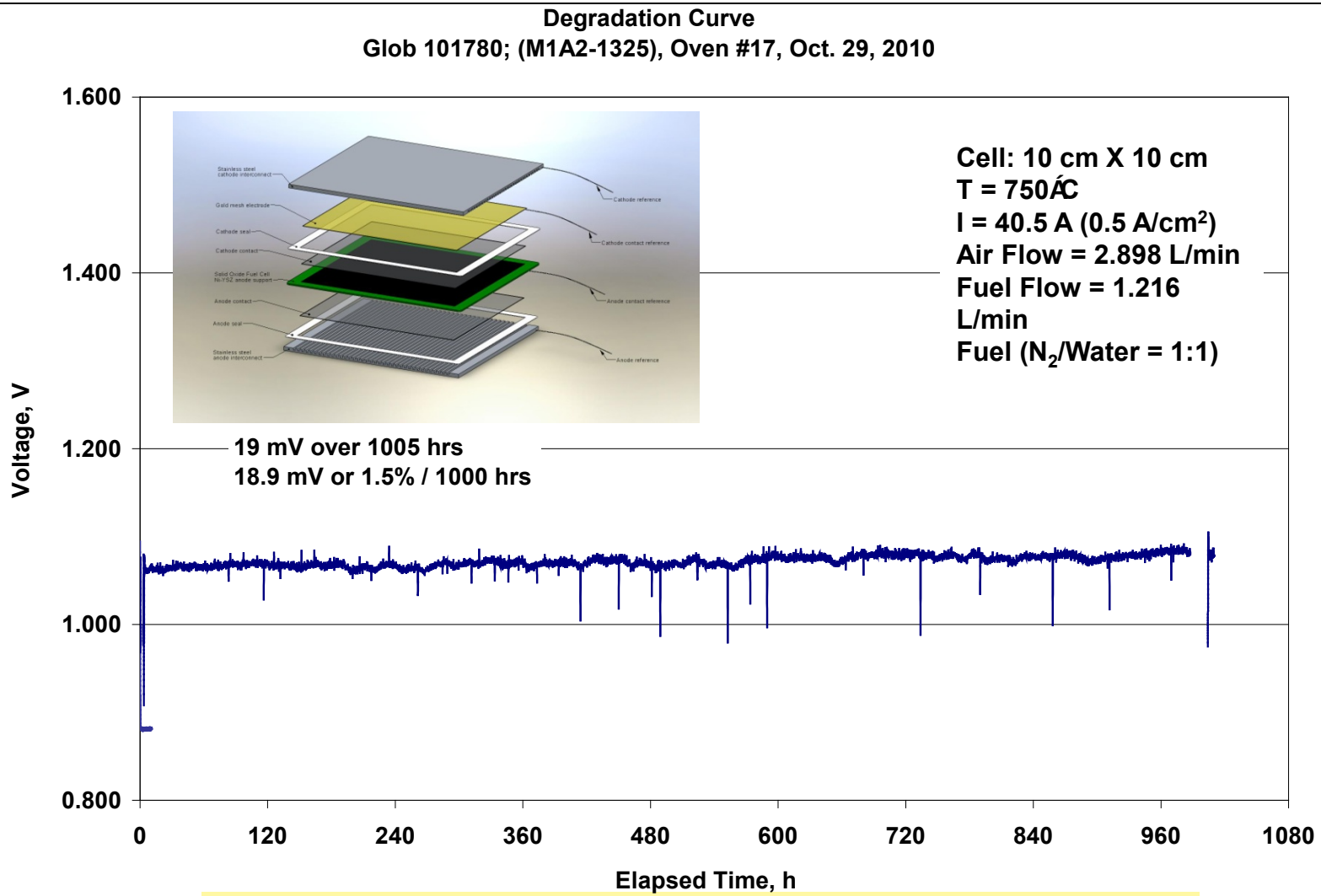
Cell Type	Electrolysis (SOEC) Degradation		
	mV / 1000 hrs	% / 1000 hrs	Duration (hrs)
Target	*< 50*	*< 4*	*> 1000*
TSC-2	91	7.3	2893
EC-1	27	2.2	8465
EC-2	~0	~0	2400
EC-3	72	5.8	1792
RSOFC-1	35	2.8	6472
RSOFC-2	120	9.6	1152
RSOFC-3	42	3.4	2653
RSOFC-4	24	1.9	3618
RSOFC-7	19	1.5	1005



Post Test Analysis After 8,000 Hours:

- **All electrochemical functional layers fully intact, no delamination between electrodes and electrolyte**
- **No chemical impurities or contaminations, such as, Cr poisoning found in cathode (air electrode)**
- **No microstructure coarsening found**

Steady-State Electrolysis Test of a RSOFC-7 Cell

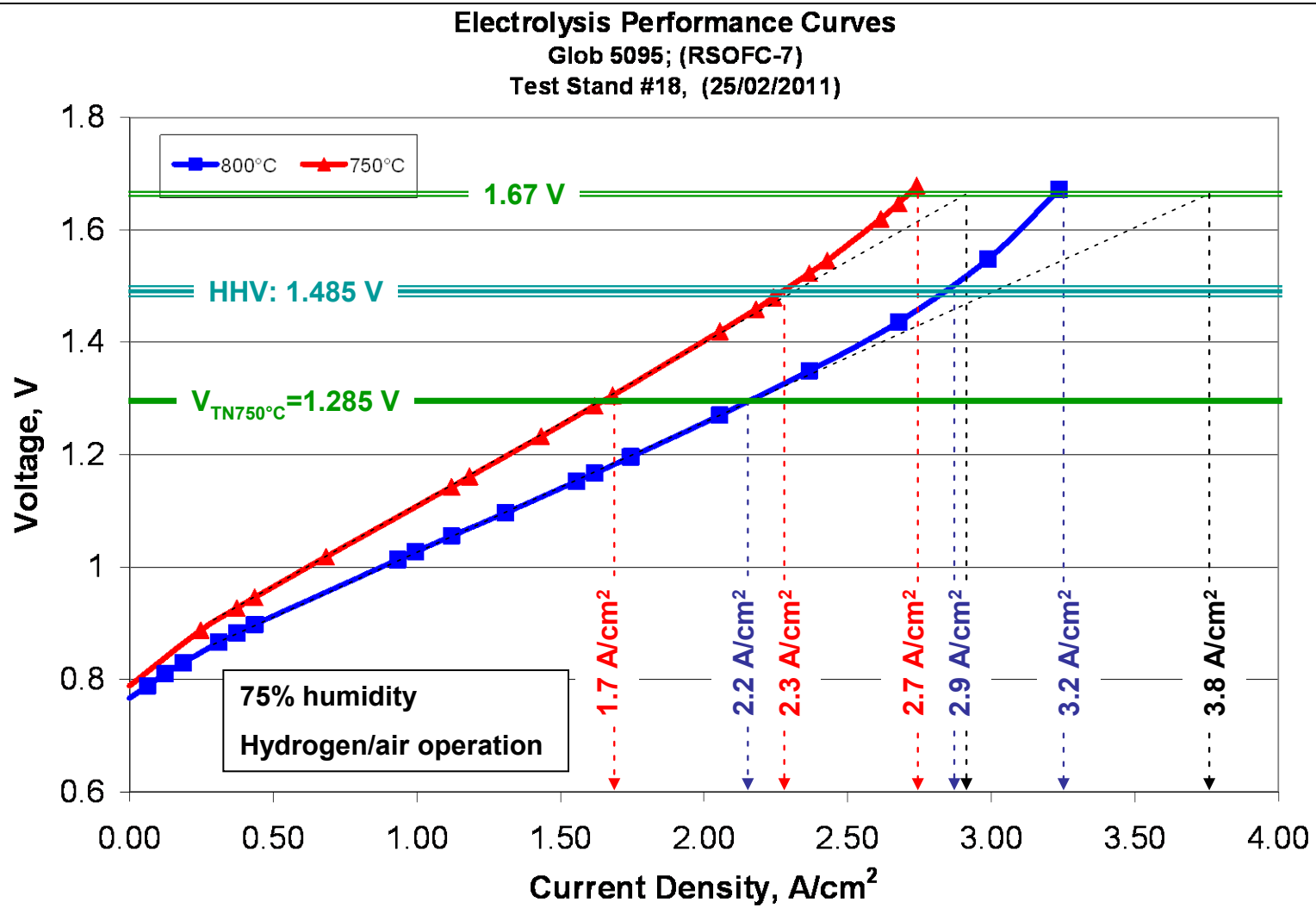


Demonstrated electrolysis mode degradation of 19 mV, or ~1.5% per 1000 hours for the Go/No-Go Decision Test

Summary of Go/No-Go Decision Points

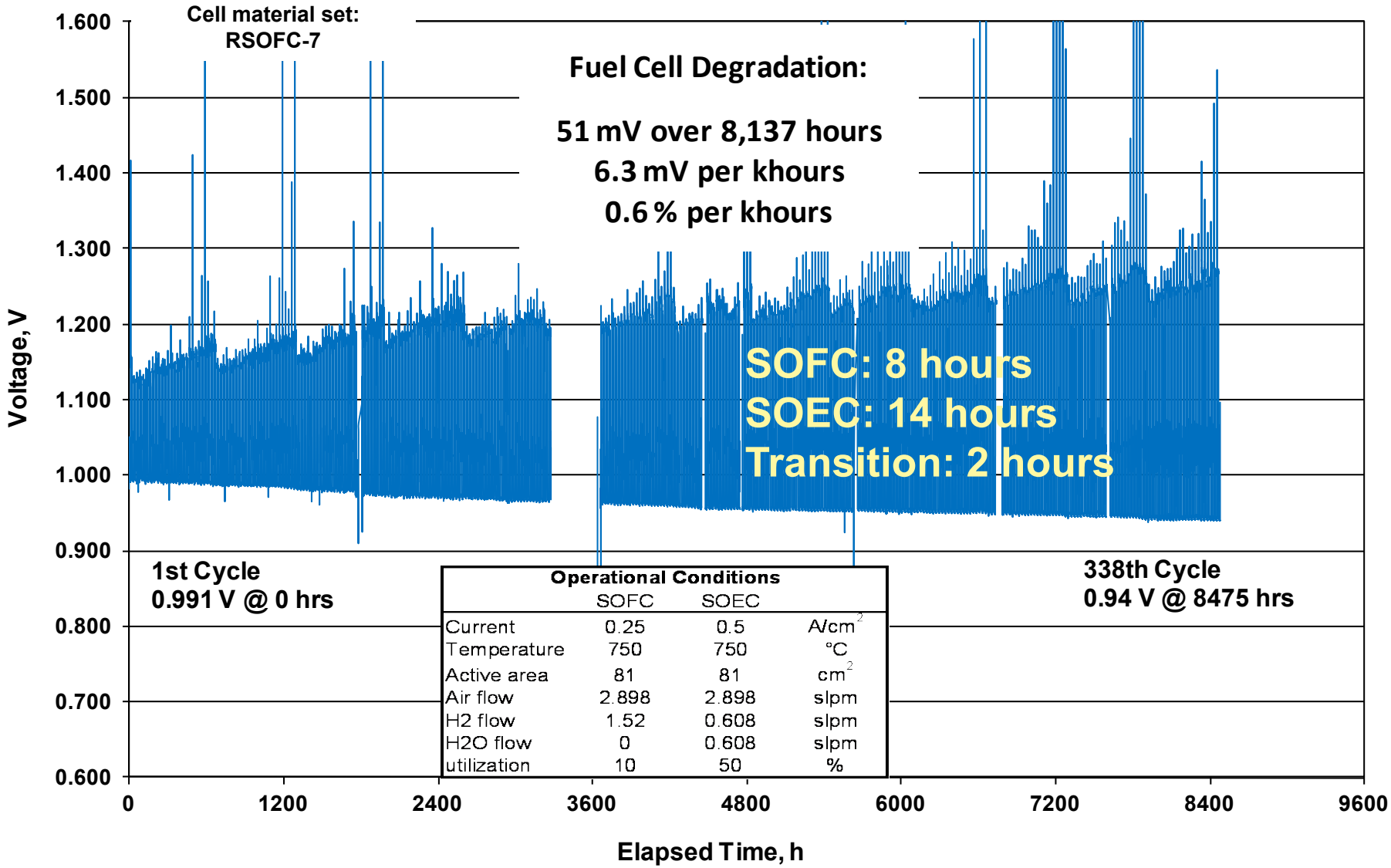
Metric	Target	Status
☑ **Performance** (Area specific resistance in both SOFC and SOEC operating modes)	< 0.3 Ω-cm^2	0.223 Ω-cm^2 in SOEC 0.224 Ω-cm^2 in SOFC
☑ **Degradation** (Overall decay rate)	< 4% per 1000 hours	~1.5% per 1000 hours
☑ **Operating Duration**	> 1000 hours	1005 hours
☑ **Operating Current Density**	> 300 mA/cm^2	500 mA/cm^2

RSOFC-7 Cell Performance at Ultra-high Electrolysis Current Density



High performance of RSOFC-7 can reduce hydrogen production cost and meet DOE water electrolysis efficiency (2017 target of 75%) at the same time

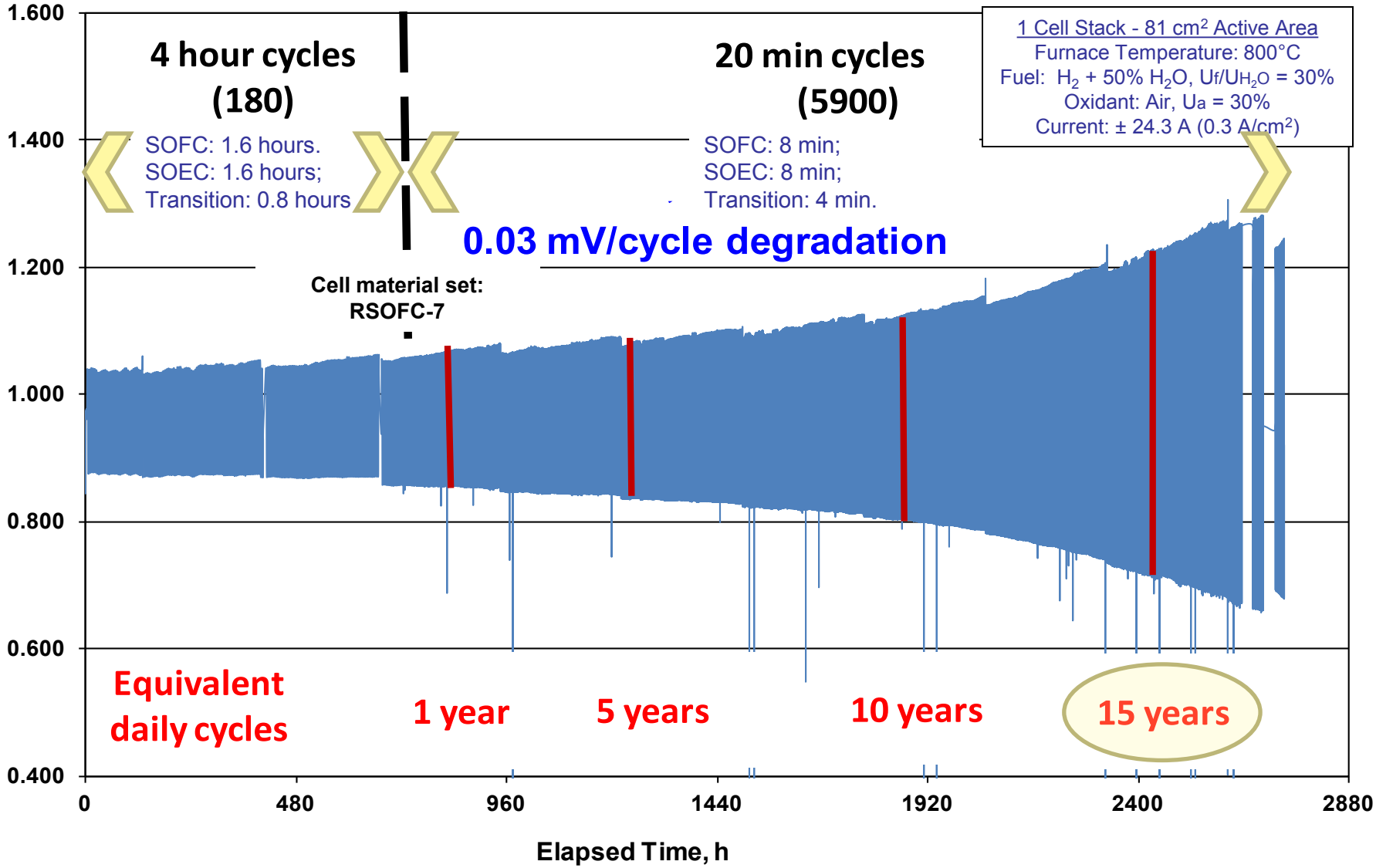
Stack Repeat Unit: Daily Cyclic Operation



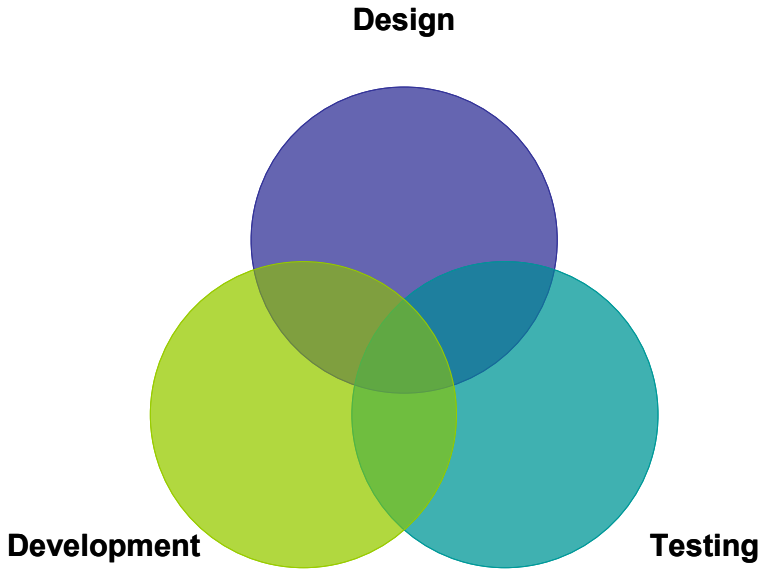
Operational Conditions

	SOFC	SOEC	
Current	0.25	0.5	A/cm^2
Temperature	750	750	°C
Active area	81	81	cm^2
Air flow	2.898	2.898	slpm
H2 flow	1.52	0.608	slpm
H2O flow	0	0.608	slpm
utilization	10	50	%

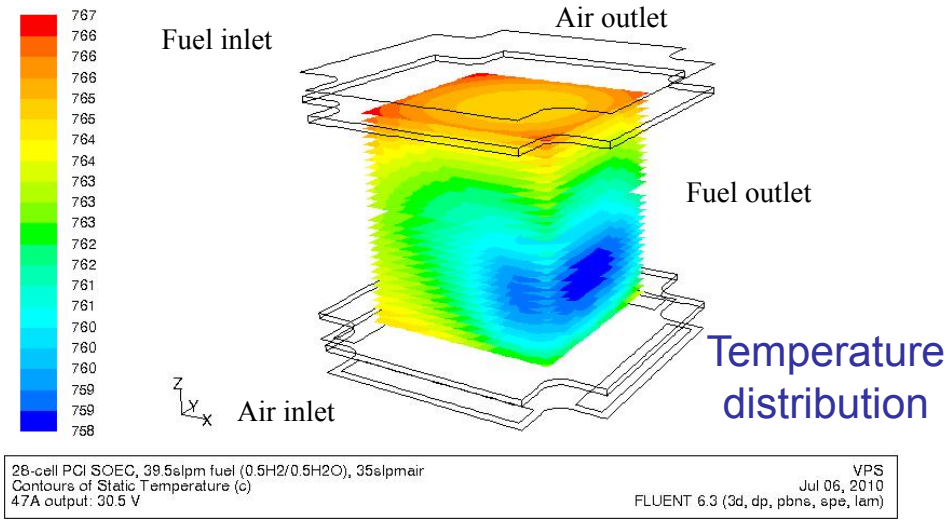
Stack Repeat Unit: Accelerated Cycling (6,080 Cycles)

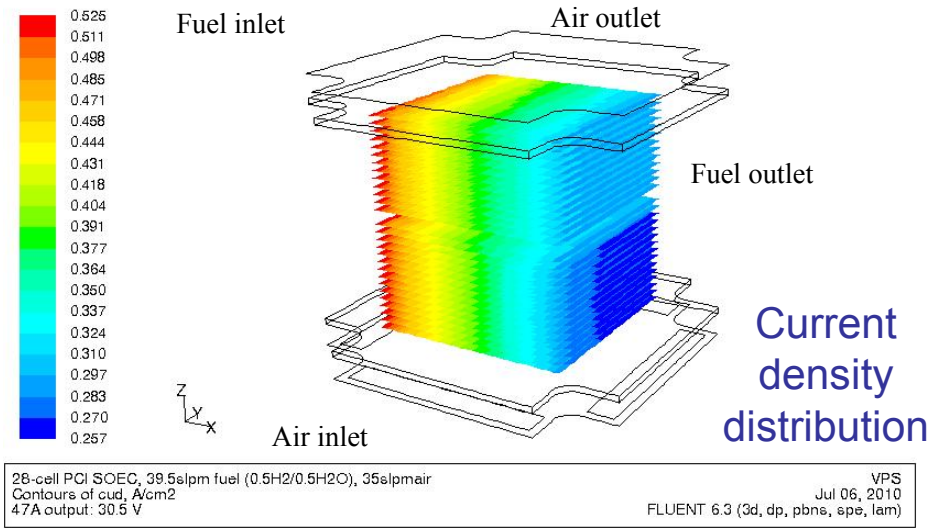


SOEC Stack Design and Development



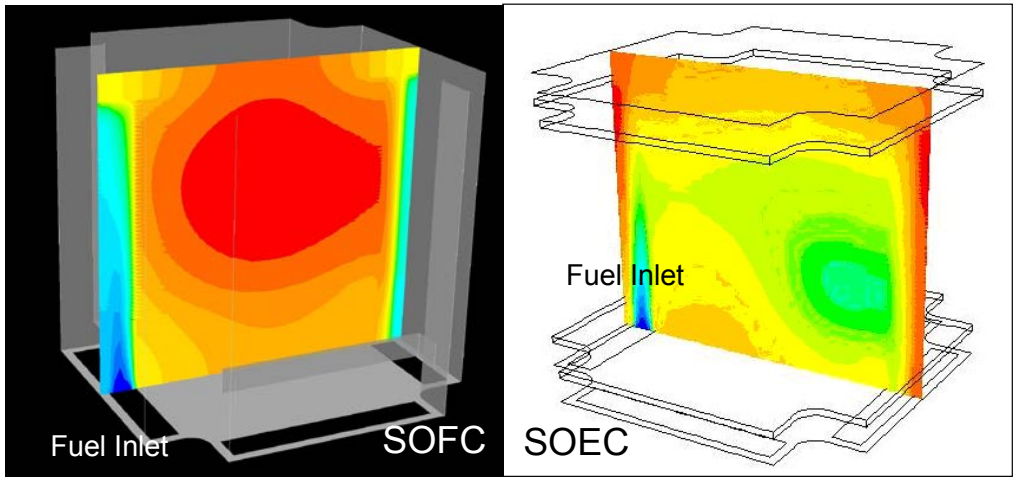
- Developed fully integrated CFD model for RSOFC stack
- Excellent stack thermal profile in SOEC operating mode
- Investigated local current density and chemical species concentration in SOEC operating conditions
- Electrolysis kinetics yet to be verified and calibrated in stack testing





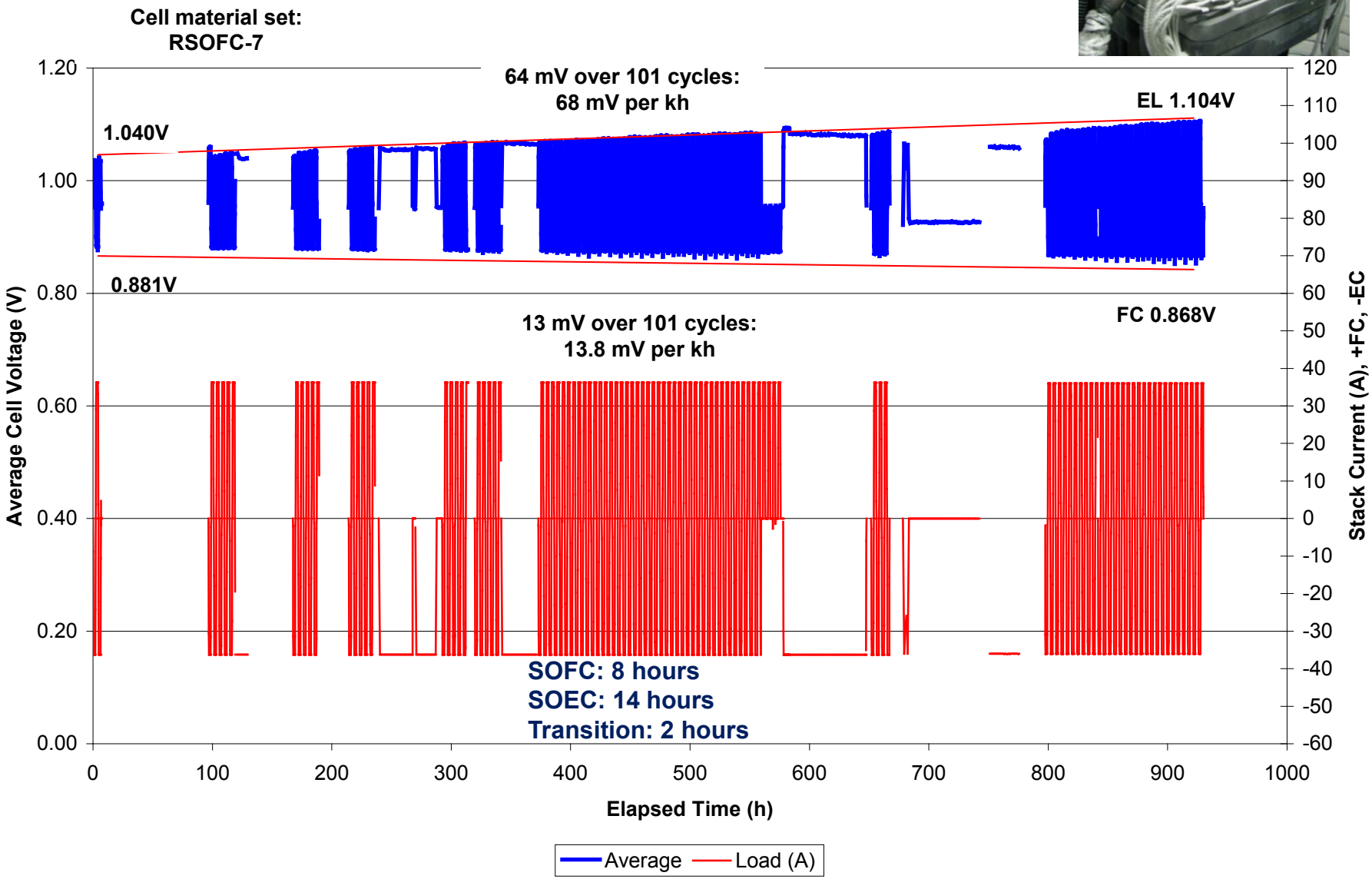
kW-Class Stack: Modeling and Cyclic Test

- CFD modeling shows thermal management challenges for RSOFC stack in cyclic operation
  - Stack operates in SOFC with hot zone in the middle of the stack
  - Stack operates in SOEC with cool in the middle of the stack
- Middle of the stack will experience increased thermal stress during SOFC/SOEC cyclic operation



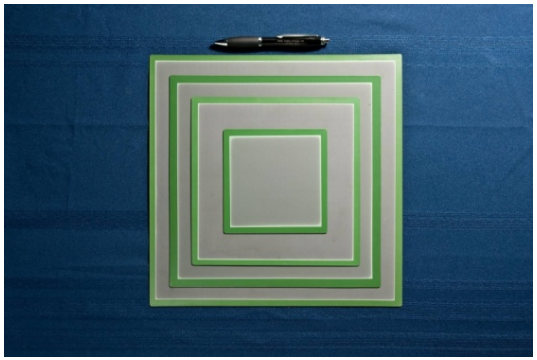
- A 20-cell, sub full area, 121 cm^2 stack was built and tested to evaluate SOFC/SOEC cyclic capability
- Characteristics
  - Improved fuel electrode contact design
  - RSOFC-7 cells
  - Five instrumentation plates with thermocouples

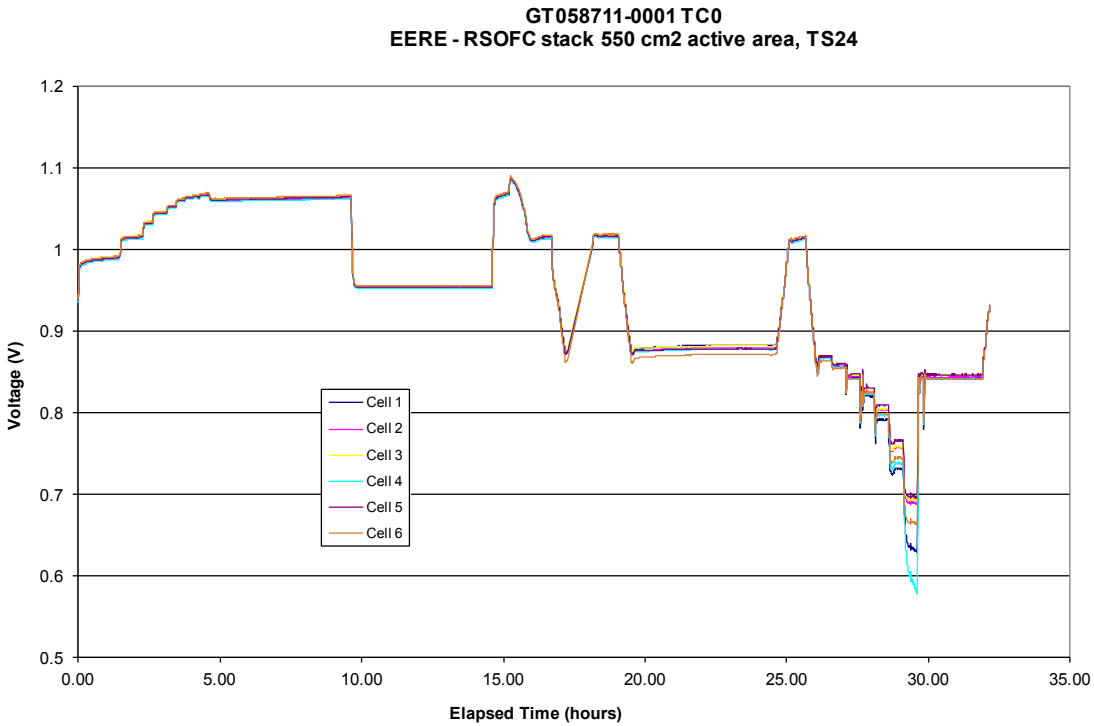
kW-Class Stack Cyclic Test: daily, SOFC, SOEC cycles



Development of a Scaled-Up kW-Class RSOFC Stack

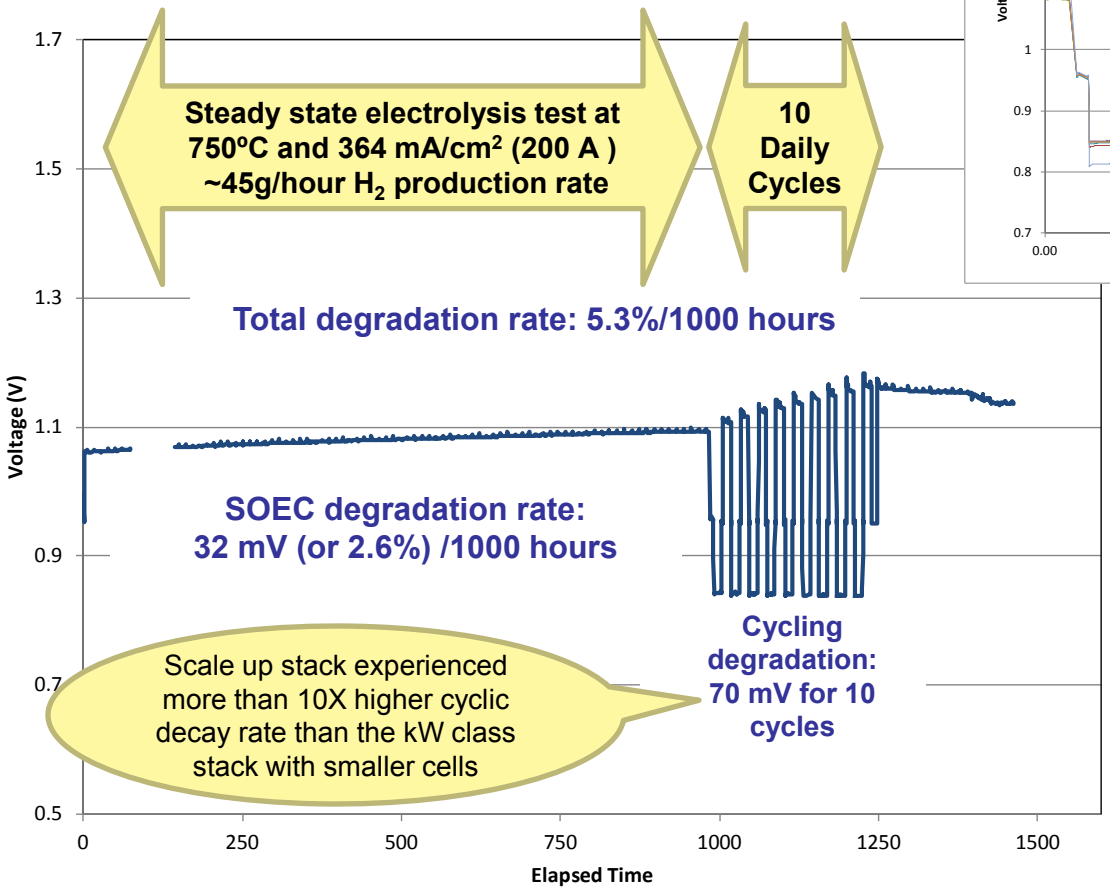
- A kW-scale RSOFC stack was developed for the milestone test
  - Using scaled up 25 by 25 cm cell (550 cm^2 active area)
  - Target operating current density: 0.364 A/cm^2, 200 A load in both fuel cell and electrolysis mode
  - Target operating temperature: 750°C
  - The stack went through conditioning and passed the VPS standard acceptance test with one thermal cycle prior to the milestone test



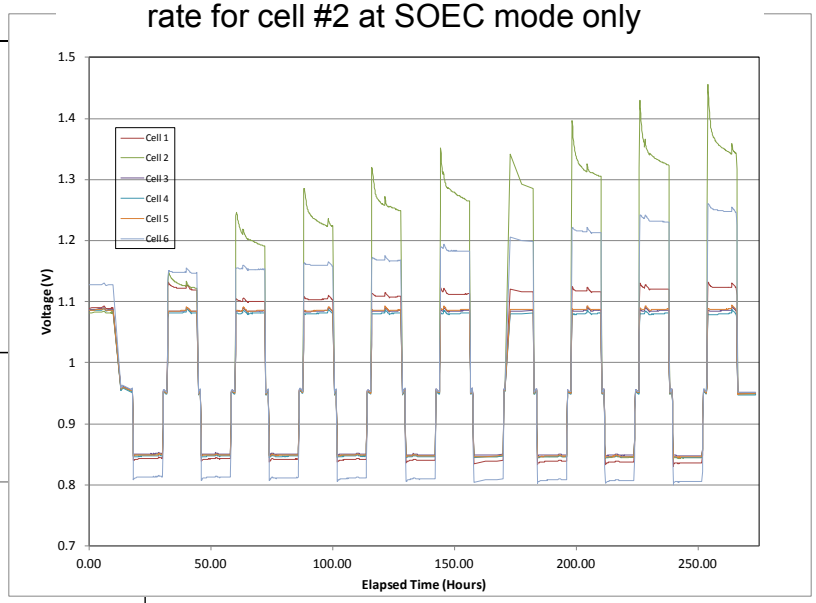


Project Milestone Test Results

- The stack did not meet the overall degradation target due to high cyclic degradation rate—higher than that obtained in previous 121 cm^2 active area, kW-class stacks
- The high cyclic degradation was mainly from cell #2 in SOEC mode and partially recovered in the subsequent testing



- Partial anode contact loss is considered the main cause of the high cyclic decay rate for cell #2 at SOEC mode only



- The milestone test started with 1000 hour SOEC steady-state test at 200A (364 mA/cm^2)—the degradation rate was 32 mV (2.6%) per 1000 hours
- Ten daily SOEC/SOFC cycles were conducted after the 1000 hour SOEC test—the degradation was 70 mV (5.6%) over 10 cycles
- The test was terminated at 1504 total operation hours due to facility issues
- The overall degradation rate was 5.3% per 1000 hours
- ***Excluding cell #2, degradation is 3.88% per 1000 hours.***

Milestone Test Results Summary

Metric	Target	Status
☑ **Performance** (Area specific resistance in both SOFC and SOEC operating modes)	**< 0.3 Ω-cm²**	**0.223 Ω-cm² in SOEC*** **0.224 Ω-cm² in SOFC***
☑ **Degradation** (Overall decay rate)	**< 4% per 1000 hours**	**5.3% per 1000 hours**
☑ **Operating Duration**	**> 1500 hours with 10 transitions**	**1504 hours with 10 transitions and one thermal cycle**
☑ **Operating Current Density**	**> 300 mA/cm²**	**364 mA/cm²**

* Single cell performance target

- VPS demonstrated less than 4% per 1000 hours in more than one kW-class stack using a 121 cm^2 cell platform
- To accelerate the scale up of the RSOFC technology, a kW-class stack based on a full area, 550 cm^2 cell platform was selected for the milestone test
- While post test analysis is on-going, contact issues associated with the combination of scale up and cyclic conditions are targeted for development and further testing to demonstrate the degradation metric deliverable before the end of the no-cost time extension

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Collaborations

- Boeing
  - Collaborated on and funded initial RSOFC development work through both Boeing and DARPA funded efforts
  - DARPA Vulture Phase 2 project was started October 2011
    - RSOFC stack integration into full reversible system
    - Stack design and development for reduced cost and weight
- NREL
  - Under EERE sponsorship, NREL re-visited energy storage system and techno-economics using RSOFC (Analysis of Solid Oxide Energy Storage, Feb 7, 2012) identifying early adopter applications and the need for more detailed alignment of duty cycles across the broad spectrum of commercial and industrial energy storage needs
- INL
  - Eventual integration of SOEC technology for hydrogen production with Next Generation High Temperature Nuclear Reactor
  - Demonstrated suitability of VPS SOEC technology for this application at the kW-class stack level
- SECA
  - The FuelCell Energy/VPS team has successfully passed through all gates to date and are now in Phase 3
  - VPS has advanced and scaled-up SOFC cell and stack technology culminating in a 50 kW stack module which has been applied in this program

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Proposed Future Work

- FY2012
  - Complete the post test analysis of the project metric test with kW-class RSOFC stack
  - Implement stack test condition and stack design improvement to meet the project metric test overall degradation target
  - Complete the final project report

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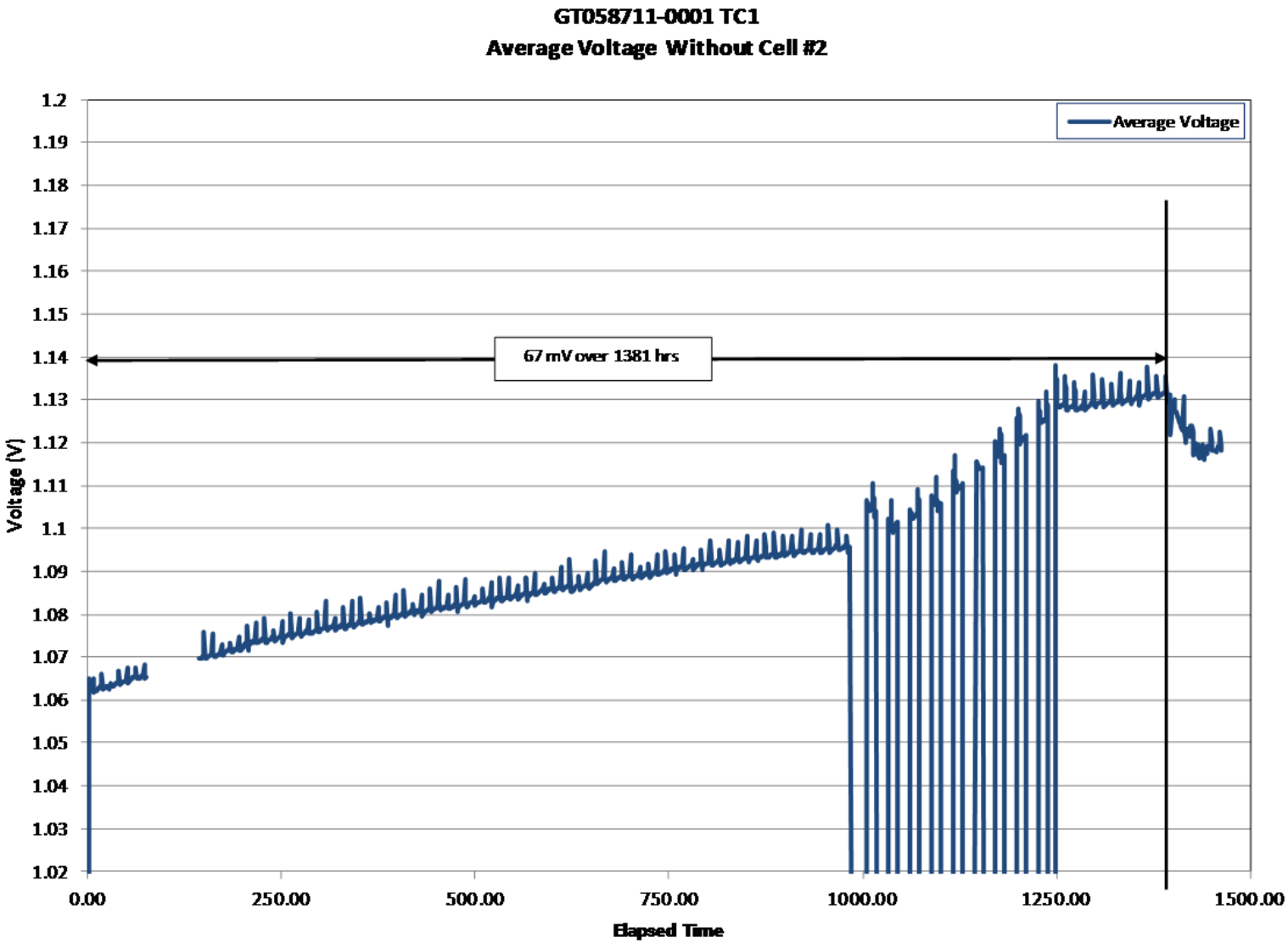
Summary

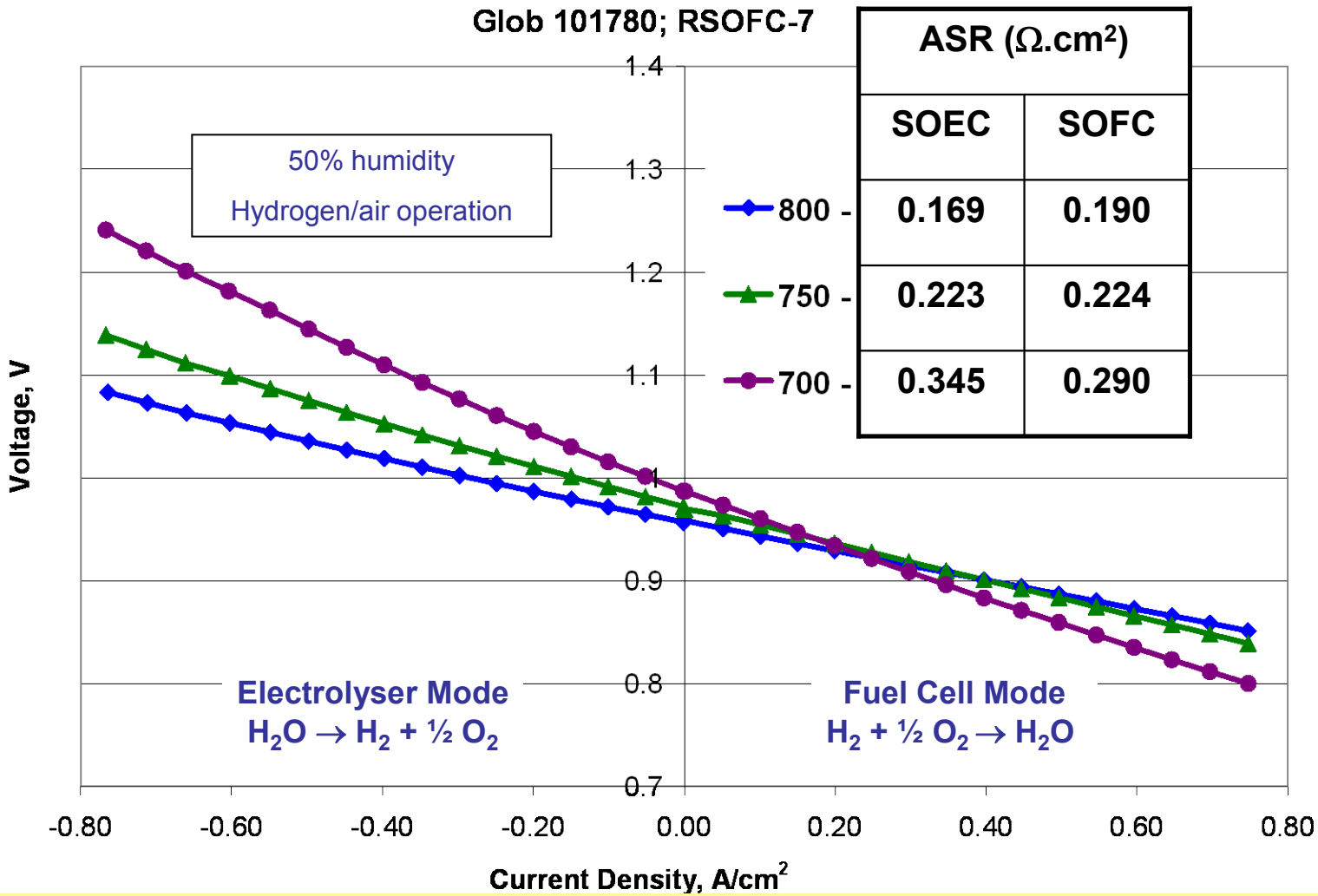
Relevance	• RSOFC can integrate renewable production of electricity and hydrogen when power generation and steam electrolysis are coupled in a system, which can turn intermittent solar and wind energy into "firm power"
Approach	• Developing high performance and low degradation RSOFC cell and stack technology is critical for the reversible SOFC/SOEC system
Technical Progress	• Over 20 types of RSOFC cells were developed in the project. Many of those exceeded both performance and degradation criteria • A steady-state single cell test of RSOFC-7 has run in electrolysis with a degradation rate of about 1.5% per 1000 hours • A single-cell test of RSOFC-7 demonstrated the capability of running electrolysis at over 3 A/cm^2 • Two single cells were tested over 8000 hours (1 year) • A single-cell test completed over 5800 SOFC/SOEC cycles • A kW-class stack was tested over 5000 hours • A kW-class stack completed 100 cycles • A kW-class stack comprising 550 cm^2 cells was developed and tested
Collaboration	▶ Boeing/DARPA, NREL, INL, and SECA
Proposed Future Research	▶ In addition to executing the original project scope, additional development activities are under consideration to accelerate RSOFC technology development for integrating with renewable energy sources, such as solar and wind.

Technical Back-Up Slides

The full area, 550cm2, kW-class, 6-cell stack- with cell 2 excluded: degradation is 3.88% per 1000 hours.



RSOFC-7 Cell Performance



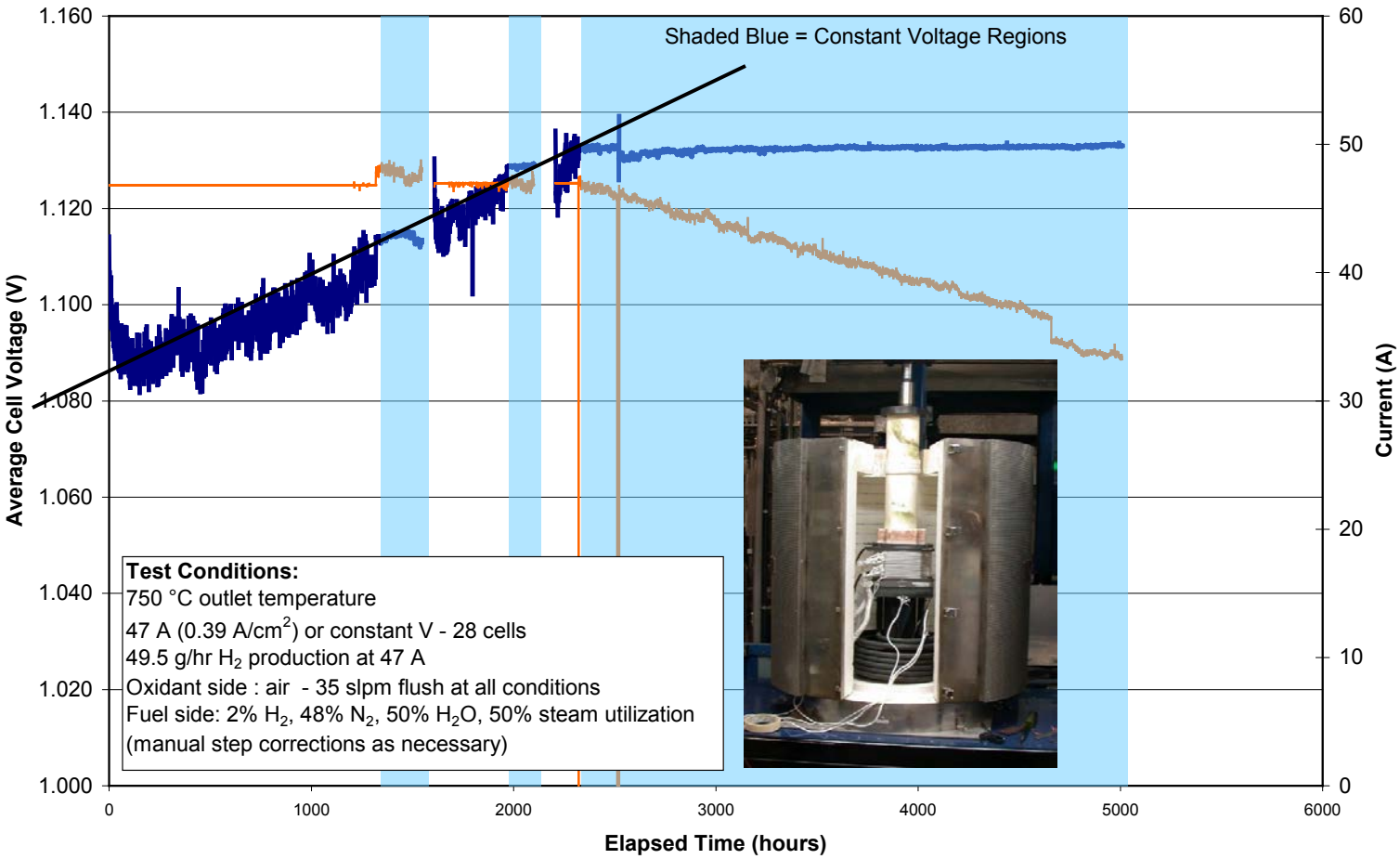
ASR (Ω.cm²)	
SOEC	SOFC
0.169	0.190
0.223	0.224
0.345	0.290

High performance of RSOFC-7 can reduce hydrogen production cost in SOEC mode and improve efficiency in SOFC mode

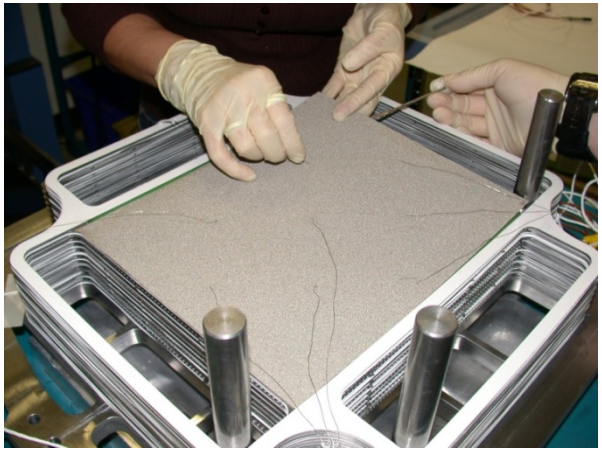
5000-Hour kW-Class Stack Testing

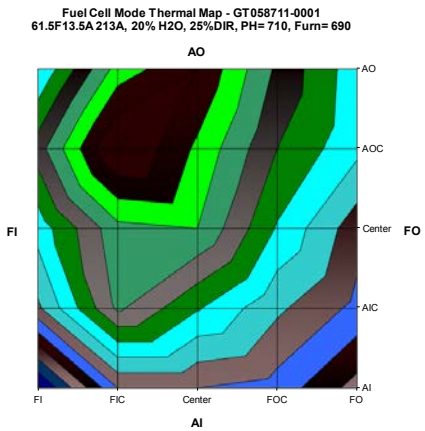
Cell material set:
RSOFC-1

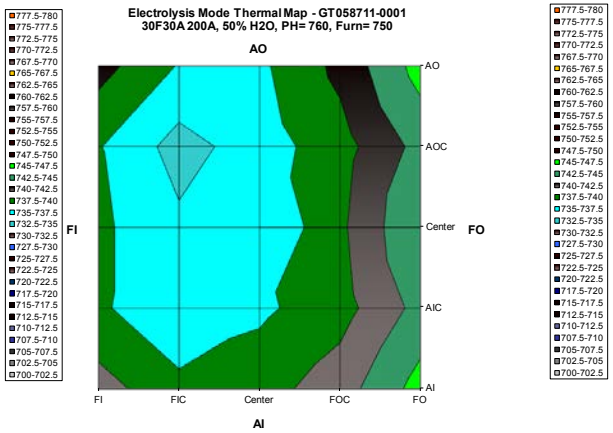
Constant Current Degradation: ~20 mV/khr
Constant Voltage Degradation: ~5 A/khr

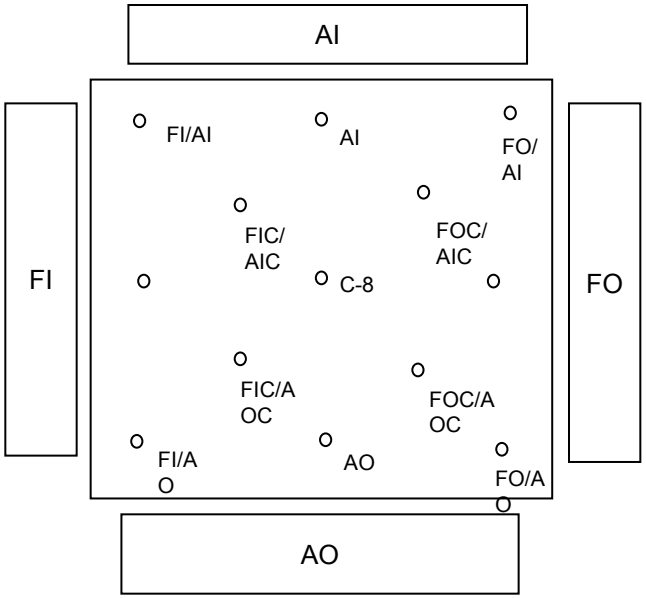


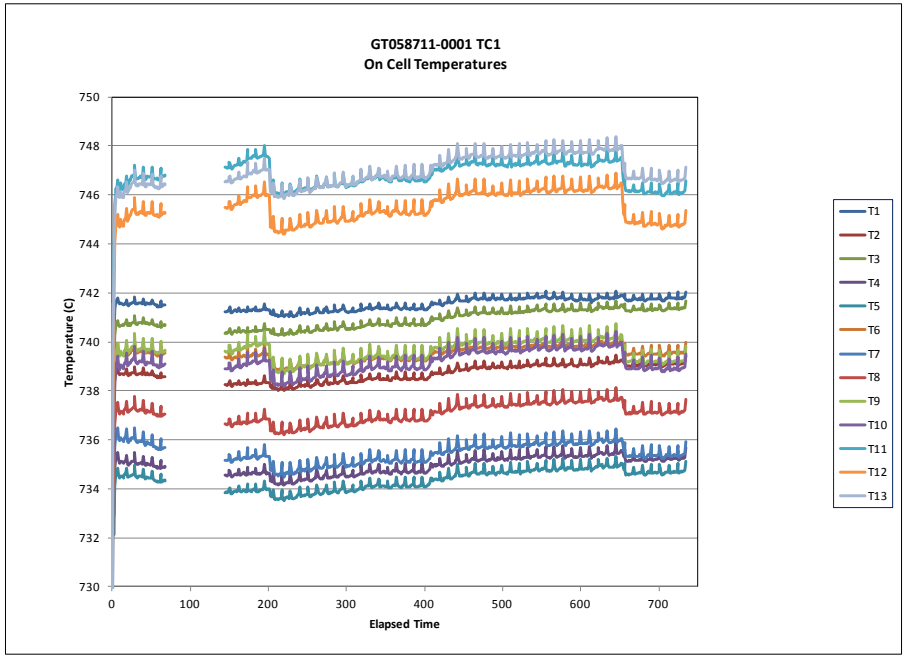
Stack Thermal Profiles





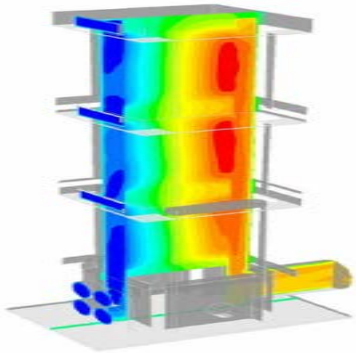


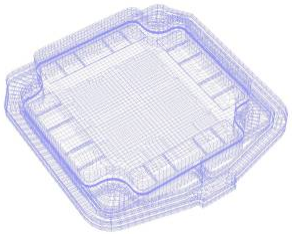


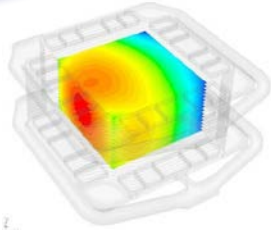


Stack Scale Up Path

- Experimental stack designs built and tested
  - Alternate components and operating conditions for cost and thermal management







- CFD and FEA models developed and validated
  - Improved resolution of thermo-mechanical challenges, input for component development