

## V.C.3 Smart Matrix Development for Direct Carbonate Fuel Cell

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### Overall Objectives

Develop an innovative durable DFC<sup>®</sup> (Direct Fuel Cell) electrolyte matrix (smart matrix) to enable >420 kW rated stack power and 10-year (80,000 h) stack service life (current generation: 350 kW rated stack power and 5-year stack service life).

- Increase market penetration for stationary fuel cells.
- Enable domestic clean energy job growth.
- Enable technology for hydrogen infrastructure and CO<sub>2</sub> capture.

### Fiscal Year (FY) 2017 Objectives

- Continue refining matrix degradation mechanistic understanding.
- Confirm smart matrix meeting all technical targets in >5,000 h accelerated cell tests.
- Verify production-ready full-area smart matrix meeting beginning of life (BOL) cell performance, sealing efficiency and resistance stability targets in >5,000 h 30 kW endurance technology stack test.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan [1].

- (A) Durability: incomplete understanding of degradation mechanism and lack of clear long-term degradation mitigation schemes
- (B) Cost: cost-effective matrix degradation–mitigation schemes

### Technical Targets

This project aims to develop an innovative smart matrix to enable combined heat and power (CHP) distributed generation fuel cell systems to meet DOE 2020 research, development, and demonstration technical targets [1] (Table 1).

**TABLE 1.** FCE Progress towards Meeting DOE Research, Development, and Demonstration Technical Targets for 100 kW–3 MW CHP Distributed Generation Fuel Cell Systems Operating on Natural Gas

Characteristic	Units	2020 Targets	DFC Baseline
Electrical Efficiency at Rated Power	%	>50	47
CHP Energy Efficiency	%	90	90
Operating Lifetime	Hours	80,000	>44,000

Specific technical targets for the smart matrix are established based on multi-year DFC field operation experience:

- >25% BOL mechanical strength increase, >20% porosity increase and improved fine-pore microstructure (>30% reduction on pores larger than 0.2 μm) compared to the baseline.
- Stable fine-pore microstructure (<50% pores larger than 0.2 μm at end of life [EOL]) for enhanced capillary electrolyte retention, projected from >5,000 h accelerated cell and 30 kW technology stack tests.
- Verify smart matrix stack performance (BOL electrochemical performance: >760 mV at 185 mA/cm<sup>2</sup> at 71% fuel utilization), sealing performance (<0.4% nitrogen crossover) and resistance stability (<30 mΩcm<sup>2</sup> increase per year) in >5,000 h 30 kW technology stack.
- Understand matrix material degradation mechanism.
- Scale-up production of smart matrix for 1 m<sup>2</sup> full-area 30 kW technology stack validation.

## FY 2017 Accomplishments

- Verified selected smart matrix meeting (by projection) EOL targets in >5,000 h accelerated single-cell tests.
- Achieved high-yield production of 1 m<sup>2</sup> full-area smart matrix.
- Met targeted electrochemical performance and seal efficiency in >5,000 h 30 kW technology stack test.



## INTRODUCTION

FCE’s DFC products based on high-temperature internal-reforming carbonate fuel cell technology are striving to meet growing worldwide demand for high-efficiency ultra-clean power generation. The electrolyte membrane (matrix), a porous microstructure consisting mainly of ultra-fine sub-micron  $\alpha$ -LiAlO<sub>2</sub> powders sandwiched between two electrodes, immobilizes liquid electrolyte, isolates fuel from oxidant, and facilitates ionic transport [2]. However,  $\alpha$ -LiAlO<sub>2</sub>, although phase stable in DFC operation, slowly coarsens lowering capillary force leading to matrix drying and electrolyte redistribution, which contributes to gas crossover and performance loss. This program aims to develop a high-yield production-ready smart matrix with robust and stable fine-pore microstructure to enable DFC meeting DOE 2020 targets for CHP distributed generation fuel cell systems.

## APPROACH

The approaches to achieve the technical targets are listed below in Table 2. The targets will be validated in long-term >5,000 h accelerated cell and full-area 30 kW technology stack tests. Full-scale production trials will be conducted to fabricate full-area smart matrices for the technology stack tests and to assure the manufacturing process ready for product implementation.

## RESULTS

Baseline  $\alpha$ -LiAlO<sub>2</sub> powders dissolve slightly in liquid carbonate and are expected to coarsen gradually via Ostwald ripening. However, the coarsening was found much accelerated at the reducing anode side at higher temperatures. The mechanism of such accelerated coarsening was not well understood. The as-made powders already exhibited some surface Li deficiency and cationic disorder. Exposure to high-temperature reducing environments, even in the absence of liquid electrolyte, enhanced not only such disorders but also aluminum metallic nature. The as-made powders also contained metastable hydrated impurities that were found transformed to less stable  $\gamma$ -LiAlO<sub>2</sub> under high-temperature reducing atmosphere.

Long-term (500–1,100 h)  $\alpha$ -LiAlO<sub>2</sub> immersion tests at 650°C under oxidizing (PO<sub>2</sub> ~0.15 atm) and reducing (PO<sub>2</sub> ~10<sup>-23</sup> atm) atmospheres with various PCO<sub>2</sub> (0–0.3 atm) were conducted to understand if the Ostwald ripening rate was controlled by equilibrium solubility (Table 3). The experiments confirmed that, under the H<sub>2</sub>-containing reducing atmosphere, increasing PCO<sub>2</sub> from 0.005 atm to 0.3 atm suppressed the equilibrium solubility as well as coarsening, agreeing with the basic dissolution mechanism suggested in the literature. However, increasing PO<sub>2</sub> to 0.15 atm (oxidizing atmosphere), while maintaining PCO<sub>2</sub> at 0.3 atm reduced the equilibrium solubility by approximately one order of magnitude. The coarsening rate was also reduced. Under extremely basic CO<sub>2</sub>-free reducing atmosphere (not a typical DFC condition), rapid  $\alpha$ → $\gamma$  phase transformation and coarsening occurred. Apparently already highly coarsened and faceted (low surface area)  $\gamma$ -LiAlO<sub>2</sub> exhibited a lower solubility probably due to Gibbs–Thomson effect. This test result suggests  $\alpha$ → $\gamma$  transformation may participate in the  $\alpha$ -LiAlO<sub>2</sub> coarsening process.

The measured higher  $\alpha$ -LiAlO<sub>2</sub> solubility under the CO<sub>2</sub>-containing reducing atmosphere could be caused by the enhanced surface non-stoichiometry/disorder as well as aluminum metallic nature, as mentioned above. Density functional theory calculation performed by University

**TABLE 2.** Approaches to Achieve Smart Matrix Technical Targets

Technical Targets	Approaches
BOL: >25% mechanical strength increase, >20% porosity increase and improved fine-pore microstructure (>30% reduction on pores larger than 0.2 $\mu$ m) than baseline	Nano-pore former for increased porosity Reinforcement additives to increase mechanical strength
	Optimize slurry formulation and processing for improved particle size distribution, particle packing and production yield
EOL: Stable fine-pore microstructure for maintaining capillary electrolyte retention (<50% pores larger than 0.2 $\mu$ m)	Stabilized LiAlO <sub>2</sub> or additives to slow down coarsening to maintain capillary electrolyte retention
Coarsening mechanistic understanding	Investigate effects of temperature, gas atmosphere, and electrolyte composition on matrix microstructure evolution, LiAlO <sub>2</sub> stability, wettability, and solubility in single-cells/stacks and controlled out-of-cell tests

**TABLE 3.**  $\alpha$ -LiAlO<sub>2</sub> Immersion Tests at 650°C in Carbonate Electrolyte under Atmospheric Pressure

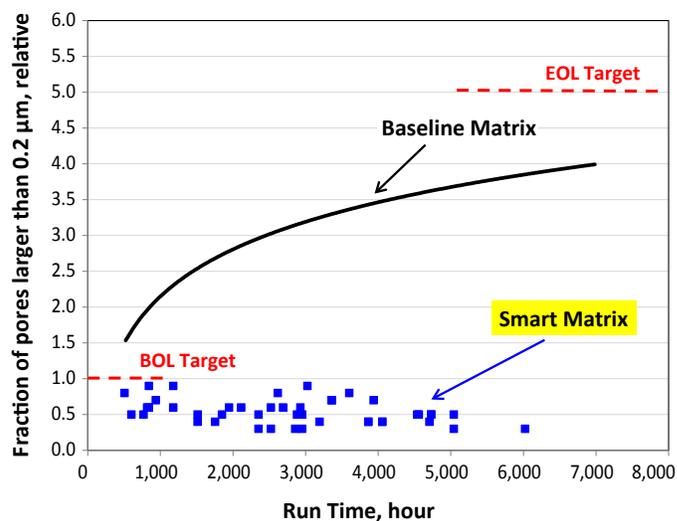
Atmosphere	Test time, h	Phase (X-Ray diffraction)	Specific surface area, relative	LiAlO <sub>2</sub> solubility, ppm
70% air–30% CO <sub>2</sub>	800	$\alpha$ -LiAlO <sub>2</sub>	1	2.7
4% H <sub>2</sub> –3% H <sub>2</sub> O–N <sub>2</sub>	500	Major $\gamma$ -LiAlO <sub>2</sub> Minor $\alpha$ -LiAlO <sub>2</sub>	0.06	1.5
4% H <sub>2</sub> –0.5% CO <sub>2</sub> –3% H <sub>2</sub> O–N <sub>2</sub>	1,100	Major $\alpha$ -LiAlO <sub>2</sub> Minor $\gamma$ -LiAlO <sub>2</sub>	0.75	28.2
4% H <sub>2</sub> –30% CO <sub>2</sub> –3% H <sub>2</sub> O–N <sub>2</sub>	1,100	$\alpha$ -LiAlO <sub>2</sub>	0.93	21.3

of Connecticut suggested that the thermodynamically equilibrated and coarsened  $\alpha$ -LiAlO<sub>2</sub> crystal shapes (observed by transmission electron microscopy) could be predicted by minimizing the surface energy levels of several preferred oxygen-terminating crystallographic planes. Therefore, the exposure conditions (temperature, gas composition, etc.) could have affected the surface energy levels of the crystallographic planes and hence stable atomic termination in the crystal, thereby influence the solubility, crystallographic plane stability, and coarsening rate.

The coarsening could also be contributed by the presence of metastable contaminants and intermediates and/or surface defects, enhanced under the reducing anode side atmospheres. Adding LiOH to the molten carbonate in the immersion tests was found to cause the formation of ultra-fine metastable intermediates such as  $\alpha$ -Li<sub>5</sub>AlO<sub>4</sub> and LiAl<sub>2</sub>(OH)<sub>7</sub>·2H<sub>2</sub>O, as well as accelerating coarsening and  $\alpha$ - $\gamma$  transformation. [OH<sup>-</sup>] may increase at the triple-phase boundary near the anode–matrix interface due to hydrogen oxidation reaction [3]. In summary, the reducing anode side atmosphere increases LiAlO<sub>2</sub> solubility as well as destabilizes the crystal surface (by creating surface defects and disorders and metastable intermediates and by promoting the growth of certain crystallographic planes), all could contribute to the accelerated  $\alpha$ -LiAlO<sub>2</sub> coarsening.

FCE has developed a smart matrix design that disrupted the above underlying accelerating coarsening mechanisms. The consistency of BOL and EOL pore structure was verified in numerous accelerated single-cells. Short-term (<1,000 h) and long-term (>5,000 h) accelerated cell tests demonstrated finer and more stable pore structure compared to the baseline. Figure 1 showed essentially little pore structure change for up to ~6,000 hours (>50% reduction of pores larger than >0.2  $\mu$ m at fuel inlet), meeting the targeted requirements.

The scale up optimization of the smart matrix formulation was continuing by fine-tuning the tape casting parameters such as slurry delivery system, drying conditions, and the lamination process in full-size production-scale (~90 gallons) trials. Results so far already show >15% improved process yield over the baseline. The BOL physical properties were all consistent with the lab-scale matrix results, confirming the reproducibility and robustness of the scaled-up process. Short- and long-term accelerated single-

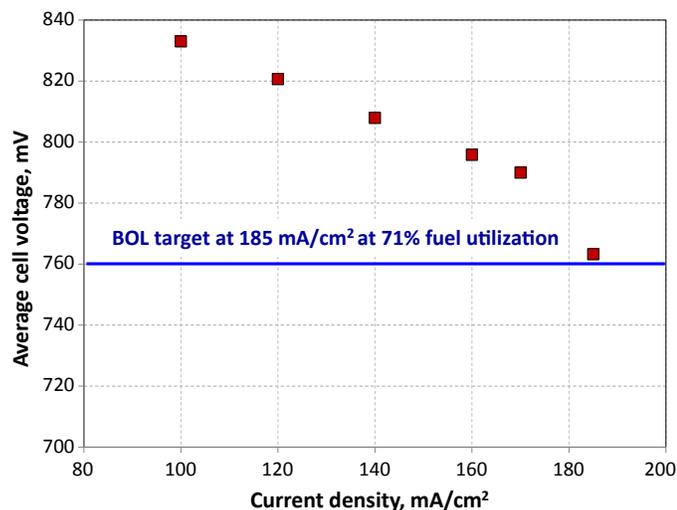


**FIGURE 1.** Excellent pore structure stability of smart matrix has been demonstrated in accelerated single-cells meeting EOL target by projection.

cell tests of these production trial matrices also validated excellent gas sealing efficiency (~0% crossover) and pore structure stability. The full area (~1 m<sup>2</sup>) smart matrices had been evaluated in a 30-cell 30 kW technology stack (Figure 2). The stack, utilizing FCE's baseline commercial DFC active cell design, also incorporated baseline matrices for comparison. Initial operating results showed that the smart matrix cells exhibited consistent higher open circuit voltage than the baseline, indicating enhanced gas sealing. Anode gain testing (increasing hydrogen concentration in fuel at open circuit voltage to assess sealing efficiency) also showed that the smart matrix cells exhibit faster and higher voltage gain, further confirming the enhanced matrix sealing efficiency. The initial BOL electrochemical performance at 185 mA/cm<sup>2</sup> demonstrated excellent electrochemical performance (~763 mV) at 71% fuel utilization (Figure 3), meeting the BOL target. Crossover target of <0.4% was successfully met during the 6,000 h test. The resistance stability of the smart matrix also met the target of <30 m $\Omega$ cm<sup>2</sup> increase per year, further confirming the improved electrolyte retention capability. The stack has been terminated for post-test validating pore structure stability and electrolyte retention capability.



**FIGURE 2.** A full-area 30 kW technology stack was built for validating selected smart matrix design. The stack was successfully operated for ~6,000 h.



**FIGURE 3.** Smart matrix cells achieved BOL electrochemical performance target in a 30 kW technology stack.

## CONCLUSIONS AND UPCOMING ACTIVITIES

Mechanistic investigation has shown that reducing anode side atmosphere increases  $\text{LiAlO}_2$  solubility, crystal defects, and metastable intermediate formation all likely contributing to the accelerated coarsening. Lab-scale and production trial smart matrices have successfully met all BOL and EOL pore structure technical targets in accelerated single-

cell tests operated for up to ~6,000 hours. The high-yield production trial smart matrix (~1 m<sup>2</sup>) consistently reproduced all targeted physical and mechanical properties. A 6,000 h, 30 kW technology stack test had validated the smart matrix electrochemical performance, resistance stability, and sealing efficiency.

The remainder of the project will focus on further refining mechanistic understanding, developing an Ostwald ripening model, and validating the pore structure stability of the production smart matrix in the technology stack test.

## FY 2017 PUBLICATIONS/PRESENTATIONS

1. S. Heo, et al., “Stability of Lithium Aluminate in Reducing and Oxidizing Atmospheres at 700°C,” *International Journal of Hydrogen Energy*, 41, 18884 (2016).
2. C. Yuh, et al., “Molten carbonate electrolyte matrix progress review,” 6th International Congress on Ceramics (ICC6), August 21–25, 2016, Dresden, Germany.
3. Program Go/No Go decision presentation to DOE-EERE, September 14, 2016.
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6. S. Heo, et al. “Role of Exposure Atmospheres on Particle Coarsening and Phase Transformation of  $\text{LiAlO}_2$ ,” *J. Electrochem. Soc.*, 168(4), H5086 (2017).
7. C. Yuh and A. Hilmi, “Smart Matrix Development for Direct Carbonate Fuel Cell,” 2017 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, Washington D.C., June 8, 2017.

## REFERENCES

1. DOE Office of Energy Efficiency and Renewable Energy (EERE) Fuel Cell Technologies Offices Multi-Year Research, Development and Demonstration (MYRD&D) Plan, Section 3.4 “Fuel Cells”, Updated June 2016, [http://energy.gov/sites/prod/files/2016/06/f32/fcto\\_myRDD\\_fuel\\_cells\\_0.pdf](http://energy.gov/sites/prod/files/2016/06/f32/fcto_myRDD_fuel_cells_0.pdf)
2. C. Yuh and M. Farooque, “Materials and Life Considerations,” in *Fuel Cells-Molten Carbonate Fuel Cells, Encyclopedia of Electrochemical Power Sources*, 497–507, Elsevier Science, 2009.
3. P. Ang and A. Sammells, “Influence of Electrolyte Composition on Electrode Kinetics in the Molten Carbonate Fuel Cell,” *J. Electrochem. Soc.*, 127(6), 1287(1980).