

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

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### Subcontractors:

- University of Connecticut, Storrs, CT
- Illinois Institute of Technology, Chicago, IL

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- (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

### 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) 2016 Objectives

- Develop matrix degradation mechanistic understanding.
- Achieve by projection end of life (EOL) targets of matrix mechanical strength, sealing efficiency, and phase-stable fine-pore microstructure.
- Scale-up manufacture and initiate 30 kW technology stack evaluation.

### 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].

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

- >25% beginning of life (BOL) mechanical strength increase, >20% porosity increase, and improved fine-pore microstructure (>30% reduction of pores larger than 0.2 μm) compared to the baseline.
- Stable fine-pore microstructure (<50% pores larger than 0.2 μm at EOL) for enhanced capillary electrolyte retention, projected from >5,000 h accelerated cell and technology stack tests.
- 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 2016 Accomplishments

- Verified selected smart matrix meeting (by projection) EOL targets in ~3,000–5,000 h accelerated single-cell tests.
- Delivered a topic report on matrix degradation mechanistic understanding.
- Successfully fabricated ~1 m<sup>2</sup> full-size high-porosity smart matrix meeting BOL targets for 30 kW technology stack evaluation.



## 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. DFC has already advanced to a single stack capable of 350 kW net alternating current power and 5-year service life. Stack power and service life increases will further enhance DFC's commercial competitiveness. The electrolyte matrix holds a very important key to higher power density operation, longer service life, and lower cost. The matrix, a porous microstructure consisting mainly of ultra-fine sub-micron  $\alpha$ -LiAlO<sub>2</sub> powders sandwiched between two electrodes, immobilizes the liquid electrolyte, isolates fuel from oxidant and facilitates ionic transport. However, LiAlO<sub>2</sub> slowly coarsens, lowering capillary force leading to matrix drying and electrolyte redistribution, contributing 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 technical 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-size smart matrices for the technology stack tests and to assure the manufacturing process ready for product implementation.

**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 of pores larger than 0.2 $\mu$ m) compared to 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

## RESULTS

Multi-year operation of DFC revealed gradual  $\alpha$ -LiAlO<sub>2</sub> coarsening, more pronounced at the reducing anode side and accelerated by temperature. Literature reported that  $\alpha$ -LiAlO<sub>2</sub> solubility increased with increasing temperature, lower CO<sub>2</sub> partial pressure, and in strong basic melts, whereas  $\alpha \rightarrow \gamma$  phase transformation also occurred at higher temperatures ( $\geq 700^\circ\text{C}$ ) [2,3]. Literature also reported that the coarsening rate increased with finer particles. All these pointed to dissolution-precipitation Ostwald ripening as the leading coarsening mechanism. However, the detailed fundamentals of the faster reducing anode-side coarsening had not yet been established.

X-ray photon spectroscopy and X-ray diffraction analyses revealed substantial surface Li deficiency and cationic disorder of the as-made baseline powders. Thermal stability tests in the absence of electrolyte at 700°C for 50 h under a reducing environment (4% H<sub>2</sub>-N<sub>2</sub>) led to powder darkening and enhancements of the nonstoichiometry and surface aluminum metallic characteristics (regardless of the presence of moisture) without apparent phase transformation. These phenomena were not observed upon exposure to the oxidizing atmospheres (air, O<sub>2</sub>-CO<sub>2</sub>-N<sub>2</sub>). Re-oxidation of the pre-reduced darkened powders at 700°C in air restored the original powder characteristics. These results attest that the reducing environment amplifies surface disorder, likely promoting phase nucleation and coarsening. Some metastable hydrated impurities were also observed transforming to less stable  $\gamma$ -LiAlO<sub>2</sub> in the reducing atmosphere. Powders synthesized with a more stoichiometric structure and without metastable hydrated phases showed minimal changes in powder characteristics upon the exposure to the same reducing atmosphere.

Electrolyte immersion tests of the baseline powder under various gas environments (such as 4% H<sub>2</sub>-H<sub>2</sub>O-N<sub>2</sub>, 4% H<sub>2</sub>-1% CO<sub>2</sub>-N<sub>2</sub>, N<sub>2</sub>, and 5% O<sub>2</sub>-N<sub>2</sub>) at 700°C showed that the CO<sub>2</sub>-free more basic environment (reducing as well as oxidizing) caused significant coarsening (>95% surface-area decay) and >90%  $\alpha \rightarrow \gamma$  transformation, whereas coarsening was significantly suppressed by CO<sub>2</sub> addition (by only ~1%). These results point to a strong relationship between the phase transformation and coarsening.

It was originally postulated that in the absence of CO<sub>2</sub>, the concentration of [O<sup>2-</sup>] in the electrolyte increases sharply, leading to a very high LiAlO<sub>2</sub> solubility and accelerated Ostwald ripening. However, the rate of coarsening and phase transformation could not be correlated well with the measured solubility difference at 650°C under the CO<sub>2</sub>-containing oxidizing (air-30% CO<sub>2</sub>) and CO<sub>2</sub>-free reducing atmospheres (4% H<sub>2</sub>-3% H<sub>2</sub>O-N<sub>2</sub>). It instead points to the formation of surface non-stoichiometry or disorder under reducing environment as the predominant factor. Based on the above fundamental understanding, more stable

powders with higher crystallinity, less surface disorder and less metastable impurities, in conjunction with innovative approaches, are being developed in this program to mitigate the coarsening.

In order to evaluate the impact of coarsening on matrix wetting properties, specially designed high-temperature, contact-angle tests under reducing atmosphere on different baseline matrix samples operated for up to ~40,000 h (single cells as well as stacks) showed rapid complete wetting and fast electrolyte absorption (indicating ~0° contact angle), suggesting little effect of coarsening on the inherent contact angle. Therefore, capillary electrolyte retention is mainly controlled by pore size distribution and a stable fine-pore matrix structure is expected to be capable of maintaining electrolyte retention.

The consistency and reproducibility of the developed smart matrix slurry formulation and process were verified in >200 lab-scale batches (~500 cc). ~250 cm<sup>2</sup> bench-scale accelerated single cells operated for up to ~3,500 h demonstrated essentially no gas cross-over (leakage) and >20-mΩcm<sup>2</sup> resistance reduction. Numerous single cells operated for up to 5,000 hours showed excellent smart matrix phase and pore-structure stability (Figure 1). In order to accurately project the durability of the developed smart matrix capable of meeting the 10-year life EOL target, an accelerated single-cell test protocol to promote matrix coarsening and electrolyte loss (higher temperature, steam content, and fuel utilization than in typical DFC) has been

established. The post-test information from accelerated single-cell and product baseline matrices operated for up to five years forms the basis of the protocol. The developed smart matrix showed essentially no increase in pores larger than 0.2 μm and stable cross-over (~0%) in accelerated single cells, projecting the capability of meeting the 10-year life EOL target (Figures 2 and 3).

Scale-up manufacturing development of the selected smart matrix, from ~500 cc lab-scale size to pilot scale (~1 gal) and production-scale full size (~90 gal slurry), has been initiated to optimize manufacturing process parameters such as mixing, milling, casting, drying, and lamination. Full-size (~1 m<sup>2</sup>) smart matrices with desired fine-pore structure were successfully fabricated for technology stack evaluation (Figure 4). It also met the BOL pore-structure target, confirming the process robustness and consistency (Figure 1). The physical and mechanical properties were consistent with the lab-scale matrices. These full-size matrices also duplicated same improved gas-sealing efficiency and cell resistance reduction in short-term single cells.

### CONCLUSIONS AND FUTURE DIRECTIONS

Lab-scale smart matrix has successfully met all BOL and EOL targets based on accelerated single-cell tests operated for up to ~5,000 h. It was successfully scaled up to full-size ~1 m<sup>2</sup> for 30 kW technology stack evaluation.

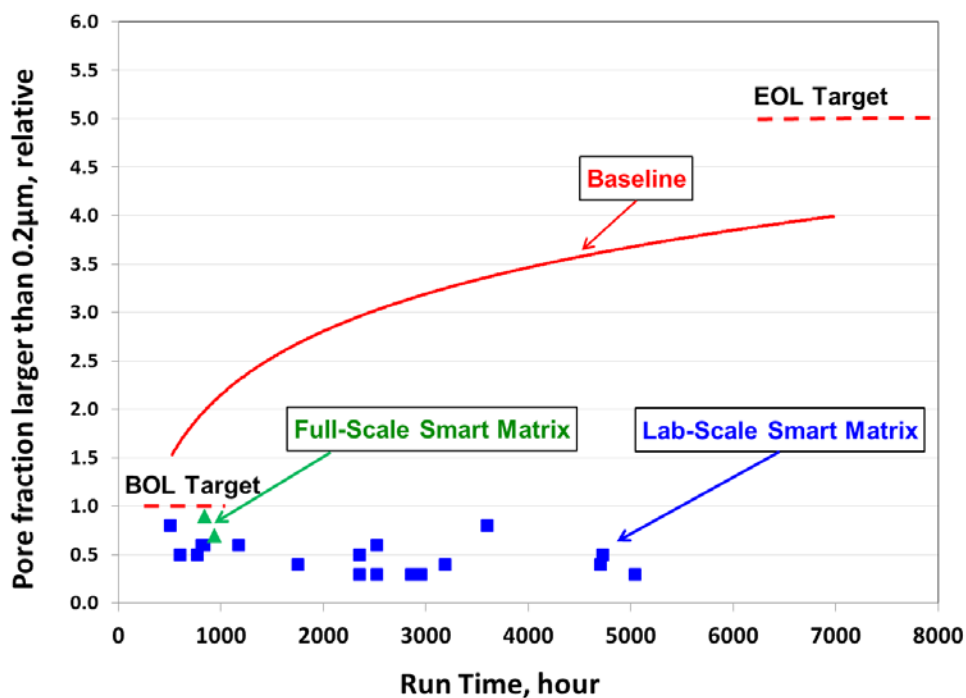


FIGURE 1. Both lab-scale and full-size smart matrices achieved excellent pore-structure stability

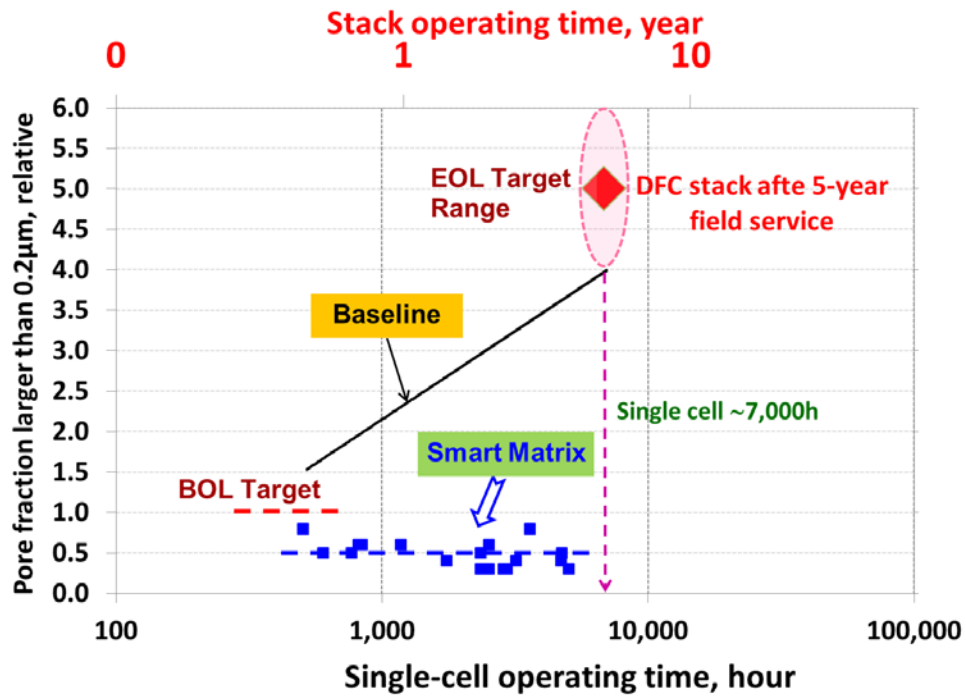


FIGURE 2. Smart matrix is projected capable of achieving EOL 10-year life pore-structure target from long-term accelerated single-cell tests

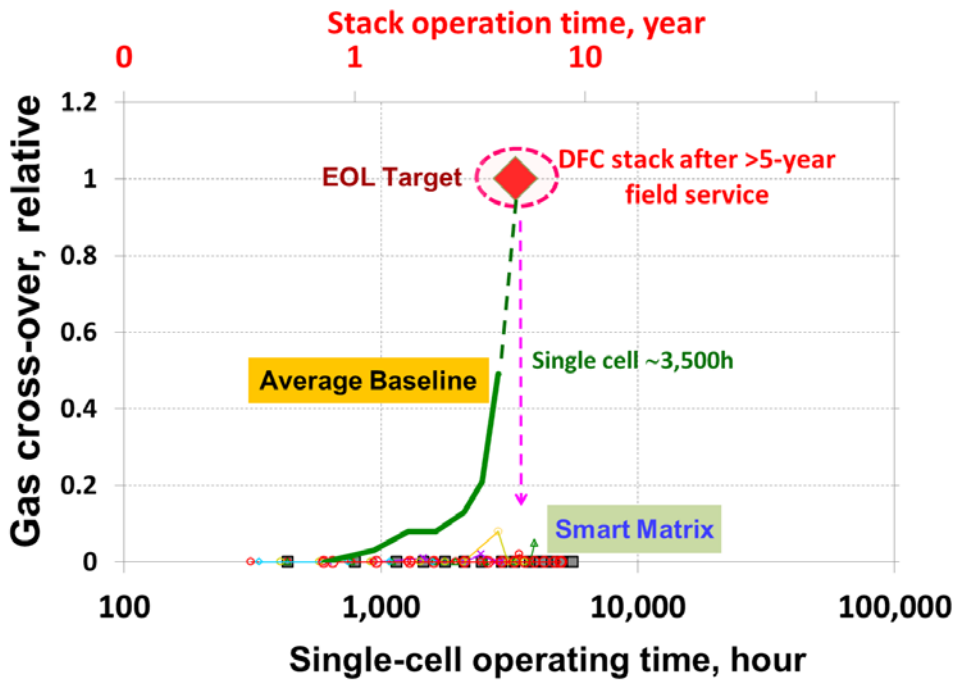
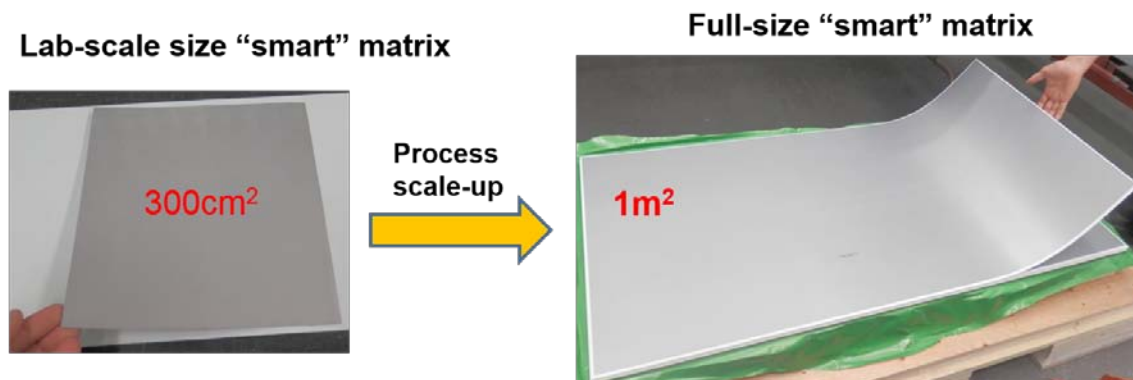


FIGURE 3. Smart matrix showed excellent sealing efficiency in accelerated single cells, projecting capable of 10-year service life



**FIGURE 4.** Full-size 1 m<sup>2</sup> high-porosity smart matrix was successfully manufactured

The remainder of the project will focus on further refining mechanistic understanding, optimizing smart matrix formulation, scale-up manufacturing, and validation in long-term technology stacks.

## FY 2016 PUBLICATIONS/PRESENTATIONS

1. Program Go/No Go decision presentation to DOE EERE, November 12, 2015.
2. Program quarterly review presentation to DOE EERE, February 16, 2016.
3. “Stability of Lithium Aluminate in Reducing and Oxidizing Atmospheres at 700°C,” manuscript accepted for publication in *International Journal of Hydrogen Energy*, 2016.
4. A. Hilmi, A. Surendranath, and C. Yuh, “The Next Generation Carbonate Fuel Cell Matrix,” Abstract# 76, 229th ECS Meeting, San Diego, CA, May 29–June 2, 2016.
5. C. Yuh and A. Hilmi, “Smart Matrix Development for Direct Carbonate Fuel Cell,” 2016 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, Arlington, Virginia, June 8, 2016.

## REFERENCES

1. DOE Office of Energy Efficiency and Renewable Energy Fuel Cell Technologies Office’s Multi-Year Research, Development, and Demonstration (MYRDD) Plan, Section 3.4 “Fuel Cells,” Updated June 2016, [http://energy.gov/sites/prod/files/2016/06/f32/fcto\\_myrrdd\\_fuel\\_cells\\_0.pdf](http://energy.gov/sites/prod/files/2016/06/f32/fcto_myrrdd_fuel_cells_0.pdf)
2. C. Yuh, M. Farooque, and H. Maru, “Advances in Carbonate Fuel Cell Matrix and Electrolyte,” in *Proc. Symp. Carbonate Fuel Cell Technology V*, The Electrochemical Society, **PV99-20**, 1999: 189–201.
3. 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.