

Solid Oxide Fuel Cell Cathode Enhancement Via Single-step Infiltration

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Outline

- **About Materials & Systems Research Inc. (MSRI)**
- **R&D Motivation**
- **Accomplishments (up to date)**
- **Results and Discussions**
- **Summary and Future Work**

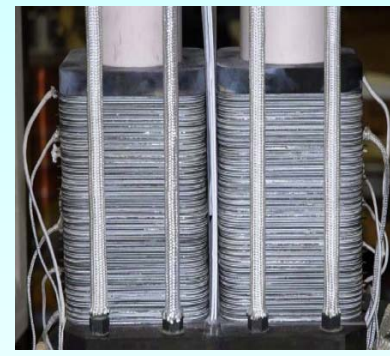
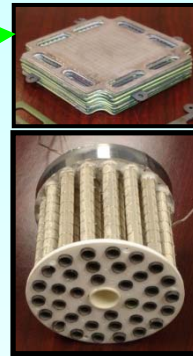
Materials & Systems Research Inc.

specializes in materials and electrochemical engineering for power generation and energy storage applications: fuel cells/electrolyzers, storage batteries, and thermoelectric converters.

has 12 employees: 5 with PhDs in material, mechanical, chemical, & chemistry

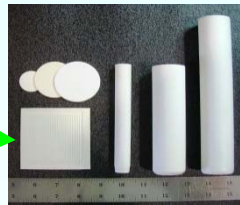
Fuel Cell/Electrolyzer

with planar and tubular cells
cell active area varying from 1 to 100 cm²
stacks/bundles from 10 W to 4 kW

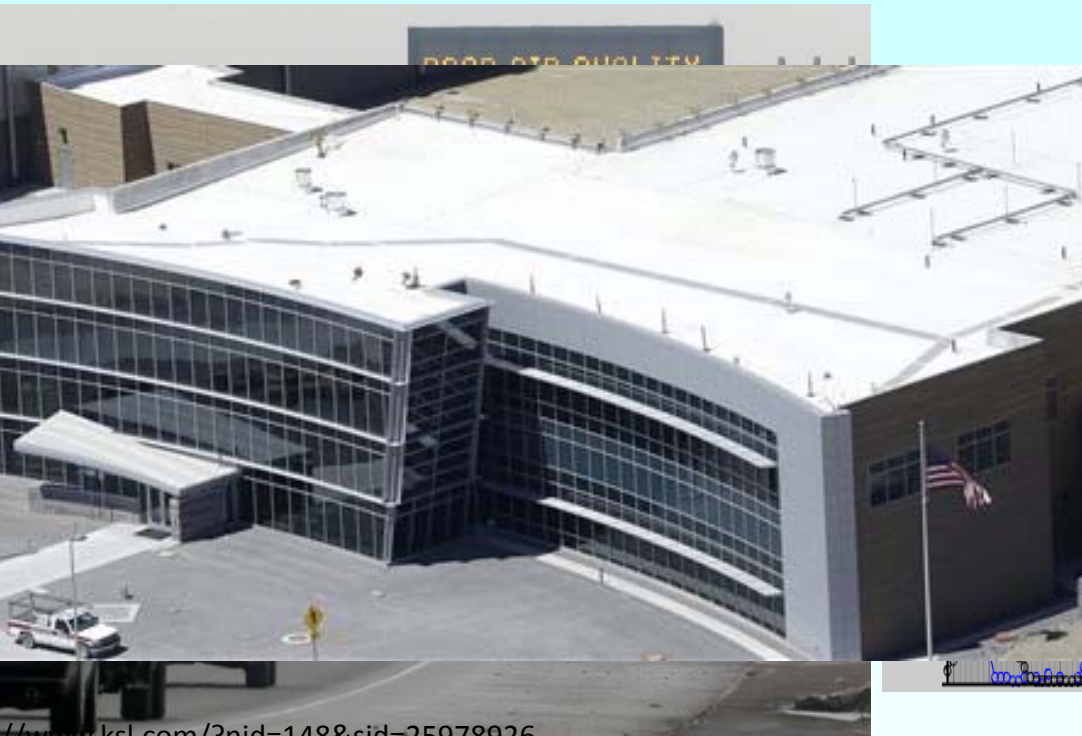


Sodium-beta Battery

Advanced Na⁺-conducting ceramic electrolyte
various battery designs

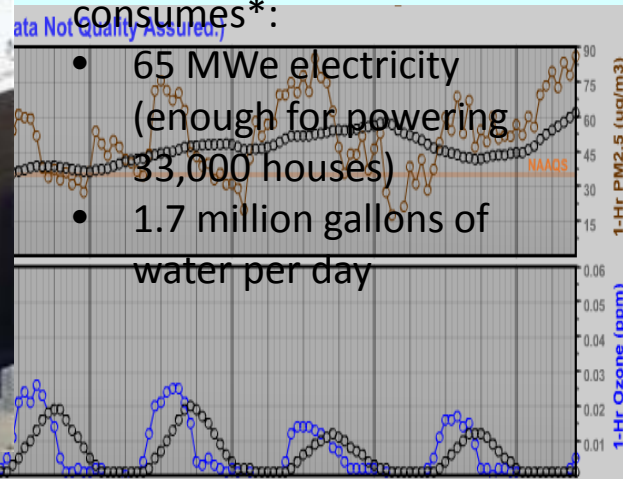


Cleaner Energy



\$1.7 billion cost of the NSA data center in Bluffdale, UT consumes*:

- 65 MWe electricity (enough for powering 33,000 houses)
- 1.7 million gallons of water per day



<http://www.ksl.com/?nid=148&sid=25978926>

<http://www.ksl.com/?nid=148&sid=25576569>

www.standard.net/stories/2013/01/23/utah-doctors-want-governor-get-aggressive-air-quality

www.deseretnews.com/article/865571239/Winter-inversions-hitting-Utah-harder-more-frequently.html?pg=all

Solid Oxide Fuel Cell is capable of converting the chemical energy of the carbon-based fuels directly into electricity with higher efficiencies while reducing the NO_x and SO_x emissions

- Power generation
- Energy storage

Motivation for Cathode Enhancement

High power density, long-term reliability & minimal degradation are critical to success of SOFC technologies and fast market penetration

- **cost target:** stack cost < \$175/kW (cathode material cost ~ 18%, or ~ \$31.5/kW)
- **degradation rate:** 0.1~1% per 1000 hours operation

Cathode polarization losses attribute significant amount to total cell losses

Cathode development: High-performing cathode materials, or/and cathode processing optimization

- infiltration of a nano-structured/nano-sized catalyst has been proven to be one of most effective/efficient means for cathode enhancement
- challenges
 - key parameters determining the success of infiltration process, including adaptability to the pre-established cathode backbones, precursor solution concentration, surfactant, wetting agent, evenness of catalyst distribution along cathode backbones
 - simplicity
 - cost-effective
 - scalable for large cells
 - durability (stability) & process repeatability

Objective & Accomplishments

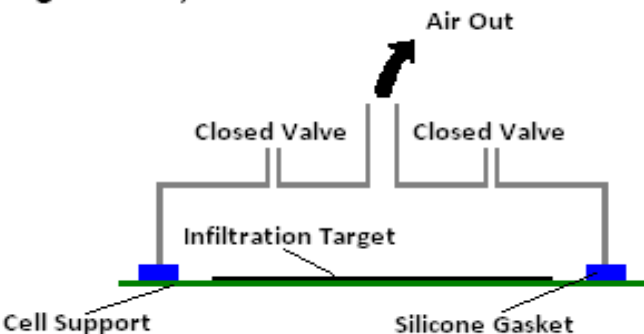
Objective: to develop and implement an advanced cathode deposition process via infiltrating a nano-catalyst(s) into pre-established cathode backbones for SOFC performance enhancement

Accomplishments:

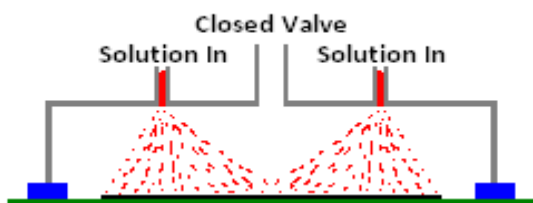
- Engineered cathode backbone microstructures for an efficient single-step infiltration
- Developed and implemented a single-step VPIT process for infiltrating a nano-sized catalyst into pre-established cathode backbones with per-cell active area varying from 2 cm² to 100 cm²
- Developed a 2nd generation of an infiltration apparatus for large cell applications
- Successfully increased the catalyst loading level to 2~2.5 mg/cm² on both button-sized cells and 10 cm x 10 cm cells via the single-step VPIT process
- Improved cell performance more than 60% after catalyst infiltration
- Developed a viable strategy to mitigate cell degradation and was validated over accumulated 25,000 cell-hour tests
- Successfully demonstrated cell degradation rates < 3%/1khrs over 5,700 hrs tests

Single-step Infiltration Concept

Align device, evacuate chamber and electrode pores



Deliver specific volume of catalyst solution



Apply heat and reintroduce atmospheric pressure

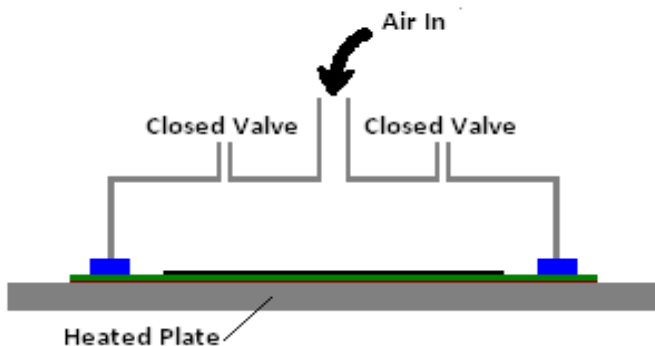


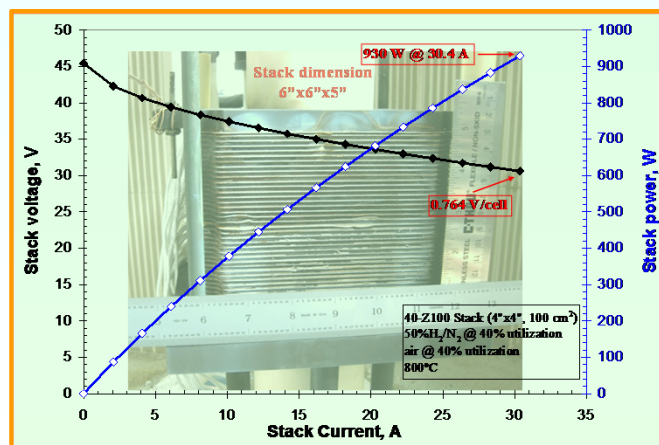
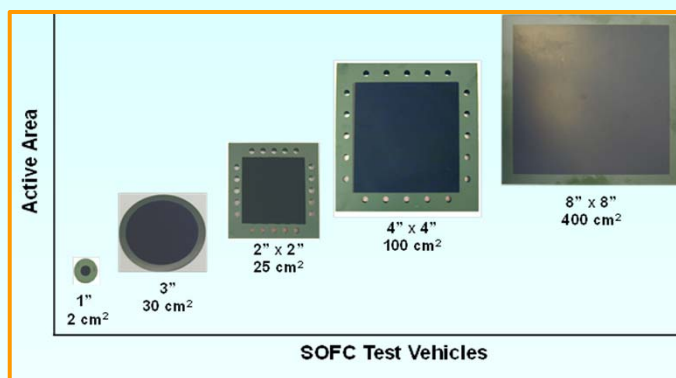
Diagram of the single-step Vacuum-Pressure-Infiltration-Thermal Treatment (VPIT) technique, involving:

- Initial vacuum step to remove air entrapped inside the cathode backbones
- precipitation of a nitrate solution into the porous cathode backbones
- and immediately followed pressurization
- gelation/decomposition at a proper rate/temperature
- Calcination at elevated $T \sim 850^\circ\text{C}$
 - Precursor concentration effects on performance, e.g. $(\text{Sm},\text{Sr})\text{CoO}_3$, or SSC
 - Repeatability/durability
 - Scaling up

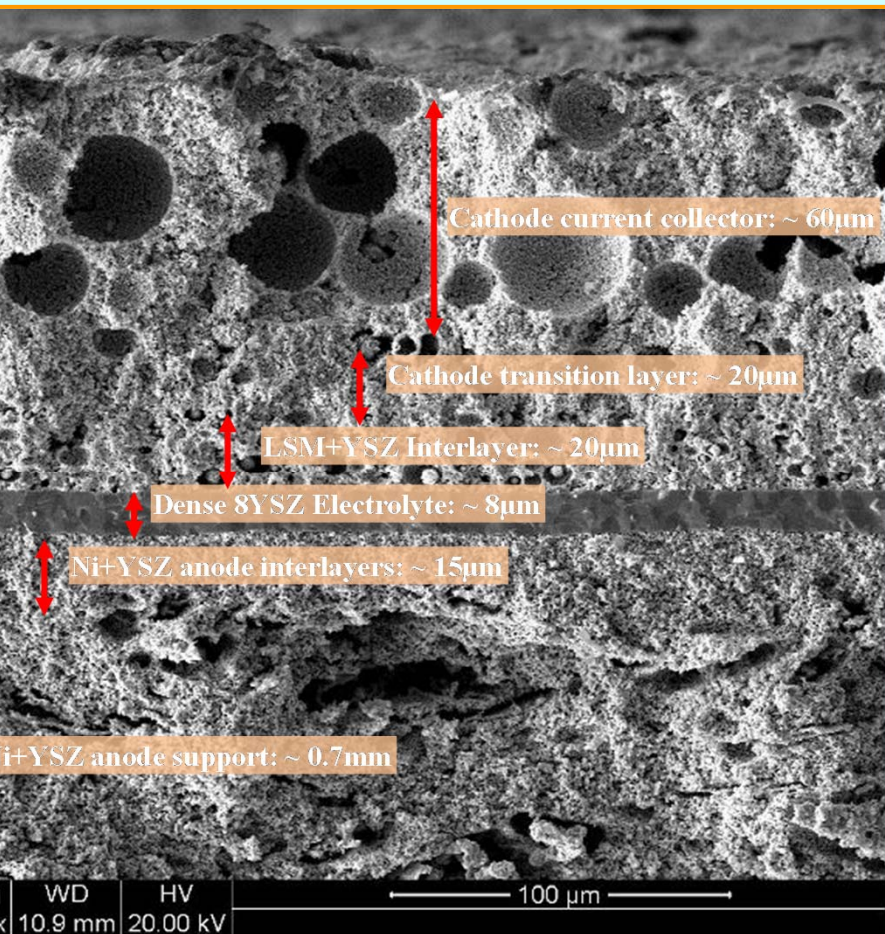
Anode-supported SOFC Fabrication

Baseline cell fabrication for infiltration studies

- MSRI's standard cell fabrication process involves sequential steps: starting from powder mixing/milling → anode tape casting → cell shaping by laser cutting → bisquing → AIL & electrolyte layer application → sintering → CIL/CTL/CCL deposition by screen-printing & firing.



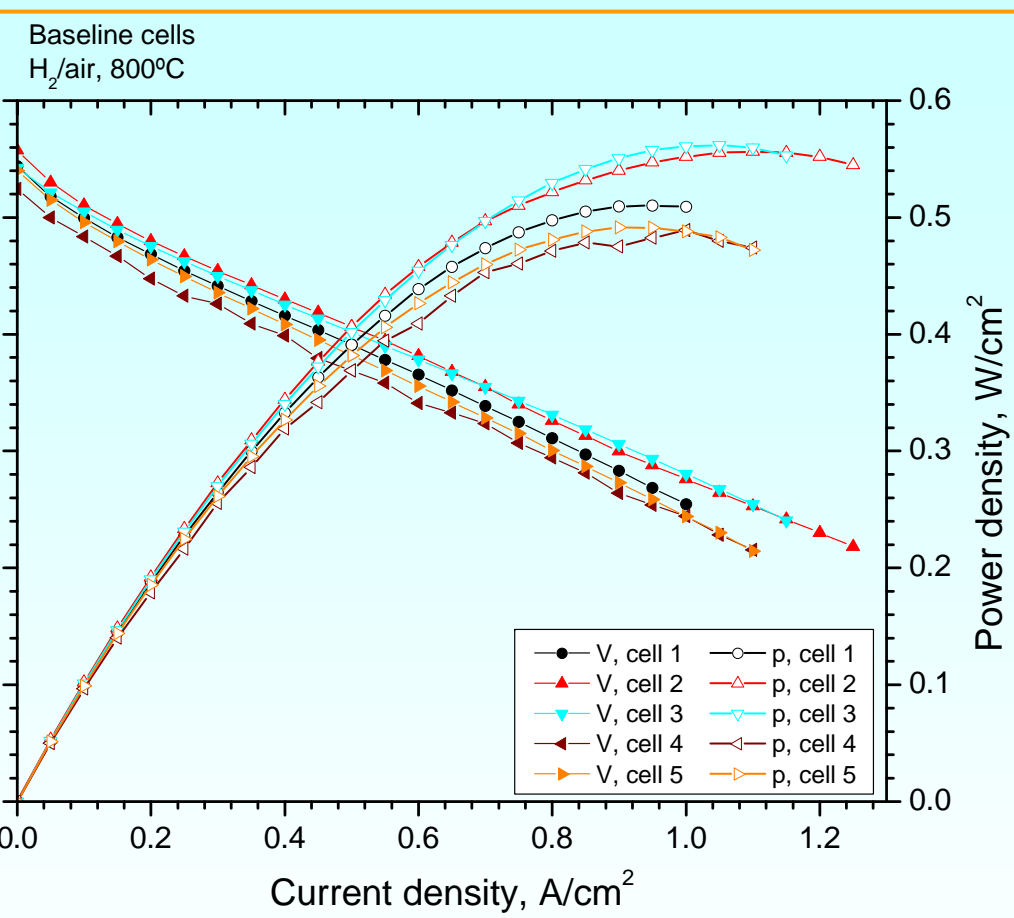
Cell Construction and Test



SEM micrograph of a base cell
(MSRI standard cell)

- In this study, all cells were constructed with:
 - Ni-YSZ anode support (~0.7 mm)
 - YSZ-based electrolyte (8 μ m)
 - **LSM-based cathode system**, consisting of LSM+YSZ as CIL, LSM+LSCF as CTL, and LSCF as CCCL
- Per-cell active area:
 - Button cell: 2 cm²
 - Single cell: 100 cm²
- Test conditions:
 - Either H₂ or a diluted H₂ as the fuel
 - Low fuel utilization for button cells
 - Controlled utilization for single cells, typically 40% ~ 60%
 - **Cell temperature** fixed @ 800°C

Baseline Cell (LSM-based) Tests

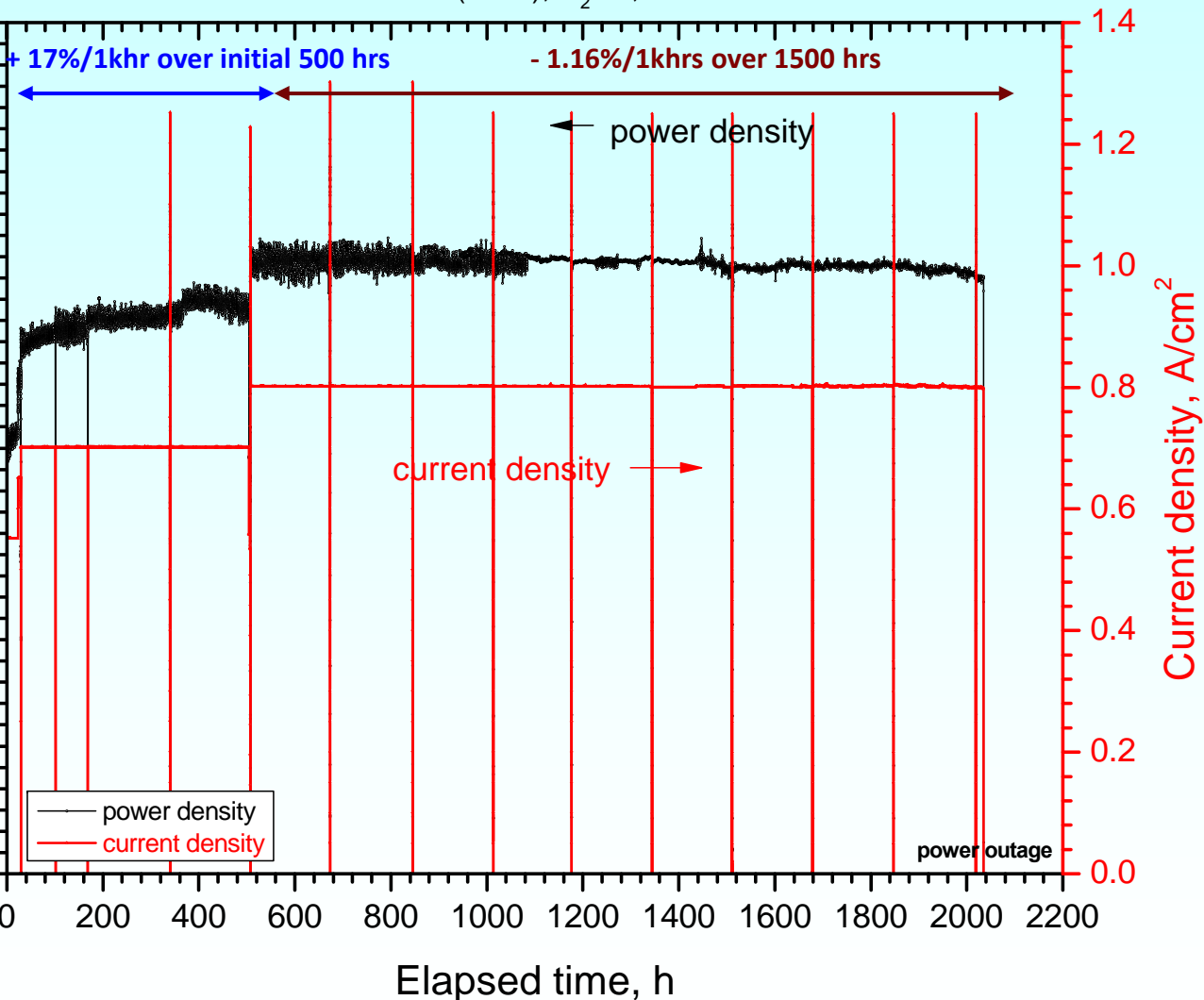


- Button cell baseline tests (w/o catalyst infiltration) for repeatability
- Typical power density: 0.4~0.5 W/cm² @ 0.7V; 0.5~0.56 W/cm² at peak

Cell No.	Peak power density W/cm ²	Power density at 0.7V W/cm ²	ASR Ωcm ²
1	0.51	0.45	0.53
2	0.557	0.5	0.506
3	0.562	0.502	0.487
4	0.489	0.4	0.515
5	0.492	0.43	0.548

Baseline Cell Long-term Tests

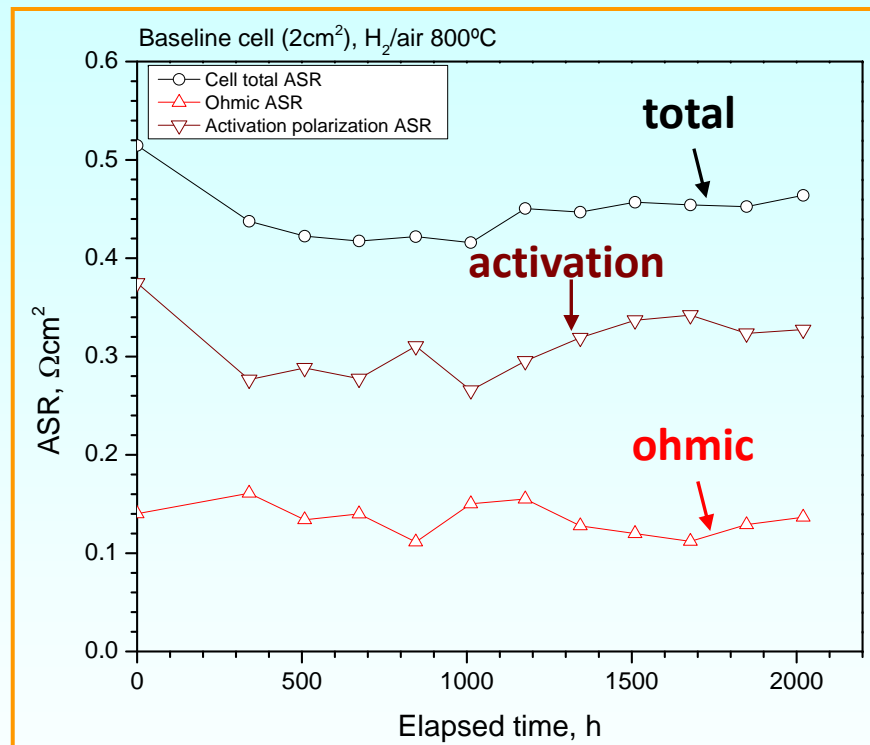
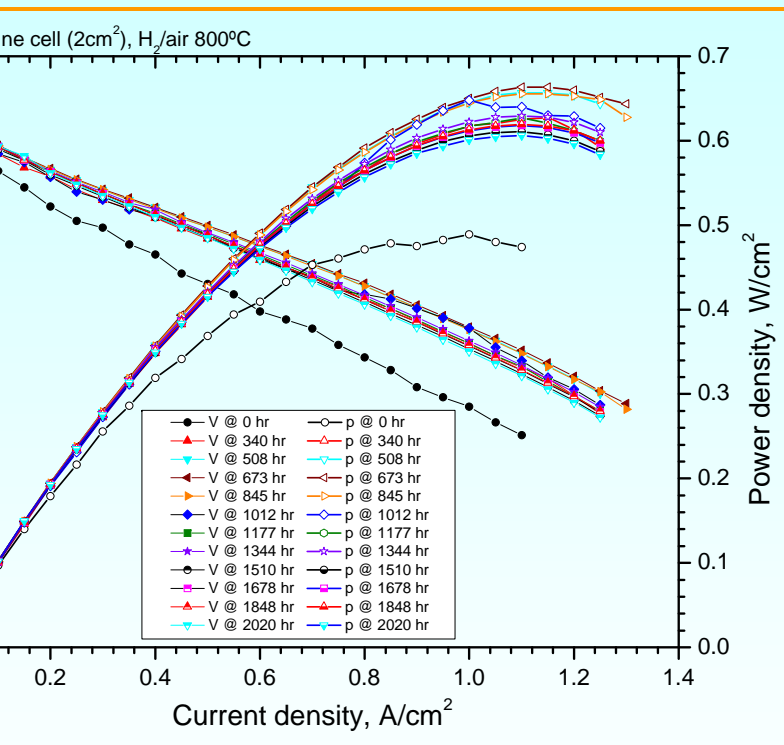
Baseline button cell w/o infiltration (2cm^2), H_2/air , 800°C



- Tested over 2000 hrs
- current density increased from $0.7 \text{ A}/\text{cm}^2$ to $0.8 \text{ A}/\text{cm}^2$ after the initial 500 hrs test
- Cell power density increased by 17%/1khrs during the initial 500 hours
- Cell degradation rate @ - 1.16%/1khrs over the last 1500 hrs

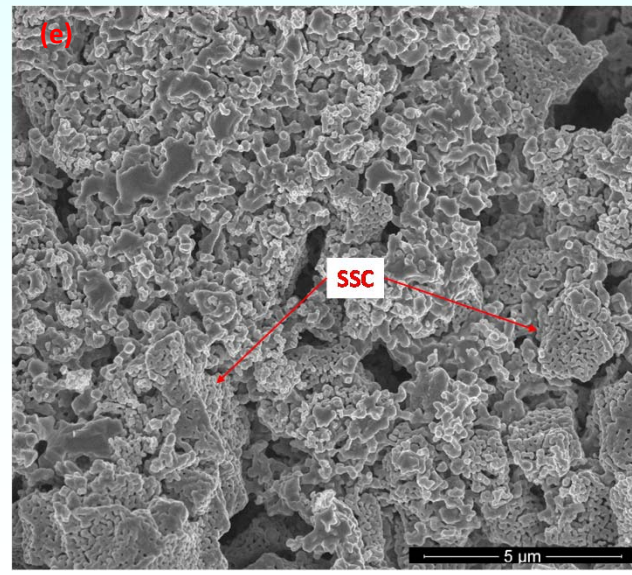
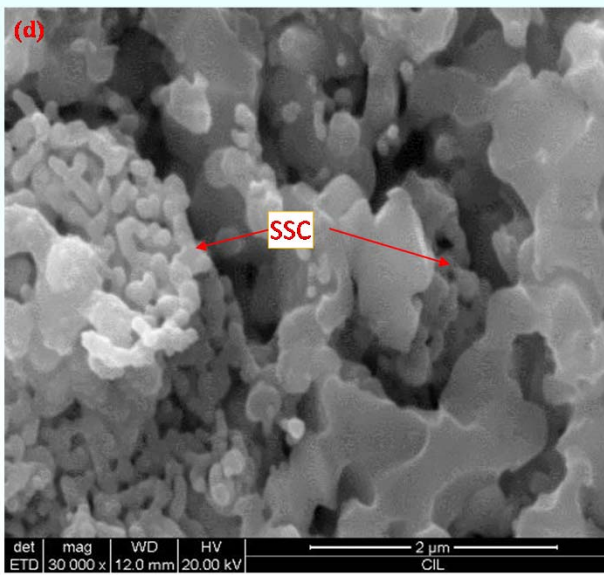
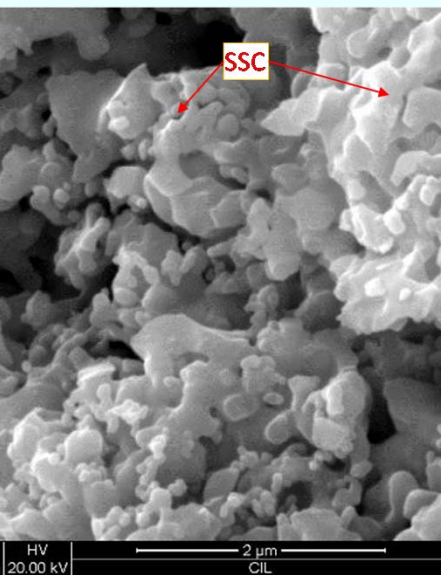
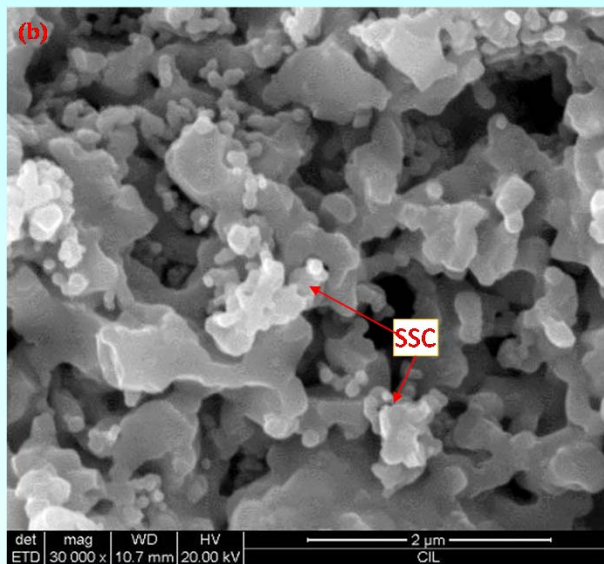
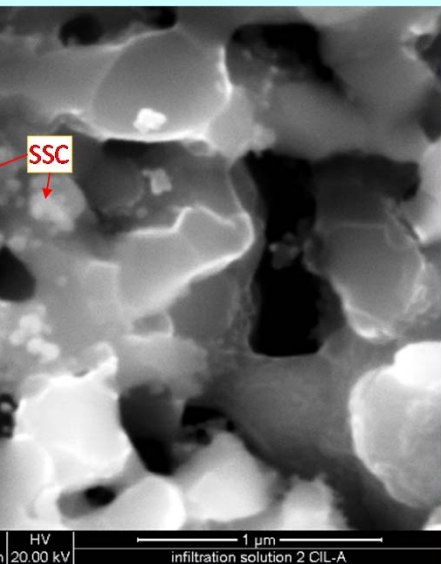
Baseline Cell Performance Characterization

VI tests & EIS measurement at scheduled time (weekly)



Activation polarization losses were much higher than Ohmic losses

Preursor Concentration Effects on Loading along CIL

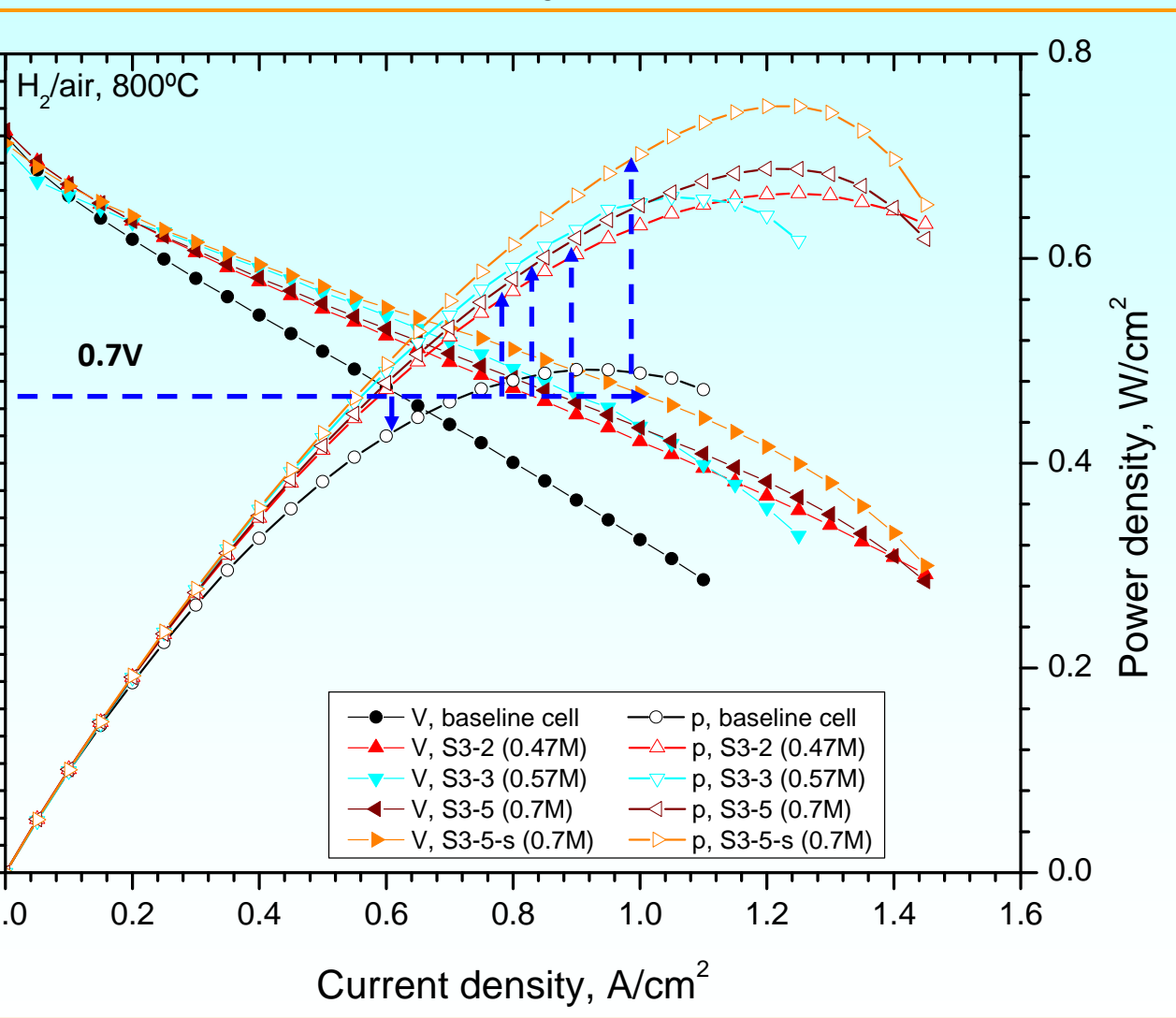


SSC concentrations: (a) 0.25 M, (b) 0.47 M, (c) 0.57 M, (d) 0.7 M, (e) 0.76M

SSC loading was increased from 1 mg/cm^2 to 2~2.5 mg/cm^2 for both button cells (2 cm^2) and large cells (100 cm^2) after the single-step VPIT process

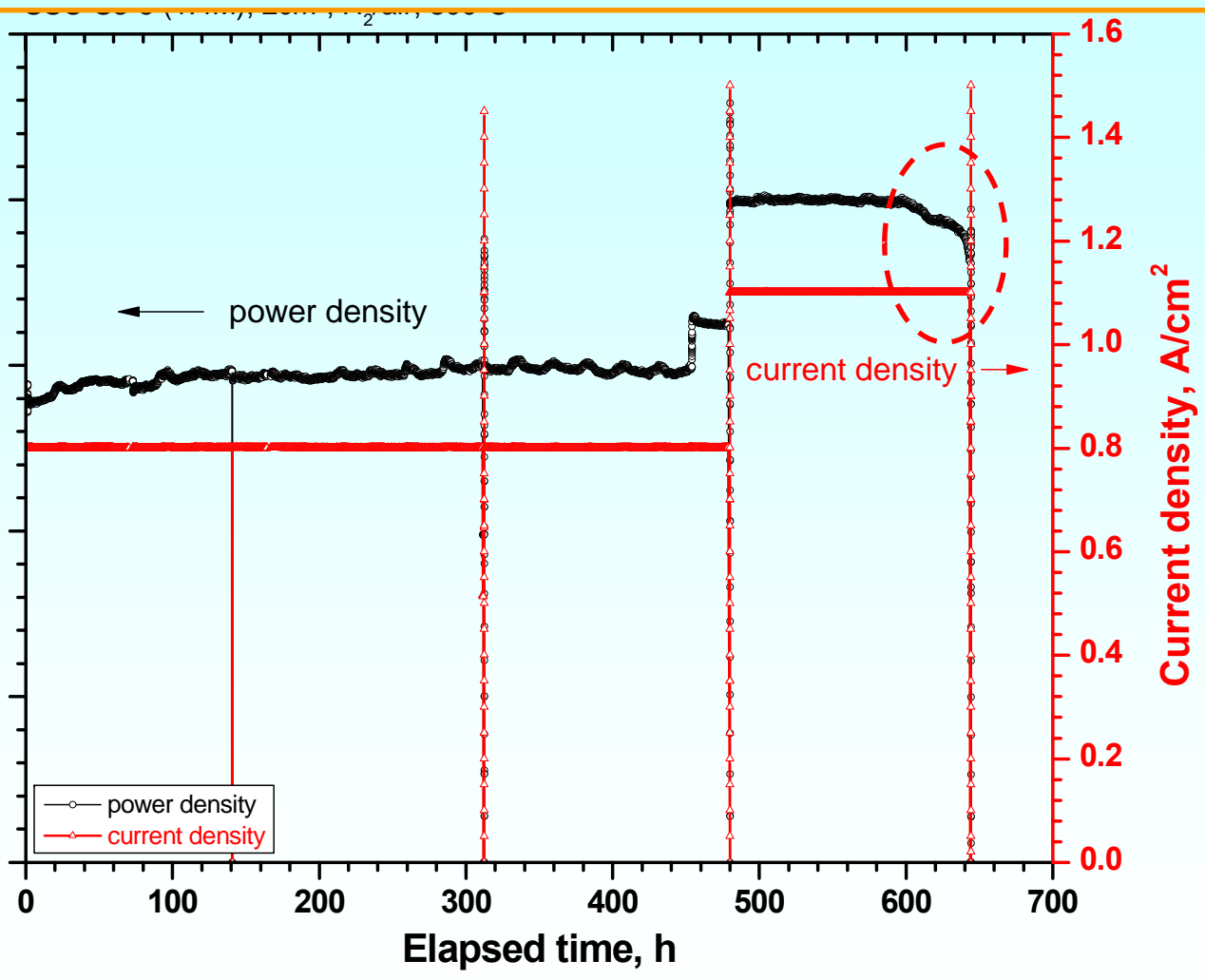
Precursor Concentration Effects on Cell Performance

Infiltration of (Sm, Sr)CoO₃ catalyst



- Three precursor solutions with concentration varied from 0.47M to 0.7M
- Power density improvement > 45% (at 0.7V)
- Cells infiltrated with 0.7M solution outperformed others

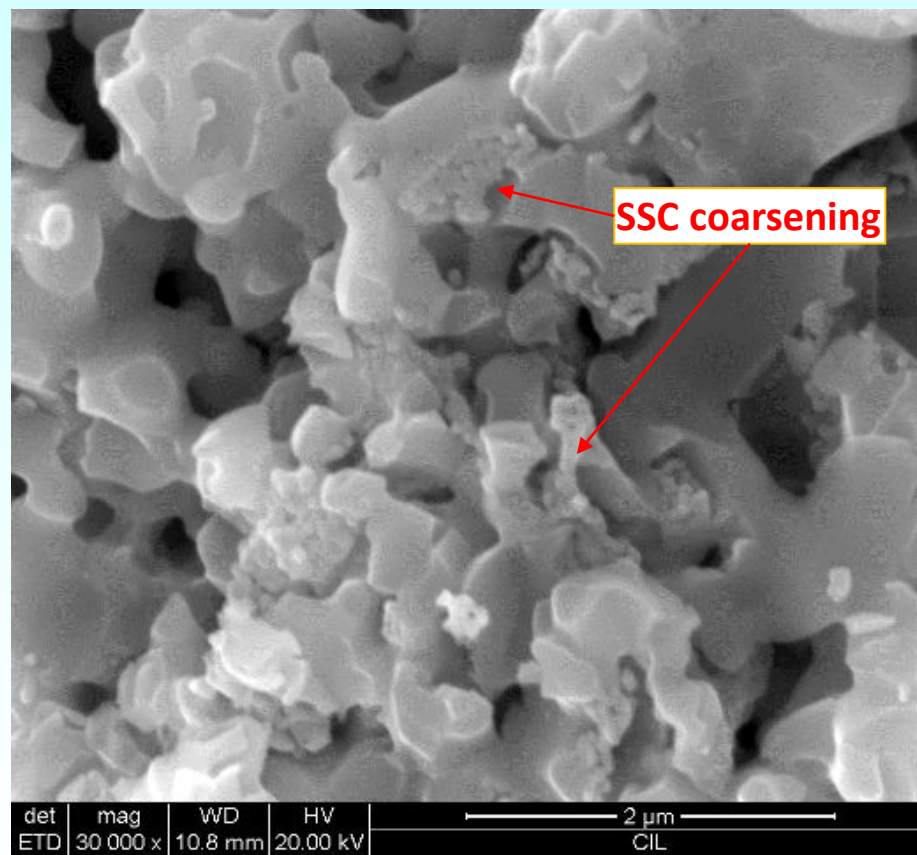
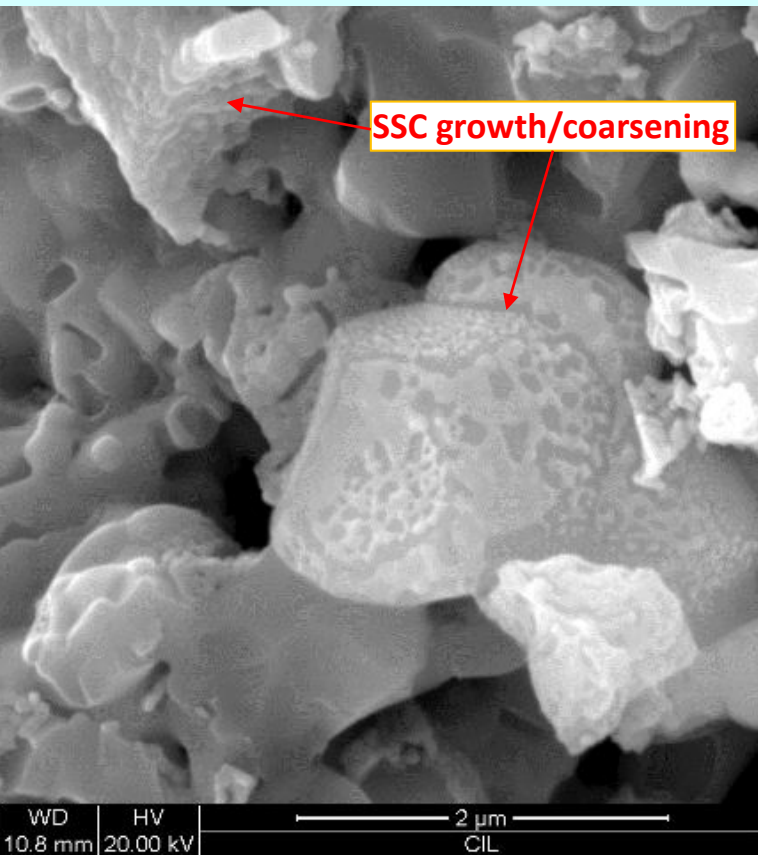
SSC-S3-5 (0.7M) Cell Long-term Test



- At 0.8 A/cm², cell performance increased by 6% over 450 hrs
- Current density increased from 0.8 A/cm² to 1.1 A/cm²
- no degradation over 600 hrs
- accelerated degradation was observed during the last 50 hrs (0.72V dropped to 0.66V within 50 hrs)

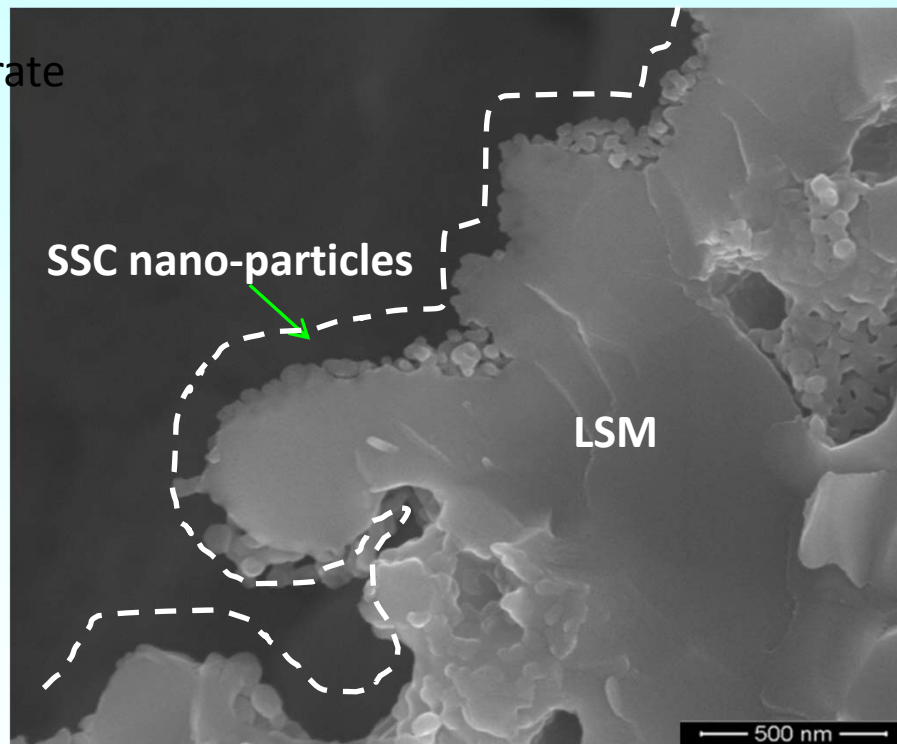
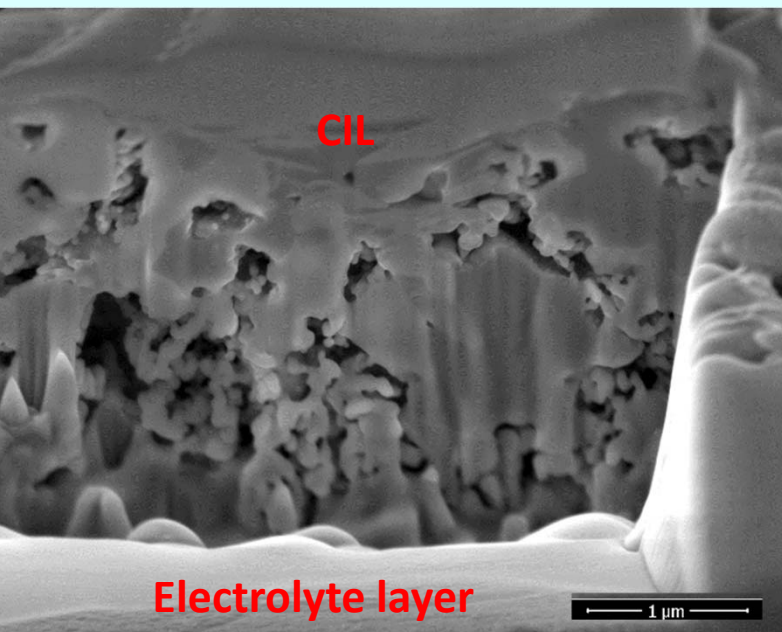
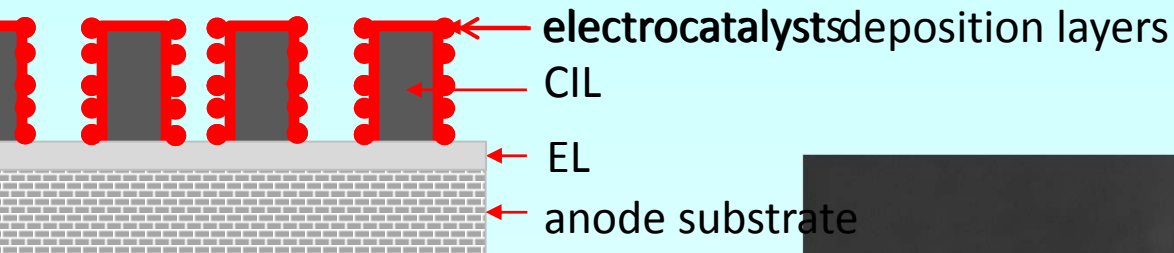
Nano-catalyst Growth/Coarsening Issue

Post-test cell (SSC-S3-5 cell after 650 hrs long-term test) characterization



Mitigate Particle Growth/Coarsening Issues

'Ideal microstructures'???

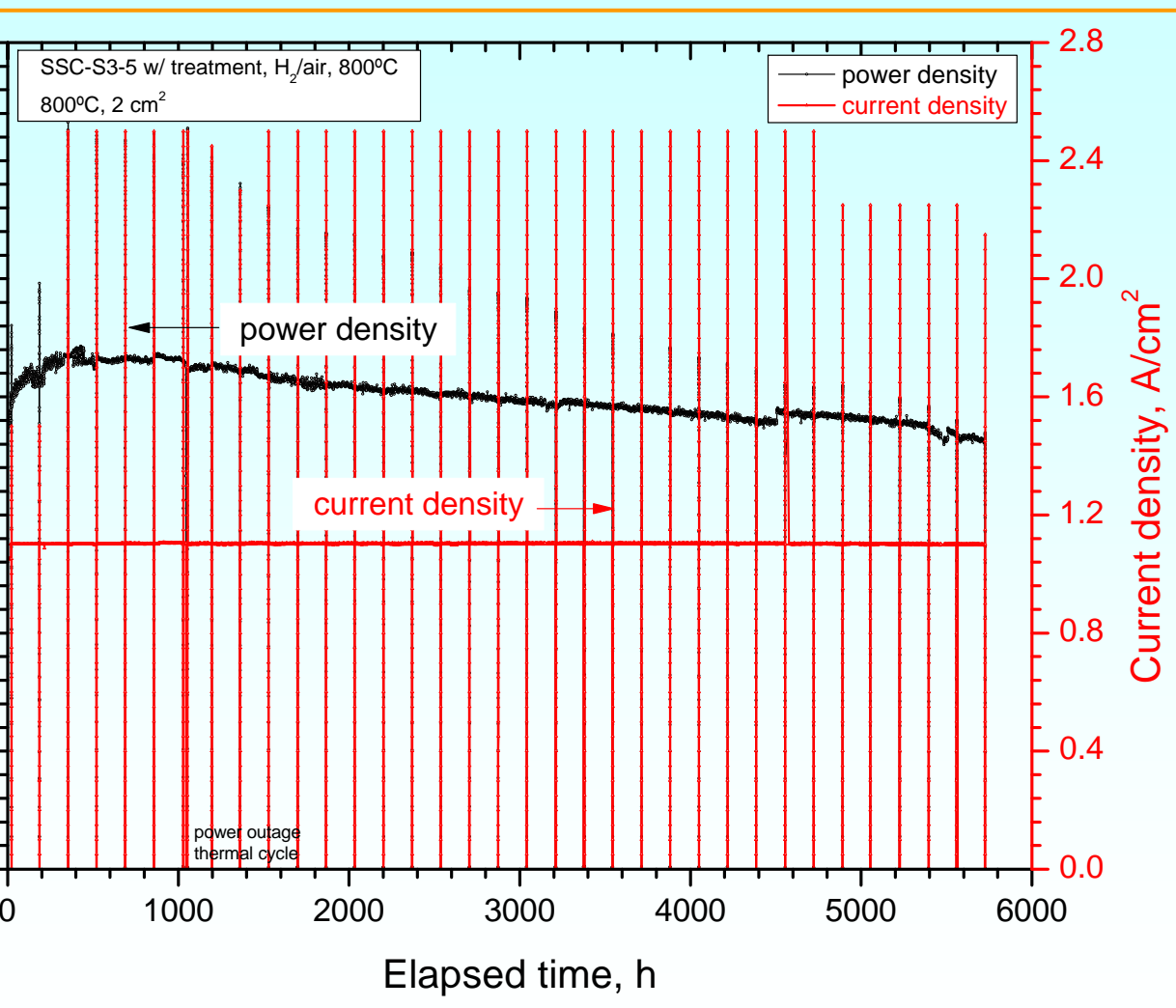


SEM of the electrolyte/CIL interface
Construct CIL and CTL to ensure an
efficient infiltration of a catalyst
precursor into the ERSs (TPB & 2PB)

- Engineer the catalyst precursor solution, upon infiltration, to avoid excessive agglomerates and to ensure a good coverage of a catalyst along the cathode grains

plement & Evaluate Mitigation Strategies

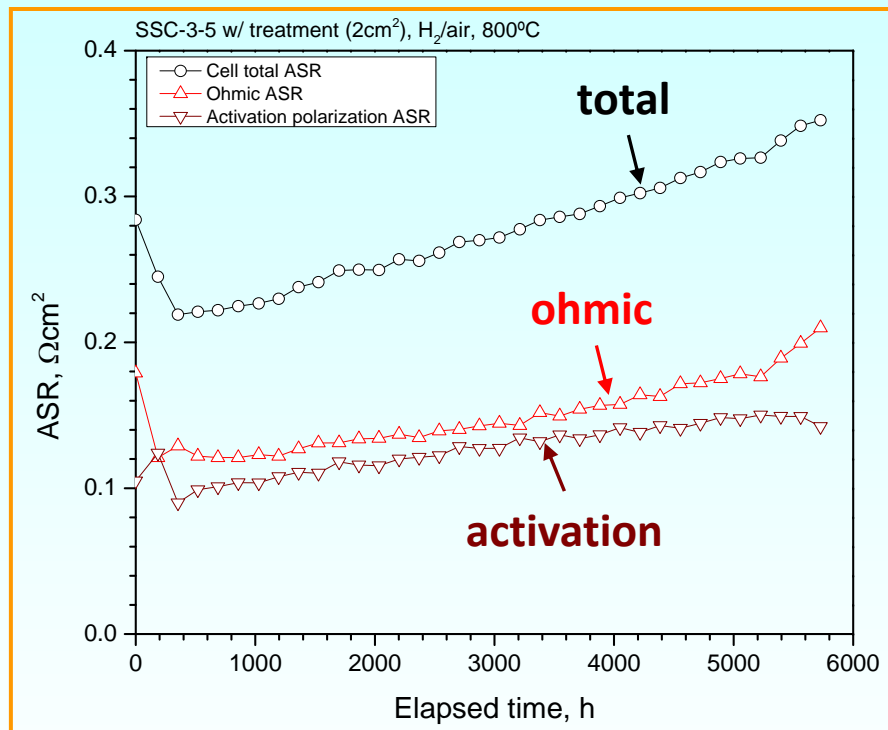
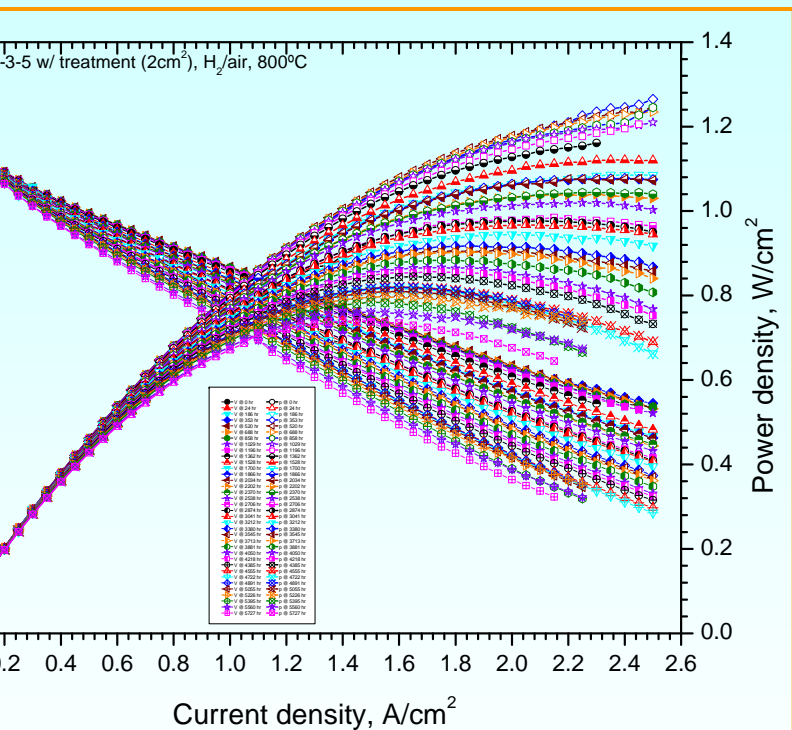
Long-term test results of a button cell



- upon infiltration, cell power density at 0.7V increased from 0.55 W/cm² to 0.86 W/cm² (> **60% improvement**)
- performance improved over **+4.5%/1khrs** during the initial 1000 hrs test until a power outage,
- cell was still under full load (2.2A, 0.27V) at 690°C during a power outage over a weekend
- cell overall degradation rate @ **-2.56%/1khrs** over **57,00 hrs (over 8 months)**
- the mitigation strategies showed great promises to improve performance and stability

Significance of Catalyst Infiltration

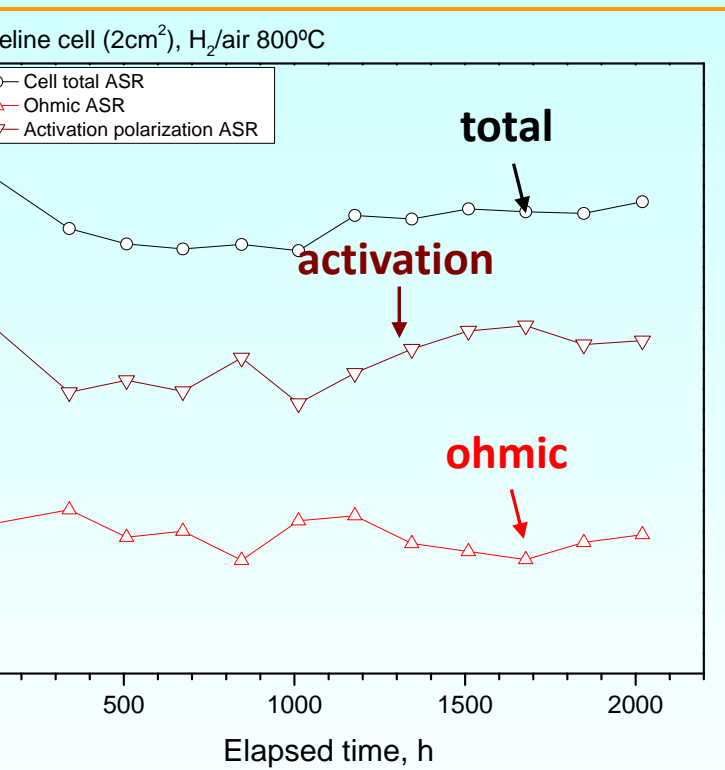
VI tests & EIS measurement at scheduled time (weekly)



Activation polarization losses were less than Ohmic losses

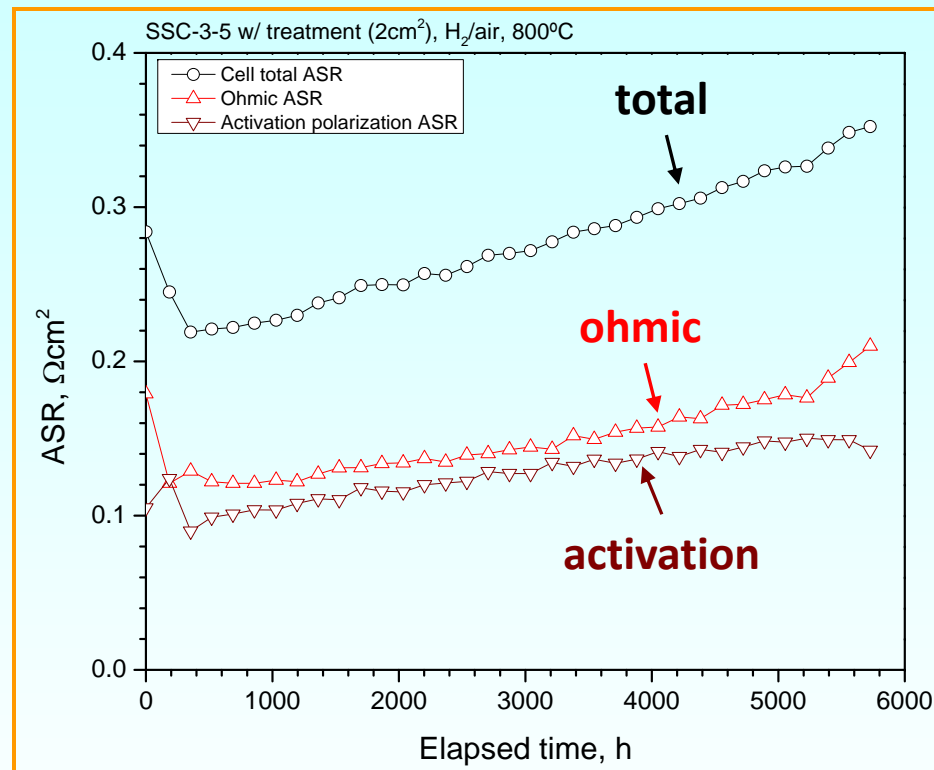
Benefits from Catalyst Infiltration – ASR standpoint

Baseline cell (w/o infiltration)



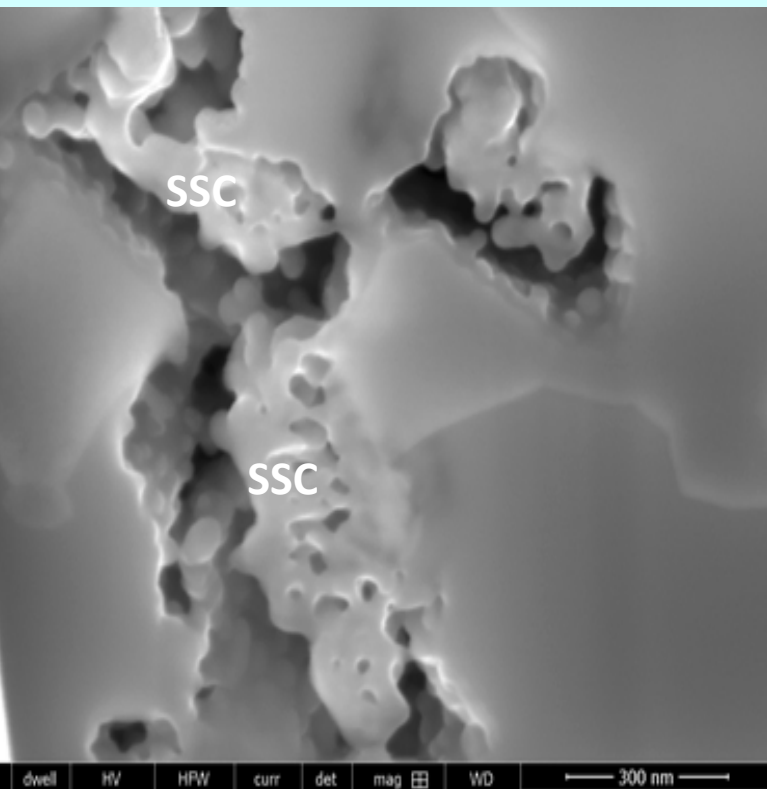
Cell ASR ~ 0.44 Ωcm² consisting of
 Ohmic ASR ~ 0.13 Ωcm²
 Activation ASR ~ 0.31 Ωcm²

Cell (infiltrated w/ SSC)

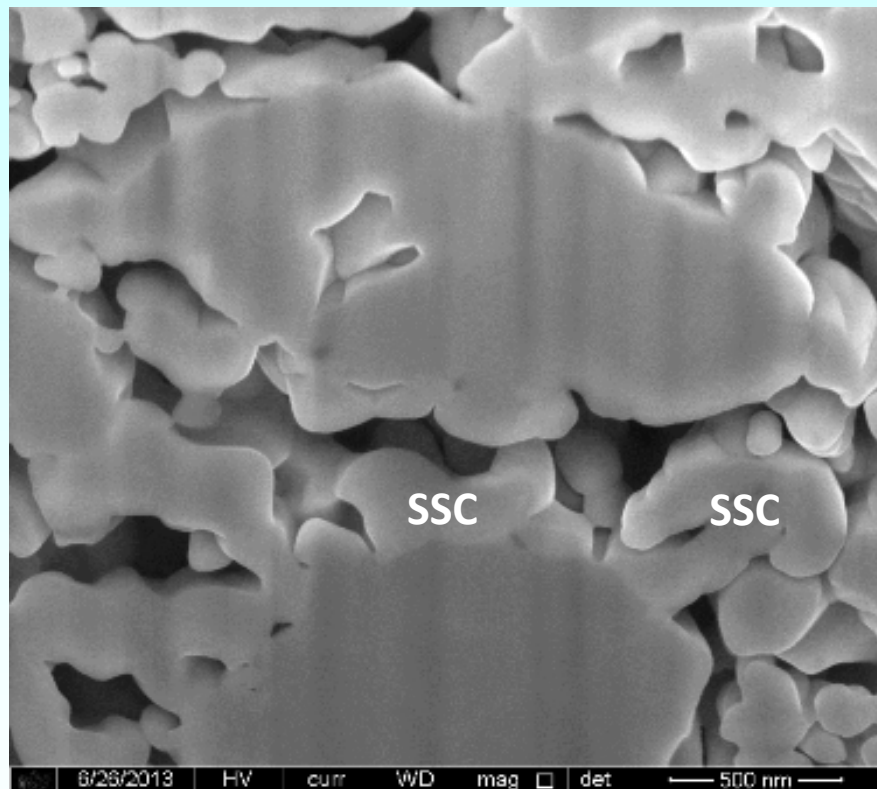


Cell ASR ~ 0.22 → 0.34 Ωcm² consisting of
 Ohmic ASR ~ 0.12 → 0.22 Ωcm²
 Activation ASR ~ 0.1 → 0.12 Ωcm²

Microstructure Changes after Long-term Tests

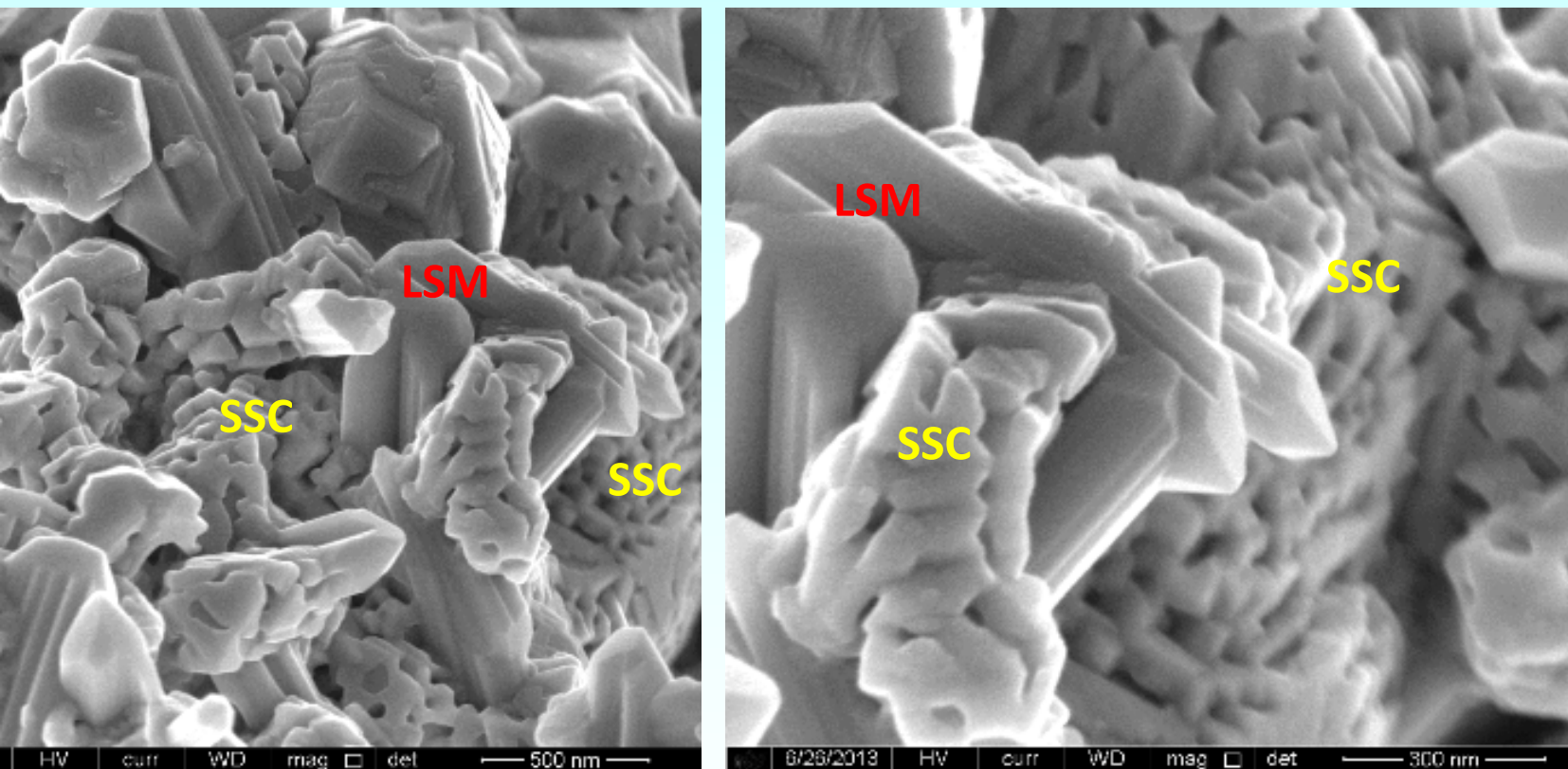


Cell w/ SSC infiltration, sample was prepared by FIB cut near electrolyte (CIL)



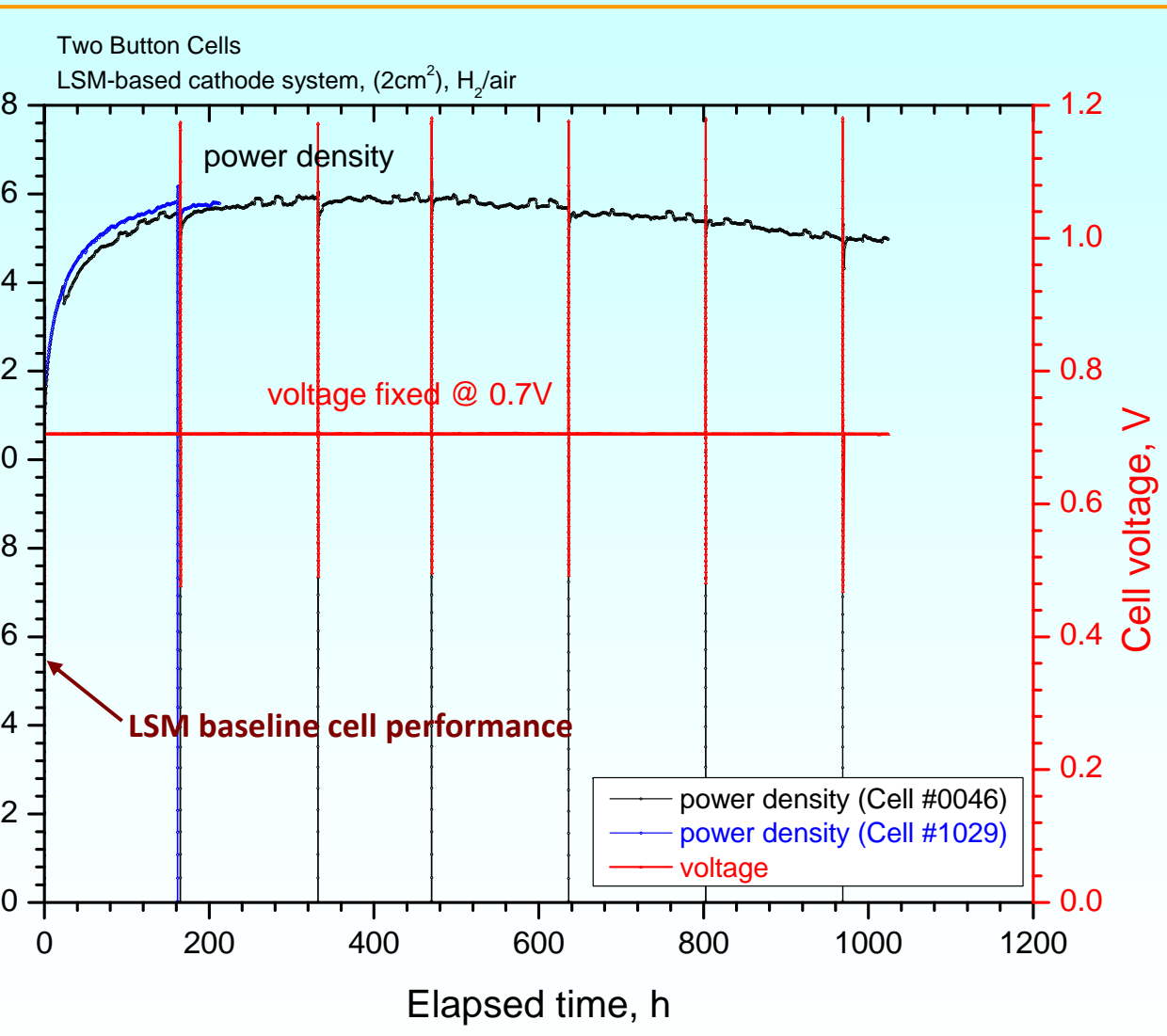
Cell after thousands of hours test. Sample was prepared by FIB cut near electrolyte (CIL)

Microstructure Changes after Long-term Tests



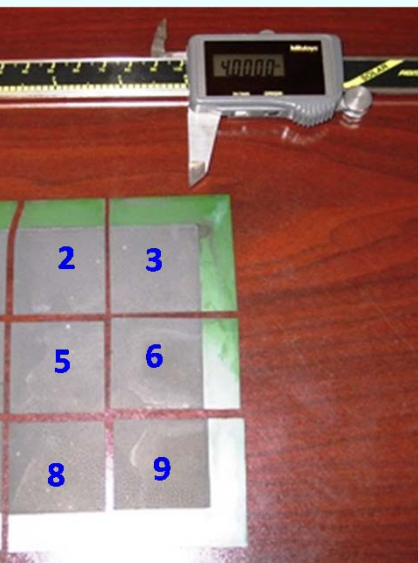
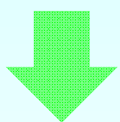
a cell after $\sim 53,00$ hours test ($1.5\text{A}/\text{cm}^2$ @ 0.7V)

Other Nano-sized Electrocatalysts

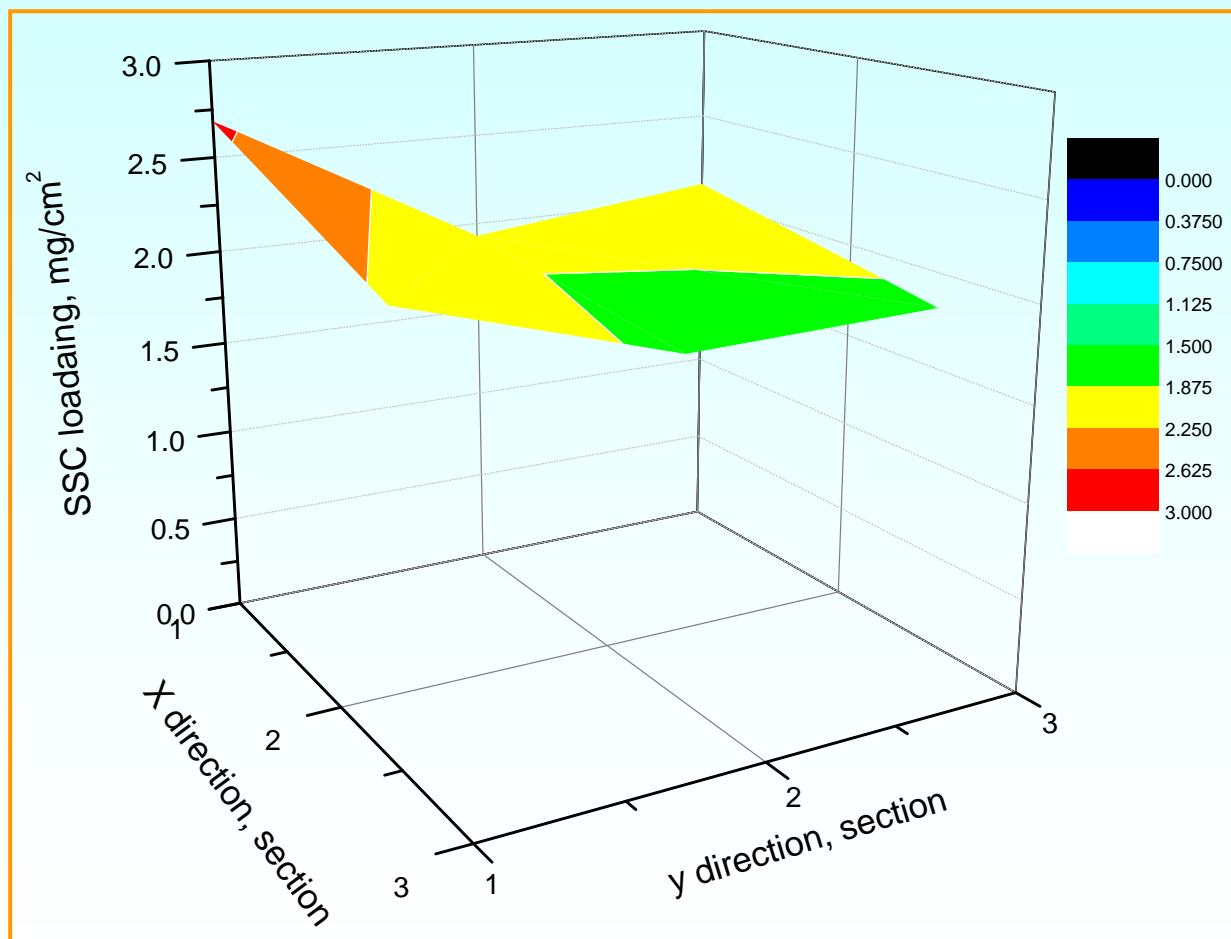


- Non-precious metal catalyst
- upon infiltration, cell power density at 0.7V increased from 0.55 W/cm² to **1.5 W/cm²** (> **170% improvement**)
- 1.5%/1khr improvement over 1khr test
- Tests are still on-going

Scaling-up from Button Cells to 100cm² Cells



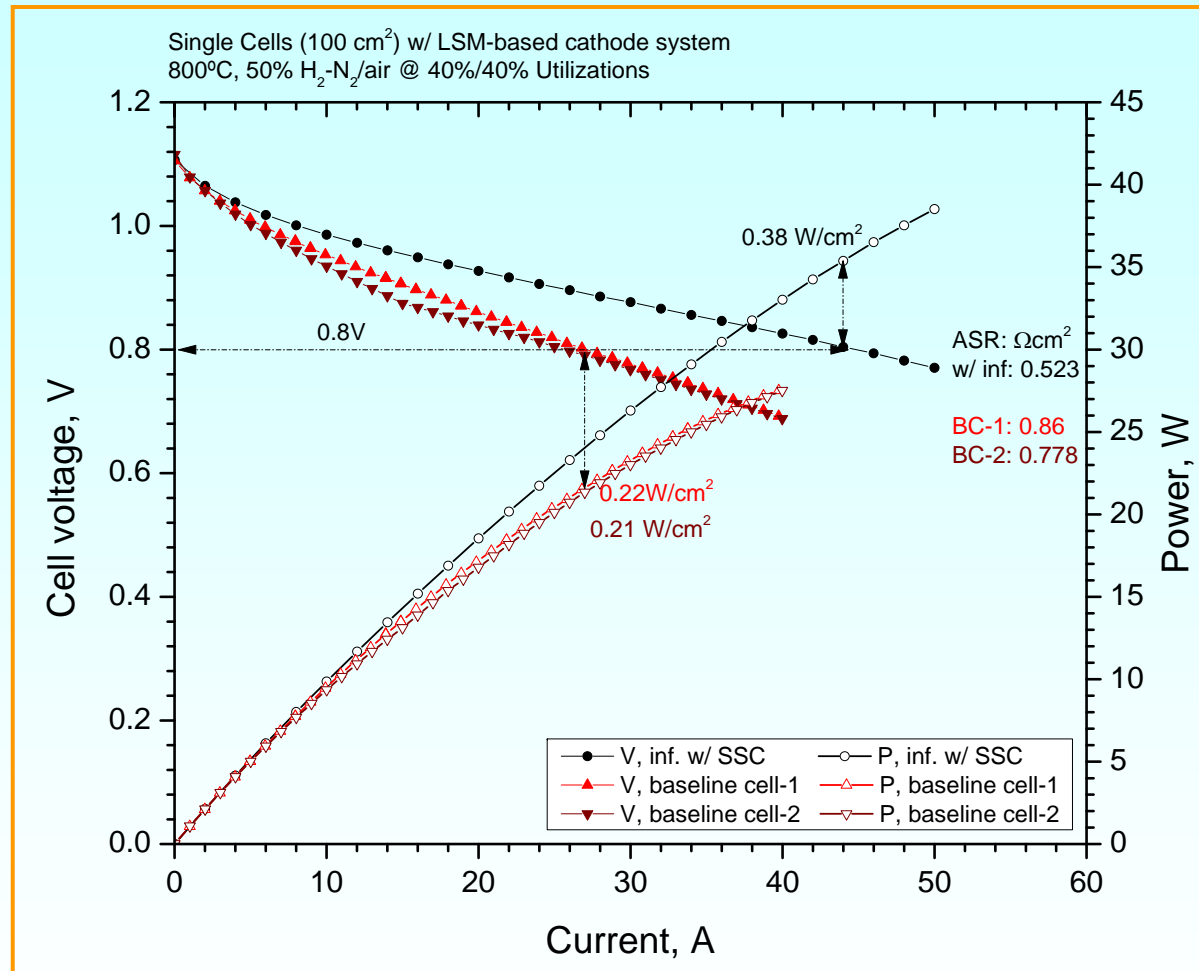
Study of SSC loading distribution along a 4"x4" single cell cathode surface (100 cm²) – from corner to corner



Single Cell (100 cm²) Evaluation



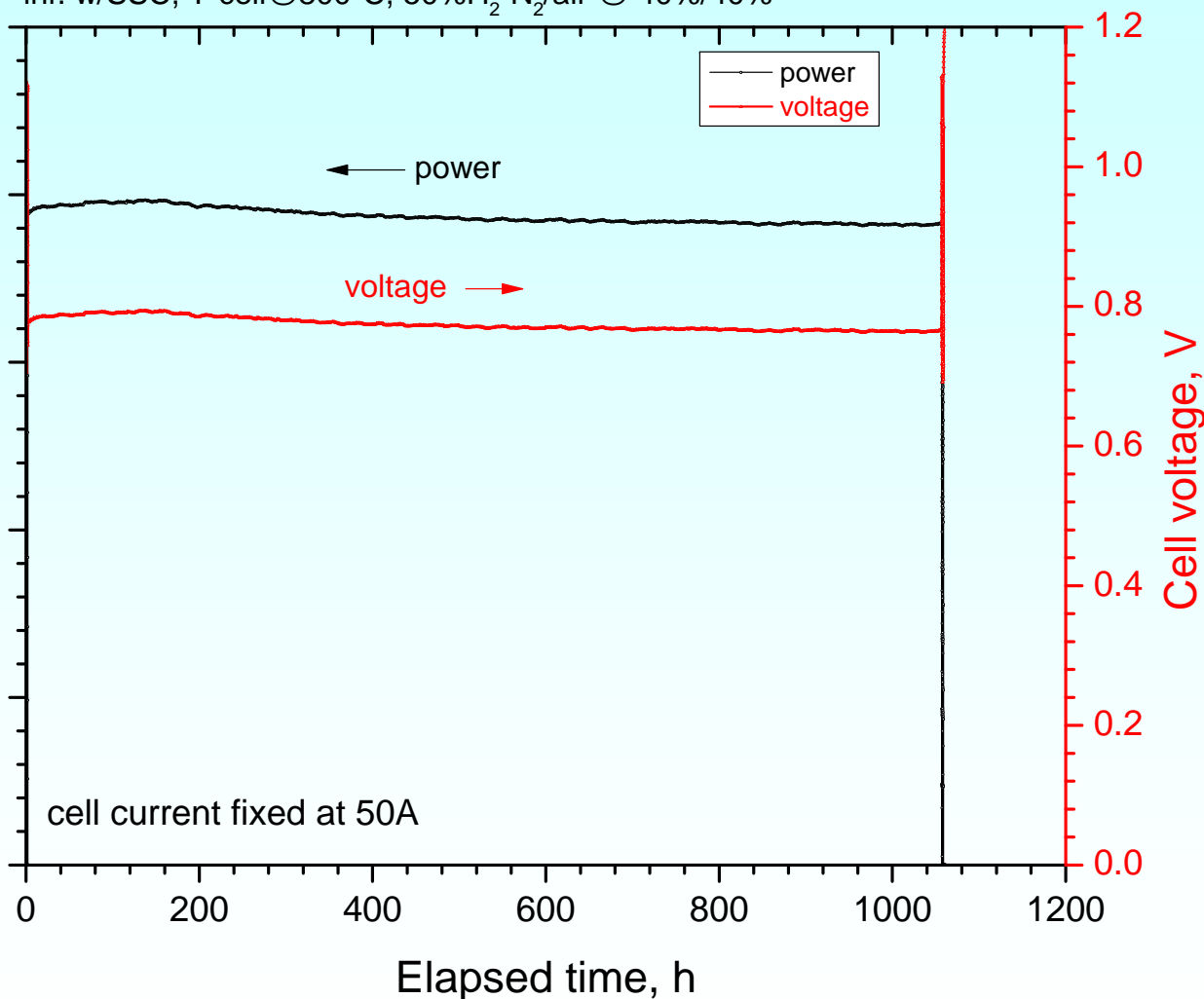
mic test-rig for single
 ts
 of Cr sources
 metallic IC
 ic stack compression &
 patterns



Single cell performance comparisons among two baseline cells and the one w/ SSC infiltration

Long-term Test of a Single Cell w/ SSC Infiltration

Single Cell w/ LSM-based cathode system (100 cm²)
inf. w/SSC, T-cell@800°C, 50%H₂-N₂/air @ 40%/40%



- ❖ Cell temperature adjusted to 800°C
- ❖ Dilute fuel w/ fixed 40% utilizations
- ❖ Under a constant current of 50 A (0.5A/cm²)
- ❖ Cell voltage ~ 0.8 V
- ❖ Power improved by ~ +2%/1khr during initial 200-hr test
- ❖ Over the 1khr test, power degradation rate: -3.5%/1khr, or -0.014 mW/cm²-hr

Long-term test result of a single cell w/ SSC infiltration

Summary/Future Work

Infiltration of an electrochemically active catalyst is an efficient and cost-effective approach to improve SOFC cathode performance

Key parameters determining the single-step infiltration efficiency are critical to the success of the SOFC performance improvement, while pre-established cathode backbones also needs modification for implementation

Cells with a catalyst infiltration outperformed the cells without infiltration by over 60% (at 0.7V), mainly attributed to the activation polarization reduction from cathodes

Continue to perfect the VPIT processes

Explore other catalyst effects

Optimize catalyst structure

Identify the anode degradation attribute

Perform techno-economic evaluation

Evaluate scale-up cells and stacks for proof-of-concept demonstration (built-on MSRI's standard SOFC products/forms)



1.5 W/cell



45 W/cell



200W/stack

4 kW/stack



Acknowledgement

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Phase II Project Manager Joseph Stoffa, Briggs White, Shailesh Vora, and the entire NETL SECA program management team

Thank you!

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