

V.F.9 Smart Matrix Development for Direct Carbonate Fuel Cell

Chao-Yi Yuh (Primary Contact), Abdelkader Hilmi,
Arun Surendranath

FuelCell Energy (FCE), Inc.
3 Great Pasture Road
Danbury, CT 06813
Phone: (203) 825-6112
Email: cyuh@fce.com

DOE Manager
Jacob Spendelow
Email: spendelow@lanl.gov

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- 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 is developing an innovative electrolyte matrix (smart matrix) to enable combined heat and power (CHP) distributed generation fuel cell systems to meet DOE 2020 research, development, and demonstration (RD&D) technical targets [1] (Table 1).

TABLE 1. FCE Progress towards Meeting DOE RD&D 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[®] (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 CO₂ capture

Fiscal Year (FY) 2015 Objectives

- Develop plans to achieve smart matrix technical goals and degradation mechanistic understanding
- Achieve targets of improved beginning of life (BOL) matrix mechanical strength and high-porosity fine-pore microstructure
- Verify smart matrix sealing efficiency and ohmic resistance in >2,000 h cell tests

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% 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 technology stack tests
- Understand matrix material degradation mechanism
- Scale-up production of smart matrix for 1 m² full-area 30 kW technology stack evaluation

FY 2015 Accomplishments

- Successfully fabricated lab-scale high-porosity smart matrix meeting target of >25% increased BOL mechanical strength
- Verified improved fine-pore microstructure (>30% reduction of pores larger than 0.2 μm) in ~2,000 h cell testing
- Verified smart matrix sealing efficiency in ~2,000 h cell tests



INTRODUCTION

Worldwide demand for high-efficiency ultra-clean power generation is growing. FCE's efficient DFC products based on high temperature internal reforming carbonate fuel cell technology are striving to meet this growing demand. DFC has already advanced to a single stack capable of producing 350 kW net alternating current power and 5-year service life. Stack power and service life increases will further enhance DFC's commercial competitiveness for larger scale deployment.

The 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-micro α -LiAlO₂ particles sandwiched between two electrodes, immobilizes liquid electrolyte, isolates fuel from oxidant and facilitates ionic transport. However, LiAlO₂ slowly coarsens during stack endurance service. Such coarsening lowers capillary force leading to matrix drying and electrolyte redistribution, contributing to performance loss and gas crossover. This program aims to develop a high yield production ready smart matrix with robust and stable fine-pore microstructure to enable DFC meeting targets of DOE 2020 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 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.

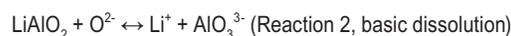
TABLE 2. Approaches to Achieve Smart Matrix Technical Targets

Technical Targets	Approaches
BOL: >25% mechanical strength increase, >20% porosity increase and improved fine-pore microstructure (>30% reduction on pores larger than 0.2 μm) 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 enhanced electrolyte retention (<50% pores larger than 0.2 μm)	Stabilized LiAlO ₂ 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 ₂ stability, wettability and solubility in single cells/stacks and controlled out-of-cell tests

RESULTS

Examination of long-term operated DFC cells and stacks revealed excellent α -LiAlO₂ phase stability but with gradual coarsening. The coarsening process is non uniform, more pronounced at the reducing anode side whereas much slower at the oxidizing cathode side. Figure 1 illustrates LiAlO₂ coarsening in accelerated $\sim 250 \text{ cm}^2$ single cells operated for up to $\sim 5,000$ hours. Analyses of additional single cells and stacks are continuing to more accurately determine coarsening kinetics and help elucidating mechanism.

LiAlO₂ dissolves slightly in the liquid carbonate electrolyte according to:



Literature reported the solubility increases with higher temperature, lower CO₂ partial pressure and in strong basic melt [2–4]. Although it is well known that dissolution could cause Ostwald ripening via dissolution-precipitation steps, the causes of the faster reducing anode side coarsening are not yet established. A detailed investigation of the effects of electrolyte chemistry, particle morphology as well as gas atmosphere and temperature on LiAlO₂ stability is required to develop fundamental understanding for helping designing mitigation schemes.

A series of controlled out-of-cell tests was initiated to investigate the effect of each parameter on coarsening. The baseline α -LiAlO₂ powder immersed in the baseline carbonate electrolyte showed significant coarsening and >90% $\alpha \rightarrow \gamma$ phase transformation at high temperature (700°C) in 150 hours, in the absence of CO₂, explainable by the higher (O²⁻) (according to Reaction 1) and higher LiAlO₂

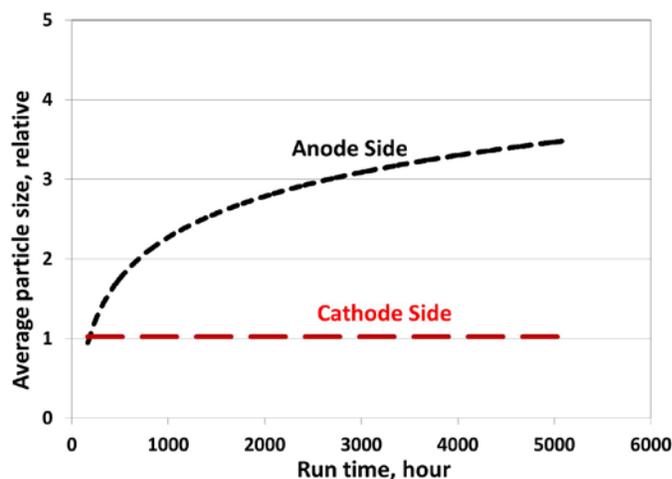


FIGURE 1. Baseline matrix coarsening in accelerated single cells: Reducing anode environment accelerates coarsening.

solubility (according to Reaction 2). These results imply that the dissolved AlO_3^{3-} might rapidly precipitate as $\gamma\text{-LiAlO}_2$ under such an extremely high solubility condition. It is also possible that $\gamma\text{-LiAlO}_2$ may likely nucleate at 700°C [3,4] and faster under the reducing anode atmosphere. The combined high solubility in the absence of CO_2 and more stable γ phase at 700°C may explain the fast simultaneous coarsening and $\alpha \rightarrow \gamma$ transformation. On the other hand, 1–10% CO_2 addition drastically improves phase and particle size stability (no coarsening or phase transformation in 150 h). DFC stack is operated typically between 550°C and 650°C and such $\alpha \rightarrow \gamma$ phase transformation was not observed. It is postulated that such higher-solubility γ or other intermediate phases may still nucleate slowly under the CO_2 -containing reducing atmosphere in DFC, promoting Ostwald ripening of the bulk α phase. Further tests to determine the transformation kinetics, wettability and solubility as a function of electrolyte composition, temperature and atmosphere are ongoing to clarify the above hypothesis.

Higher matrix porosity is desired to increase electrolyte storage capacity and reduce cell ohmic resistance. The electrolyte matrix has to remain substantially crack resistant in order to provide effective gas sealing to minimize gas leakage induced electrolyte loss and cell resistance increase. Stronger matrix is desired to withstand thermo-mechanical stress experienced during both initial start-up conditioning and endurance operation. The Ostwald ripening process that contributes to the coarsening and resulting pore-structure degradation needs to be mitigated to maintain a desired stable fine-pore microstructure.

Nano-pore formers meeting key requirements such as particles size, chemical compatibility with the electrolyte, complete removal during conditioning and low sulfur content (<30 ppm) have been utilized. Several promising additives to enhance mechanical strength and to disrupt the Ostwald ripening process have also been selected. In order to achieve an ultra-fine and tighter pore microstructure, matrix formulation and slurry processing were modified to improve dispersion, milling efficiency, particle packing and slurry tape-casting characteristics.

Lab scale (~10 in wide) high-porosity smart matrices with a reinforced fine-pore microstructure have successfully been fabricated. The consistency and reproducibility of the slurry and the matrix physical properties were verified in many lab scale batches (~20 batches). The target of ~20% higher porosity compared to the current baseline has been successfully achieved. Verification of the BOL mechanical strength was conducted in de-bindered matrices from >20 lab scale batches. The debindered matrix before electrolyte filling (during start-up conditioning) is at the mechanically weakest state. Three-point bending tests showed that the smart matrix has >40% higher snap (fracture) strength compared to the current baseline, thus meeting the BOL

mechanical strength target (Figure 2). This fracture strength improvement minimizes matrix cracking during conditioning and enables enhanced BOL gas sealing; essentially no gas cross-over (leakage) was detected in ~250 cm^2 bench-scale single cell tests operated for ~2,000 h. The pore structure of the smart matrix in greater than eight single cells operated for up to 1,700 h also meets the BOL target of >30% reduction on pores larger than 0.2 μm (Figures 3 and 4) at the fuel inlet, compared to the baseline. The fuel inlet location was selected for comparison because it is the most reducing location and showing the fastest coarsening, >5,000 h. Endurance cell tests under thermal cycling condition are continuing to evaluate longer term pore-structure stability and matrix sealing capability under transient conditions.

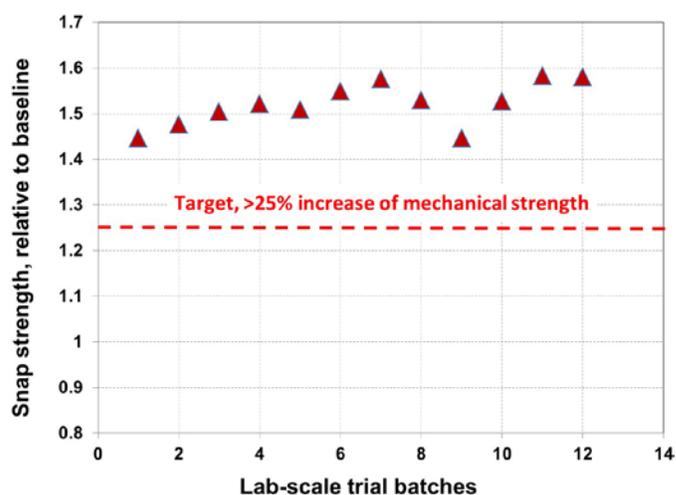


FIGURE 2. BOL mechanical strength of lab-scale smart matrix: Target of >25% increased mechanical strength was achieved.

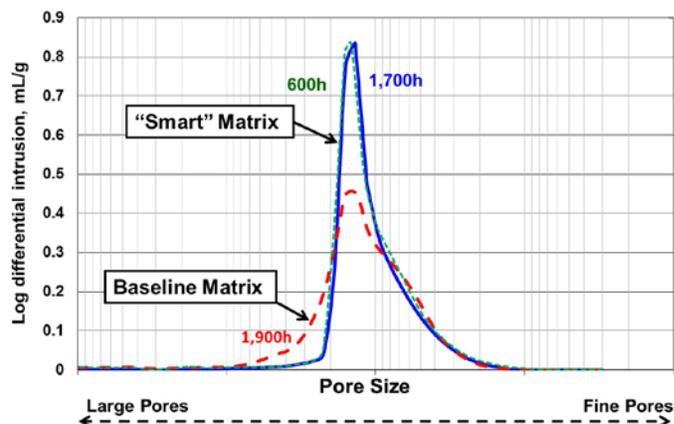


FIGURE 3. Comparison of pore structure of smart matrix vs. baseline in accelerated single cells: >30% reduction of larger pores in smart matrix has been demonstrated.

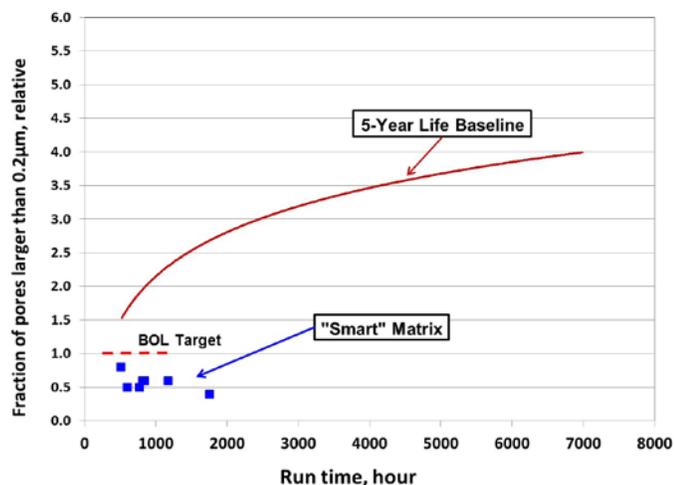


FIGURE 4. Large-pore fraction comparison (pore fraction larger than $0.2\ \mu\text{m}$): >30% reduction of large pores in smart matrix has been demonstrated in accelerated single cells.

CONCLUSIONS AND FUTURE DIRECTIONS

Lab-scale smart matrix has been successfully verified in single cells operated for ~2,000 h. Accomplishments and conclusions for this reporting period include the following.

- Developed slurry formulation and processing parameters to produce lab-scale (10 in wide) smart matrices with improved fine-particle packing
- Met BOL targets of >20% higher porosity, >25% increase of mechanical strength and >30% reduction on pores larger than $0.2\ \mu\text{m}$ (up to 1,700 h cell testing)
- Degradation mechanistic understanding
 - Identified accelerated coarsening in reducing anode environment
 - Developed hypothesis of accelerated coarsening mechanism

The remainder of the project will focus on optimizing smart matrix formulation, additive improvement, endurance validation and scale-up manufacturing trials.

- Verify smart matrix durability in endurance cell tests (>5,000 h)
- Understand degradation mechanism
- Perform scale-up manufacturing trials and validate smart matrix in 30 kW technology stacks

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Program Kickoff Review, held at FuelCell Energy, Inc., February 26, 2015.
2. Abdelkader Hilmi, Arun Surendranath, and Chao-Yi Yuh, “An Innovative Carbonate Fuel Cell Matrix,” Abstract #188, Joint General Session: Battery and Energy Storage-and-Fuel Cells, Electrolytes, and Energy Conversion, paper presented at 227th ECS Meeting, Chicago, IL, May 28, 2015.
3. Chao-Yi Yuh and Abdelkader Hilmi, “Smart Matrix Development for Direct Carbonate Fuel Cell,” 2015 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, Arlington, Virginia, June 12–16, 2015.
4. Chao-Yi Yuh, Abdelkader Hilmi, and Ramki Venkataraman, “High-Temperature Direct Fuel Cell Material Experience,” paper presented at the 11th International Conference on Ceramic Materials and Components for Energy and Environmental Applications, T1-Ceramics for Energy Conversion, Storage, and Distribution Systems, T1S1: High-Temperature Fuel Cells and Electrolysis, American Ceramic Society, Vancouver, Canada, June 14–19, 2015.

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2. Chao-Yi Yuh, Mohammad Farooque, and Hans 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. Chao-Yi Yuh and Mohammad Farooque, “Materials and Life Considerations,” in *Fuel Cells-Molten Carbonate Fuel Cells, Encyclopedia of Electrochemical Power Sources*, 497–507, Elsevier Science, 2009.
4. Chao-Yi Yuh and Mohammad Farooque, “High-Temperature Direct Fuel Cell Material Experience,” in *Advances in Solid Oxide Fuel Cells X, Ceramic Engineering and Science Proceedings*, 11th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology in 38th International Conference and Exposition on Advanced Ceramics and Composites (38th ICACC 2014), American Ceramic Society, **(35)** 9–21, John Wiley & Sons, Hoboken, NJ, 2015.