

Smart Matrix Development for Direct Carbonate Fuel Cell



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

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 CO₂ 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

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

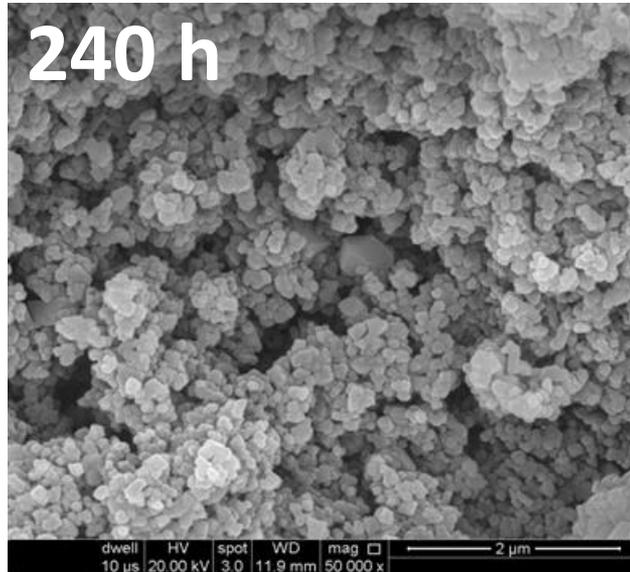
- Scale up manufacturing “Smart” Matrix and ready for stack evaluation

Impact since 2015 AMR

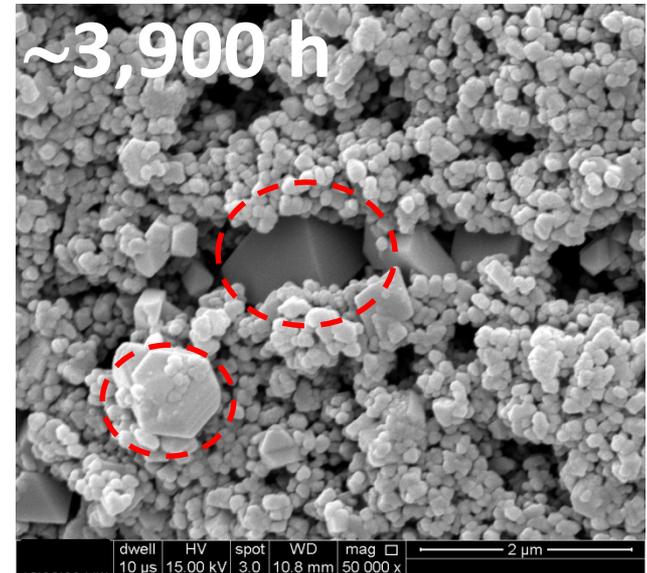
- Projected “Smart” Matrix design capable of achieving 80,000h life target (**Barriers A and B**)

Why Do We Need “Smart” Matrix?

Enhance Matrix Material Stability



Coarsening via
Ostwald Ripening
dissolution/deposition



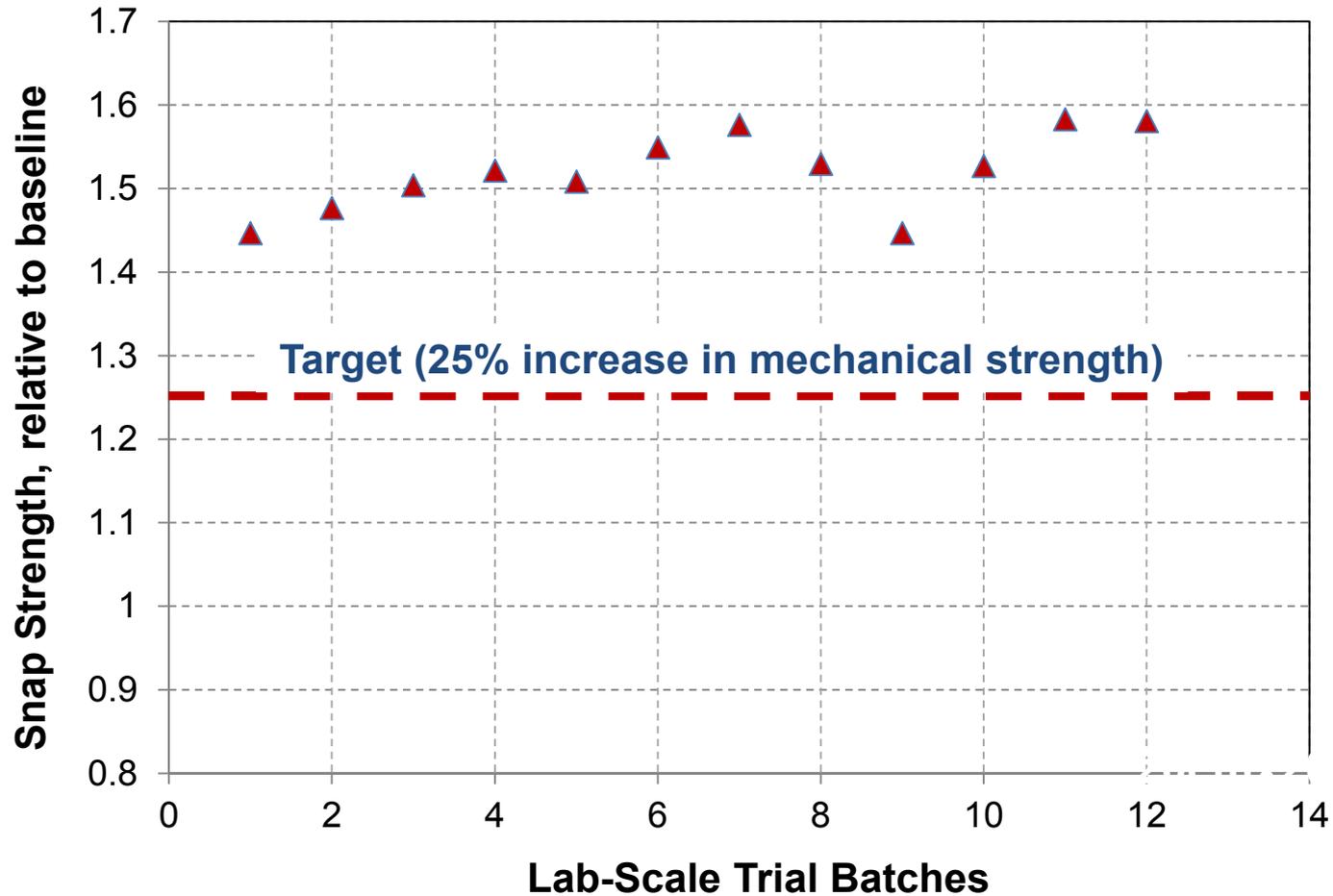
- Coarsening of α -LiAlO₂ support material leading to pore growth
 - Reduced electrolyte retention capability
 - Increased cross-leakage
 - Increased ohmic resistance
 - Electrolyte mal-distribution and cell performance impact
- Besides enhancing matrix material stability under “Smart” Matrix program, FCE is actively developing other advanced cost-effective 10-year life stack components.

Goals	Approaches	Desired Properties	Status
<p>>20% porosity increase and improved fine-pore structure (>30% reduction on pores larger than 0.2μm)</p> <p>>25% increased mechanical strength</p> <p>Verify matrix sealing efficiency</p>	Proprietary pore former	Chemical compatibility	✓
	<p>Optimize slurry formulation and processing</p> <p>Engineered additives</p>	<p>Uniform particle size distribution</p> <p>Improved slurry rheology, particles packing & manufacture yield</p>	✓
<p>Stable fine pores for enhanced electrolyte retention (<50% pores larger than 0.2μm and <5% phase transformation) in endurance tests (>5,000h)</p>	<p>Stabilized LiAlO₂</p> <p>Cost-effective LiAlO₂ manufacturing process</p> <p>Engineered additives</p>	<p>Stable phase (100% α-LiAlO₂ phase purity)</p> <p>Low solubility</p> <p>Slow coarsening</p>	✓
<p>Understand matrix phase, microstructure and wettability changes</p>	<p>Effect of temperature, gas composition and cell location</p>	<p>Fundamental parameters governing matrix material stability and wettability</p>	✓

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

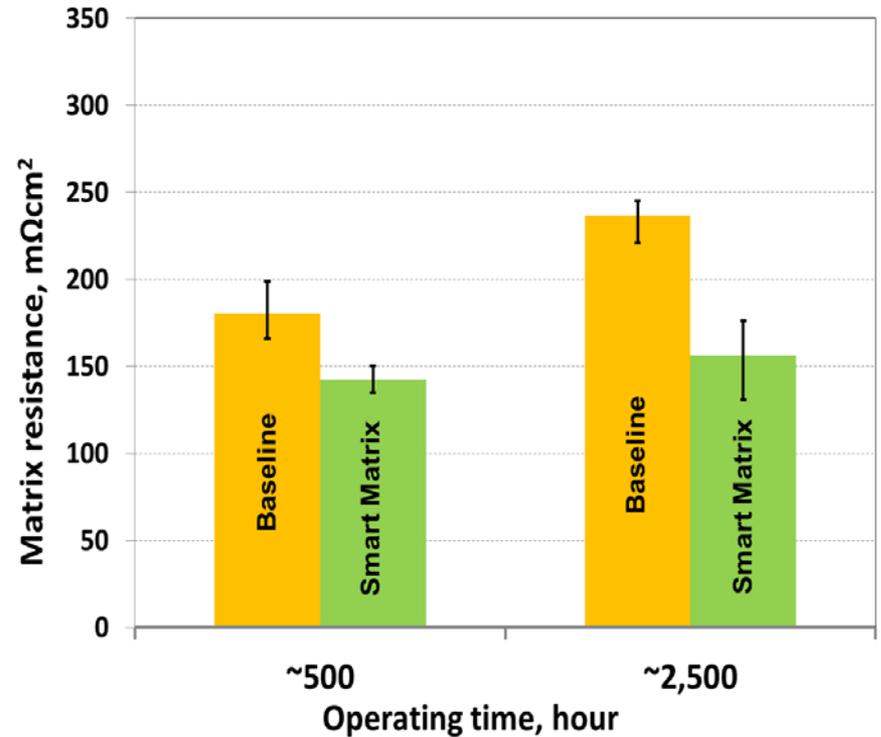
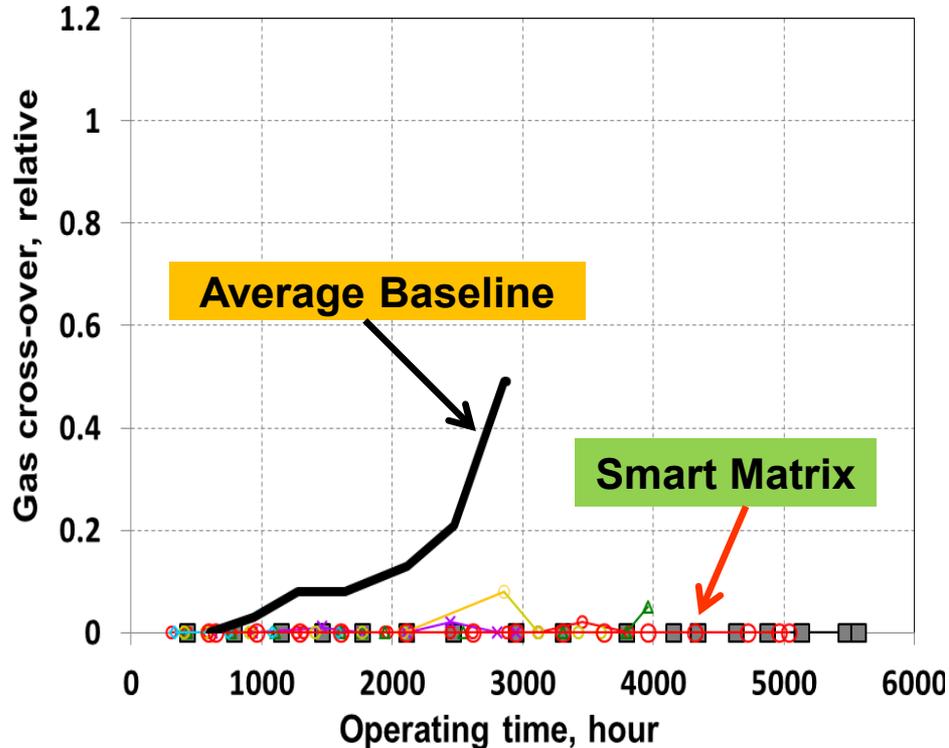


- Smart matrix consistently demonstrated increased mechanical strength (verified in >30 batches)

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

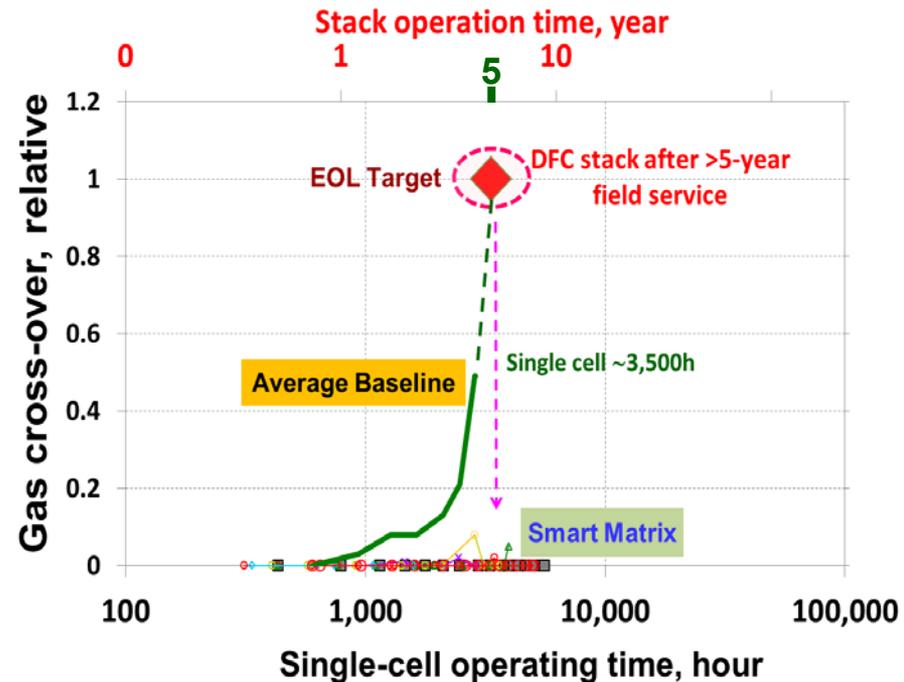
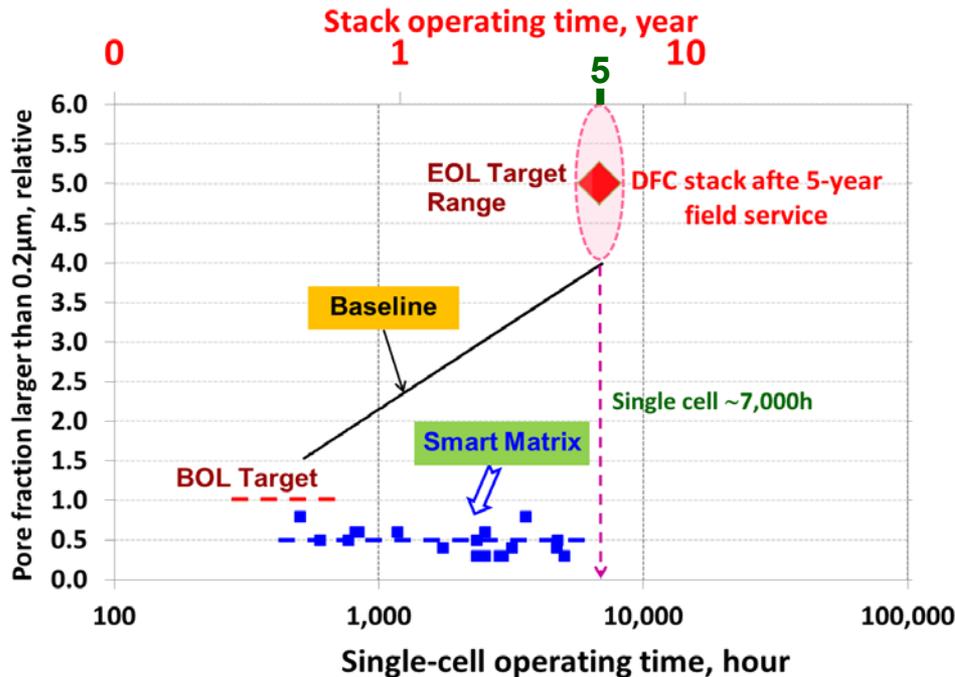


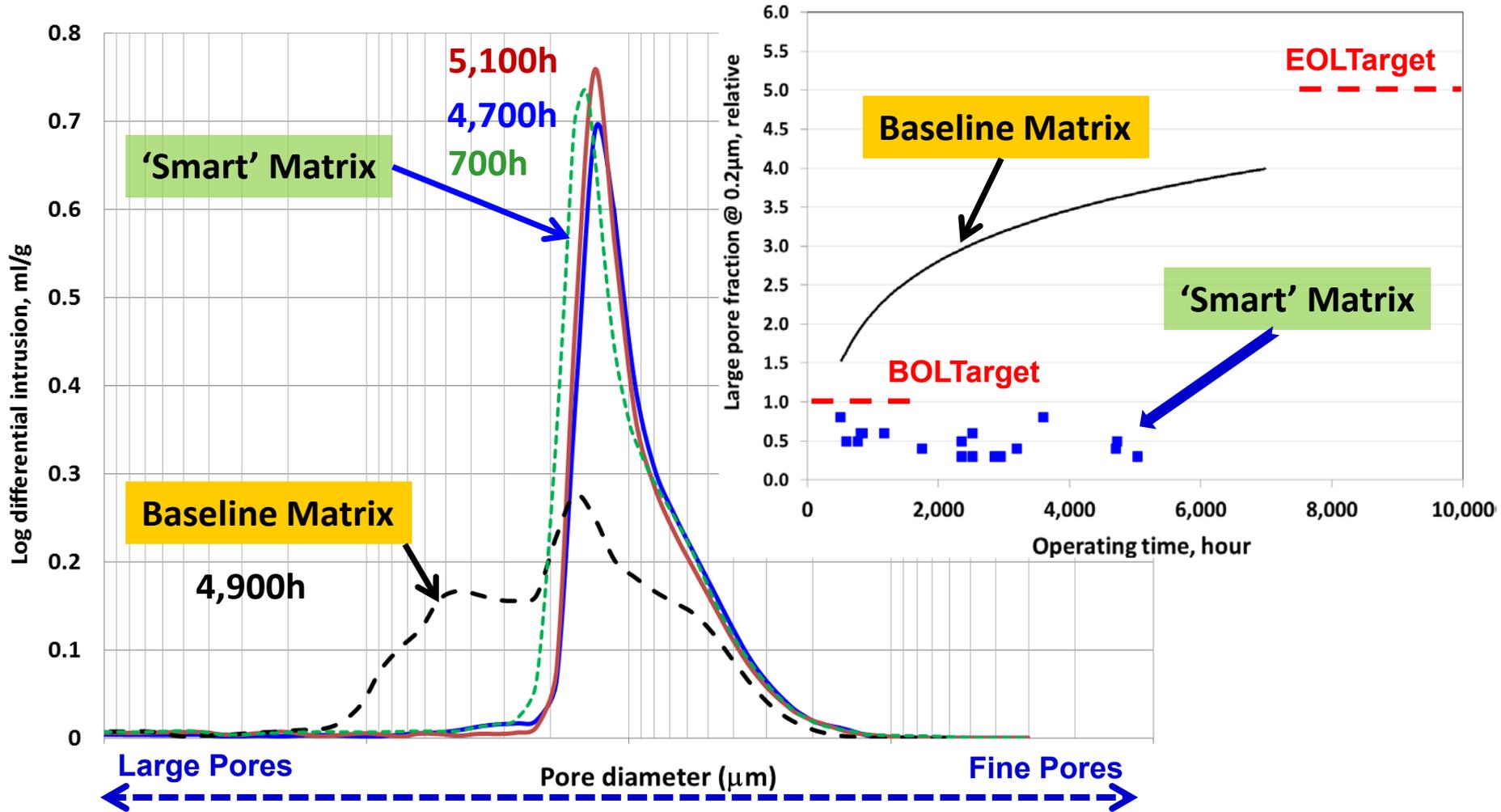
☐ Demonstrated significantly improved gas sealing (cross-over) efficiency (>20 single cell tests)

☐ Achieved targeted >20mΩ cm² resistance reduction in >20 cells

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.



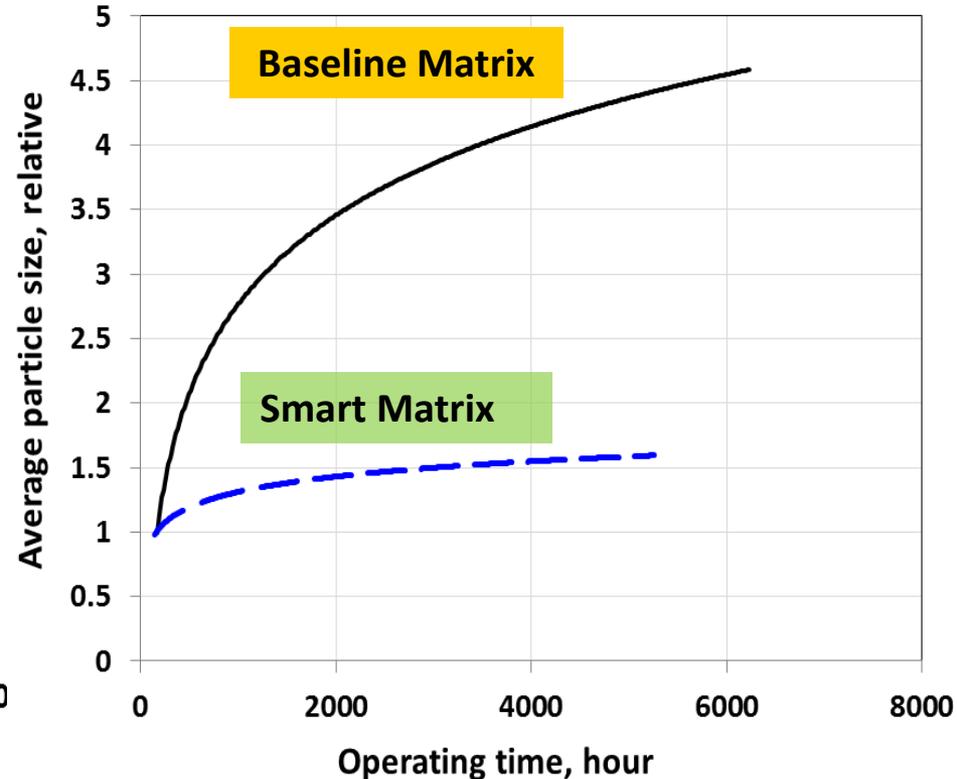
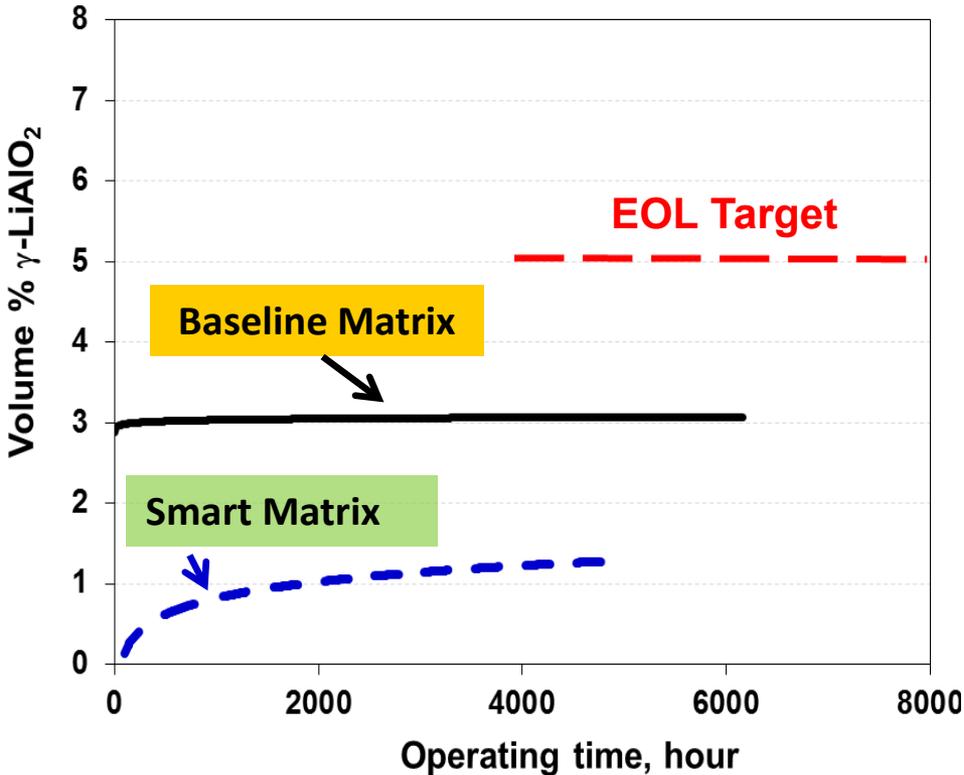


☐ Achieved projected EOL stable pore structure target (<50% of pores >0.2μm in 10 years)

Improved “Smart” Matrix Phase and Particles Stability

Accelerated cell tests

Particles coarsening at reducing anode side (fuel inlet)



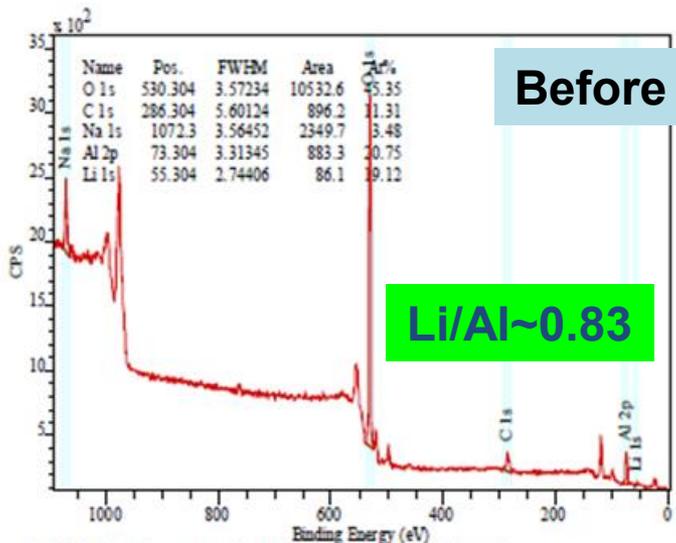
- ❑ Smart matrix shows excellent phase and particle-size stability
- ❑ Projecting <3% phase transformation and ~3.5× reduction in coarsening in 10-years, meeting EOL targets

LiAlO₂ Dissolution

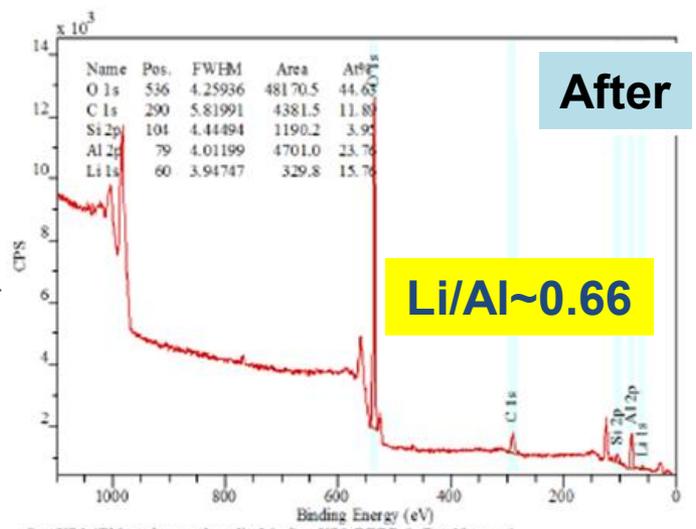
- ❖ Carbonate dissociation: $\text{CO}_3^{2-} \leftrightarrow \text{CO}_2 + \text{O}^{2-}$ (basicity)
- ❖ Basic dissolution: $\text{LiAlO}_2 + \text{O}^{2-} \leftrightarrow \text{Li}^+ + \text{AlO}_3^{3-}$

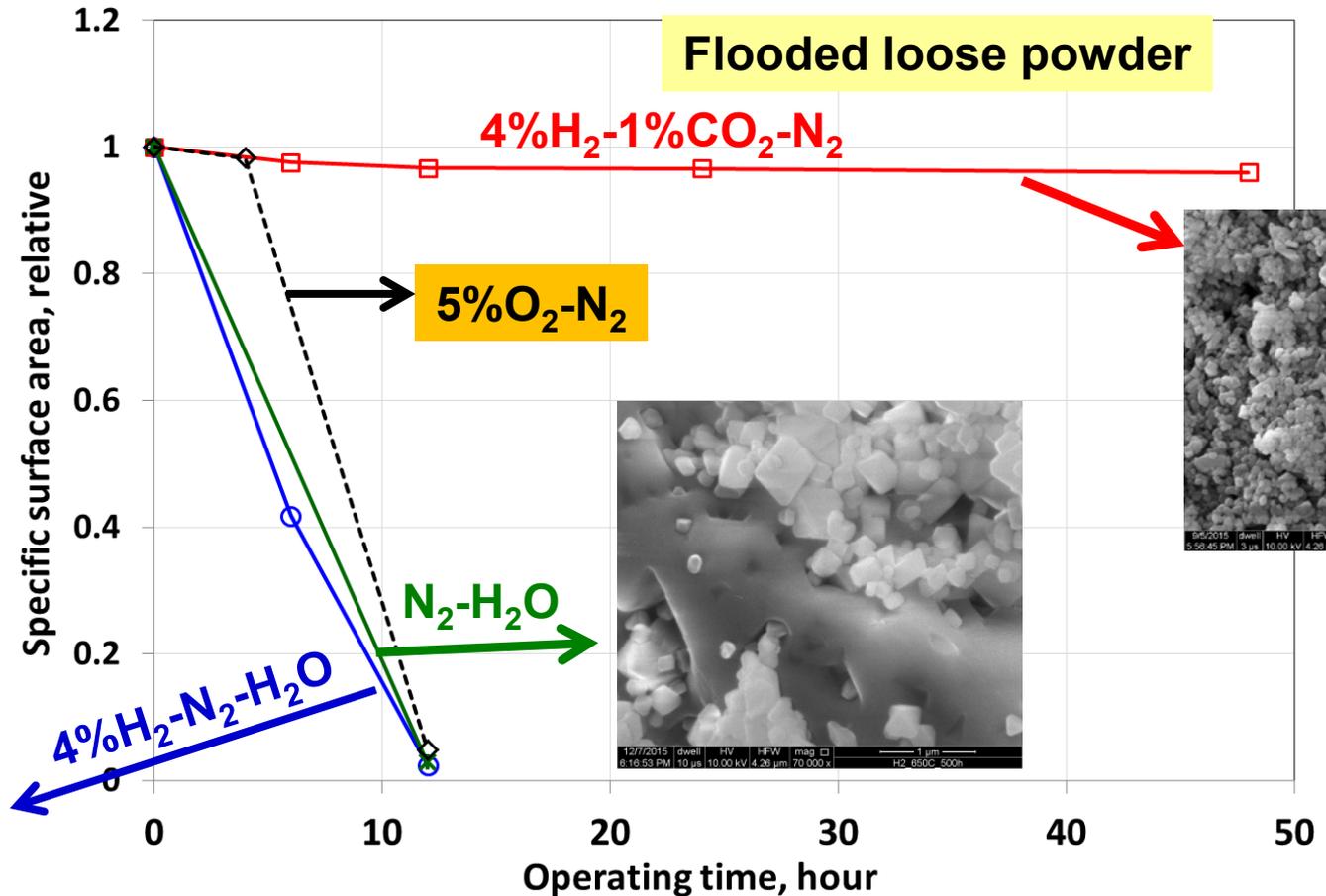
Coarsening mechanism

- ❖ 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)



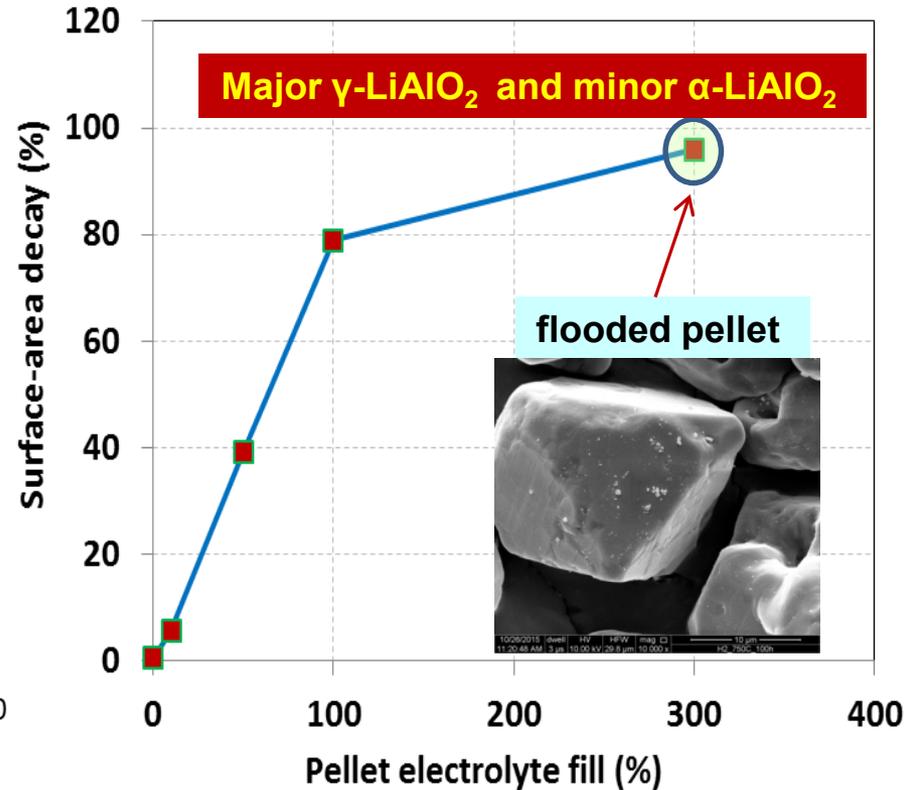
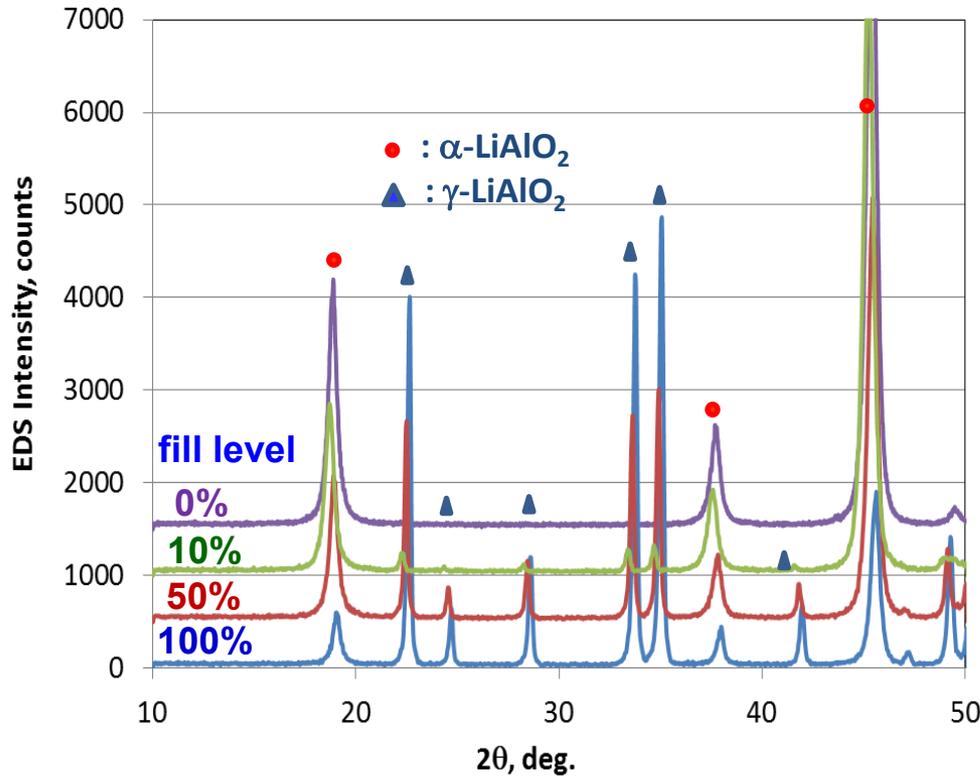
Exposure to
4% H₂-N₂-3% H₂O
(w/o electrolyte)





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

LiAlO₂ pellets - 4%H₂-3%H₂O-N₂

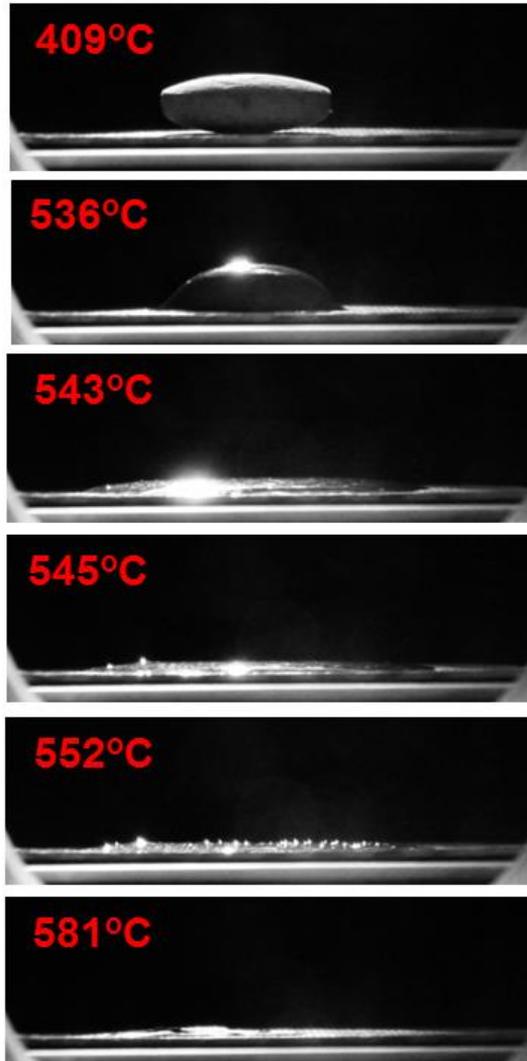


- Higher electrolyte fill level promotes dissolution and diffusion, hence accelerates Ostwald ripening.

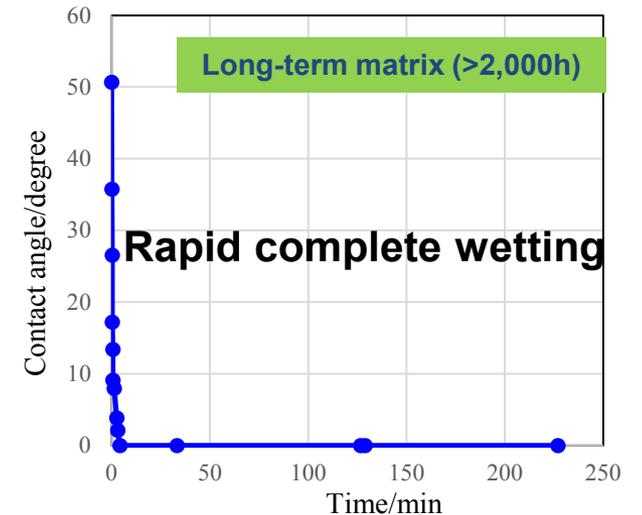
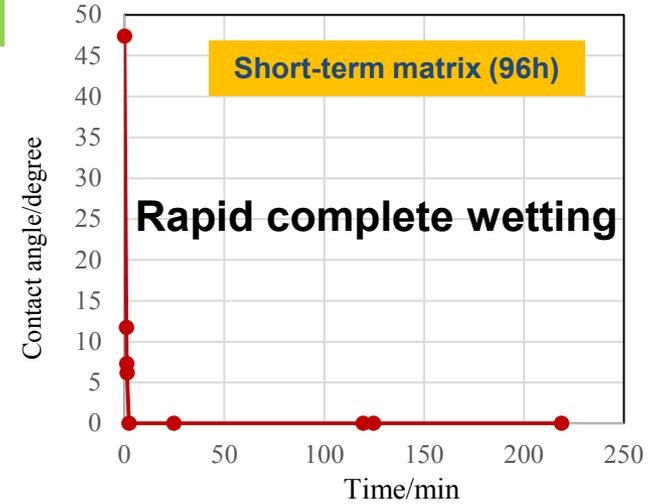
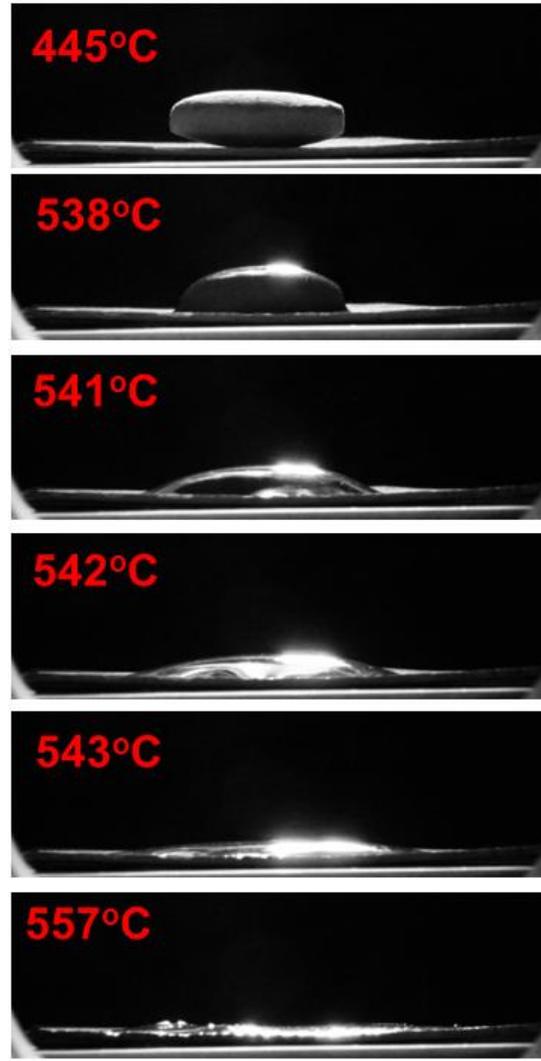
Baseline matrix wettability characterization

No effect of coarsening on LiAlO_2 inherent wettability

Short-term tested matrix (96h)



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



➤ **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 CO₂ 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.

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



Expertise in high temperature fuel cell, material stability and characterization

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



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

- Evaluate matrix electrolyte wettability

Prof. JR Selman

- Consulting on electrolyte contact angle/distribution

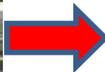
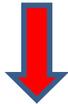
Understand matrix coarsening mechanism & electrolyte retention capability

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

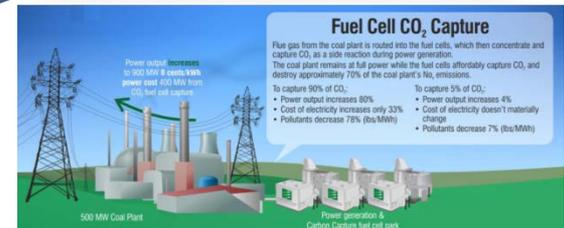
Proposed Future Work

Milestone Description		Approach	% Complete
Remaining FY2016	Perform scale-up manufacturing trials and start technology stack	<ul style="list-style-type: none"> ❖ 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	<ul style="list-style-type: none"> ❖ Perform long-term (>5,000h) tests of cell and technology stacks: measure electrochemical performance, matrix gas sealing efficiency, ohmic resistance, and material stability. 	10

- 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-H₂ system
 - Enable DFC-CO₂ capture for reducing CO₂ emission



Trigen: power+H₂+heat



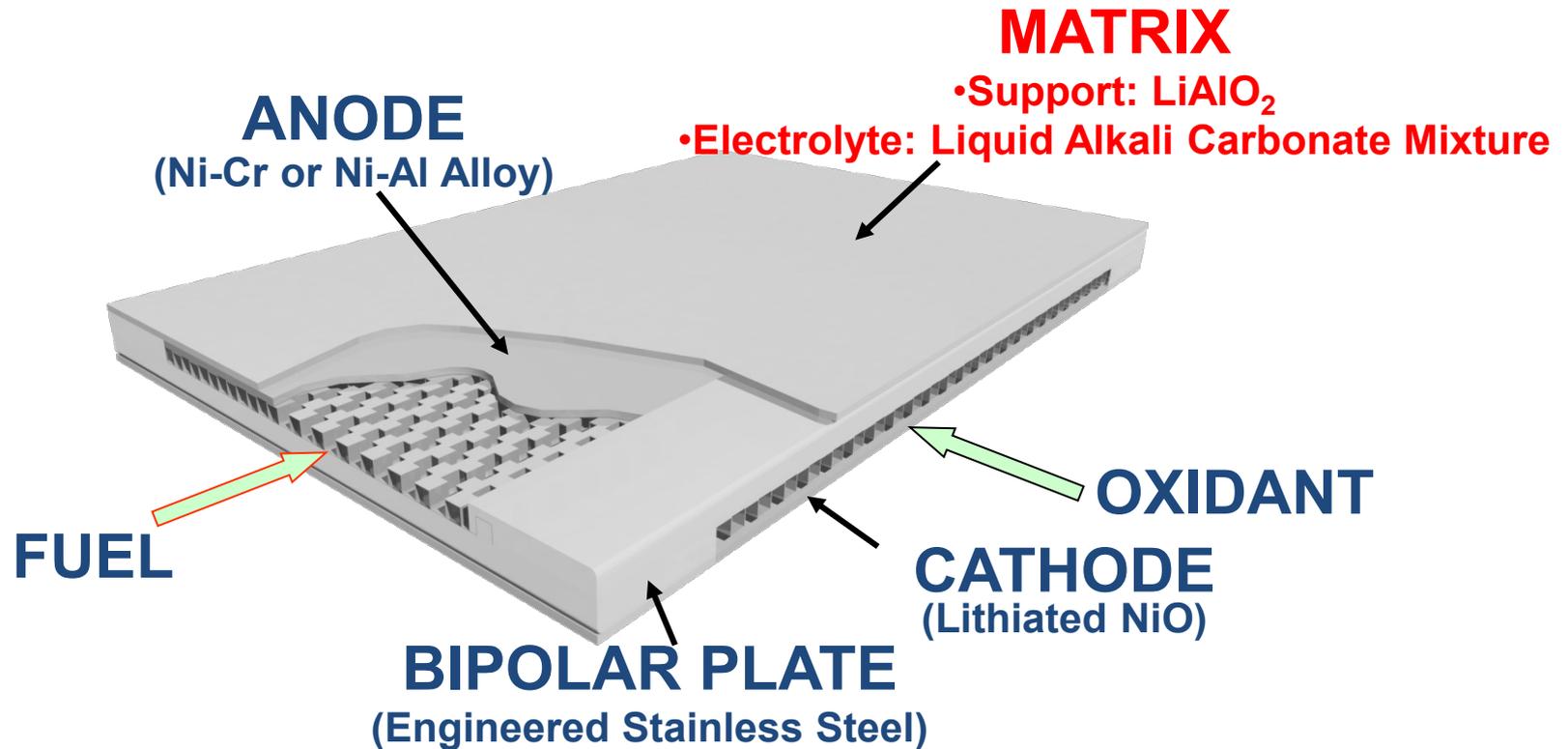
- ❑ **Achieved all quarterly and Go/No Go milestones**
 - ✓ Met target of >25% improved matrix mechanical strength compared to baseline
 - ✓ Achieved targets of sealing efficiency and >20mΩcm² ohmic resistance reduction
 - ✓ Successfully verified smart matrix support material stability in lab-scale endurance cells (>5,000h)
 - ✓ Met targeted milestones of projected <5% phase transformation ($\alpha \rightarrow \gamma$ -LiAlO₂) 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-stoichiometry, hence enhancing Ostwald ripening

Technical Back-Up Slides



- **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.**



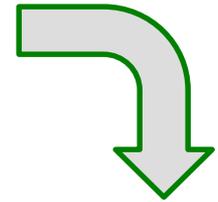
Matrix: a key cell component for enabling 80,000h stack life



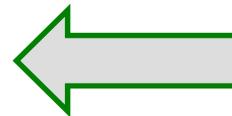
Individual fuel cell component



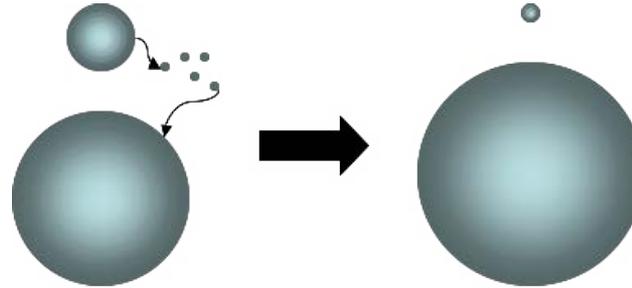
400 components are used to build one 350 kW fuel cell stack



Two modules are used for a 2.8 MW power plant



4 stacks are combined to build a 1.4 MW modules



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 LiAlO₂ coarsening mechanism

- **Investigate controlling parameters under this program**
 - Temperature, gas atmosphere
 - Particle-size distribution
 - Solubility
 - Powder defect chemistry
 - Phase transformation, deposition kinetics
 - Additive

- **Possible LiAlO_2 Dissolution Mechanism**
 - Carbonate dissociation: $\text{CO}_3^{2-} \leftrightarrow \text{CO}_2 + \text{O}^{2-}$ (**basicity**)
 - Basic dissolution: $\text{LiAlO}_2 + \text{O}^{2-} \leftrightarrow \text{Li}^+ + \text{AlO}_3^{3-}$
 - Higher PCO_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**