Smart Matrix Development for Direct Carbonate Fuel Cell

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Project ID FC116

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Overview

Timeline

- Project Start Date: 09/22/2014
- Project End Date: 10/31/2017

Budget

- Total Project Budget: $4,519K
  - Total Recipient Share: $1,356K
  - Total Federal Share: $3,163K
  - Total DOE Funds Spent*: ~$2,540K

* As of 3/31/17

Barriers

Barrier	Target
A (durability): Incomplete understanding of degradation mechanism	**80,000h operating lifetime (2020)**
A (durability) & B (cost): Develop cost-effective matrix degradation-mitigation schemes	

Partners

- **FuelCell Energy, Inc. (project lead)**
- **University of Connecticut - Center for Clean Energy Engineering (C2E2)**
  - Degradation mechanistic understanding
- **Illinois Institute of Technology (IIT)**
  - Electrolyte wettability investigation

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Relevance

Overall Objectives: Develop an innovative durable DFC (Direct Fuel Cell) electrolyte matrix ('Smart' Matrix) to enable >420kW rated stack power and 10-year (80,000h) stack service life*

- Increase market penetration for stationary fuel cells
- Enable hydrogen infrastructure
- Enable CO_2 capture
- Enable domestic clean-energy job growth

100 kW–3 MW Combined Heat and Power and Distributed Generation Fuel Cell Systems Operating on Natural Gas		
Characteristic	DFC Baseline	DOE-EERE MYRD&D 2020 Targets
Electrical efficiency at rated power	47%	>50%
CHP energy efficiency	90%	90%
Operating lifetime	>40,000h	80,000h

- **FCE confirmed >5 years stack life during field operation at customer sites**

*current-generation: 350kW rated stack power and 5-year stack service life

Relevance

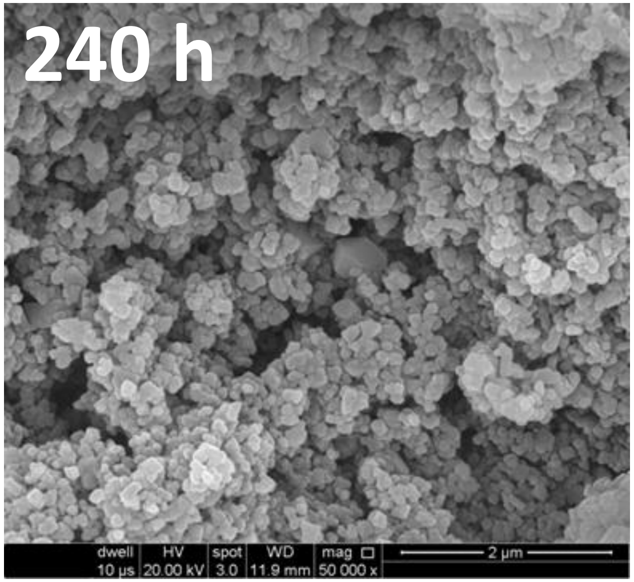
Objectives for Current Project Year (April 2016 - April 2017)

- \- Scale up manufacturing 'Smart' Matrix and perform endurance stack test
- \- Confirm 'Smart' Matrix meeting technical targets in >5,000h accelerated cell tests

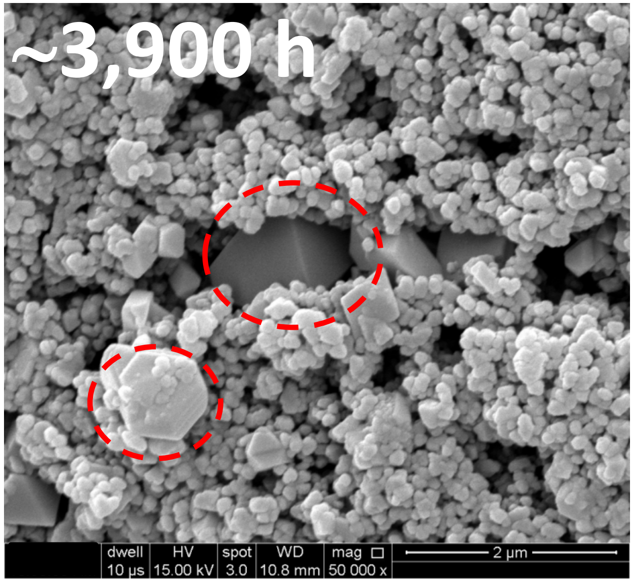
Impact since 2016 AMR

- \- Successfully scaled up 'Smart' Matrix to ~10,000 cm^2 area (Barrier B)
- Met targeted electrochemical performance and seal efficiency in 30 kW technology stack (Barrier A)

Why Do We Need 'Smart' Matrix?
Enhance Matrix Material Stability



Coarsening via Ostwald Ripening
dissolution/deposition



- **Coarsening of α-$LiAlO_2$ support material leading to pore growth**
  - **Reduced electrolyte retention capability**
  - **Increased cross-leakage**
  - **Increased ohmic resistance**
  - **Electrolyte mal-distribution and cell performance impact**

- **Besides enhancing matrix material stability under 'Smart' Matrix program, FCE is actively developing other advanced cost-effective 10-year life stack components.**

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Approaches to Achieve ‘Smart’ Matrix

Goals	Approaches	Desired Properties	Status
>20% porosity increase and improved fine-pore structure (>30% reduction on pores larger than 0.2μm) >25% increased mechanical strength Verify matrix sealing efficiency	Proprietary pore former	Chemical compatibility	✓
	Optimize slurry formulation and processing Engineered additives	Uniform particle size distribution Improved slurry rheology, particles packing & manufacture yield	✓
Stable fine pores for enhanced electrolyte retention (<50% pores larger than 0.2μm and <5% phase transformation) in endurance tests (>5,000h)	Stabilized $LiAlO_2$ Cost-effective $LiAO_2$ manufacturing process Engineered additives	Stable phase (100% α-$LiAlO_2$ phase purity) Low solubility Slow coarsening	✓
Understand matrix phase, microstructure and wettability changes	Effect of temperature, gas composition and cell location	Fundamental parameters governing matrix material stability and wettability	✓
‘Smart’ Matrix ready for field validation	Production manufacturing trials Develop cell and 30kW technology stack condition and operation procedures	High-yield manufacturing Optimized stack condition/operation procedures	✓

Approach: Near-term Milestones & Go/No-Go Decisions: Program on track

Milestone	Description	Status
Through 3/31/2017	❖ Scale-up manufacturing process	100%
	❖ Start evaluation in technology stack	100%
	❖ Confirm meeting initial stack performance and gas seal efficiency	100%
	❖ Confirm meeting technical targets in >5,000h accelerated endurance cell tests	100%
Remaining FY2017	❖ Verify sealing performance and resistance stability in >5,000h technology stack	70%
	❖ Confirm meeting technical targets in >5,000h 30kW technology stack test	50%

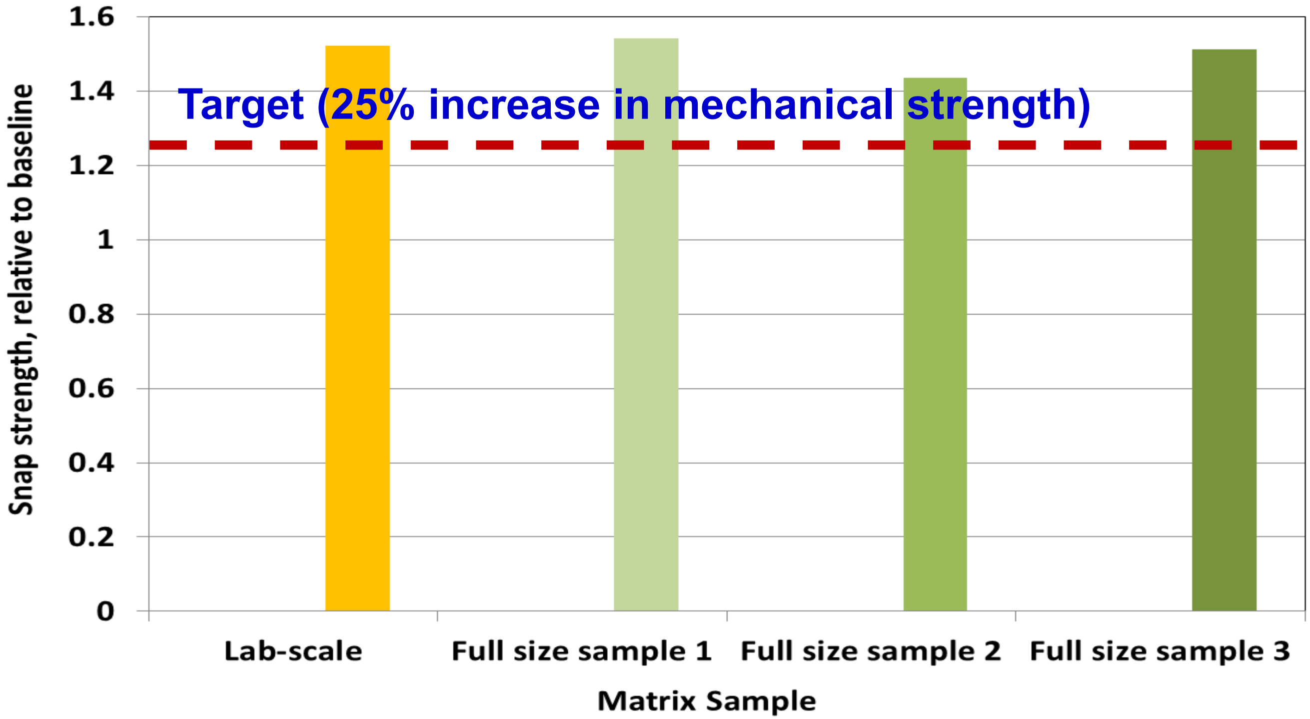
Go/No-Go	Description	Status
FY2016 (10/31/2016)	❖'Smart' Matrix technical targets confirmed in >5,000h accelerated endurance cell tests	100%

Accomplishment: Verified >25% Improved Mechanical Strength in Full-Area 'Smart' Matrix

Lab-scale size 'smart' matrix

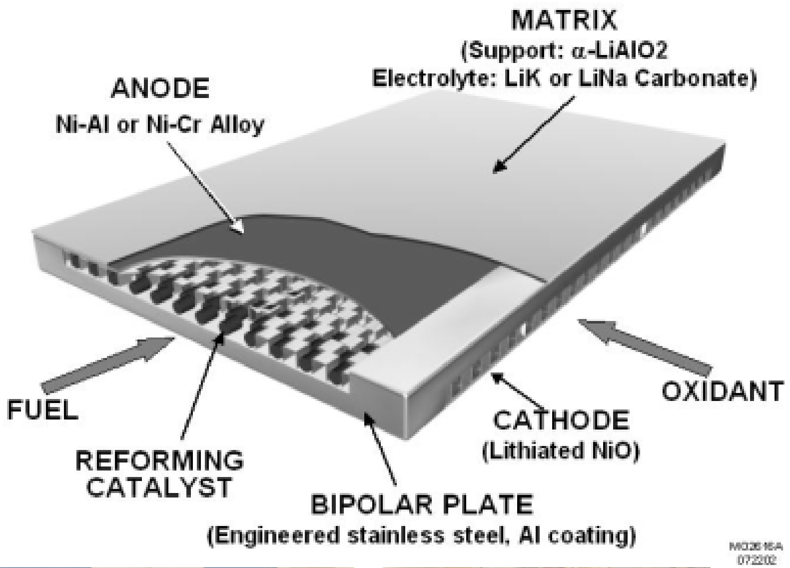
Process scale-up

Full size 'smart' matrix



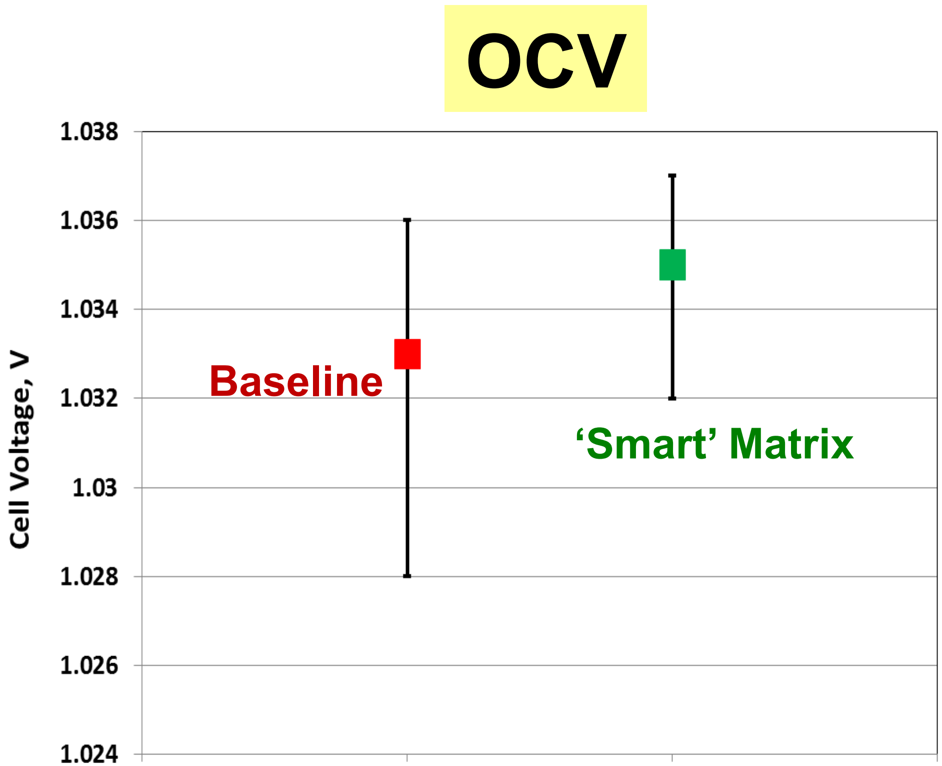
- **Successfully scaled up to full area: ~10,000 cm^2**
- **Consistently demonstrated exceeding mechanical strength target (verified in >12 full-area production manufacturing trials)**

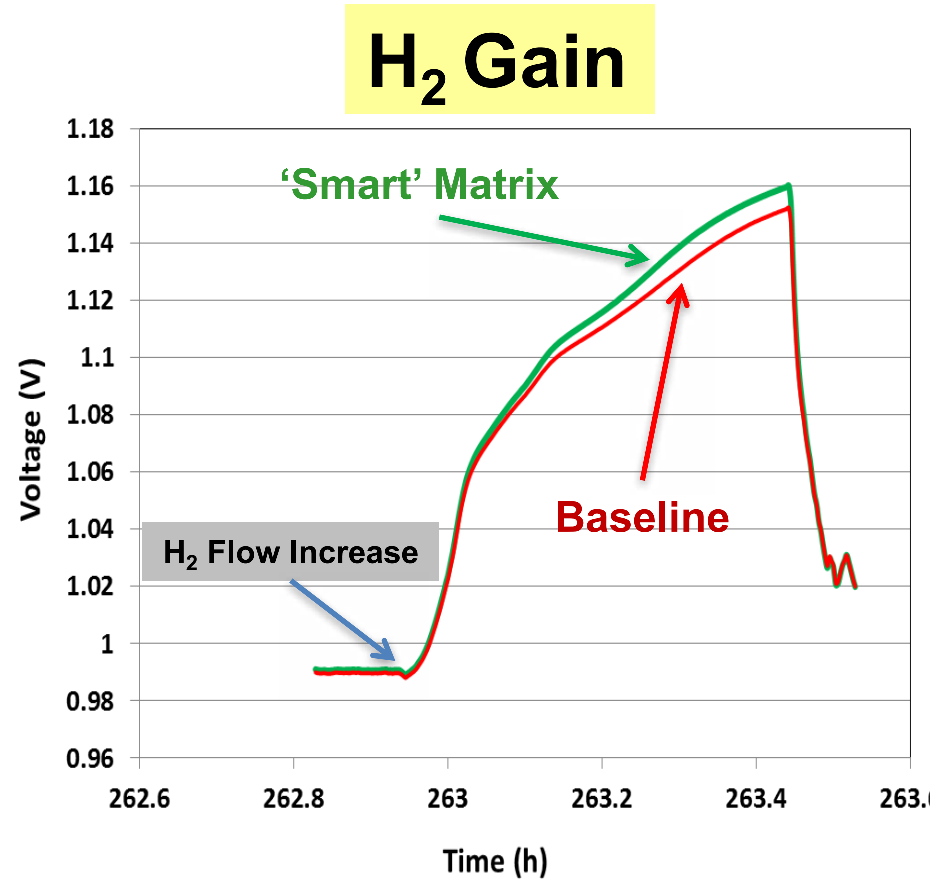
30kW Technology Stack



- **Electrodes: Ni-based**
- **Matrix: 'Smart' Matrix & production baseline as a control**
- **Electrolyte: Baseline alkali carbonate**
- **Baseline Cell Hardware: Austenitic stainless steels**
- **Stack Hardware: Baseline design**

Achieved Improved Gas Sealing Efficiency In 30kW Technology Stack

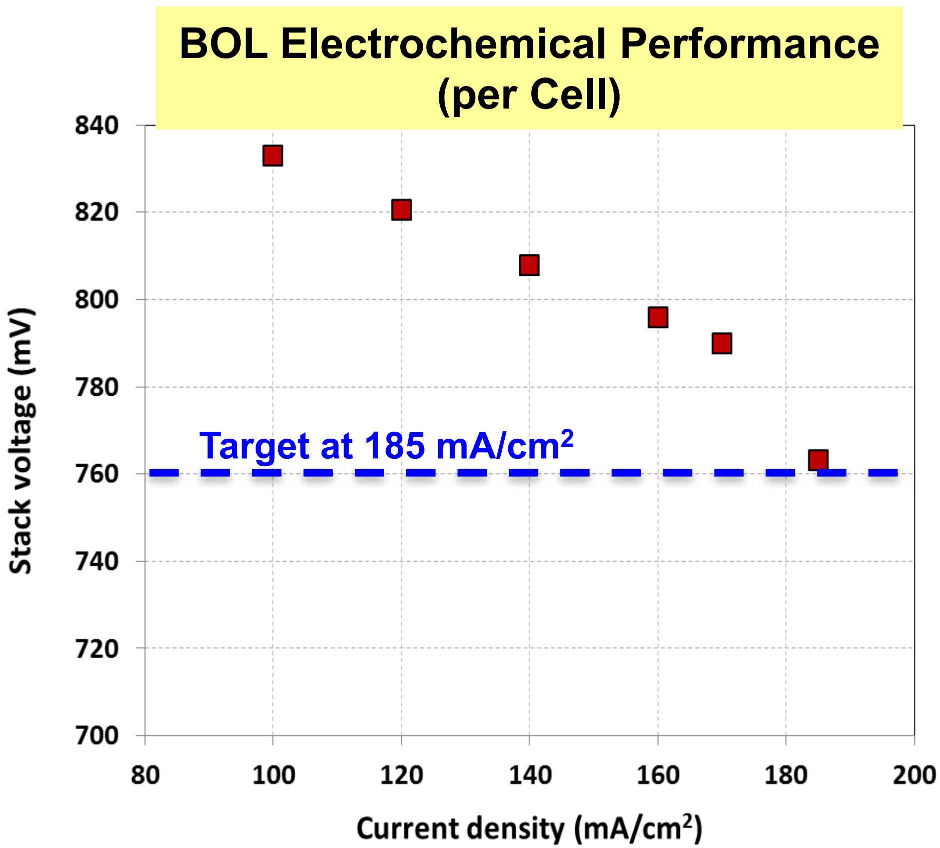


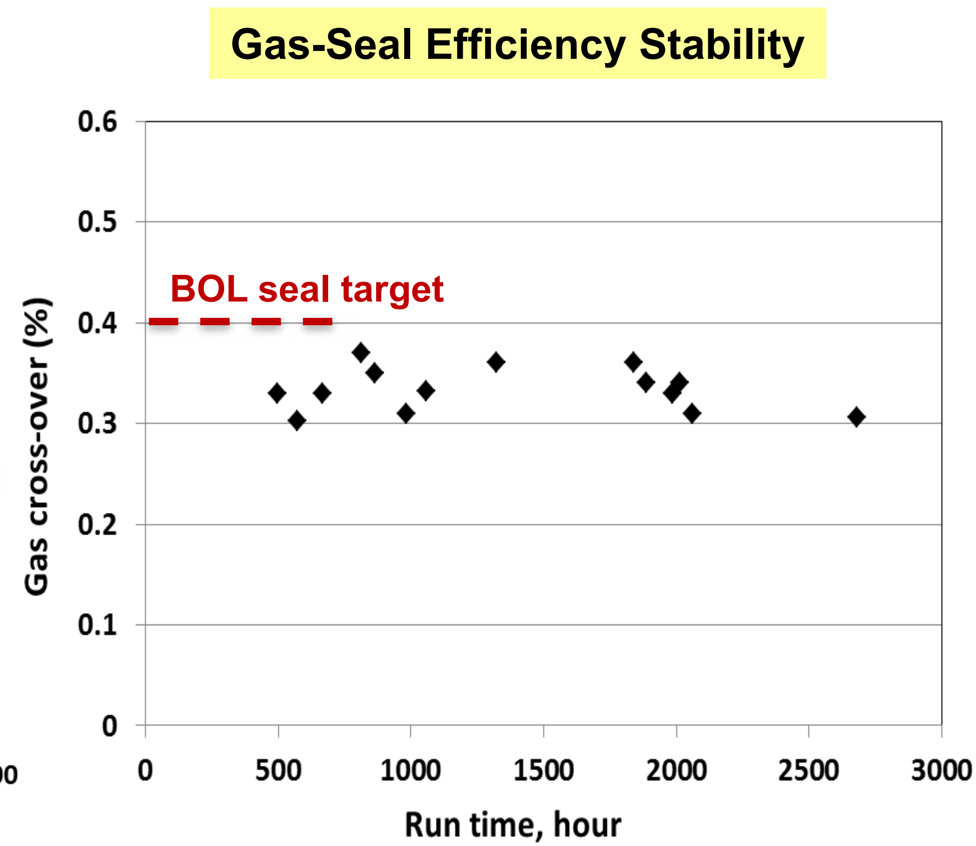


- **BOL* open-circuit voltage (OCV) and H_2-gain tests confirmed improved gas sealing efficiency of 'Smart' Matrix.**

*BOL: Beginning-of-Life

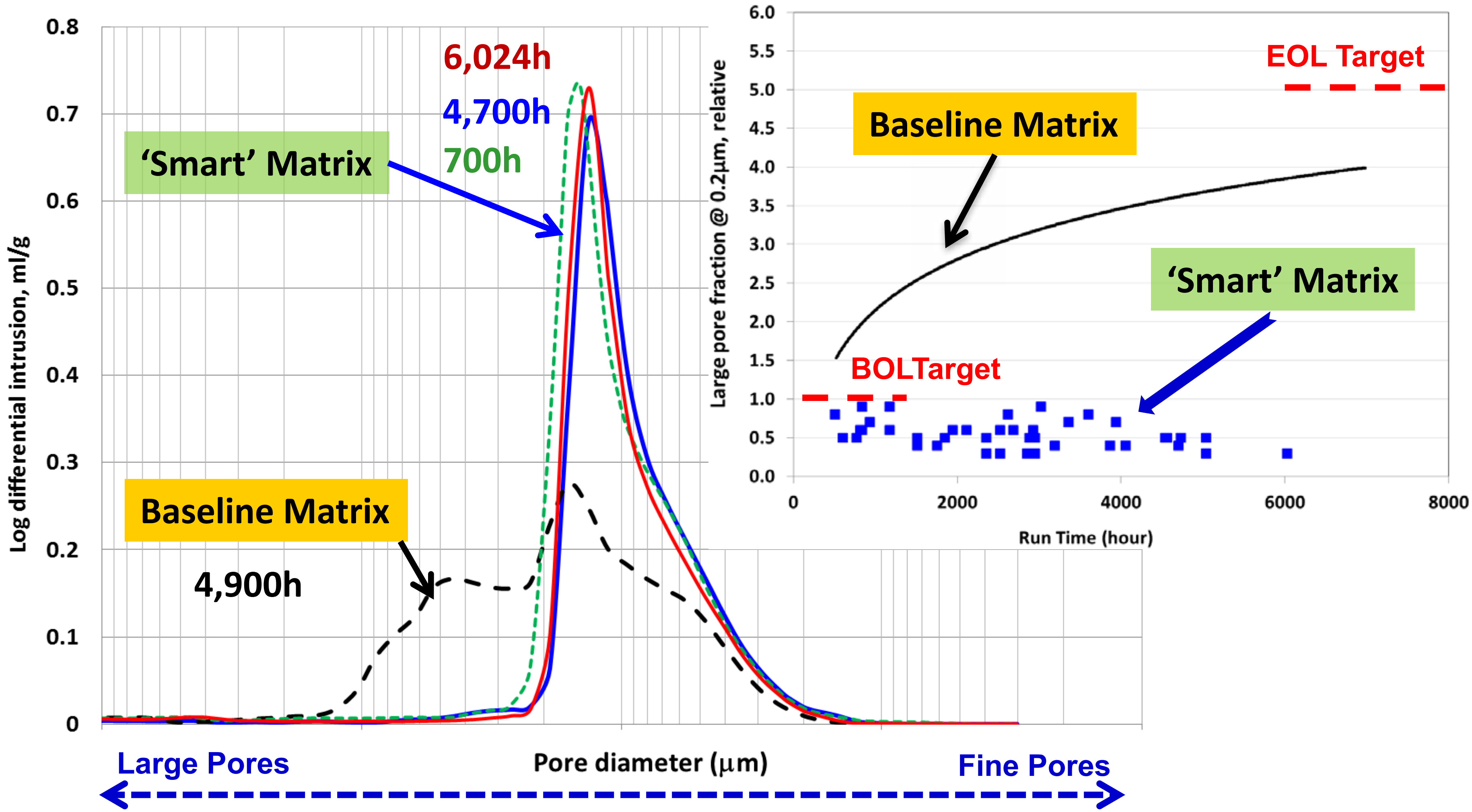
'Smart' Matrix Met Technology Stack
Initial Performance and Gas cross-over





- Achieved initial electrochemical performance and stable low gas cross-over

Confirmed 'Smart' Matrix Pore Structure Stability

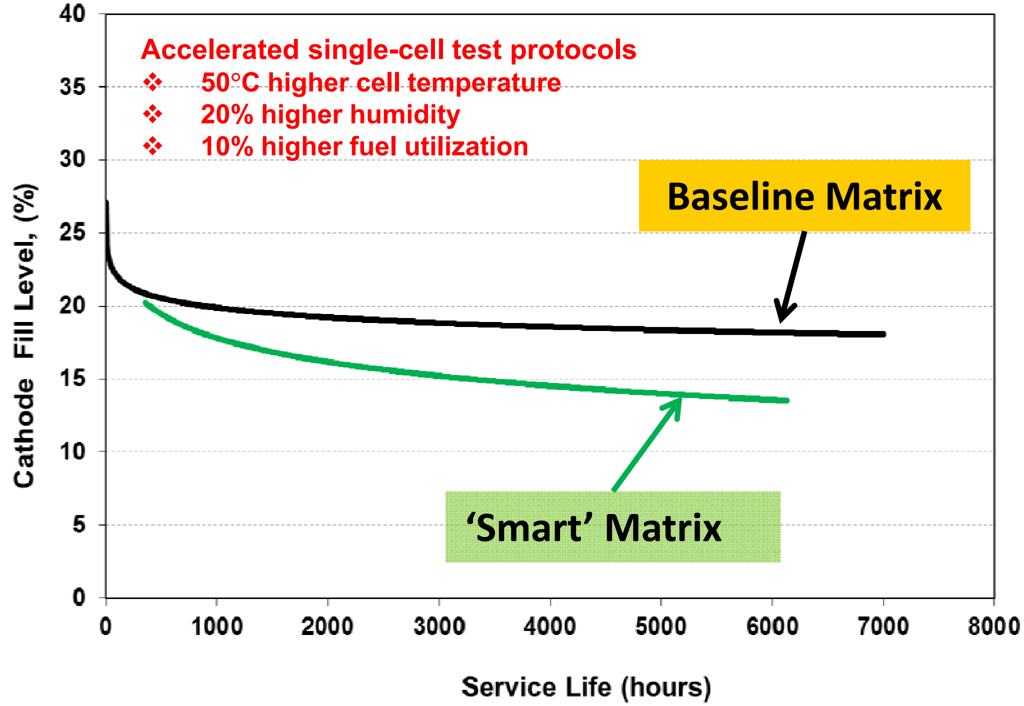


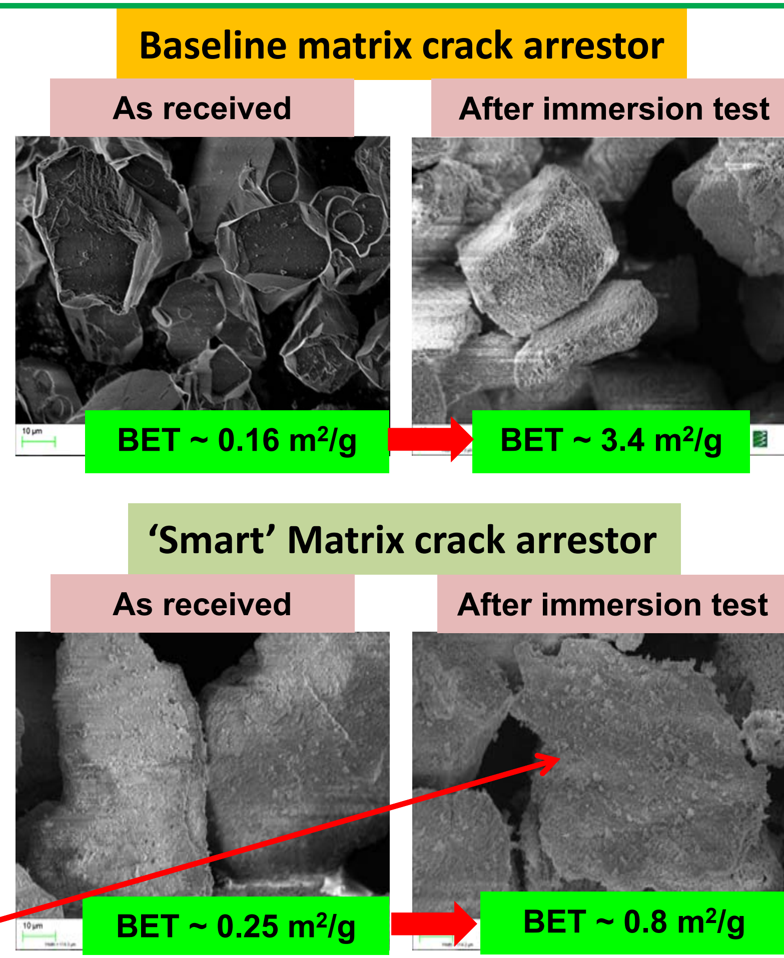
- ❑ **Projected meeting EOL* pore-structure target (<50% of pores >0.2μm in 10 years) in accelerated cells**

*EOL: End-of-Life

‘Smart’ Matrix Enables Improved Matrix Electrolyte Retention and Reduced Electrolyte Consumption

Cathode fill level comparison

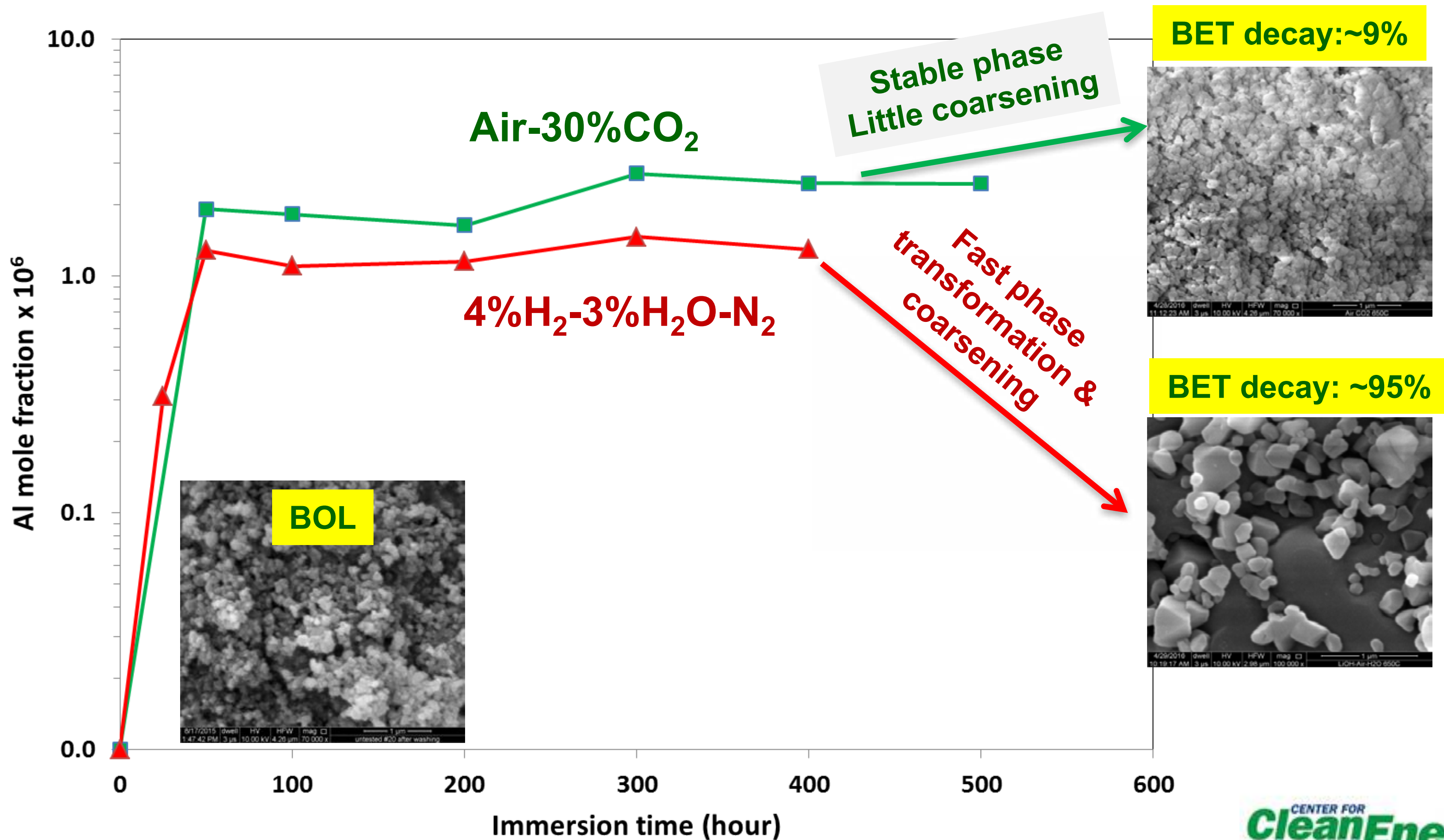




Reduced surface fine-oxide formation and ~40% reduction of Li consumption compared to baseline

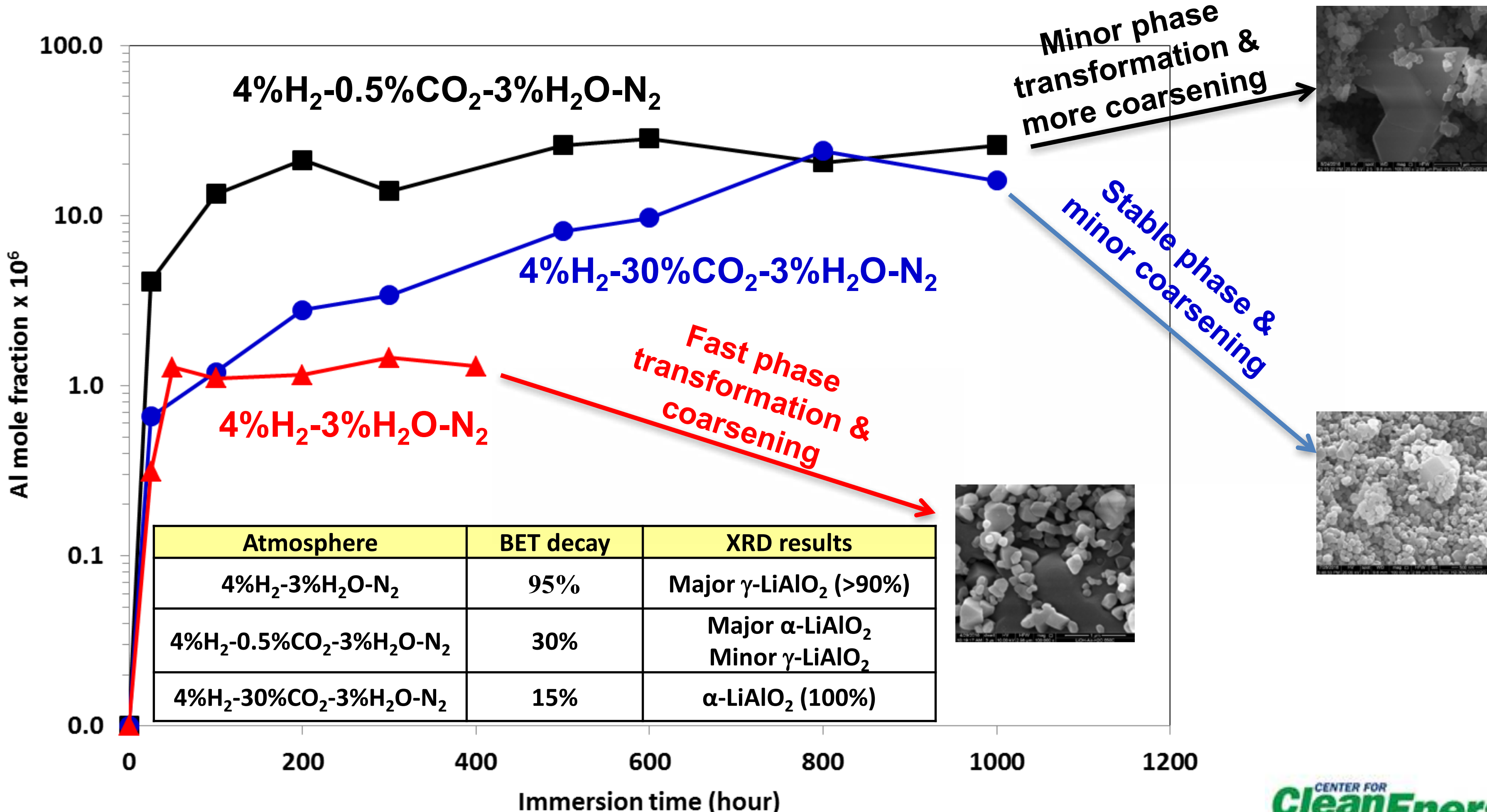
- Demonstrated improved matrix capillary electrolyte retention (avoiding high cathode electrolyte fill)
- ‘Smart’ Matrix offers >30% reduced electrolyte consumption by utilizing alternate low Li-consumption crack arrestor

Solubility of Baseline $LiAlO_2$ at 650°C
Reducing vs. Oxidizing Environment



- **Similar equilibrium solubility**
  - **Equilibrium solubility may not be the only controlling factor on coarsening**

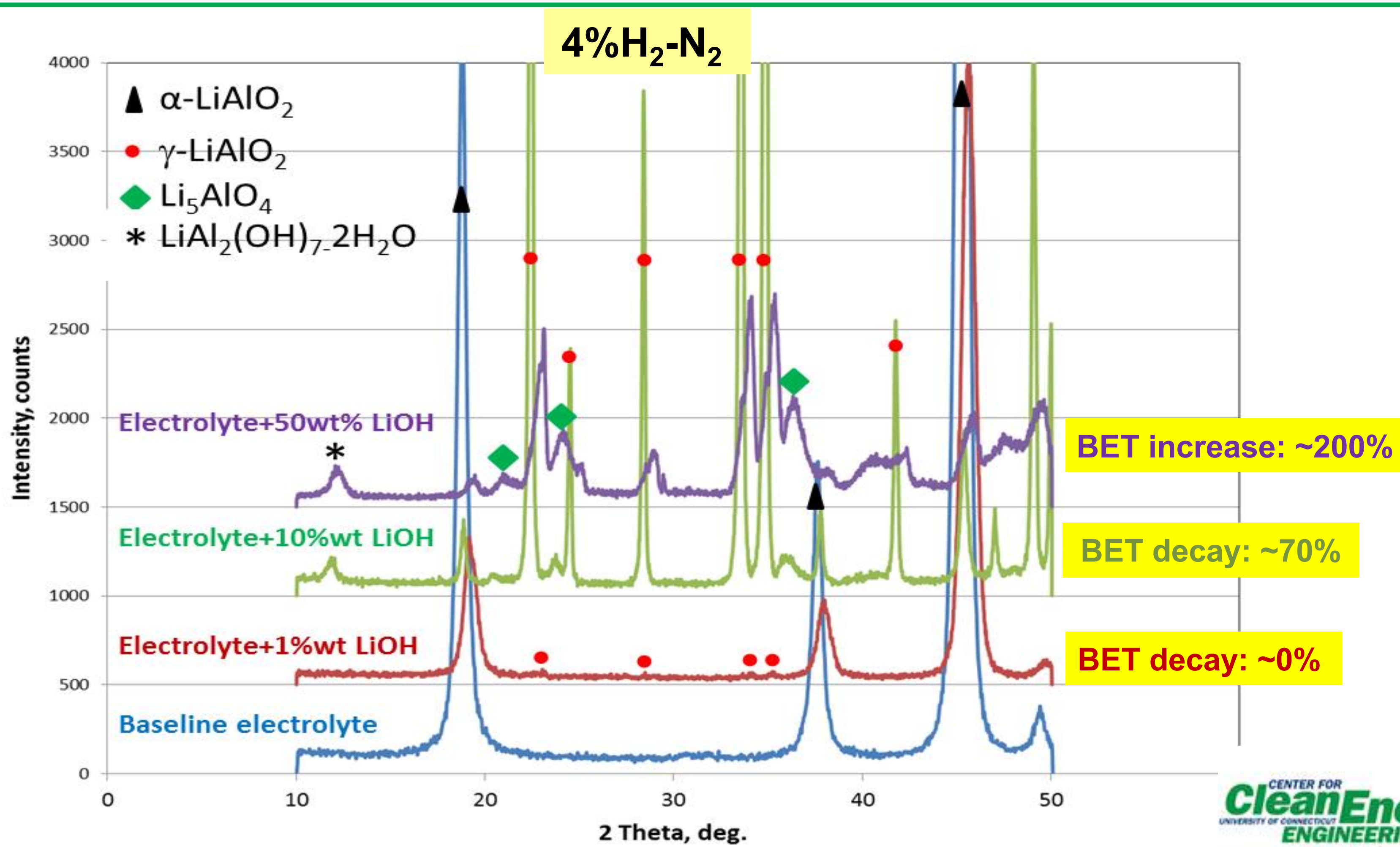
Effect of CO_2 on Solubility of Baseline $LiAlO_2$
Reducing Atmosphere at 650°C



Atmosphere	BET decay	XRD results
$4\%H_2$-$3\%H_2O$-N_2	95%	Major γ-$LiAlO_2$ (>90%)
$4\%H_2$-$0.5\%CO_2$-$3\%H_2O$-N_2	30%	Major α-$LiAlO_2$ Minor γ-$LiAlO_2$
$4\%H_2$-$30\%CO_2$-$3\%H_2O$-N_2	15%	α-$LiAlO_2$ (100%)

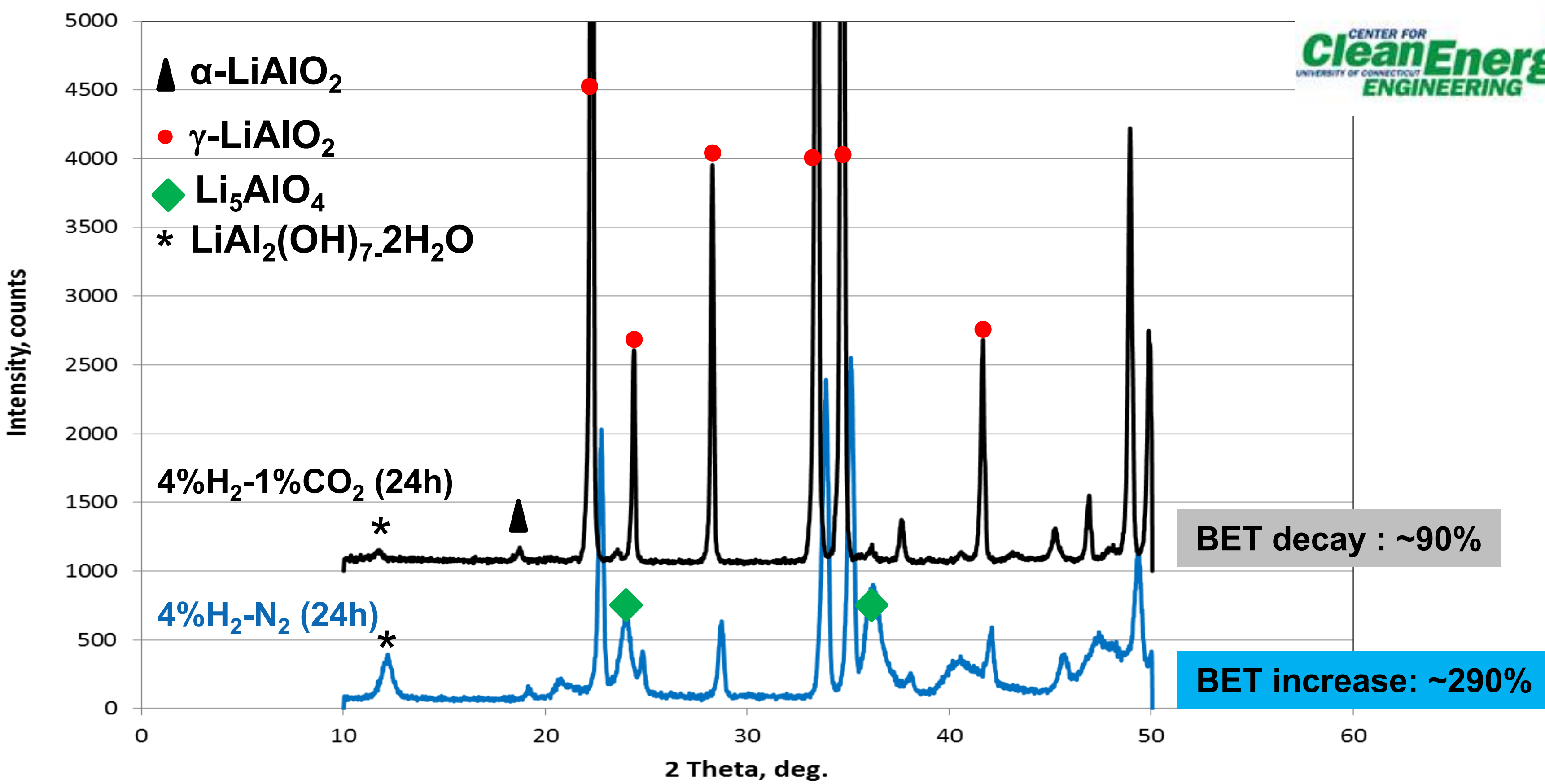
- ❑ CO_2 promotes phase and particle-size stability
- ❑ CO_2 decreases dissolution rate
- ❑ Coarsened γ-$LiAlO_2$ has a lower solubility (Gibbs-Thomson equation)

$LiAlO_2$ Phase Transformation and Coarsening in Reducing Environment: Effect of Hydroxide (700°C/2h)



- LiOH (<10wt%) promotes forming γ-$LiAlO_2$
- Higher LiOH promotes fine intermediates: α-Li_5AlO_4 and $LiAl_2(OH)_7$-$2H_2O$
  - Fine intermediates may preferably transform to γ-$LiAlO_2$

Stability of Baseline $LiAlO_2$ in Pure LiOH at 700°C: Effect of CO_2



- Hydroxide promotes forming fine intermediates: α-Li_5AlO_4 and $LiAl_2(OH)_7$-$2H_2O$
- CO_2 appears to promote intermediate phases transforming to γ-$LiAlO_2$.

$$Li_5AlO_4 + 2CO_2 \rightarrow 2Li_2CO_3 + \gamma\text{-}LiAlO_2$$

- TEM and theoretical DFT/Ostwald-ripening modeling are underway to further clarify coarsening mechanism.

Responses to AMR16 reviewers comments

- **Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals:**
  - 5,000h stack test is underway to validate the developed ‘smart’ matrix. Longer-term stack testing (>10,000h) is planned beyond the current program.
  - The pore-structure degradation result projected no concern on coarsening during extended cell operation.
- **More technical details of how the improvements have been achieved:**
  - As already pointed out by reviewers, this may be unavoidable given the proprietary nature. In essence, FCE devised an innovative approach to stabilize the $LiAlO_2$ structure by disrupting the phase transformation and Ostwald dissolution-precipitation ripening process. A patent application has been submitted to USPTO.
- **Details on partner work:**
  - Fundamental studies (SEM, XPS, high-temperature XRD, solubility, wettability, etc.) have been extensively performed by subcontractors (both UConn and IIT) and reported in the AMR review presentations. The fundamental studies (including TEM and ripening modeling) by the subcontractor UConn is continuing to enhance the understanding.
- **Degradation mechanistic understanding:**
  - The justification of the acceleration factors are based on FCE’s extensive matrix degradation experience from operation of accelerated cells and >5-year operated field commercial product stacks.
  - The mechanistic model development will continue during the remainder of this program.
  - The Li loss (Li non-stochiometry) created crystalline disorder and metastable intermediate formation, an important factor contributing to coarsening. Identification of the metastable intermediates is underway.
  - Recent solubility results have shown that PCO_2 (or $[O^=]$) may not be the only factor contributing to coarsening. Identifying metastable intermediates is being focused during the remainder of the program. FCE believed phase transformation studies in conjunction with additional electrolyte-immersion and accelerated single-cell tests will provide more direct results than static oxide-concentration electrochemical measurements.
  - Additional effort beyond the current program scope may be needed to understand the impact of other factors besides matrix degradation on resistance stability.

Collaborations: *UConn/IIT has significant prior experience and analytical capability*

- **FCE collaborates with subcontractors UConn and IIT to develop fundamental understandings of matrix coarsening and wettability and to help design mitigation approaches**

FuelCell Energy
Ultra-Clean, Efficient, Reliable Power

UCONN
UNIVERSITY OF CONNECTICUT
CENTER FOR CleanEnergy ENGINEERING

Expertise in high temperature fuel cell, material stability and characterization

- **Characterize matrix microstructure evolution**
- **Measure $LiAlO_2$ solubility**
- **Develop mechanistic understanding of coarsening**

ILLINOIS INSTITUTE OF TECHNOLOGY

Expertise in high temperature fuel cell fundamental, modeling, electrolyte wetting

- **Evaluate matrix electrolyte wettability**

Prof. JR Selman

- **Consulting on electrolyte contact angle/distribution**

Understand matrix coarsening mechanism & electrolyte retention capability

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Remaining Challenges and Barriers

Challenges	Barrier
Confirm ‘Smart’ matrix performance and material stability in endurance technology stack (>5,000h)	A

Proposed Future Work

Milestone Description		Approach	% Complete
Remaining FY2017	Confirm design meeting technical requirements in accelerated technology stack tests (>5,000h): sealing efficiency, performance and material stability	Perform long-term (>5,000h) cell and technology stack tests: measure electrochemical performance, matrix gas sealing efficiency, ohmic resistance, and material stability	70

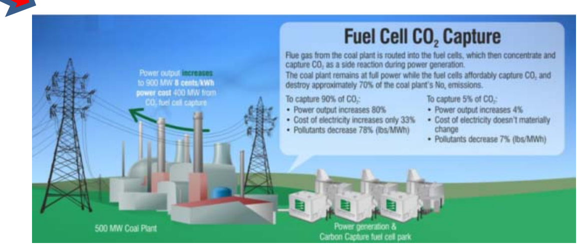
Any proposed future work is subject to change based on funding levels.

Technology Transfer Activities

- **FCE plans to further validate developed 'Smart' Matrix in endurance technology (30kW) and full-size prototype product stacks tests (>1 year operation)**

- **Controlled release 'Smart' Matrix in DFC products**
  - **Enhance DFC market penetration and clean-energy job creation**
  - **Enable cost-effective distributed hydrogen-production DFC-H_2 & REP systems**
  - **Enable DFC-CO_2 system for CO_2 capture**

Trigen: power+H_2+heat



Summary

- Achieved all quarterly and Go/No Go milestones
  - ✓ Successfully scaled up ‘Smart’ Matrix manufacturing process and initiated technology stack test evaluation
    - ✓ Full-area ‘Smart’ Matrix met targets of yield, mechanical strength and pore structure
  - ✓ Achieved targeted initial electrochemical performance and gas sealing efficiency in 30 kW technology stack
  - ✓ Confirmed ‘Smart’ Matrix phase stability and coarsening reduction in accelerated lab-scale endurance cells (>5,000h)
    - ✓ Met targeted milestones of projected <20% cathode fill, reduced electrolyte loss and <50% of pores larger than 0.2μm in 10 years

- Degradation mechanistic understanding
  - ✓ Confirmed accelerated coarsening and phase transformation in reducing environment
  - ✓ Reducing environment promotes surface non-stoichiometry, Al reduction, and crystalline cationic disorder
  - ✓ CO_2 promotes particle-size and phase stability. It is not the only factor controlling observed reducing-side accelerated coarsening.
  - ✓ Hydroxide promoted $\alpha \rightarrow \gamma$ phase transformation via intermediates observed under reducing-atmosphere electrolyte-immersion testing may be a more dominant factor.
  - ✓ TEM/Ostwald-ripening modeling underway to further elucidate coarsening mechanism.

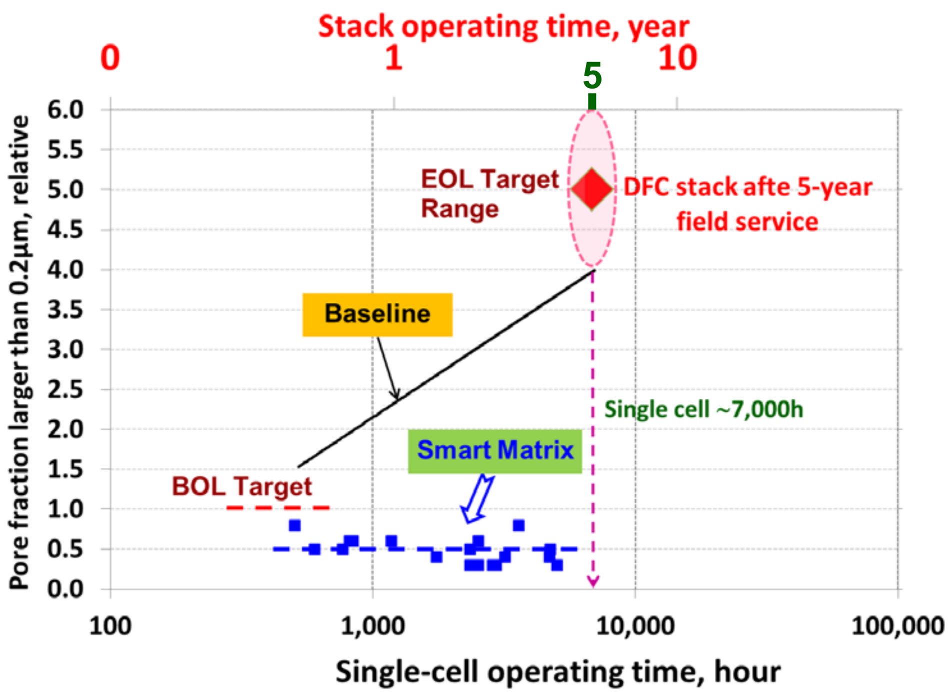
Technical Back-Up Slides

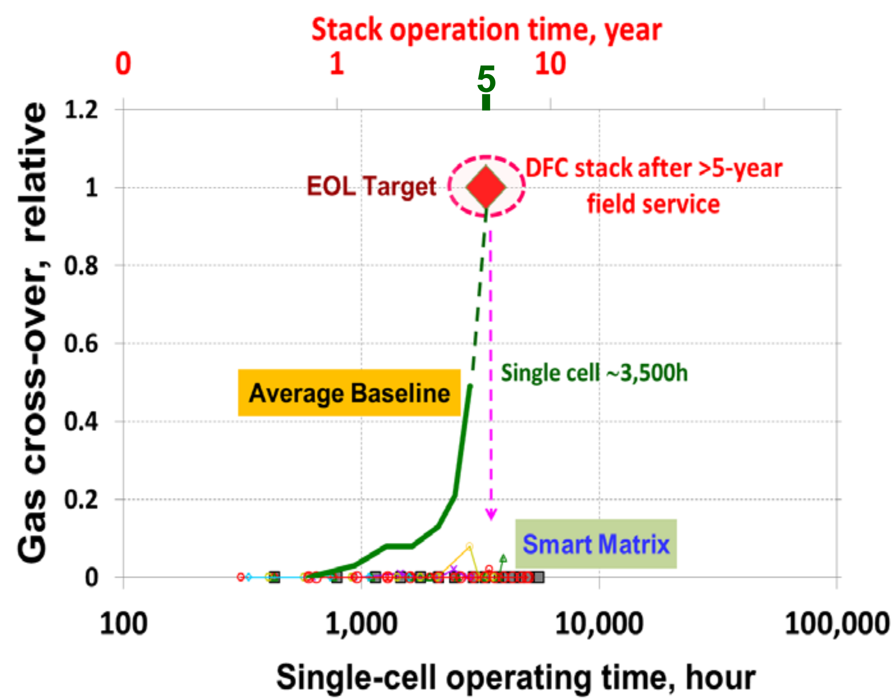
Acceleration Test Protocols

Basis:

- ❖ **Baseline matrices already verified >5-year field-service life in many commercial units.**
- ❖ **Accelerated single-cell test protocols**
  - ❖ **50°C higher cell temperature**
  - ❖ **20% higher humidity**
  - ❖ **10% higher fuel utilization**
- ❖ **Acceleration factors: pore coarsening and sealing stability (6X-12X)**

➢ **~5,000h accelerated cell test demonstrated 80,000h stack durability, by projection.**





DFC Product Commercialization

- More than 300 MW capacity installed/backlog.
- Generating power at about 50 locations worldwide.
- Generated ~5 billion kWh ultra-clean electricity.
- Annual production run-rate 70 megawatts.

DFC Configuration

Individual fuel cell component

400 components are used to build one 350 kW fuel cell stack

4 stacks are combined to build a 1.4 MW modules

Two modules are used for a 2.8 MW power plant