FuelCell Energy
Ultra-Clean, Efficient, Reliable Power

Smart Matrix Development for Direct Carbonate Fuel Cell



UCONN
UNIVERSITY OF CONNECTICUT
Center for Clean Energy Engineering

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ILLINOIS INSTITUTE OF TECHNOLOGY

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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*: ~$430K

* As of 3/31/15

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)**
  - Matrix 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 technology for hydrogen infrastructure & CO_2 capture**
- **Enable domestic clean-energy job growth**

Objectives for Current Project Year (October 2014 - April 2015):

- **Develop plans to achieve 'Smart' Matrix technical goals**
- **Develop plans to enhance degradation mechanistic understanding**
- **Initiate cell testing of 'Smart' Matrix**

Impact since 2014 AMR

- **Identified environmental factors impacting degradation (Barrier A)**
- **Fabricated 'Smart' Matrix meeting beginning-of-life porosity and pore-structure targets (Barriers A and B)**

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

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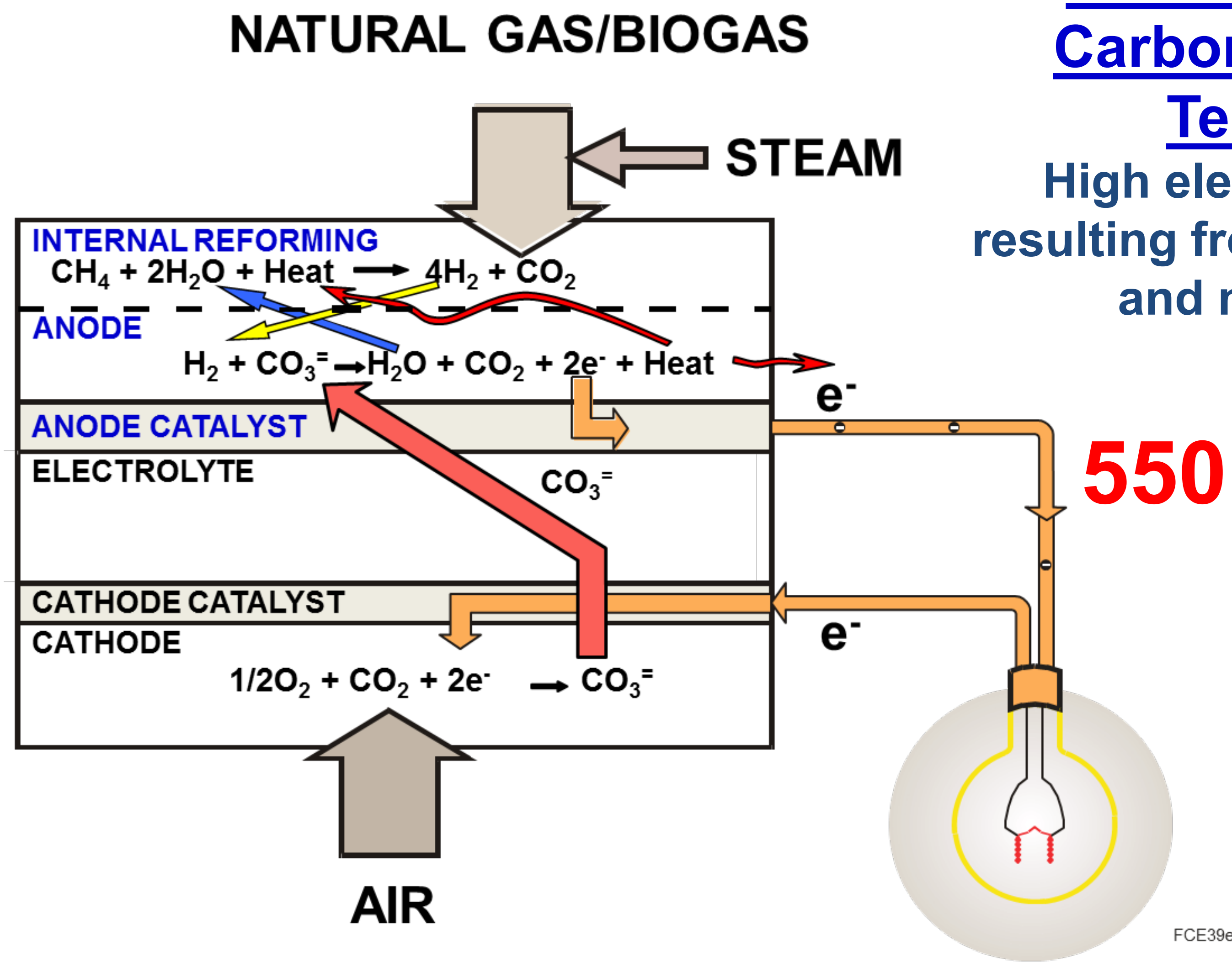
Relevance to RD&D Technical Targets

'Smart' Matrix aims to enable 80,000h DFC stack life by 2020

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	**>43,000h**	**80,000h**

What is DFC?



Internal-Reforming Carbonate Fuel Cell Technology

High electrical efficiency resulting from synergistic heat and mass transfer

550-650°C

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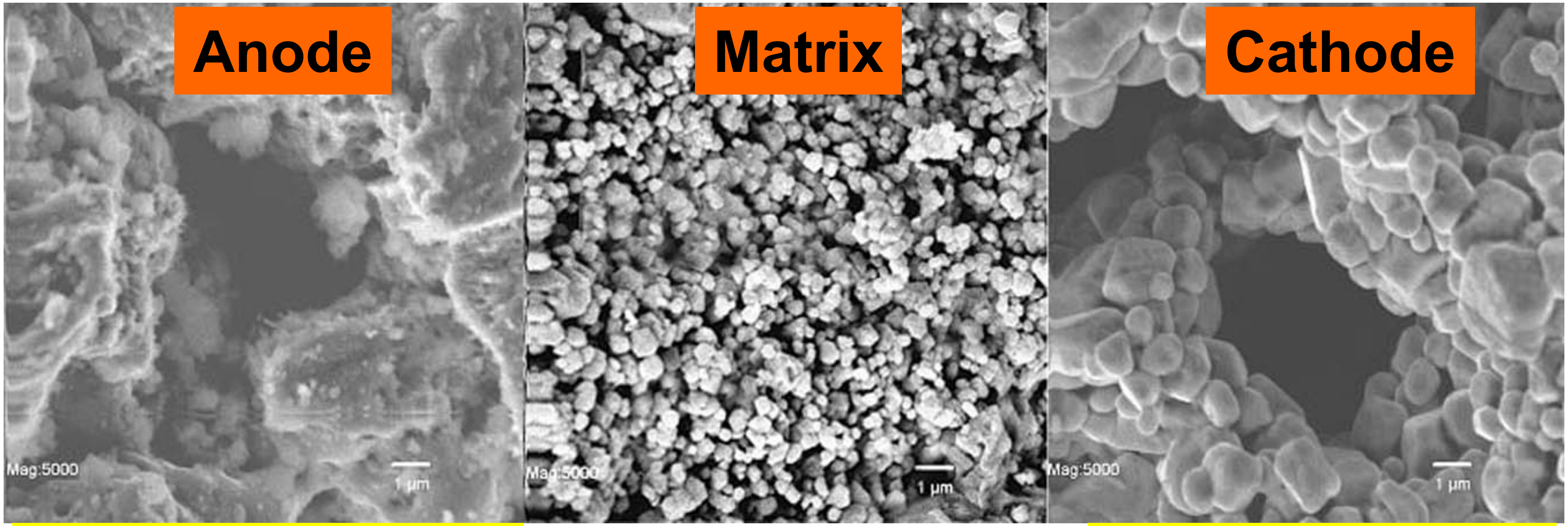
DFC Active Cell Components



Ni-Based ODS Alloy

$LiAlO_2$

Lithiated NiO

Matrix Requirements

- **Stable fine-pore structure for capillary electrolyte retention**
- **High porosity for low ionic resistance**
- **High strength and toughness to withstand thermo-mechanical stress**

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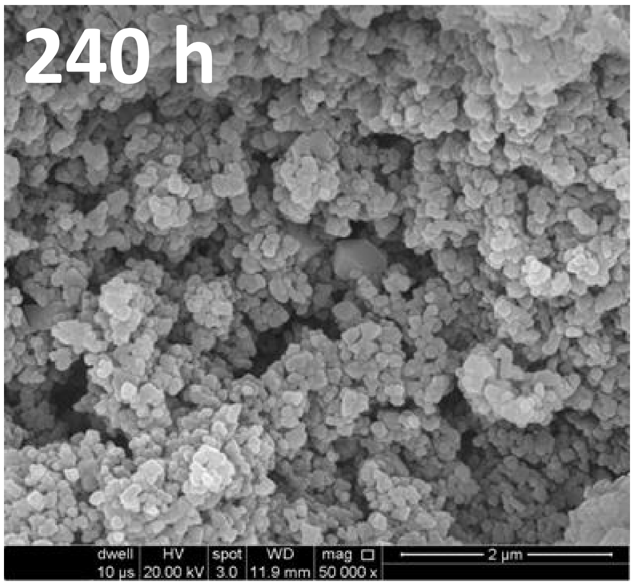
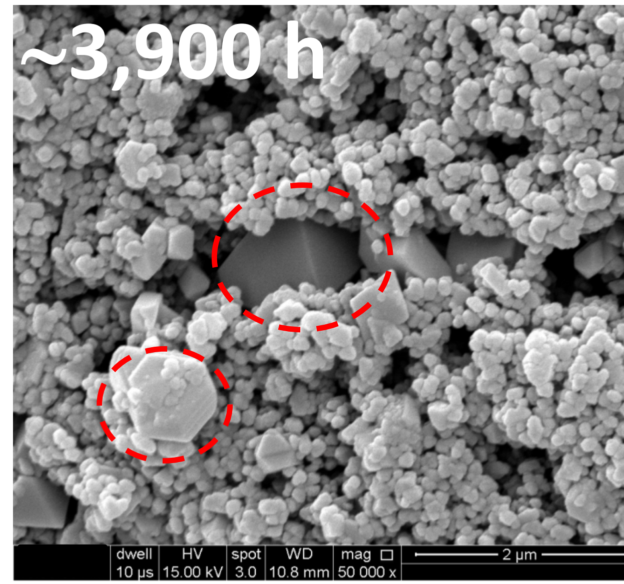
Observed Matrix Coarsening in Single Cell



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**

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Approaches to Achieve 'Smart' Matrix

Goals	Approaches	Desired Characteristics
BOL* >20% porosity increase and improved fine-pore structure (>30% reduction on pores larger than 0.2μm)	Pore former	• Chemical compatibility • Free of contaminant • No undesirable residue
	Optimize slurry formulation and processing	• Improved slurry rheology & manufacture yield
EOL* Stable fine pores for enhanced electrolyte retention (<50% pores larger than 0.2μm)	Stabilized $LiAlO_2$	• Stable phase • Low solubility • Slow coarsening

*BOL: beginning-of-life, EOL: end-of-life

Approaches to Enhance Coarsening Mechanistic Understanding

Goals	Tests/Experiments	Characterization Methods
Matrix microstructure change	**Effect of temperature, gas composition & cell location on coarsening rate**	**FCE/UConn** **HRSEM, XRD, BET, porosimetry, electrolyte fill level**
$LiAlO_2$ solubility & phase stability	**Solubility, coarsening and defect chemistry (550-800°C, reducing/oxidizing atmosphere)**	**FCE/UConn** **HRSEM, ICP, XRD, BET, Density, FTIR, XPS**
Matrix wettability	**Effect of time, temperature and gas composition**	**FCE/IIT** **Optical Sessile drop**

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

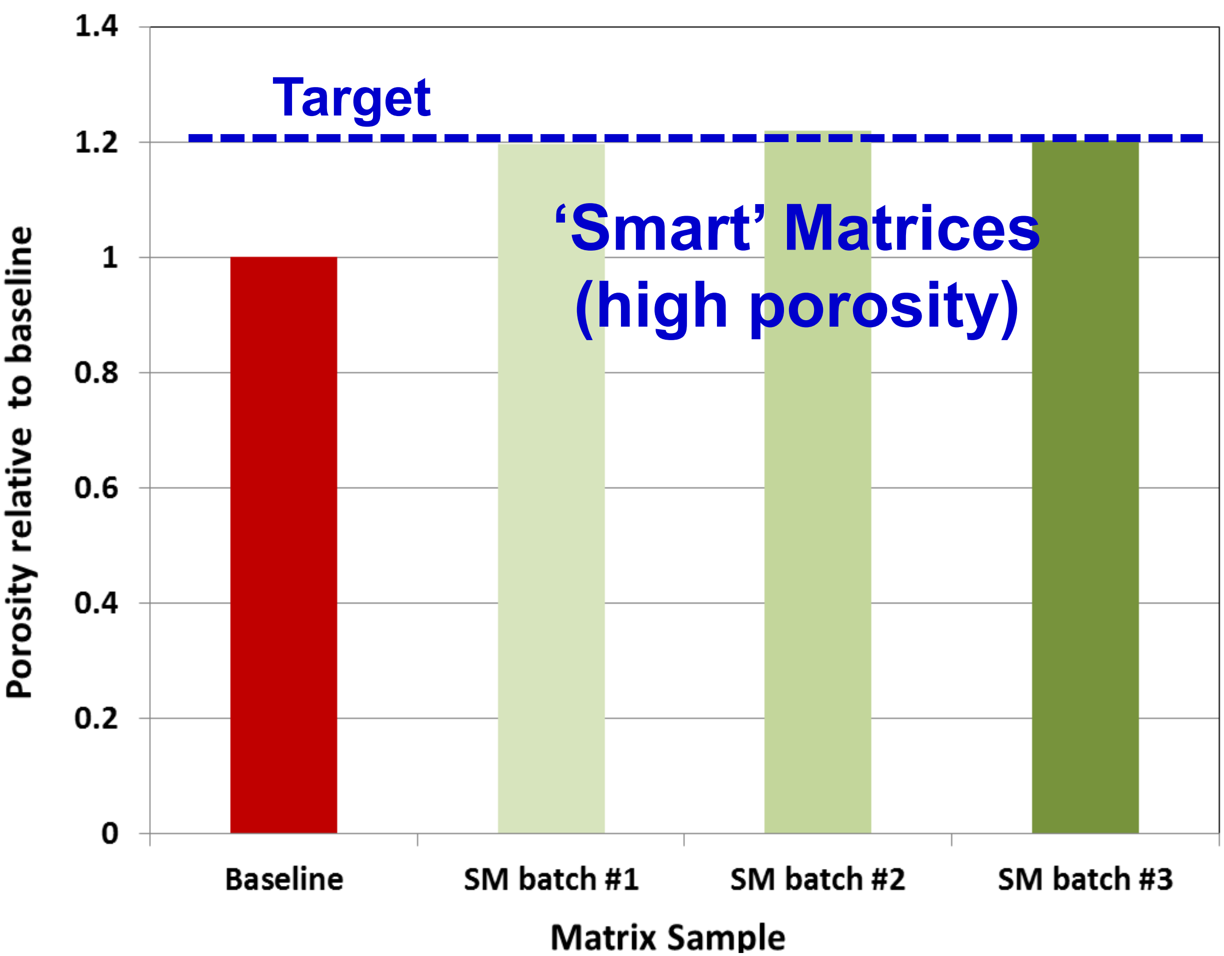
Program on track

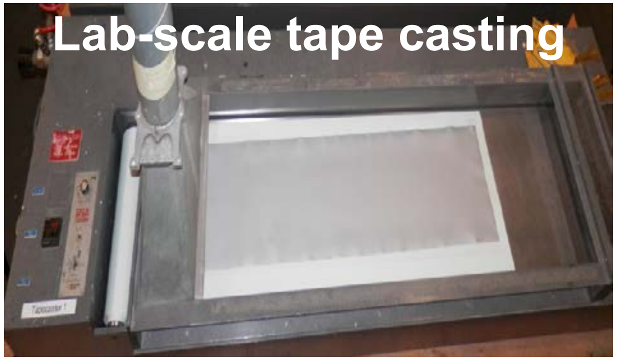
Milestone	Description	Status
Through 3/31/2015	❖ Deliver technical plans ❖ Achieve high-porosity stable fine-pore structure ❖ Enhance degradation mechanistic understanding ❖ Initiate "Smart' Matrix cell testing	100%
Remaining FY2015	Achieve BOL mechanical strength (>30% increase) and improved fine-pore structure	75%
	Verify preliminary 'smart' matrix sealing efficiency & ohmic resistance in >2,000h cell tests	40%
FY2016	Verify "Smart' Matrix durability in >5,000h endurance cell tests	20%
	Deliver report on degradation mechanistic understanding	10%
	Perform scale-up manufacturing trial and start technology stack	10%

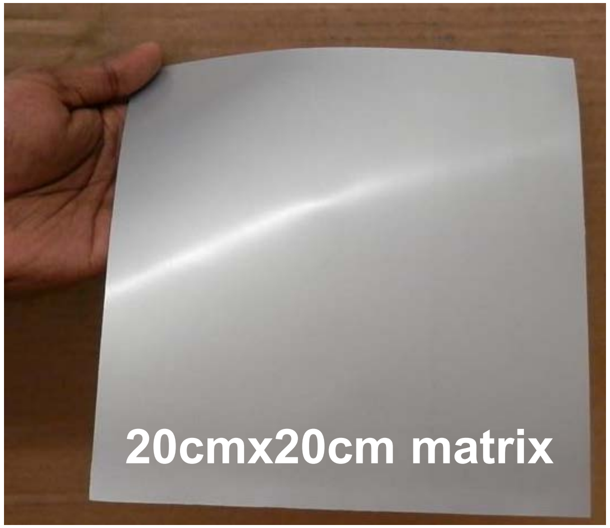
Go/No-Go	Description	Status
FY2015 (9/30/2015)	'Smart' Matrix technical targets verified in <3,000h cell tests	50%
FY2016 (9/30/2016)	❖ 'Smart' Matrix technical targets verified in >5,000h cell tests ❖ Tech stack ready for start-up	

Achieved High Porosity

Successfully manufactured lab-scale high-porosity 'Smart' Matrix



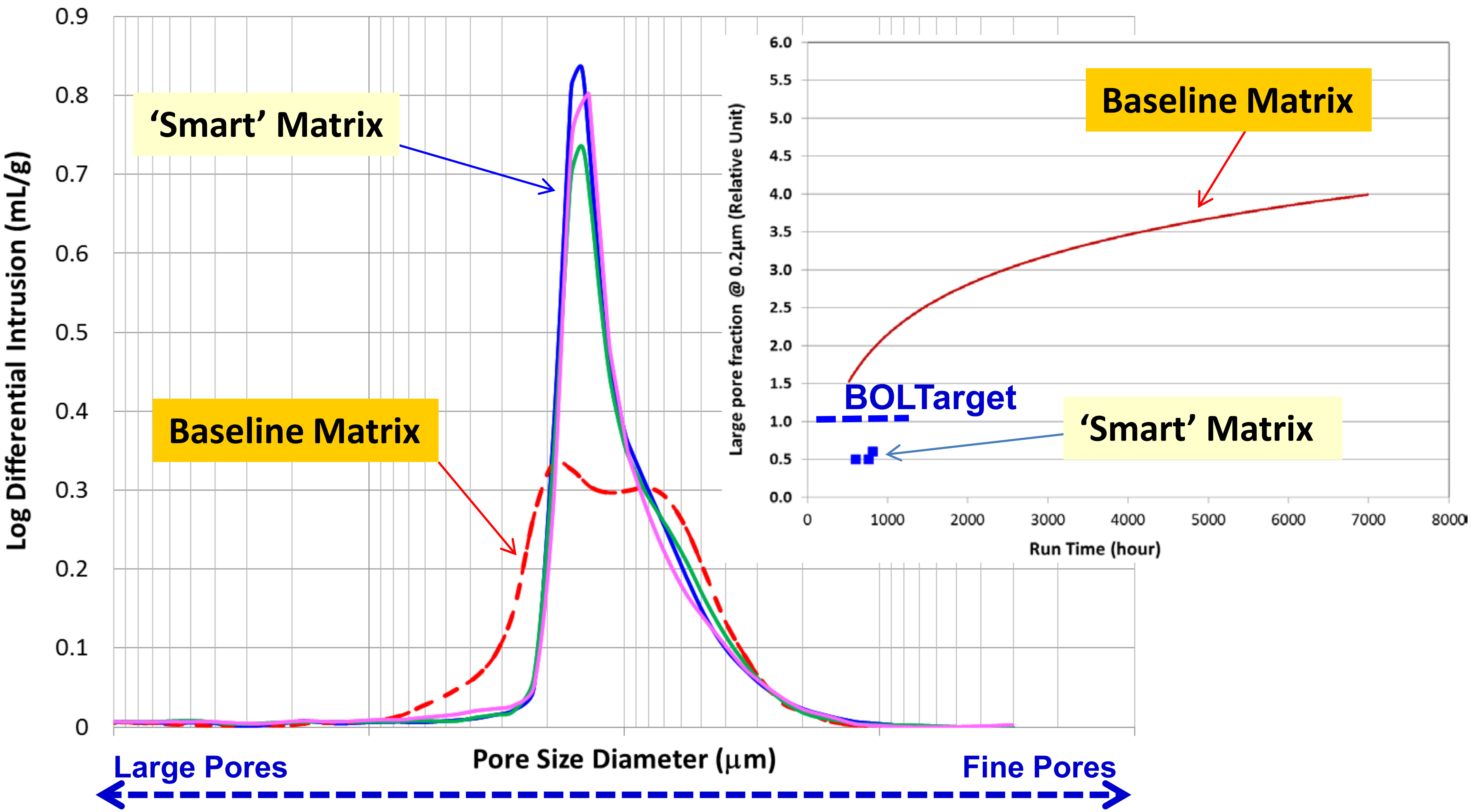




- **Verified process consistency and reproducibility (> 20 batches)**

Improved 'Smart' Matrix Pore Structure

BOL (~600-700h) pore-structure comparison



- Achieved significant reduction of pores larger than 0.2μm at BOL
- Endurance cell testing ongoing (>1,000h)

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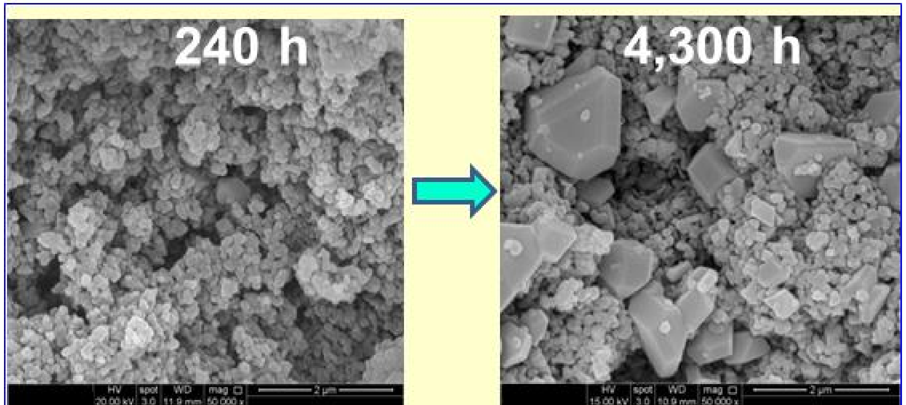
Understanding Matrix Pore-Structure Change

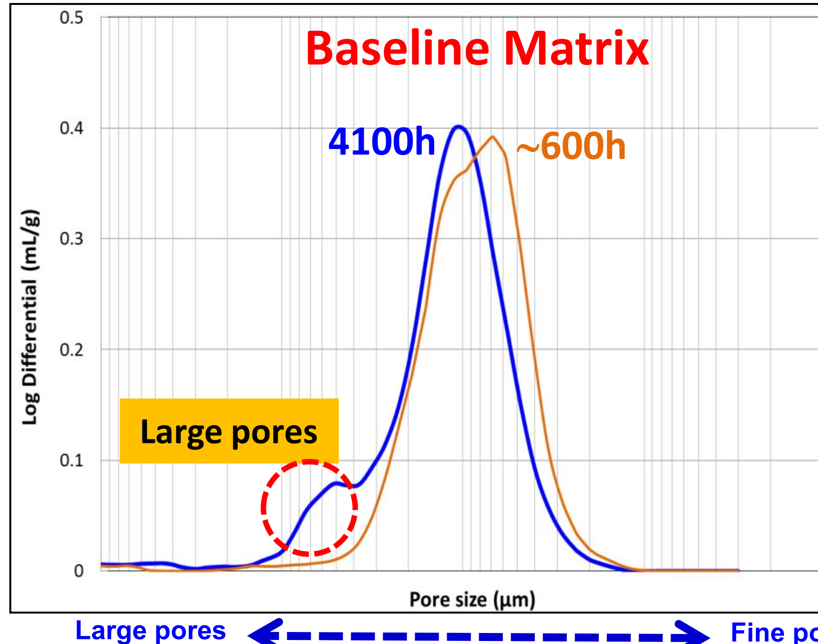


Matrix coarsening (anode side)

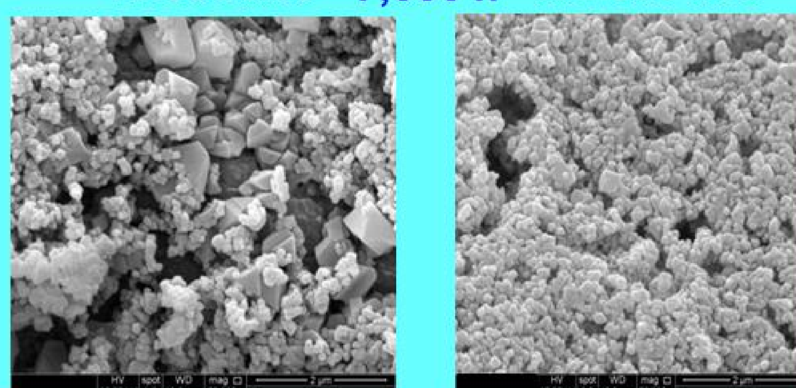
α-$LiAlO_2$ coarsening & large-pore formation (via Ostwald ripening)

- More coarsening at anode side than at cathode side
- Little phase transformation

- **Mechanistic Understanding**
  - **Investigate environmental impact on $LiAlO_2$**
    - **Powder structure**
    - **Solubility**



Anode side 7,000 h Cathode side



Effect of gas atmosphere on coarsening

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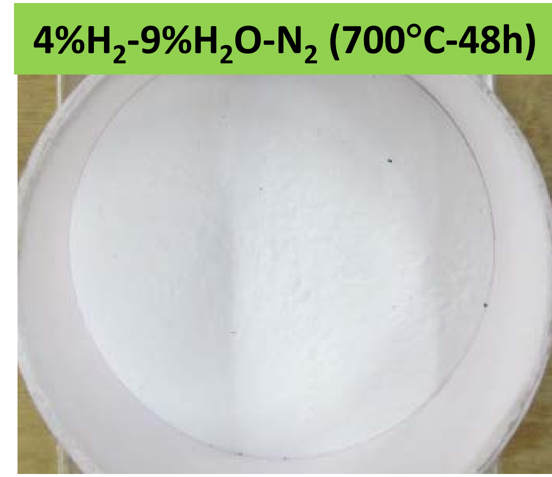
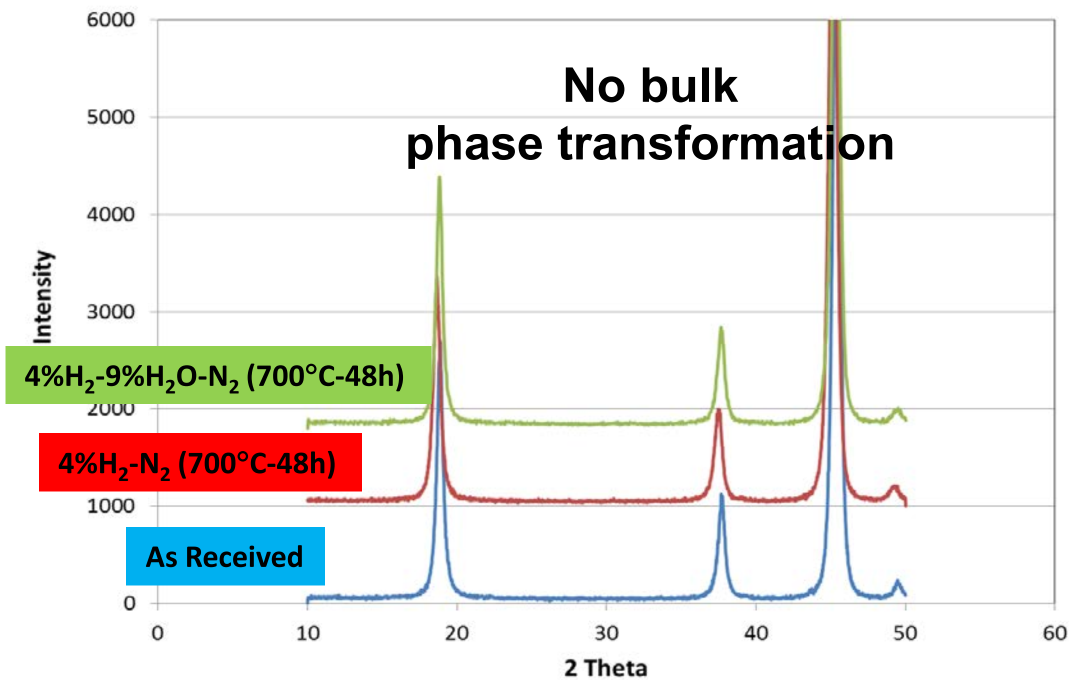
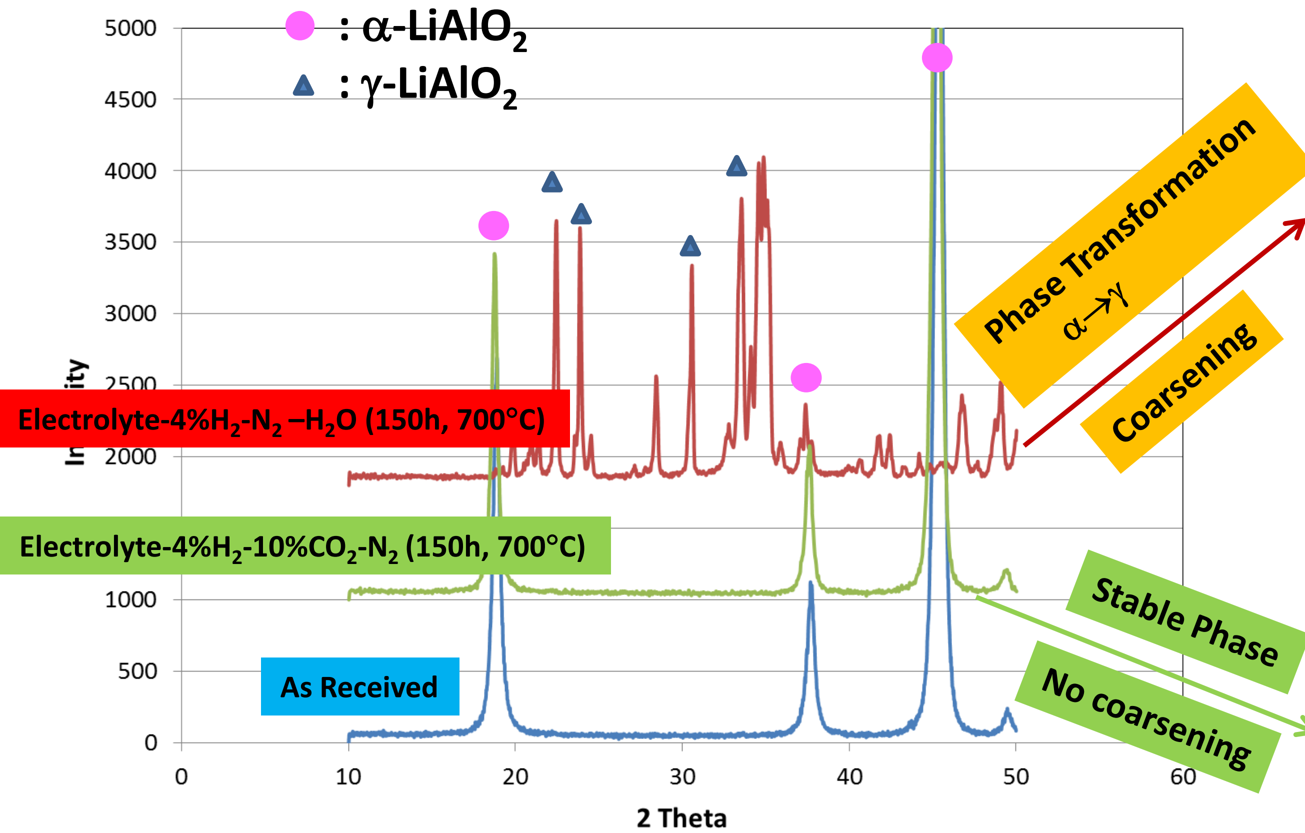
Understanding Stability of Baseline $LiAlO_2$ Powder
Reducing anode atmosphere (absence of electrolyte)

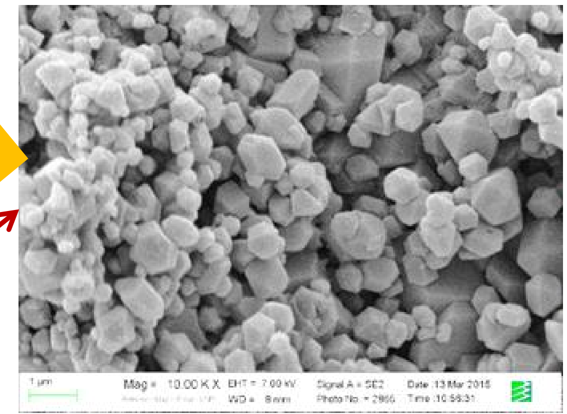


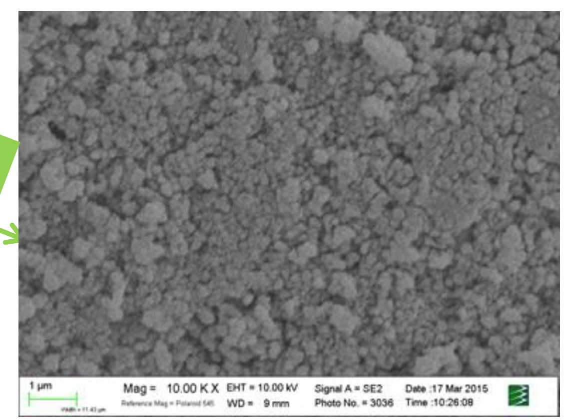


- **Investigate reducing atmosphere on powder structure change**
  - **At extremely low PO_2, color change observed without bulk phase transformation**
  - **Root cause analysis ongoing**
    - **Li loss, oxygen vacancy generation, Al/O ratio change, etc.**
    - **Any relationship with coarsening in presence of electrolyte?**

Electrolyte basicity strongly affects α-$LiAlO_2$ stability







- **High basicity [O^{-2}] (low PCO_2) accelerates coarsening**

  $LiAlO_2 + O^{2-} \leftrightarrow Li^+ + AlO_3^{3-}$

- **Mechanistic investigation ongoing**
  - **Any effect of PO_2 and/or α→γ transformation on coarsening**

$CO_3^{2-} \leftrightarrow CO_2 + O^{2-}$ **(basicity)**

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

- FCE collaborates with subcontractors UConn and IIT to develop fundamental understandings on matrix coarsening and wettability and to help design mitigate approaches

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

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- Evaluate matrix electrolyte wettability

Prof. JR Selman

- Consulting on electrolyte contact angle

Understand matrix coarsening mechanism & electrolyte retention capability

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Remaining Challenges and Barriers

Challenges	Barrier
Root cause of $LiAlO_2$ coarsening in reducing atmosphere	A
Develop cost-effective mitigation schemes (stabilized support materials)	A, B
Demonstrate ‘Smart’ Matrix stability in endurance cells (>5,000h)	A
Manufacture full-size production ‘Smart’ Matrix and validate in full-area DFC stacks	A, B

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Proposed Future Work

Milestone Description		Approach	% Complete
Remaining FY2015	Achieve technical targets of BOL mechanical strength and fine-pore structure	• Optimize matrix formulation & processing conditions • Develop stabilized materials based on mechanistic understanding	60
	Verify sealing efficiency and matrix resistance in long-term (>2,000h) cell tests		

FY2016	Verify 'Smart' Matrix durability in endurance cell tests (>5,000h)	• Validate stabilized materials in endurance cells
		• Mechanistic understanding
		  • Out-of-cell tests
		  • Cell post-test analysis
		• Scale-up manufacturing trials
			10

	Deliver report on degradation mechanistic understanding		
	Perform scale-up manufacturing trial and start technology stack		

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)**

- **Implement "Smart" Matrix in DFC products**
  - **Enhance DFC market penetration and clean-energy job creation**
  - **Enable hydrogen production DFC-H_2 system currently under demonstration**
  - **Enable DFC-CO_2 capture for reducing CO_2 emission**

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Summary

- **Achieved FY2015 Q1 & Q2 milestones**
  - **Developed test plans for achieving 'Smart' Matrix technical goals and mechanistic understanding**
  - **High-Porosity 'Smart' Matrix**
    - **Developed slurry formulation and processing parameters to produce lab-scale (9" wide) 'Smart' Matrices with improved fine-particle packing**
    - **Initiated cell evaluation**
    - **Met BOL targets of >20% higher porosity and >30% reduction of pores larger than 0.2μm.**
- **Degradation mechanistic understanding**
    - **Identified accelerated coarsening in reducing environment**
    - **Initiated further mechanistic characterization**
      - **In-cell testing (detailed post-test matrix characterization)**
      - **Out-of-cell testing ($LiAlO_2$ powder structure & solubility under various environments)**

Technical Back-Up Slides

DFC Product Commercialization

- **More than 300 MW capacity installed/backlog.**
- **Generating power at about 50 locations worldwide.**
- **Generated >3 billion kWh ultra-clean electricity.**
- **Annual production run-rate 70 megawatts.**

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DFC Configuration

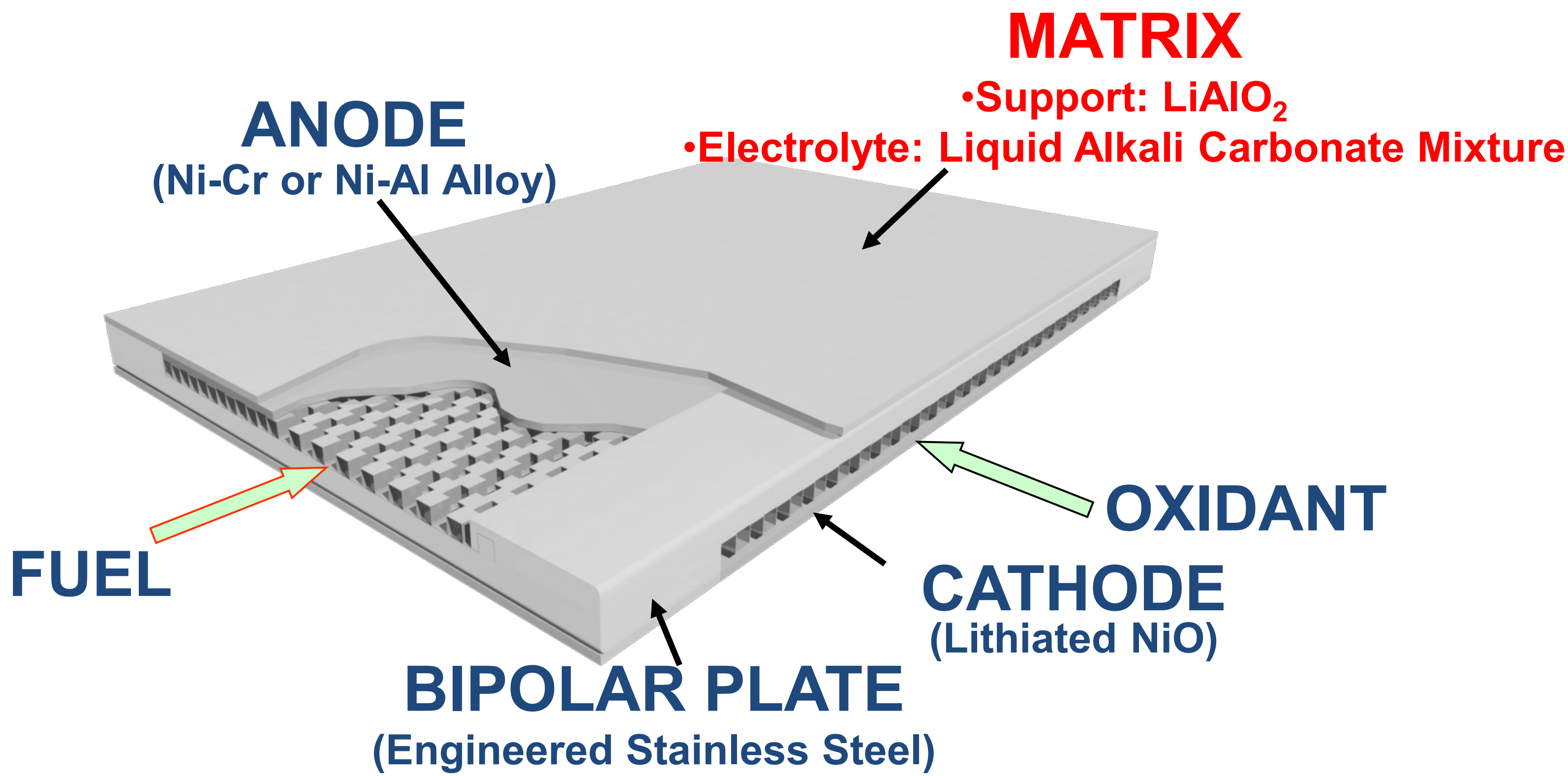
Individual fuel cell component

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

CARBONATE FUEL CELL MATERIALS



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

MO2616BW
042701

Matrix Support Material Experience

- **MgO, ZnO, Al_2O_3, CeO_2, $SrTiO_3$, $LiAlO_2$, etc. evaluated in early years**
- **$LiAlO_2$ selected by developers**
  - Three allotropic phases: α, β and γ
  - γ- $LiAlO_2$ widely used before 2000
  - α-$LiAlO_2$ adopted for lower solubility and better phase stability
  - Continue enhancing powder consistency and reducing cost
- **Particulate or fiber crack arrestors**

Phase	<650° C	>700° C
α-$LiAlO_2$	Phase stable	Changes to γ
β-$LiAlO_2$	Changes to α	Changes to γ
γ-$LiAlO_2$	Changes to α	Phase stable

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**