FuelCell Energy
Ultra-Clean, Efficient, Reliable Power

Smart Matrix Development for Direct Carbonate Fuel Cell



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ILLINOIS INSTITUTE OF TECHNOLOGY

Project ID FC116

Ultra-Clean | Efficient | Reliable Power

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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*: ~$1,424K

* As of 3/31/16

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*

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

RD&D Technical Targets: 100 kW–3 MW Combined Heat and Power and Distributed Generation Fuel Cell Systems Operating on Natural Gas		
Characteristic	DFC Baseline	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

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Relevance

Objectives for Current Project Year (April 2015 - April 2016)

- **Scale up manufacturing "Smart" Matrix and ready for stack evaluation**

Impact since 2015 AMR

- **Projected "Smart" Matrix design capable of achieving 80,000h life target (Barriers A and B)**

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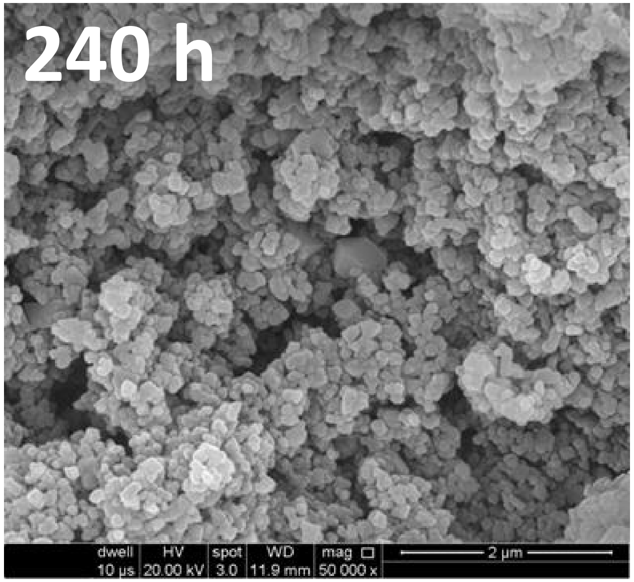
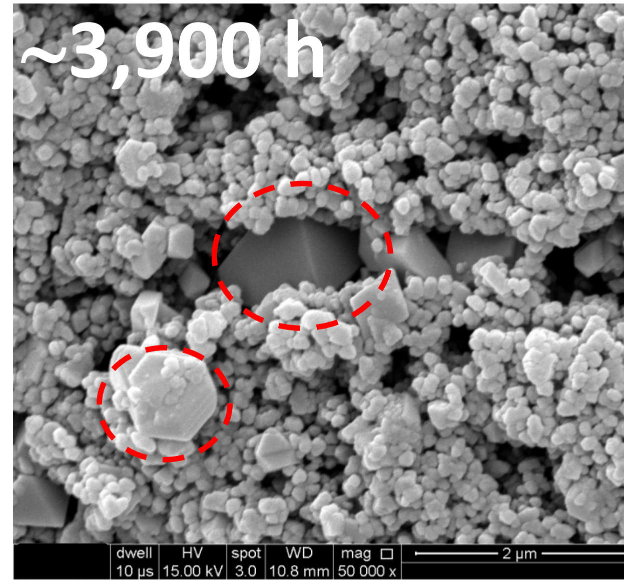
Why Do We Need "Smart" Matrix?
Enhance Matrix Material Stability



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	✓

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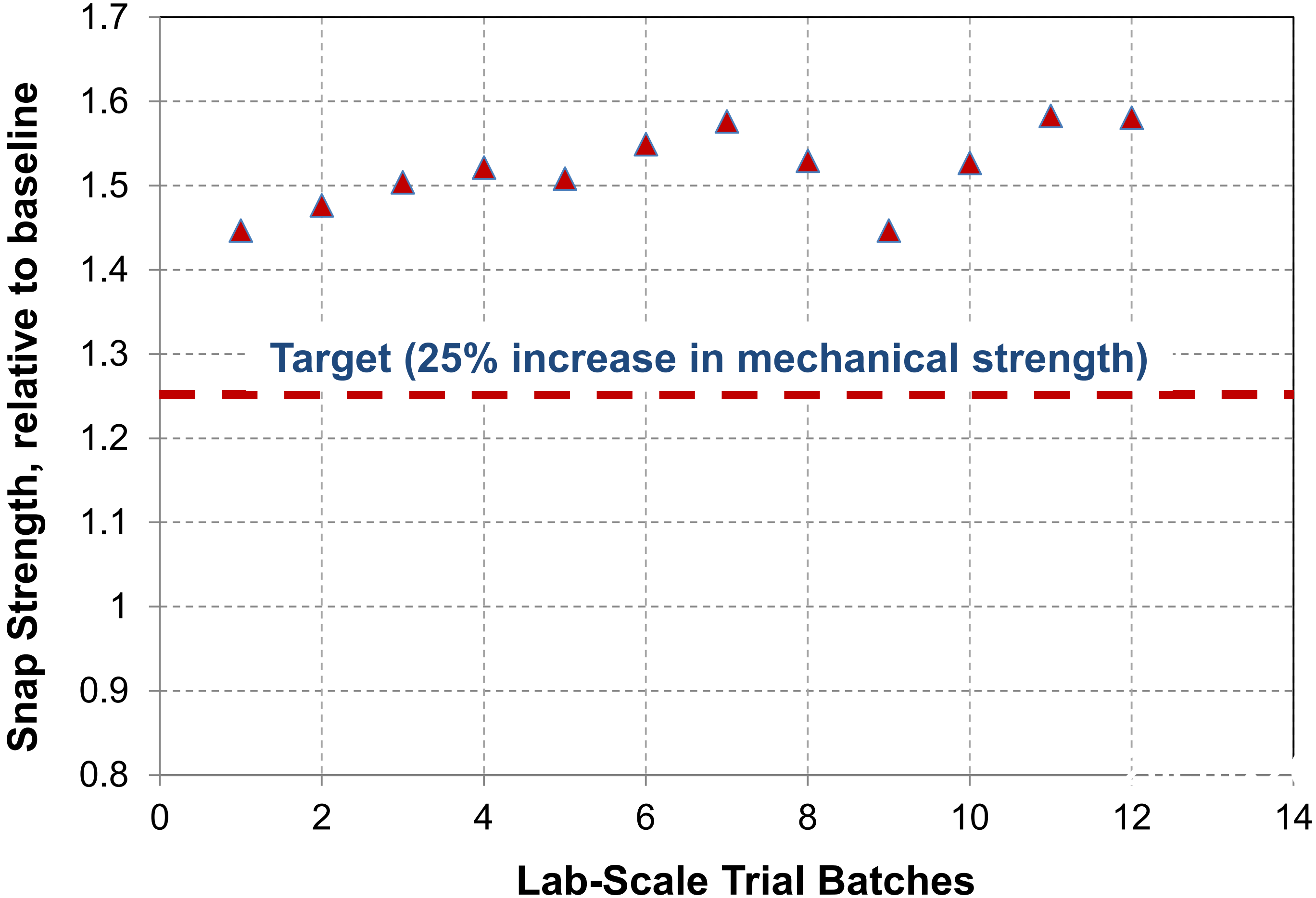
Approach: Near-term Milestones & Go/No-Go Decisions

Program on track

Milestone	Description	Status
Through 3/31/2016	❖ Verify “Smart’ Matrix durability in >5,000h endurance cell tests	100%
	❖ Report on degradation mechanistic understanding	100%
Remaining FY2016	❖ Scale-up “Smart” Matrix manufacturing process	50%
	❖ Start “Smart” Matrix evaluation in technology stack	0%
FY2017	❖ Verify “Smart” Matrix performance, endurance and gas sealing efficiency in >5,000h cells and technology stack	10%

Go/No-Go	Description	Status
FY2016 (10/31/2016)	❖“Smart” Matrix technical targets verified in >5,000h cell tests ❖ Start technology stack	50%

Accomplishment: Achieved Targeted >25% Increase in Mechanical Strength



- Smart matrix consistently demonstrated increased mechanical strength (verified in >30 batches)

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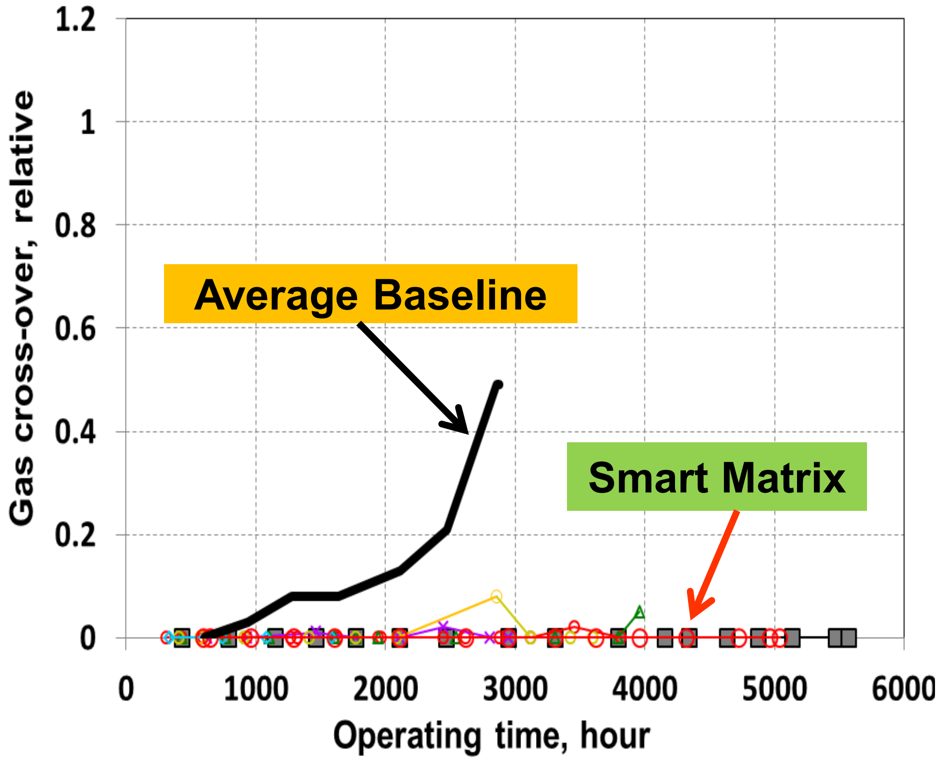
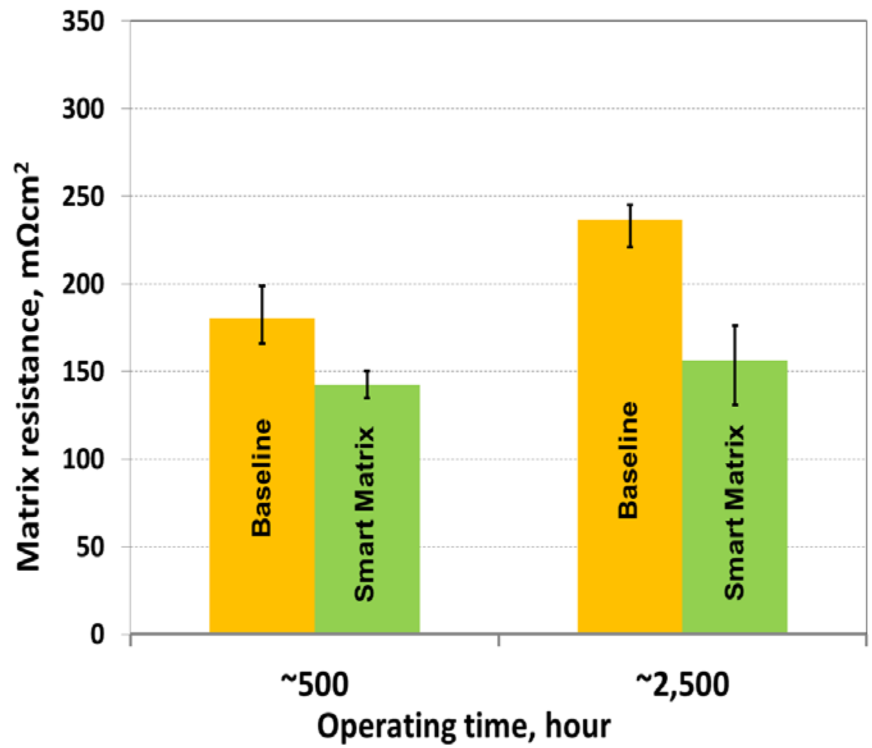
Achieved Targeted Matrix Sealing Efficiency and Ohmic Resistance Reduction

Accelerated cell test conditions

- 50°C higher temperature
- 20% higher steam content
- 10% higher fuel utilization





- Demonstrated significantly improved gas sealing (cross-over) efficiency (>20 single cell tests)
- Achieved targeted >20mΩ cm^2 resistance reduction in >20 cells

Acceleration Test Protocols

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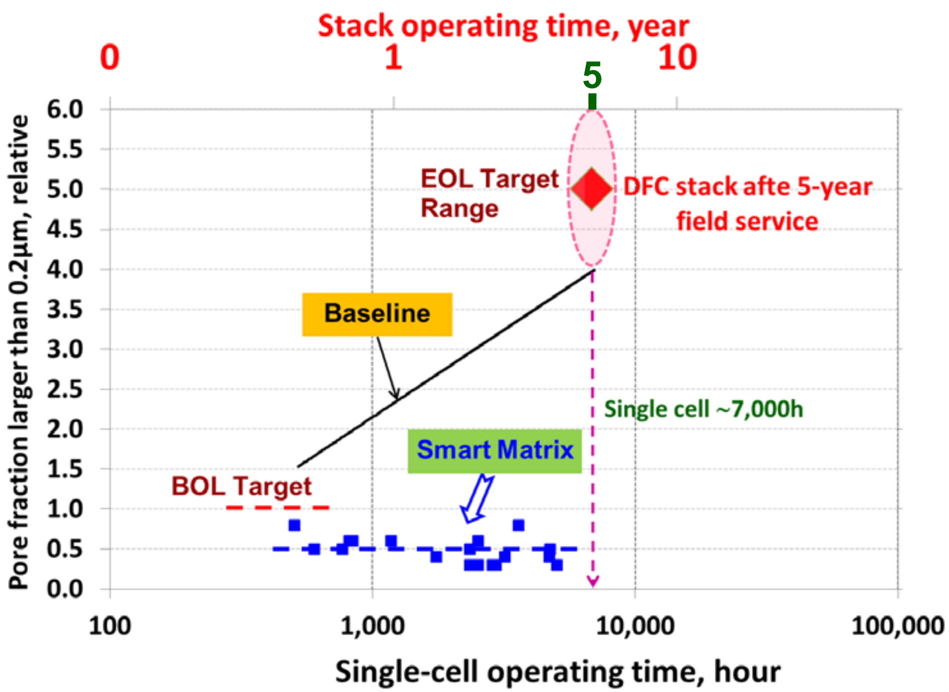
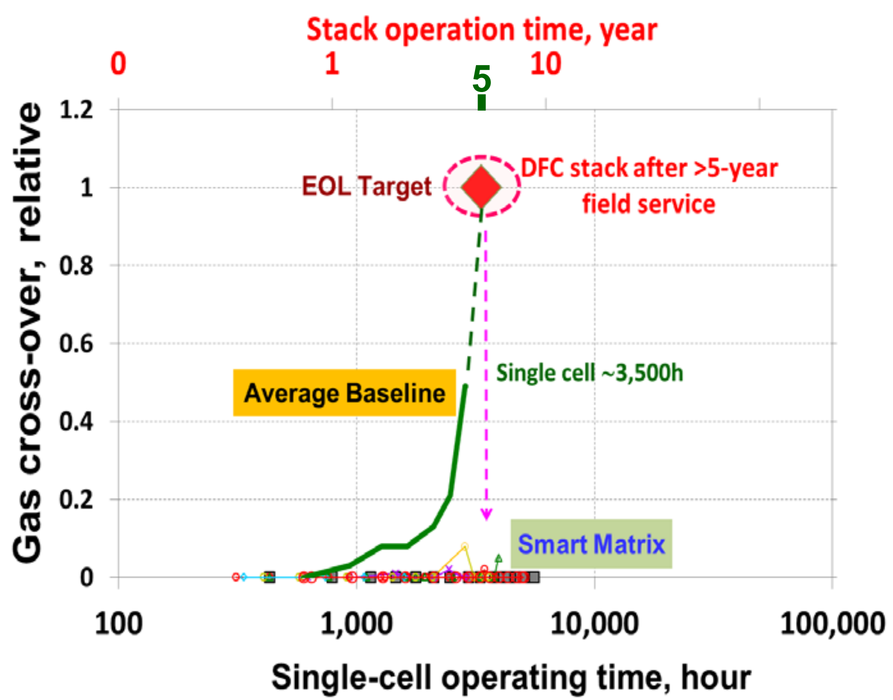
Basis:

- ❖ **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)**

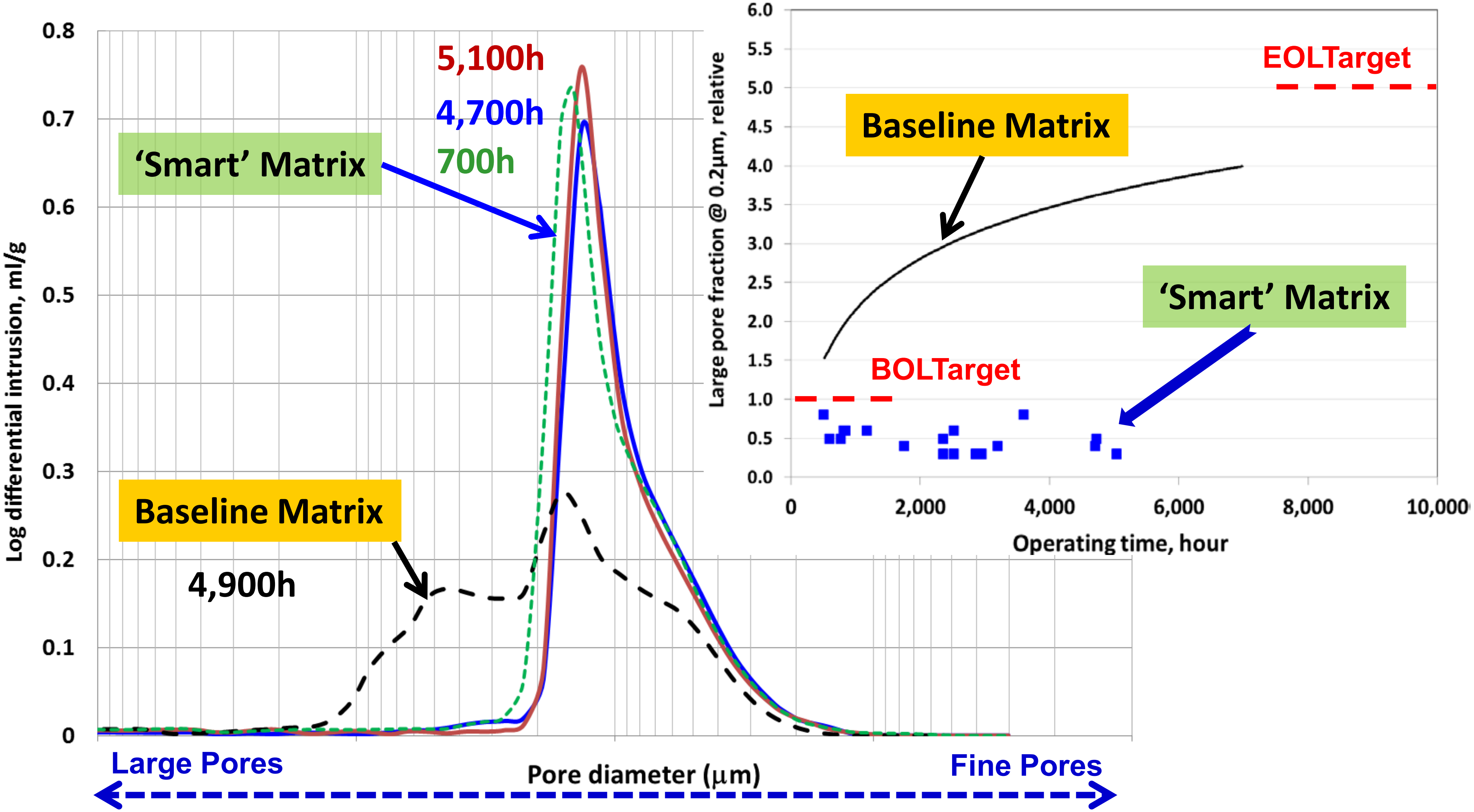
➢ **~5,000h accelerated cell test demonstrated 80,000h stack durability, by projection.**





Verified 'Smart' Matrix Pore Structure Stability

Endurance (~5,000h) pore-structure comparison



- Achieved projected EOL stable pore structure target (<50% of pores >0.2μm in 10 years)

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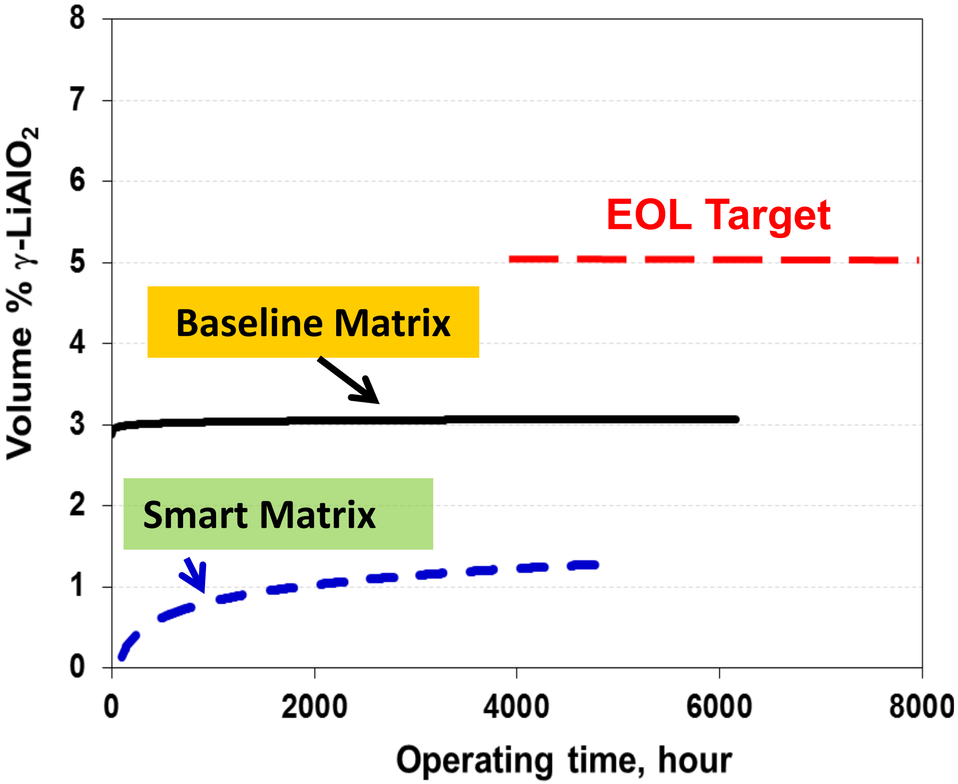
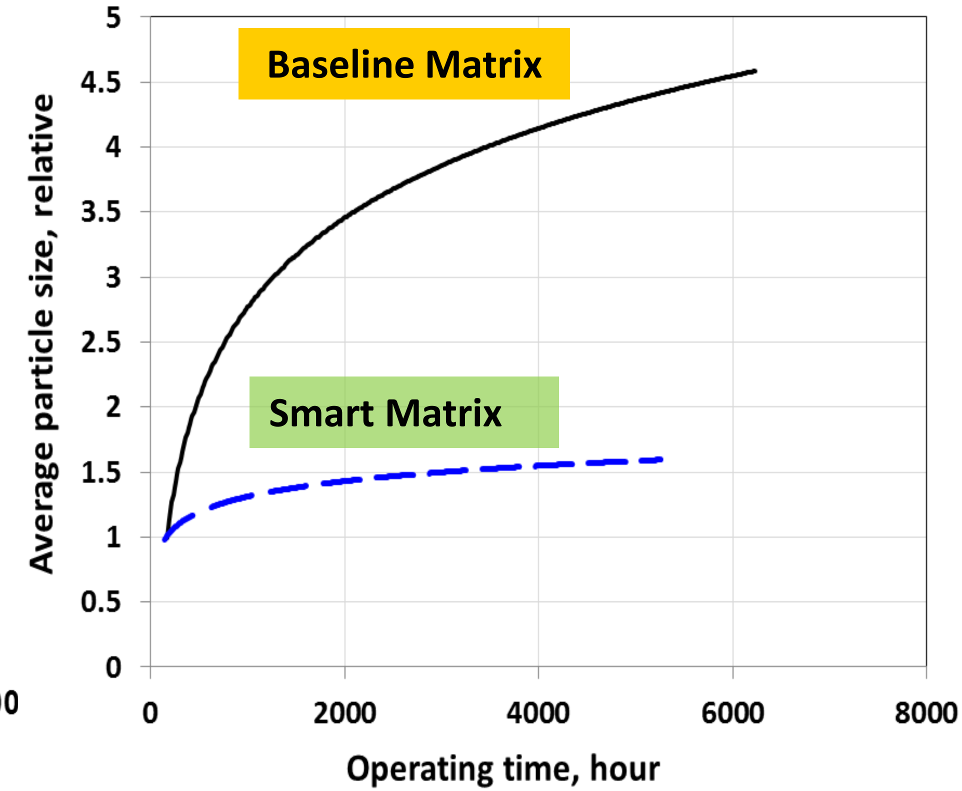
Improved "Smart" Matrix Phase and Particles Stability

Accelerated cell tests

Particles coarsening at reducing anode side (fuel inlet)





- **Smart matrix shows excellent phase and particle-size stability**
- **Projecting <3% phase transformation and ~3.5× reduction in coarsening in 10-years, meeting EOL targets**

$LiAlO_2$ Coarsening Mechanism

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$LiAlO_2$ Dissolution

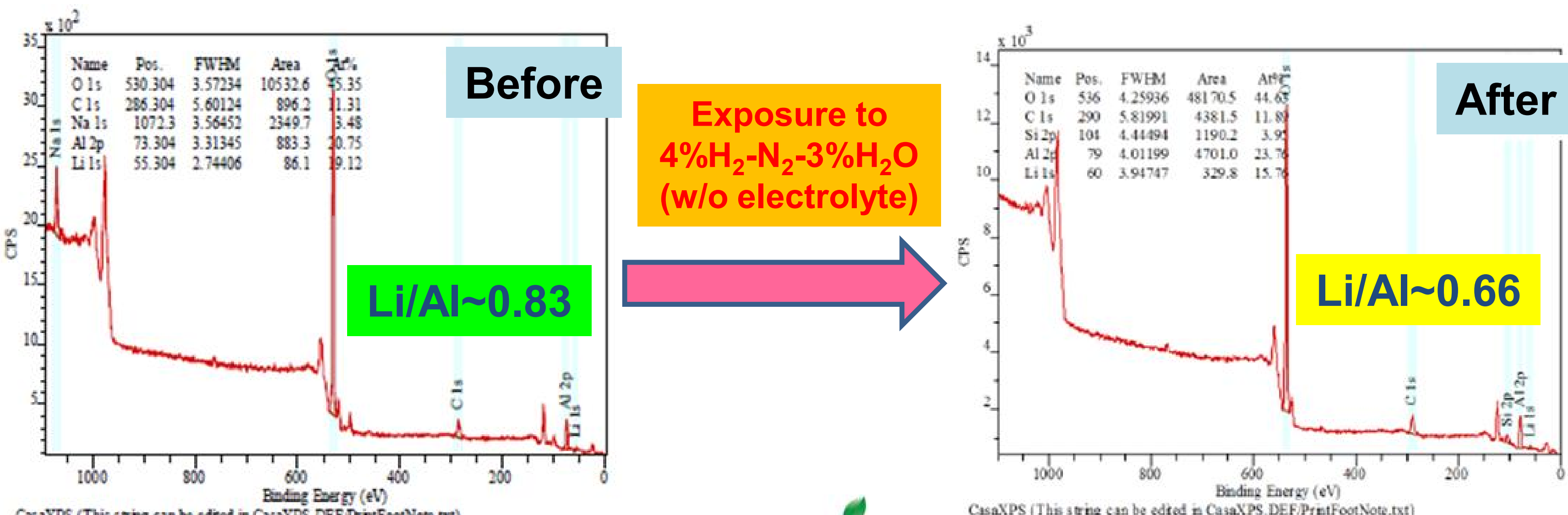
❖ Carbonate dissociation: $CO_3^{2-} \leftrightarrow CO_2 + O^{2-}$ (basicity)

❖ Basic dissolution: $LiAlO_2 + O^{2-} \leftrightarrow Li^+ + AlO_3^{3-}$

Coarsening mechanism

❖ Reducing environment promotes surface non-stoichiometry, Al reduction and crystalline cationic disorder (verified by XPS/XRD)

- ➢ Less stable/more soluble intermediate surface/phases dissolve and deposits on α phase (Ostwald ripening)



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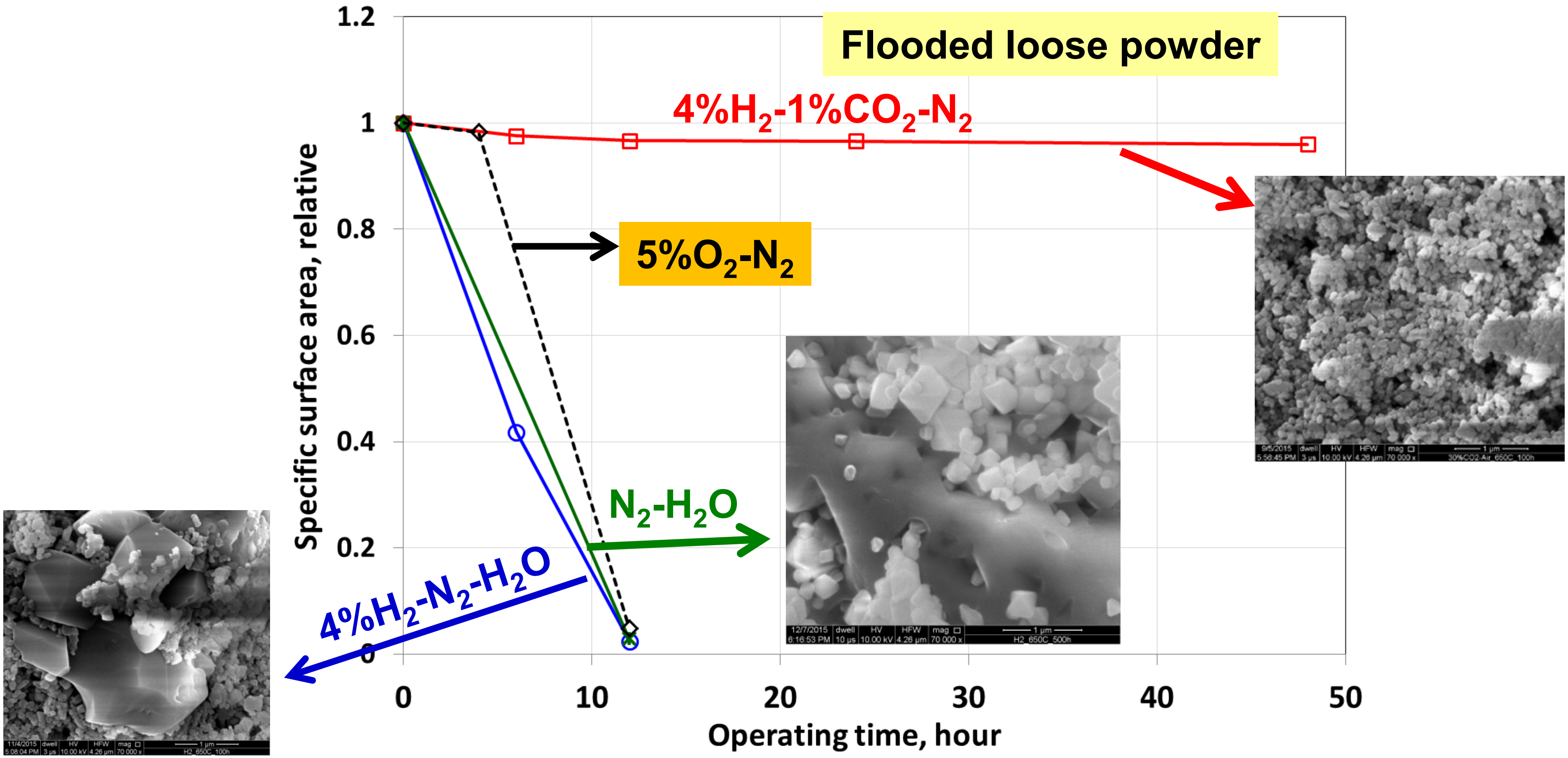
Stability of Baseline $LiAlO_2$ Powder

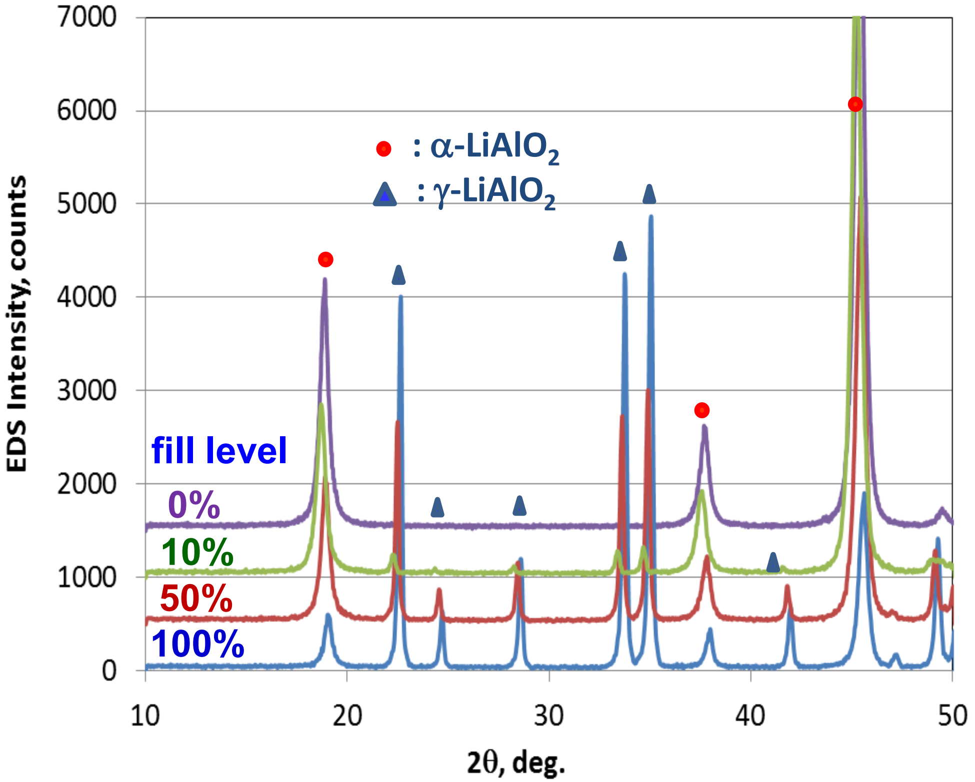
Effect of gas atmosphere at 700℃ in the presence of electrolyte

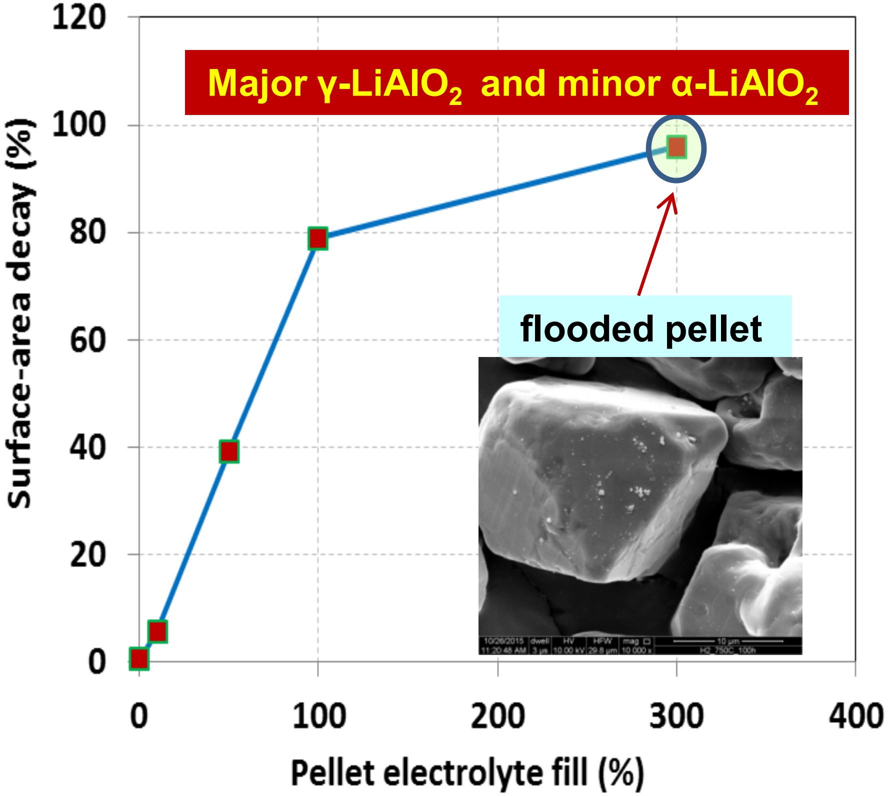


- **Highly basic electrolyte under extremely low PCO_2 accelerates dissolution, phase transformation and coarsening**
- **Reducing environment accelerates coarsening**

$LiAlO_2$ phase transformation and coarsening in reducing environment: Effect of electrolyte fill level (700℃/100h)

$LiAlO_2$ pellets - $4\%H_2$-$3\%H_2O$-N_2





- Higher electrolyte fill level promotes dissolution and diffusion, hence accelerates Ostwald ripening.

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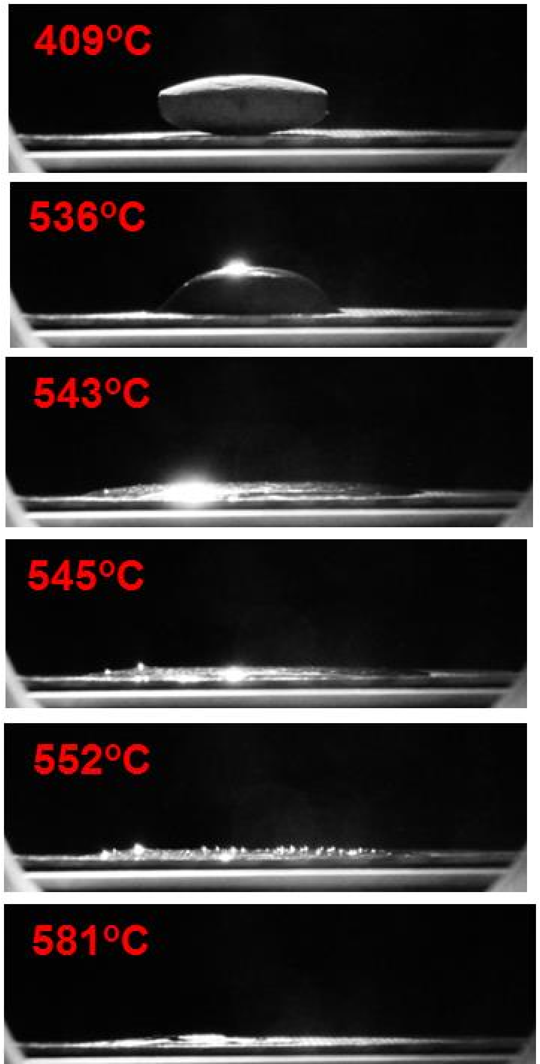
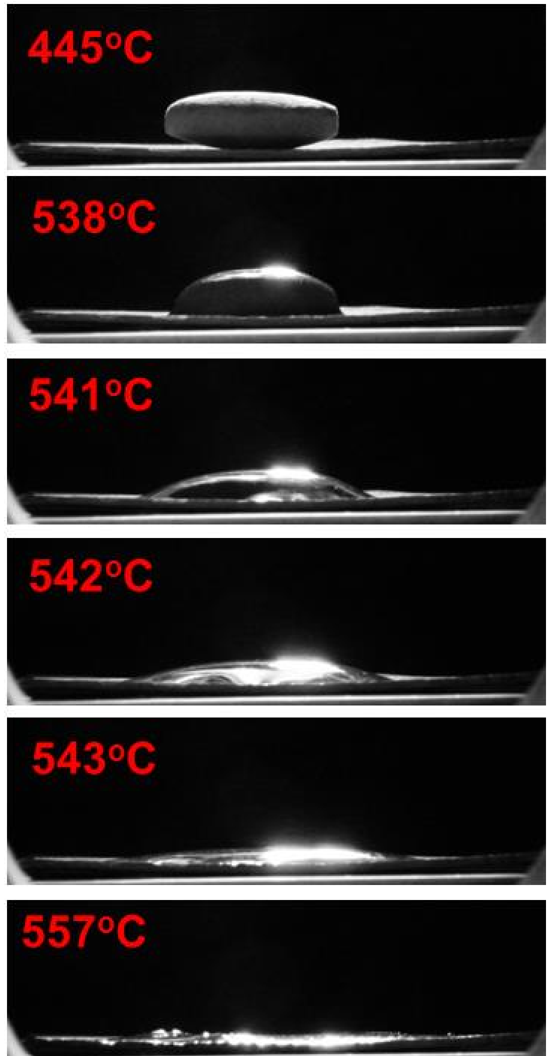
Baseline matrix wettability characterization

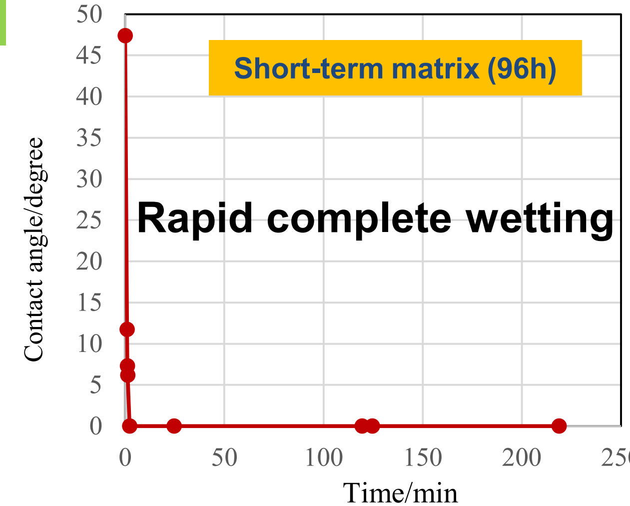
No effect of coarsening on $LiAlO_2$ inherent wettability

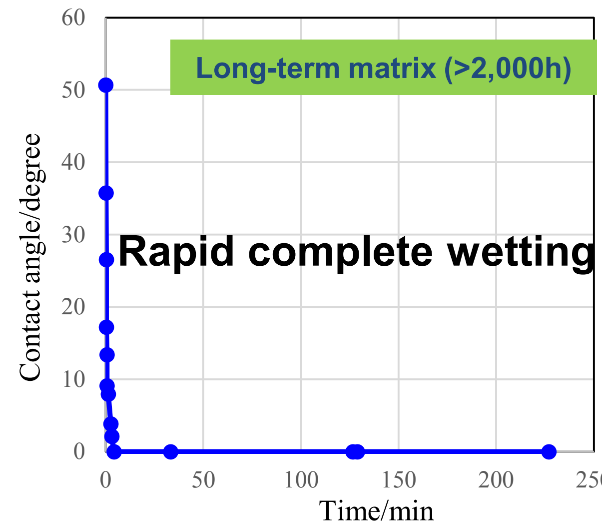
Short-term tested matrix (96h)



Long-term tested & coarsened matrix (2,500h)







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Responses to previous year reviewers comments

- **Program relevance to DOE-EERE RD&D targets:**
  - ✓ The program objective is very relevant to EERE RD&D technical targets of 100 kW–3 MW CHP and DG fuel cell systems operating on natural gas by 2020. The program success will also enable cost-effective distributed hydrogen production and CO_2 capture. DFC electrolyte matrix life enhancement is key to achieve this target.
- **Define acceleration protocols and acceleration factors to assure technical improvements projecting to 10-year stack life:**
  - ✓ Acceleration protocols and factors are reported in this presentation.
- **Cost reduction as an important program effort:**
  - ✓ Doubling stack life to 10 years can result in a substantial reduction of cost-of-electricity (COE). FCE's technical approach adopts low-cost additives and commercial standard manufacturing processes.
- **Matrix stability as 10-year stack life controlling factor:**
  - ✓ Matrix durability is one of the key DFC life-controlling factors ("Molten Carbonate and Phosphoric Acid Stationary Fuel Cells: Overview and Gap Analysis" Technical Report, NREL/TP-560-49072, September 2010). FCE is also actively developing other advanced components to achieve 10-year stack life for future-generation products.

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

UCONN – University of Connecticut, Center for Clean Energy 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

Remaining Challenges and Barriers

Challenges	Barrier
Confirm "Smart" Matrix material stability in endurance cells (>5,000h)	A
Scale up formulation and process to manufacture full-size production "Smart" Matrix and validate in full-area DFC technology stack (>5,000h)	A, B

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Proposed Future Work

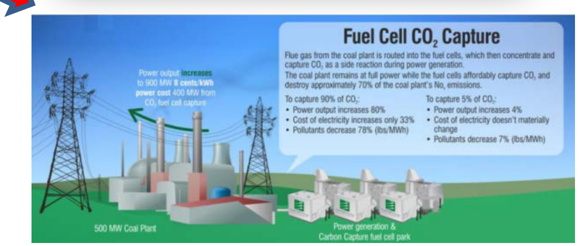
Milestone Description		Approach	% Complete
Remaining FY2016	Perform scale-up manufacturing trials and start technology stack	❖ Optimize parameters & processing conditions ❖ Scale-up trials in production facility	50
FY2017	Confirm design meeting technical requirements in accelerated cell and technology stack tests (>5,000h): sealing efficiency, performance and material stability	❖ Perform long-term (>5,000h) tests of cell and technology stacks: measure electrochemical performance, matrix gas sealing efficiency, ohmic resistance, and material stability.	10

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 system**
  - **Enable DFC-CO_2 capture for reducing CO_2 emission**

Trigen: power+H_2+heat



Summary

- **Achieved all quarterly and Go/No Go milestones**
  - ✓ Met target of >25% improved matrix mechanical strength compared to baseline
  - ✓ Achieved targets of sealing efficiency and >20mΩcm^2 ohmic resistance reduction
  - ✓ Successfully verified smart matrix support material stability in lab-scale endurance cells (>5,000h)
    - ✓ Met targeted milestones of projected <5% phase transformation ($\alpha \rightarrow \gamma$-$LiAlO_2$) and <50% pores larger than 0.2μm in 10 years

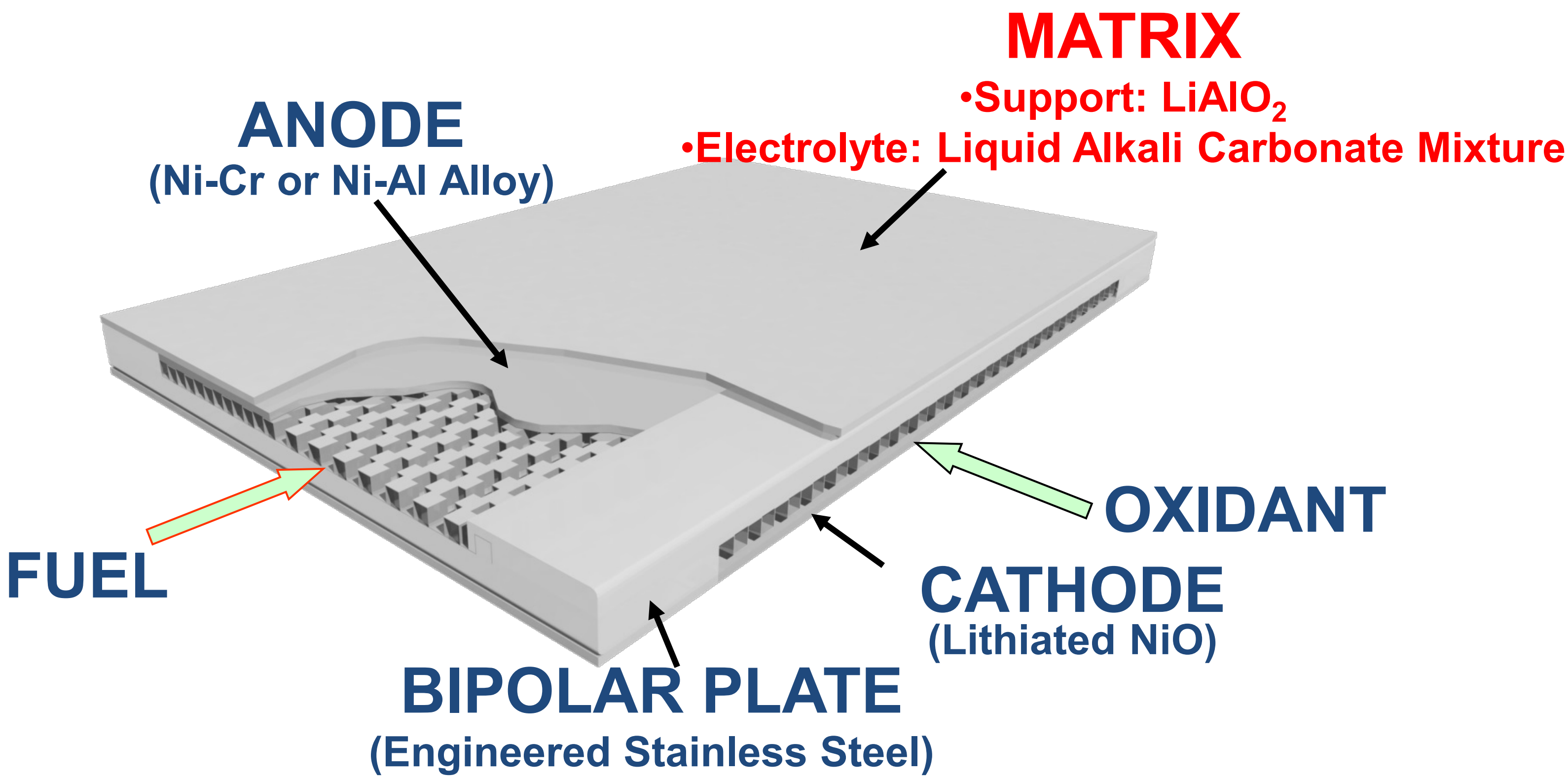
- **Degradation mechanistic understanding**
  - ✓ Confirmed accelerated coarsening in highly basic electrolytes
  - ✓ Demonstrated strong effect of electrolyte fill and temperature on coarsening rate and phase transformation.
  - ✓ Reducing environment promotes surface non-stochiometry, hence enhancing Ostwald ripening

Technical Back-Up Slides

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.

CARBONATE FUEL CELL MATERIALS



Matrix: a key cell component for enabling 80,000h stack life

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DFC Configuration

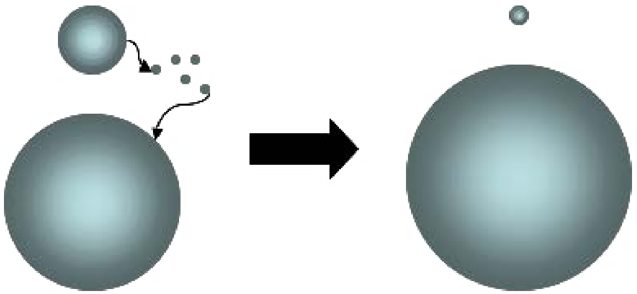
Individual fuel cell component

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

$LiAlO_2$ Ostwald Ripening Understanding



Ostwald Ripening: smaller particles dissolve and deposit on larger particles in order to reach a more thermodynamically stable state

- High solubility promotes coarsening
- Diffusion and/or dissolution/deposition control

Understand $LiAlO_2$ coarsening mechanism

➢ **Investigate controlling parameters under this program**

- ➢ Temperature, gas atmosphere
- ➢ Particle-size distribution
- ➢ Solubility
- ➢ Powder defect chemistry
- ➢ Phase transformation, deposition kinetics
- ➢ Additive

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Literature Information on $LiAlO_2$ Stability

- **Possible $LiAlO_2$ Dissolution Mechanism**
  – **Carbonate dissociation: $CO_3^{2-} \leftrightarrow CO_2 + O^{2-}$ (basicity)**
  – **Basic dissolution: $LiAlO_2 + O^{2-} \leftrightarrow Li^+ + AlO_3^{3-}$**

  ➢ **Higher P_{CO_2} and lower temperature: lower solubility and slower coarsening**

  ➢ **Solubility $\beta > \gamma > \alpha$**

- **Additional factors:**
  – **Intermediate phase formation or Li elution**
  – **Agglomeration, non-uniform particle-size distribution**

➢ **Very limited study on $LiAlO_2$ coarsening under reducing anode atmosphere**