Solid Oxide Fuel Cell Cathode Enhancement Via Single-step Infiltration

DOE SBIR Phase II Award # DE-SC0006374
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15th Annual SECA Workshop
Pittsburgh, PA, July 22-23, 2014

Outline

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

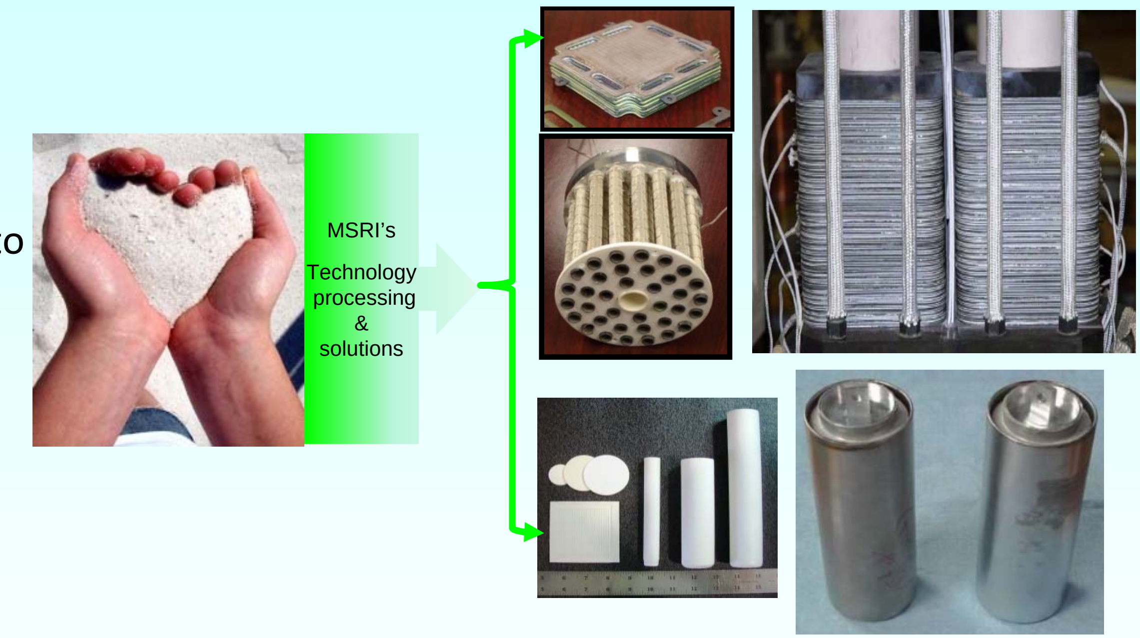
Materials & Systems Research Inc.

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

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

Fuel Cell/Electrolyzer

- Start from off-the-shelf powders
- Both planar and tubular cells
- Per-cell active area varying from 1 to 400 cm^2
- Stacks/bundles from 10 W to 4 kW



Sodium-beta Battery

- Advanced Na^+-conducting ceramic electrolyte
- Unique battery designs

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 < $225/kWe (cathode material cost ~ 18%, or ~ $40/kWe)
  - **degradation rate**: 0.2~1% 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

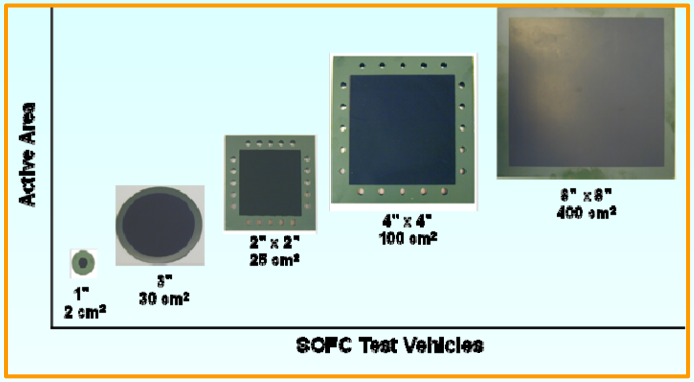
Accomplishments:

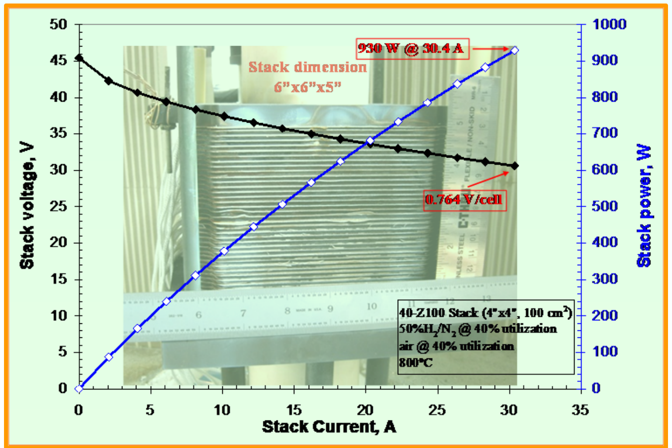
- Developed and implemented a single-step VPIT process for infiltrating a nano-sized electrocatalyst into pre-established cathode backbones with per-cell active area varying from 2 cm^2 to 100 cm^2
- Developed a Gen-3 infiltration apparatus for large cell applications
- Investigated electrocatalyst loading profile along the CIL and CCCL of 100 cm^2 cells after the single-step VPIT process
- Developed a viable strategy to mitigate cell degradation and was validated over accumulated 35,000 cell-hour tests
- Improved single cell performance more than 80% after catalyst infiltration
- Demonstrated single cell (100 cm^2) degradation rates ~ 3.5%/1khrs @ 0.5A/cm^2 (>1100 hrs) and 5%/1khr @ 0.75 A/cm^2 (>1400hrs, on-going)
- Improved short stacks performance by 40% upon catalyst infiltration, and demonstrate stack degradation rate ~ 3.1%/1khr @ 0.5A/cm^2

Anode-supported SOFC Fabrication

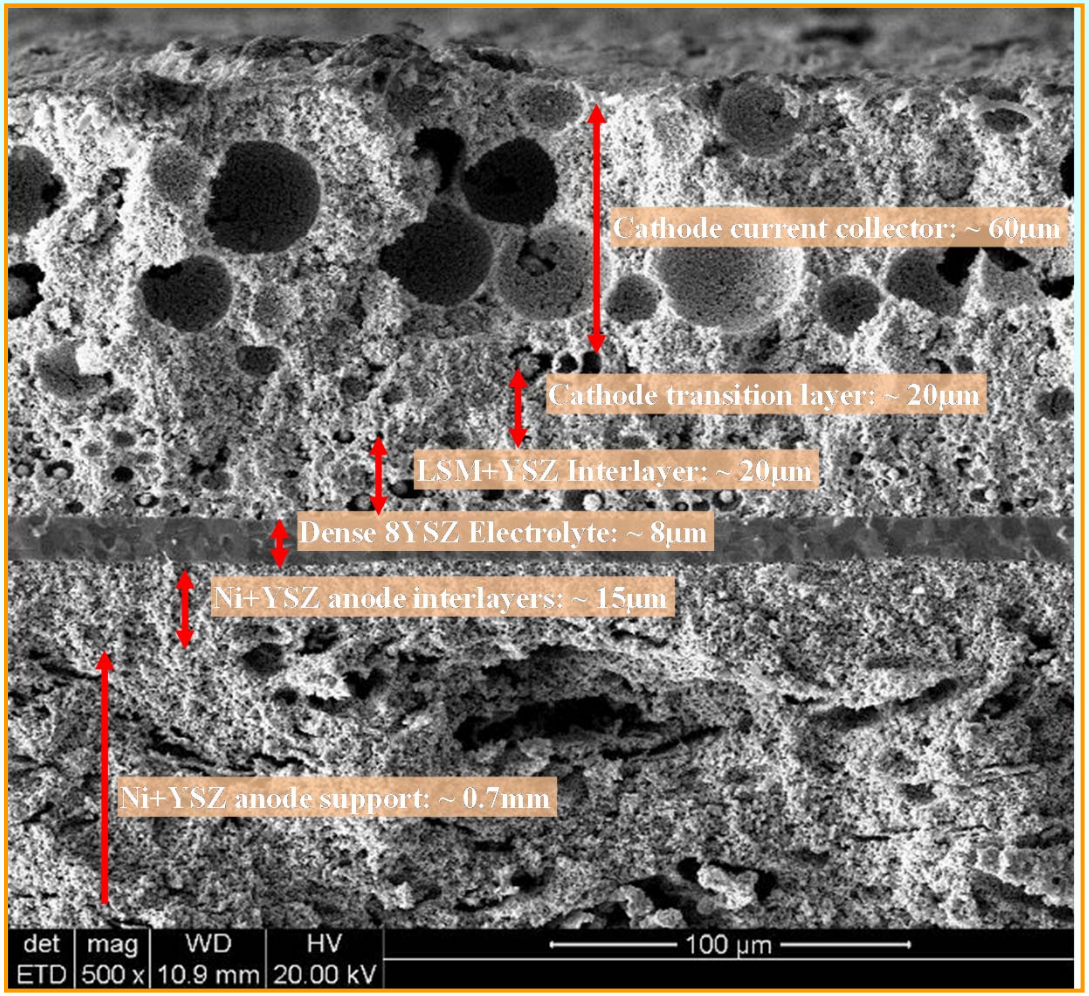
Baseline cell fabrication for infiltration studies

- 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/CCCL deposition by screen-printing & firing.





Cell Construction and Test



SEM micrograph of a baseline cell

- In this study, all cells were constructed with:
  - Ni-YSZ anode support (~0.7 mm)
  - YSZ-based electrolyte (8 μm)
  - **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 cm^2
  - Single cell: 100 cm^2
- Test conditions:
  - Either H_2 or a diluted H_2 as the fuel
  - Low fuel utilization for button cells
  - Controlled utilization for single cells and stacks, typically 40% ~ 80%
  - **Cell temperature** fixed @ 800ºC for LSM-based cathode cells and 700ºC for LSCF-based cathode cells

Single-step Infiltration Technique

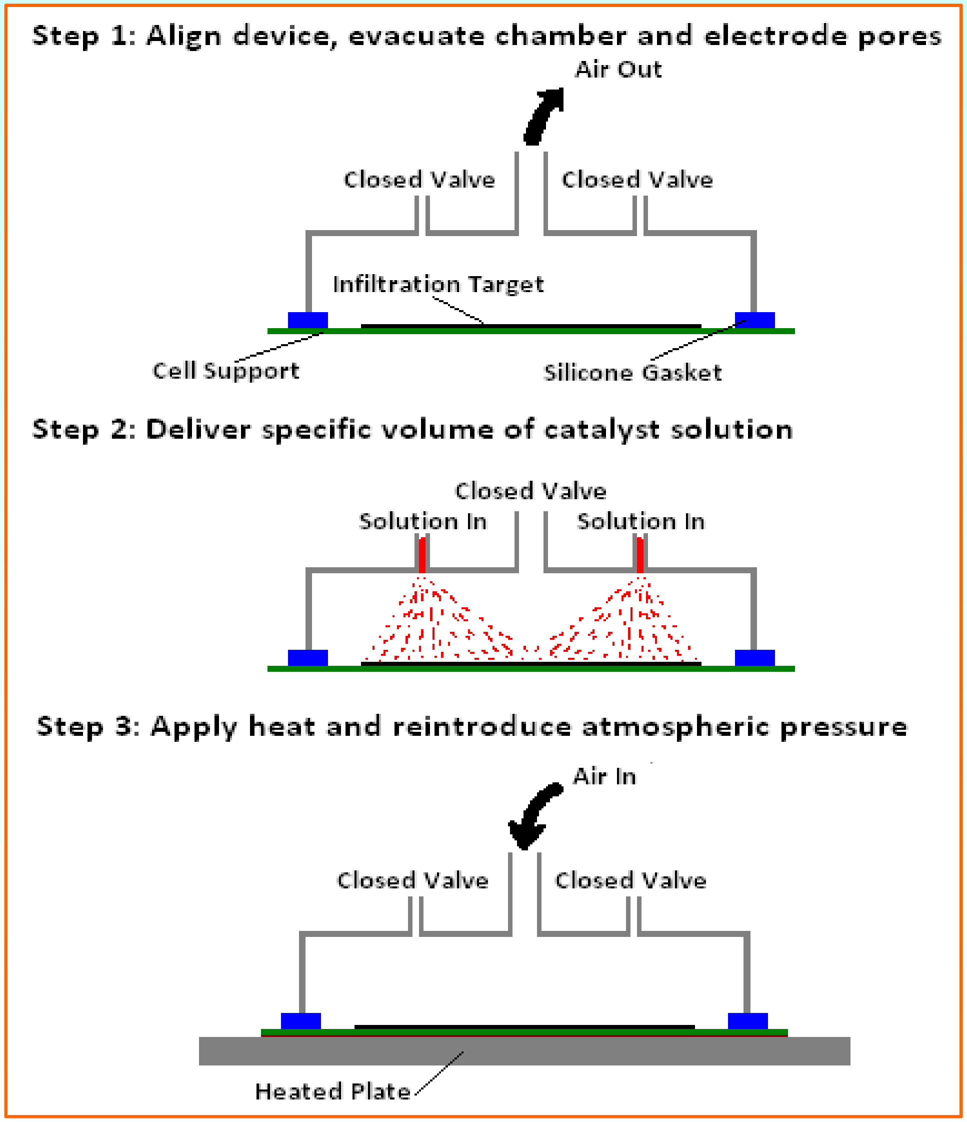
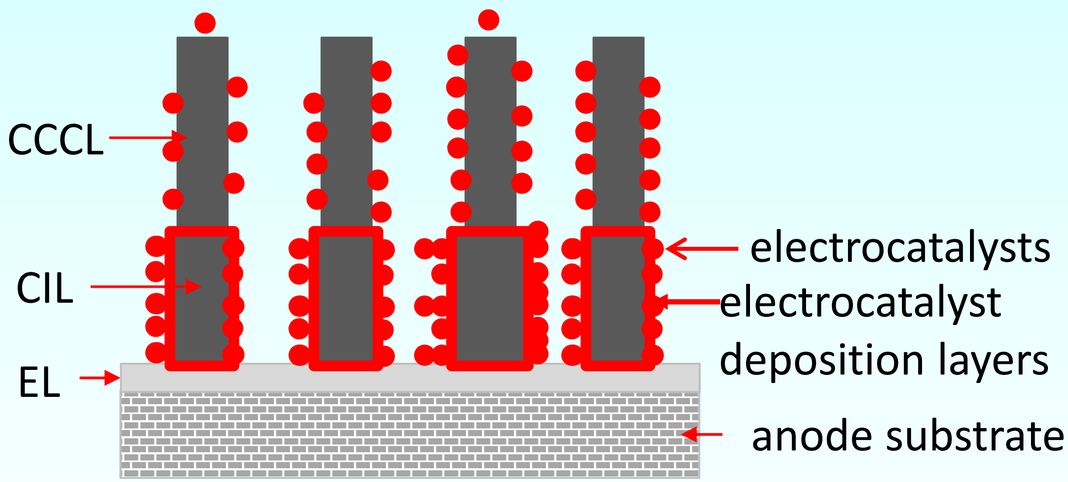
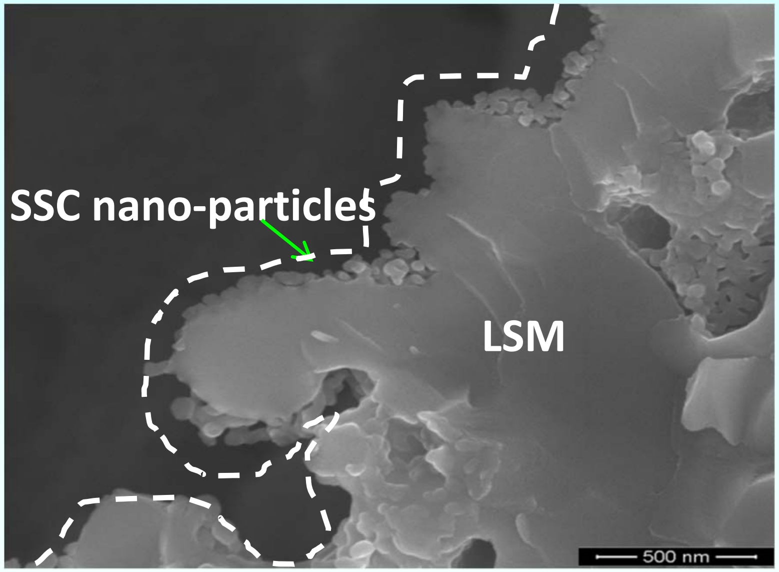


Diagram of the single-step Vacuum-Pressure-Infiltration-Thermal Treatment (VPIT) technique, involving:

- 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 ~850ºC
  - Evaluate effects of various electrocatalysts on performance improvement, e.g. SSC, LSC, LSM, LSCF
  - Repeatability/durability
  - Scaling up from 1”-button to 4”x4”

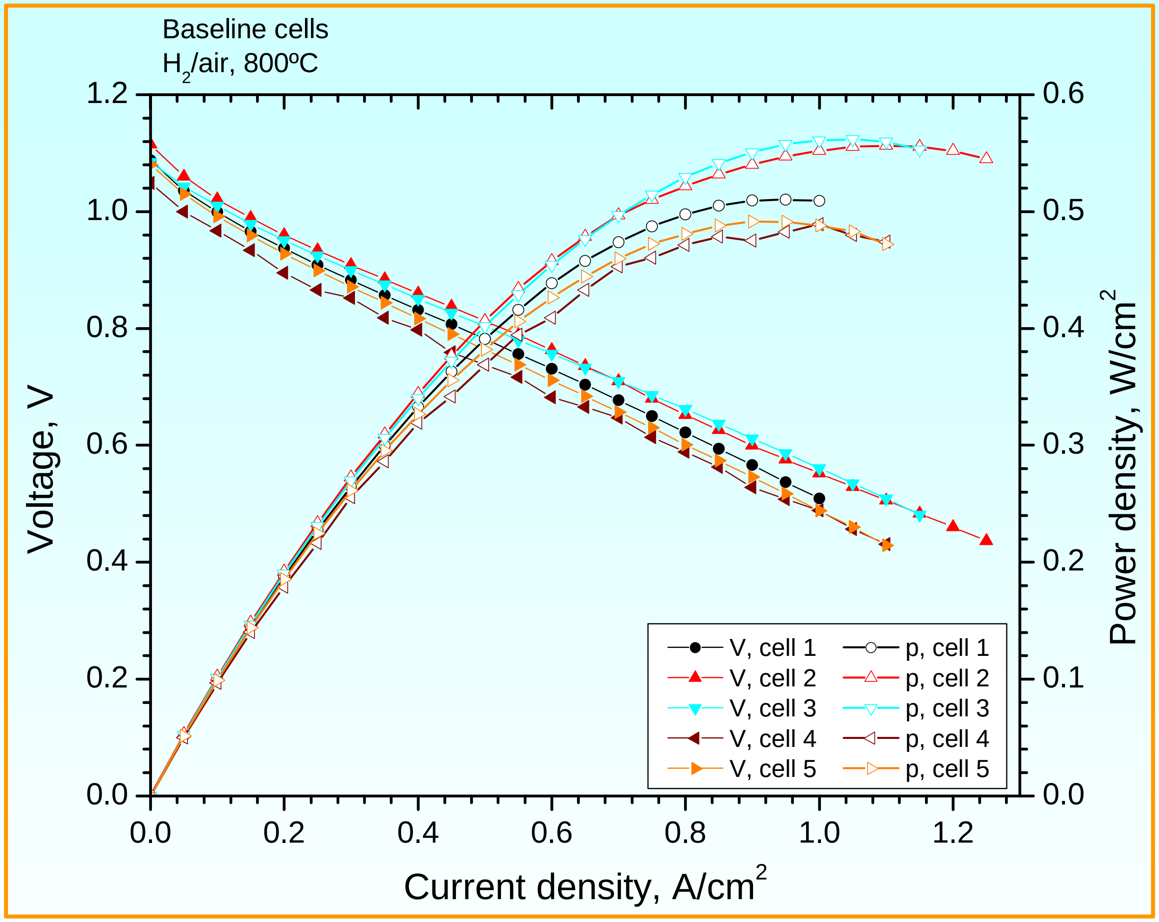
Infiltration Technique Implementation





- Reconstruct CIL and CTL to ensure an efficient infiltration of a catalyst quickly to the ERS (TPB & 2PB)
- Avoid excessive agglomerates and to ensure a good coverage of a catalyst along the cathode grains

Baseline Cell (LSM-based) Tests

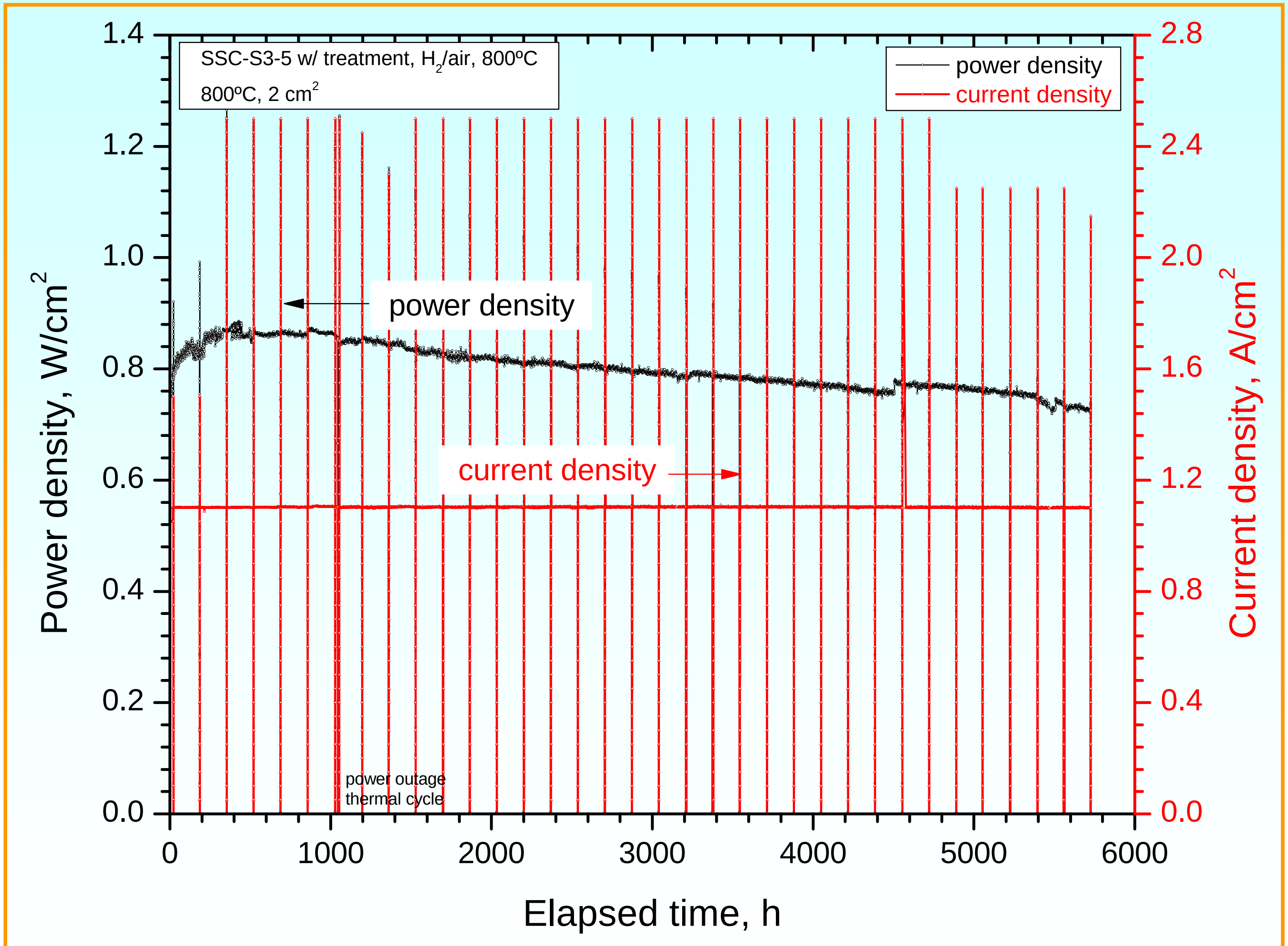


- Button cell baseline tests (w/o catalyst infiltration) for repeatability
- Typical power density: 0.4~0.5 W/cm^2 @ 0.7V; 0.5~0.56 W/cm^2 at peak

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

Nano Electrocatalyst Infiltration Effects

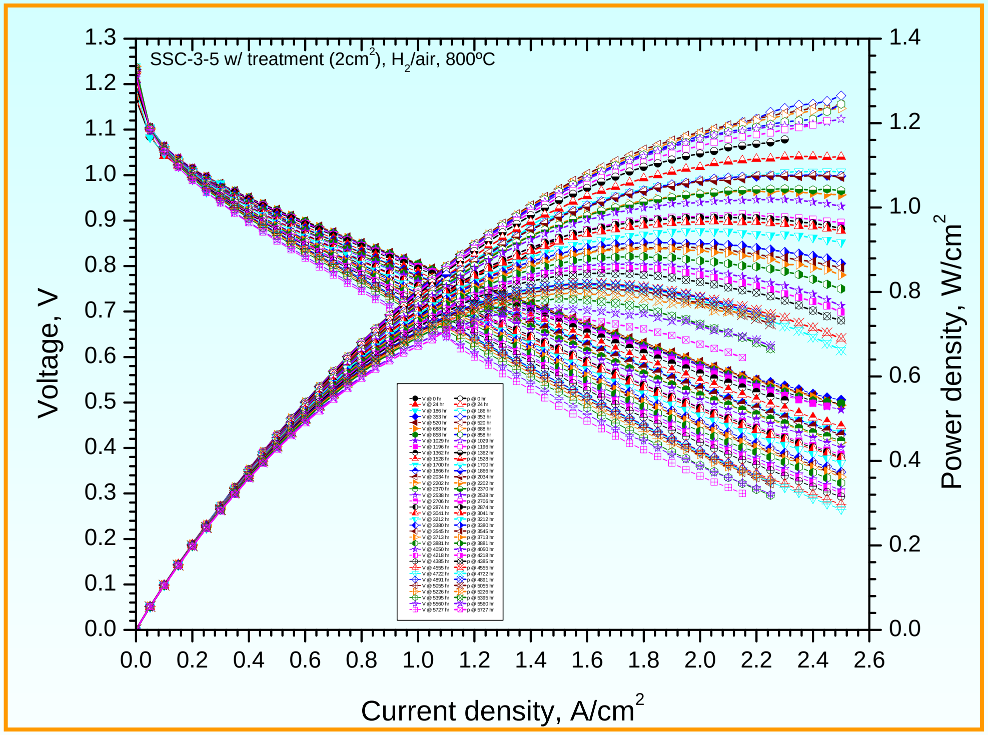
Long-term test results of a button cell

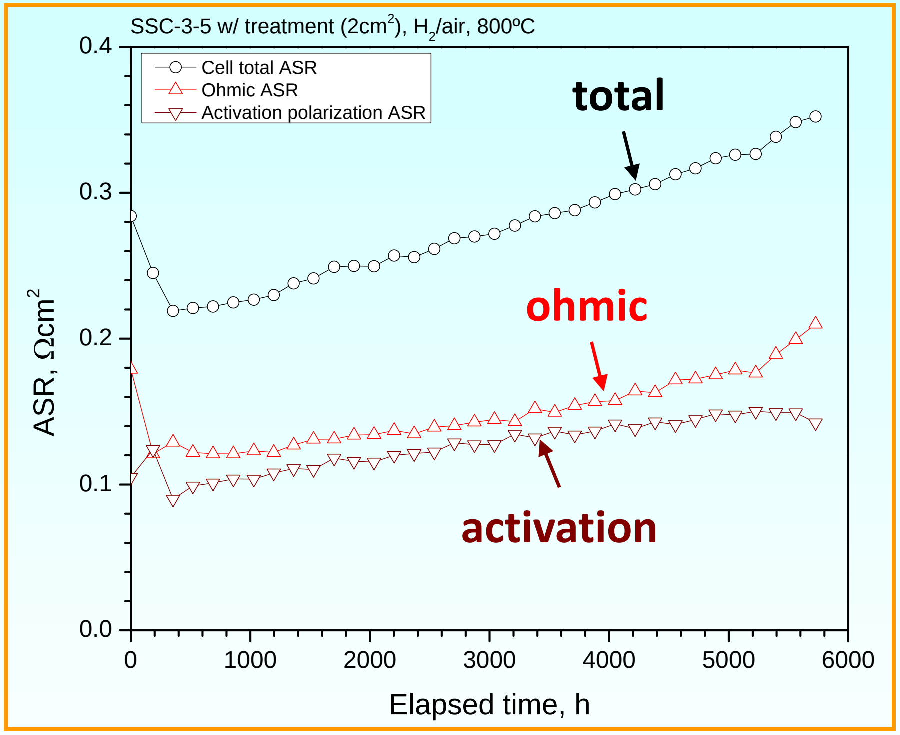


- 1" button cell (2cm²)
- T_cell @ 800C, H_2/air
- upon infiltration, cell power density at 0.7V increased from 0.55 W/cm² to 0.86 W/cm² (> **60% improvement**)
- performance improved over **+4.5%/1khrs** during the initial 1000 hrs test until a power outage,
- cell overall degradation rate @ **-2.56%/1khrs** over **57,00 hrs (over 8 months)**

Significance of Catalyst Infiltration

VI tests & EIS measurement at scheduled time (weekly)

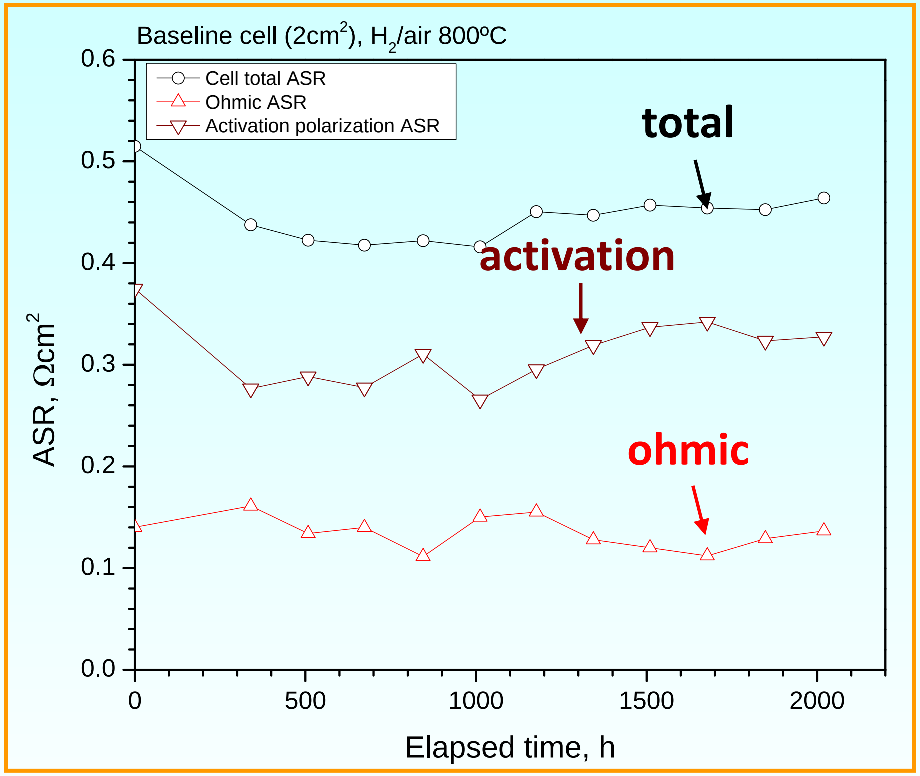




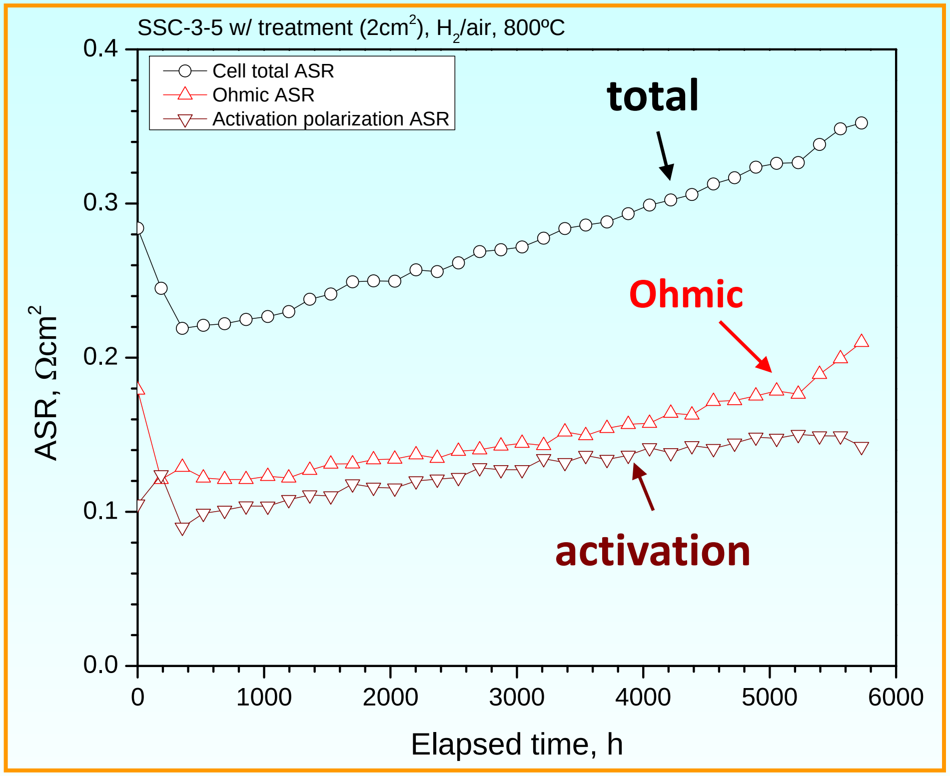
Activation polarization losses were less than Ohmic losses

Benefits from Catalyst Infiltration – ASR standpoint

Baseline cell (w/o infiltration)



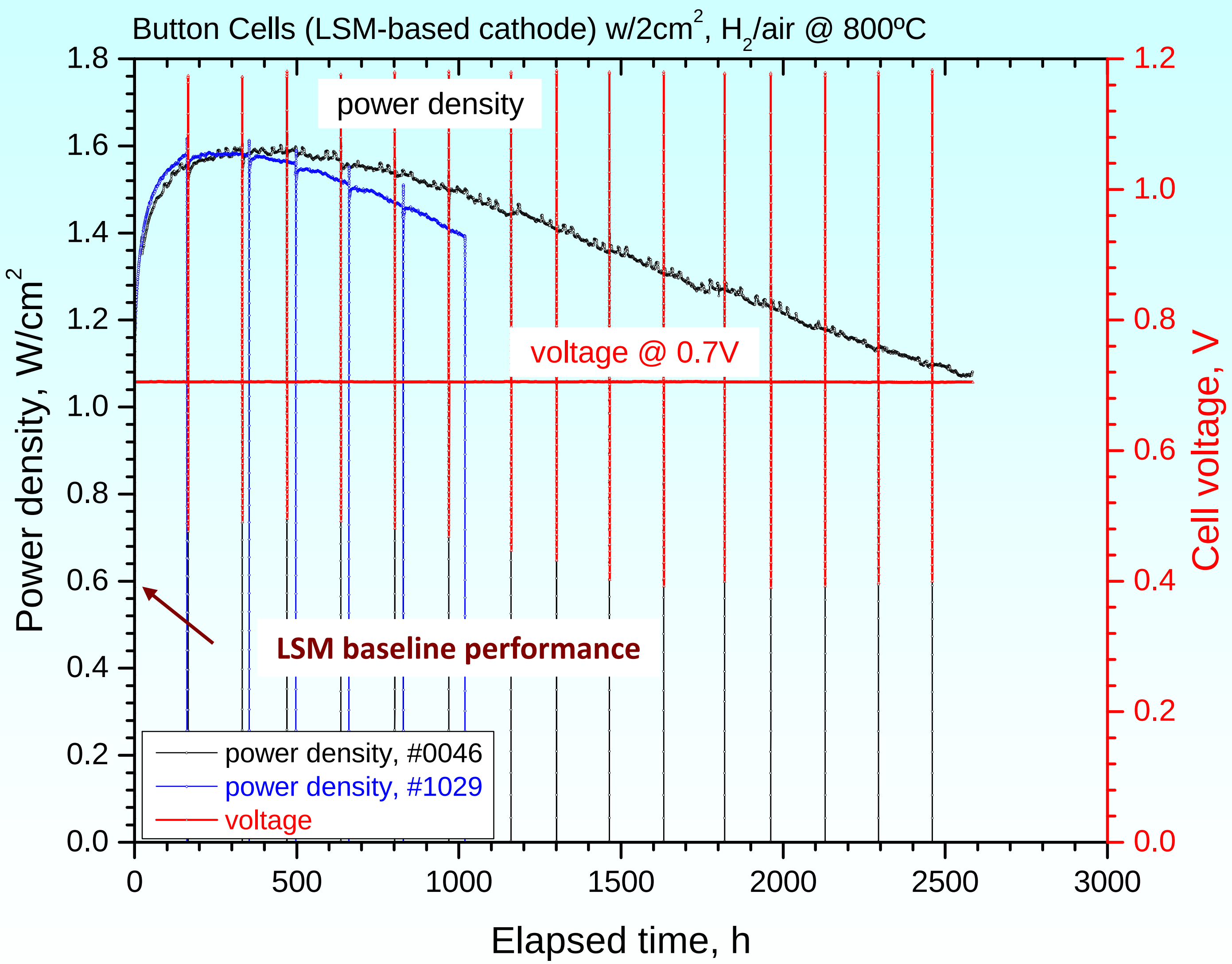
Cell (infiltrated w/ SSC)



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

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

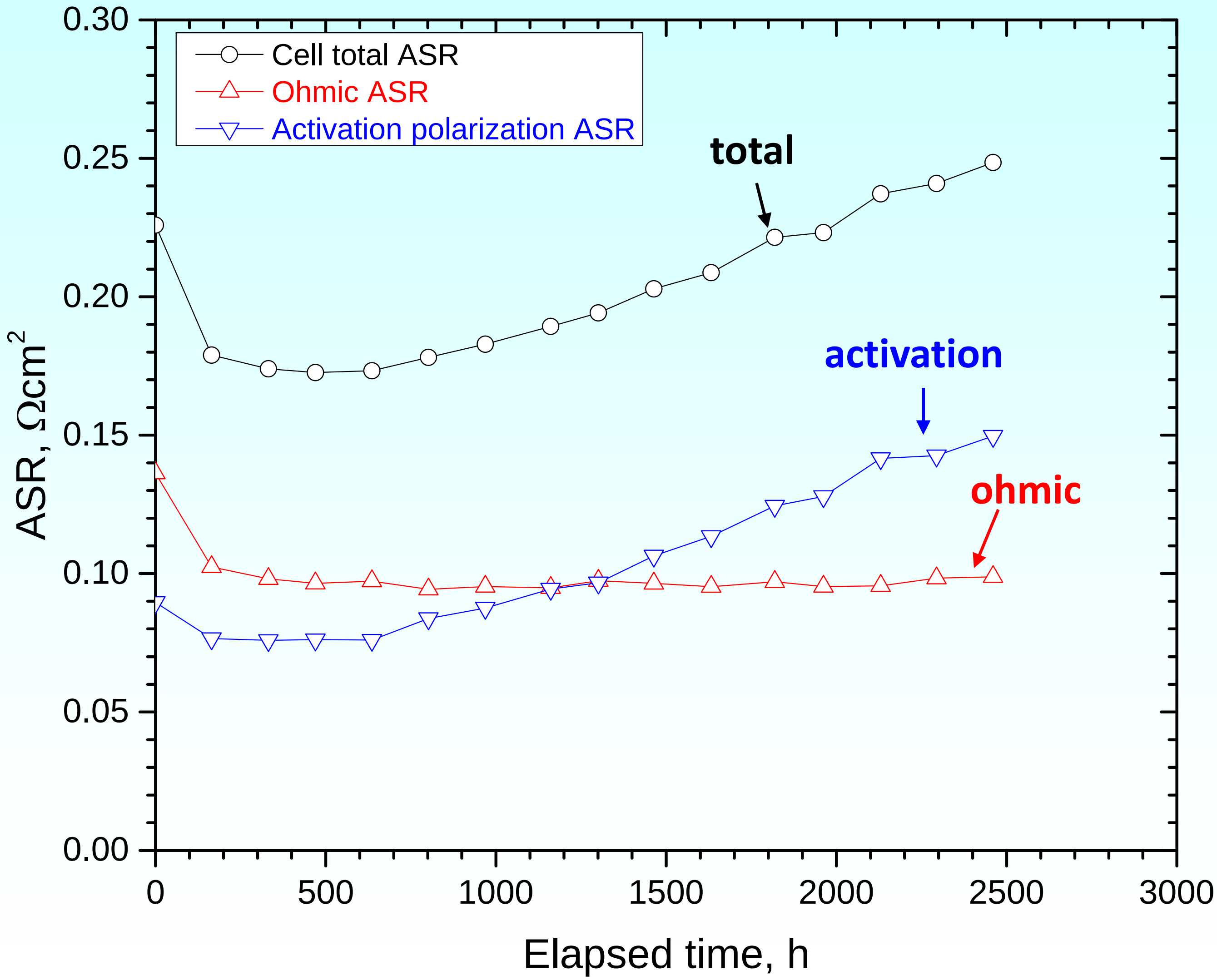
Nano-sized Super Electrocatalysts



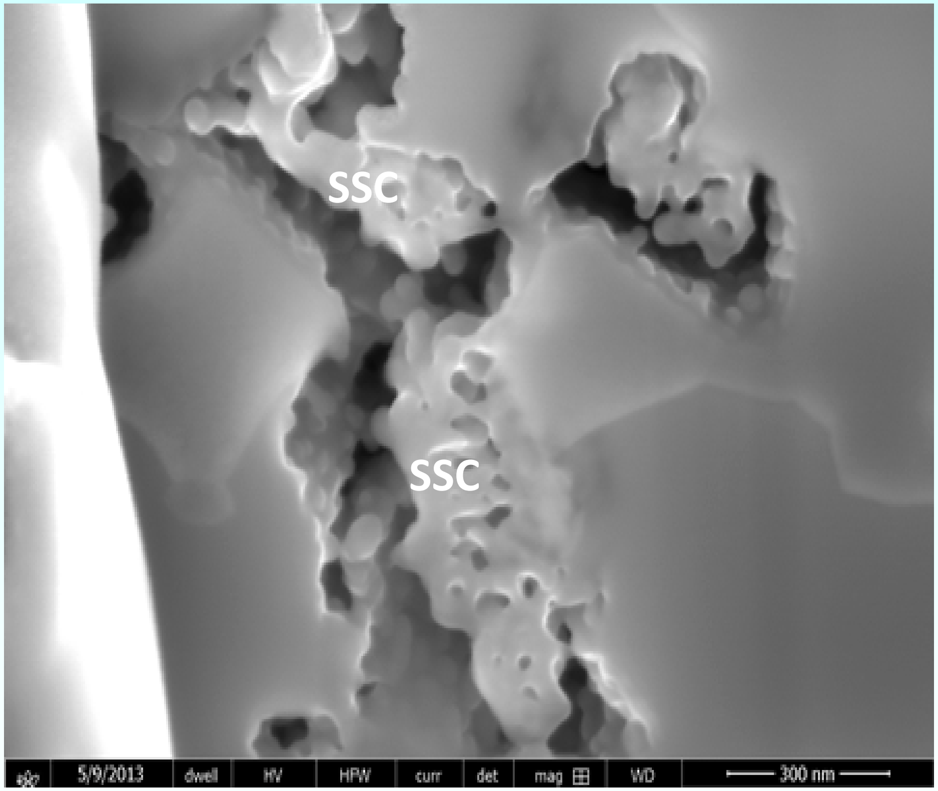
- Nano-sized electrocatalyst
- upon infiltration, cell p-density @ 0.7V increased from 0.55 W/cm^2 to **1.58 W/cm^2** (> **180% improvement**)
- 1.5%/1khr improvement over 1khr test
- High degradation rate

Performance Characterization

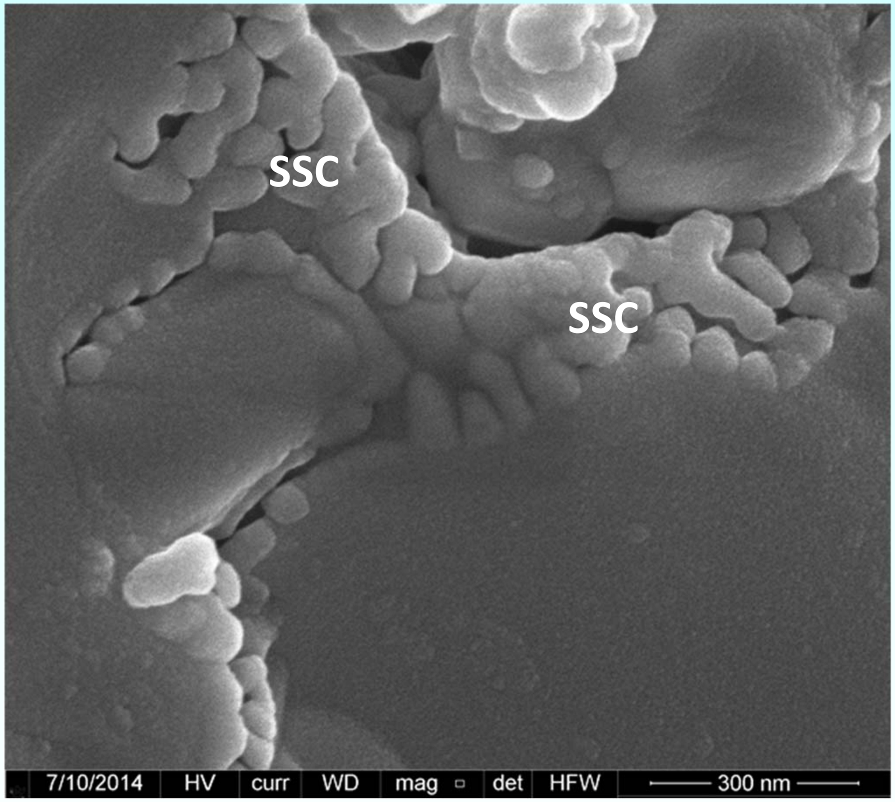
VI tests & EIS measurement at scheduled time (weekly)



Microstructure Changes after Long-term Tests

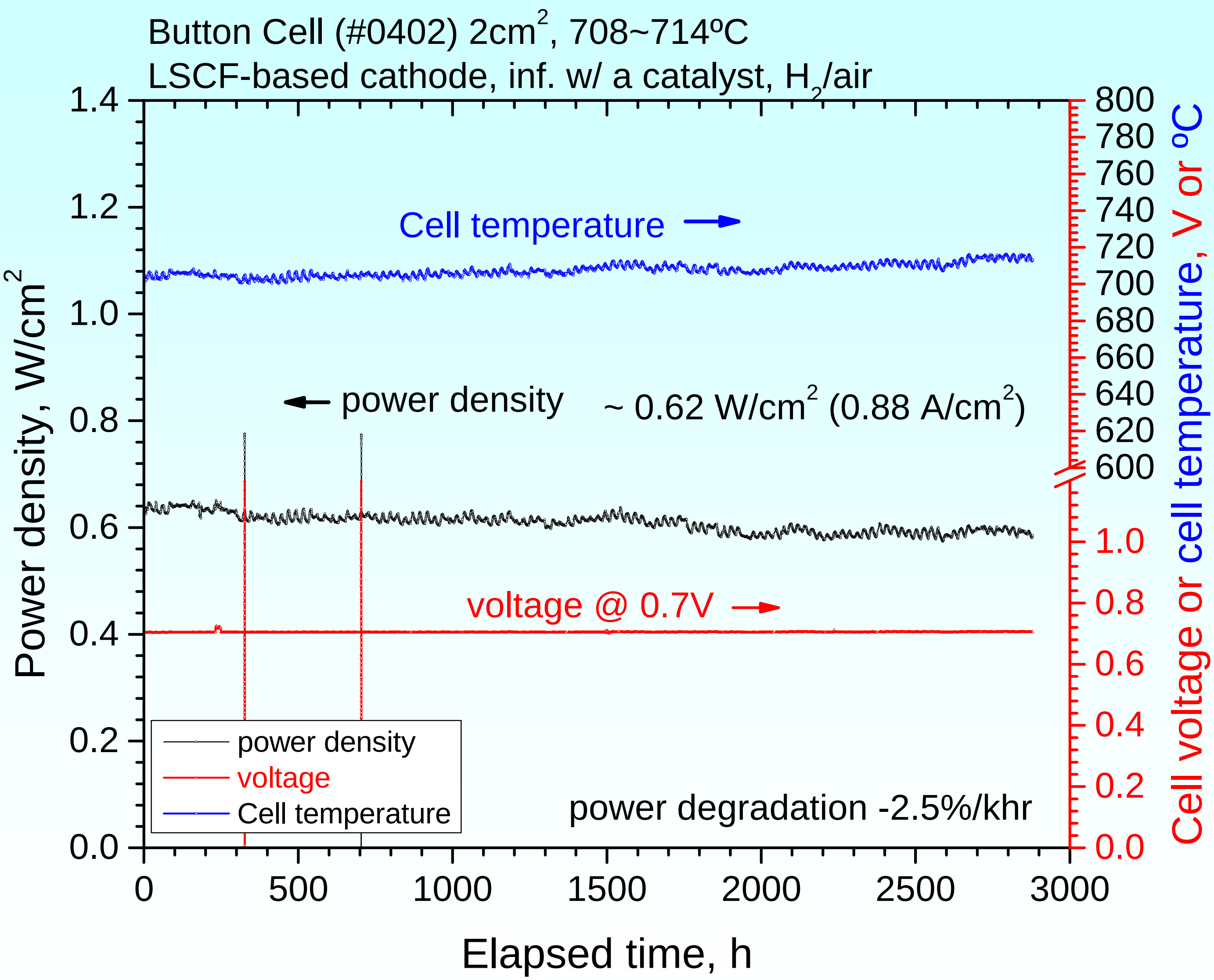


Pristine cell w/ SSC infiltration, sample was prepared by FIB cut near electrolyte (CIL)



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

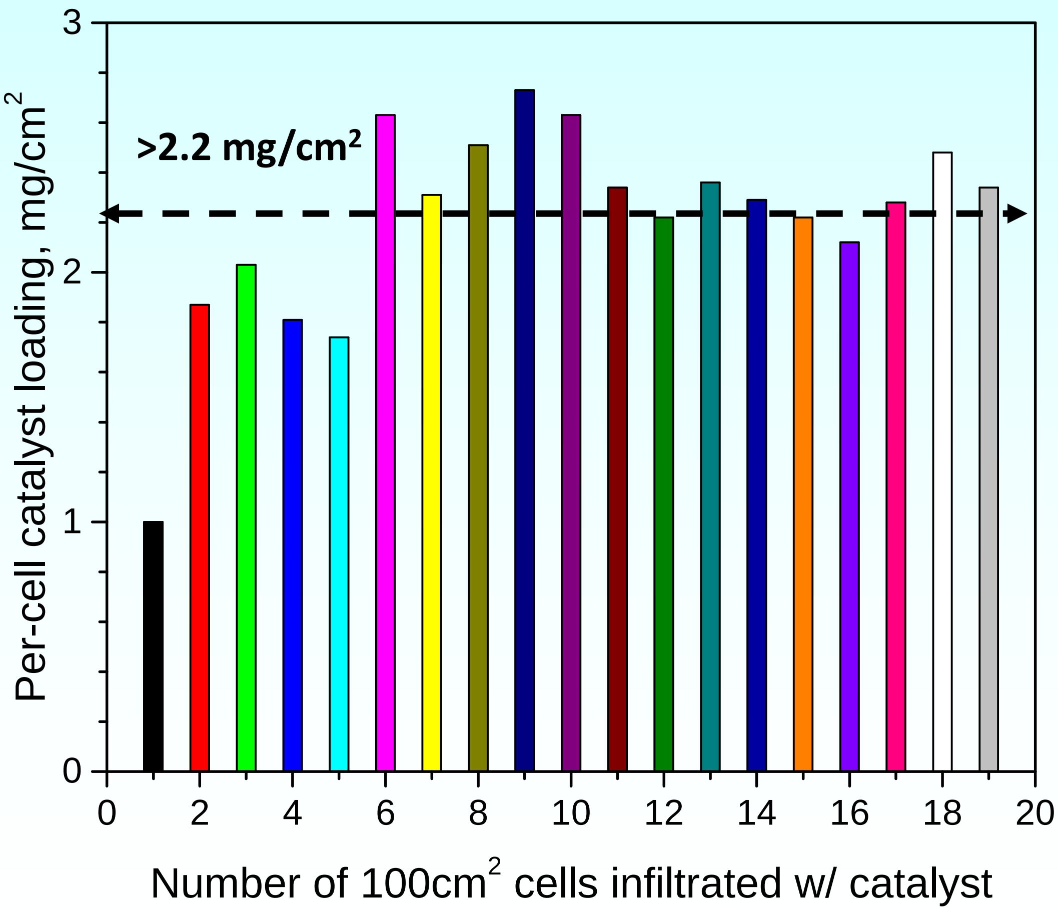
Electrocatalyst Effects on LSCF-base Cathode



- LSCF-based cathode system experienced higher degradation @ high T
- A complex system compared to LSM-based
- Lowering operating T improves stability
- Fixed V@0.7V. (j @ ~ 0.88 A/cm^2)
- Over 35% improvement upon electrocatalyst infiltration
- Power degradation rate ~ -2.5%/khr

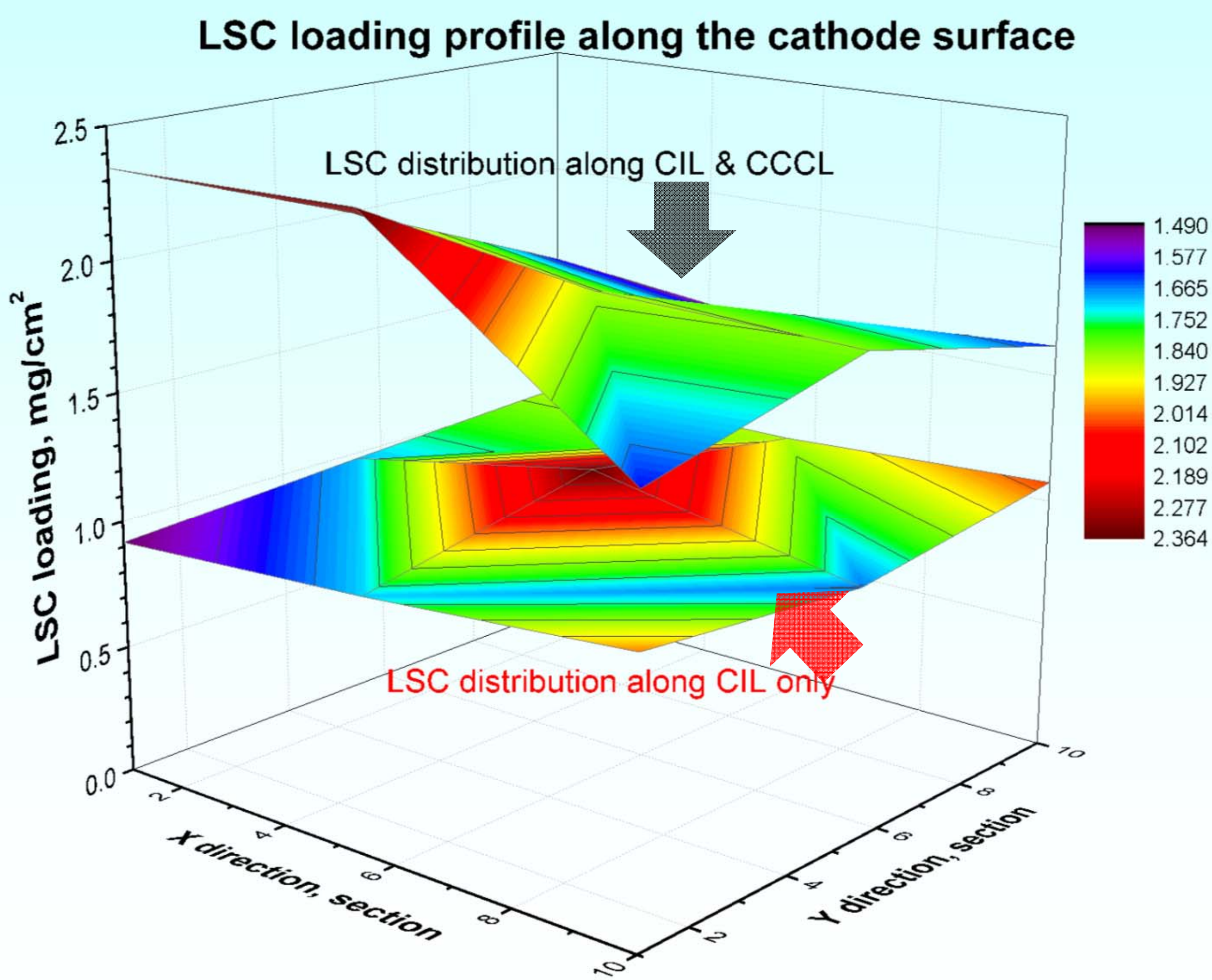
From Button Cells to 100cm² Cells

- Implement the infiltration technique to large cells
  - Scaleability
  - Nano electrocatalyst distribution
  - Repeatability



Catalyst Loading Profile Study

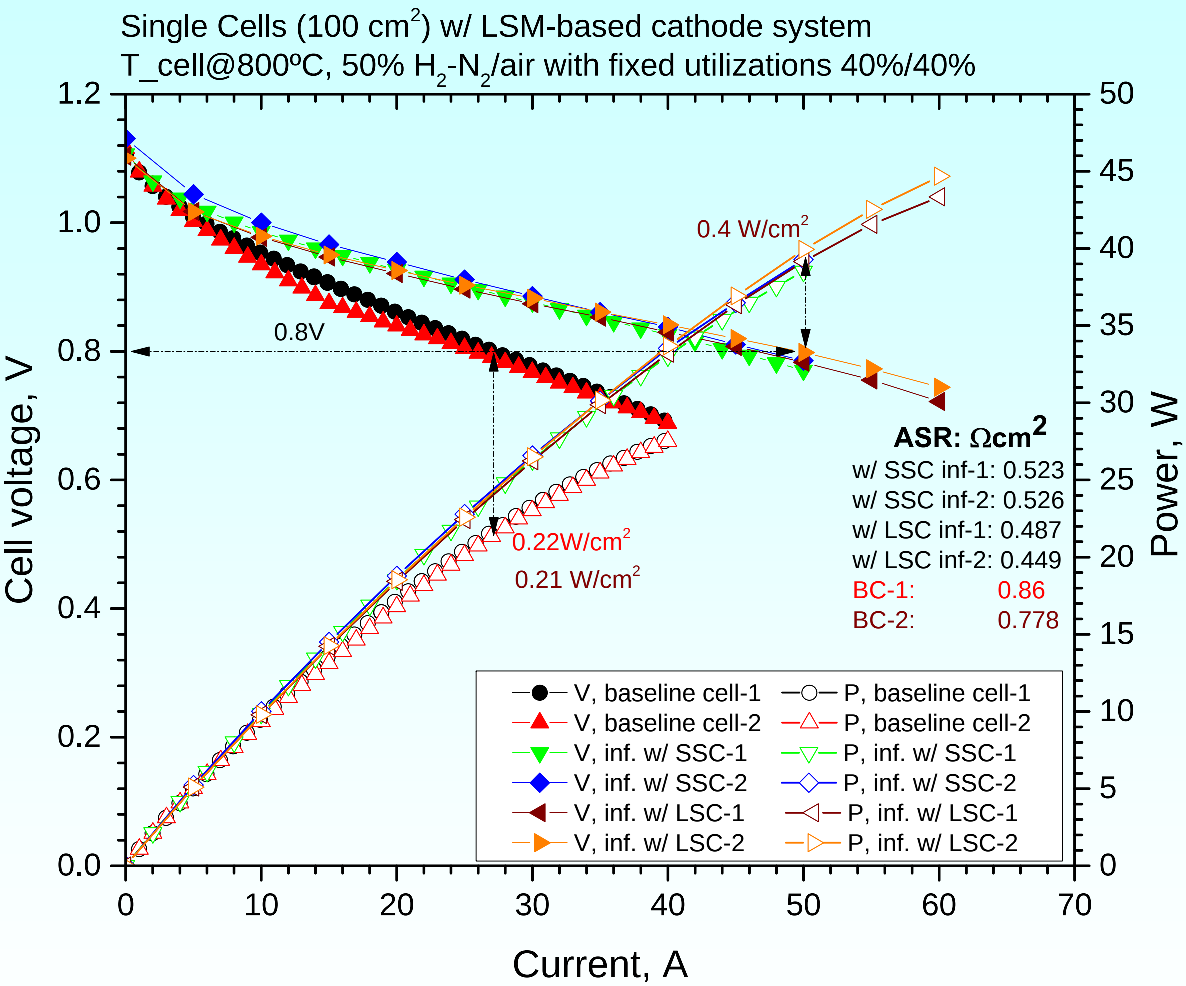
Study of LSC loading distribution along 4”x4” single cells (100 cm^2) – characterization from corner to corner



Single Cell (100 cm^2) Evaluation

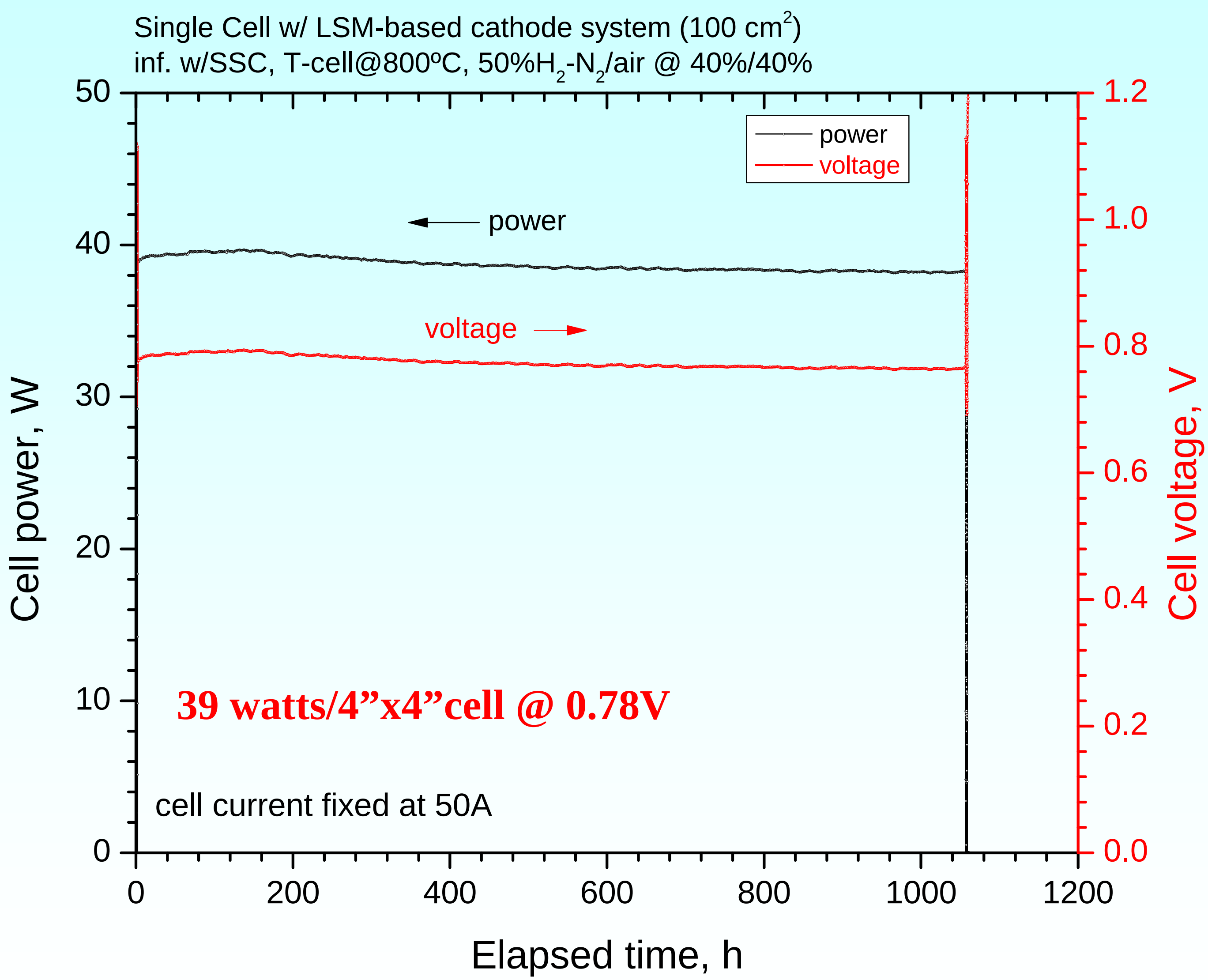
all-ceramic test-rig for single cell tests

- free-of Cr sources, but Cr-source can be introduced in a controlled fashion
- no metallic IC
- mimic stack compression & flow patterns
- Moisture can be introduced to both electrodes
- Flexible fuel feeds



Six-single cell performance comparison:
two baseline cells, two w/ SSC inf. & 2 w/ LSC inf.

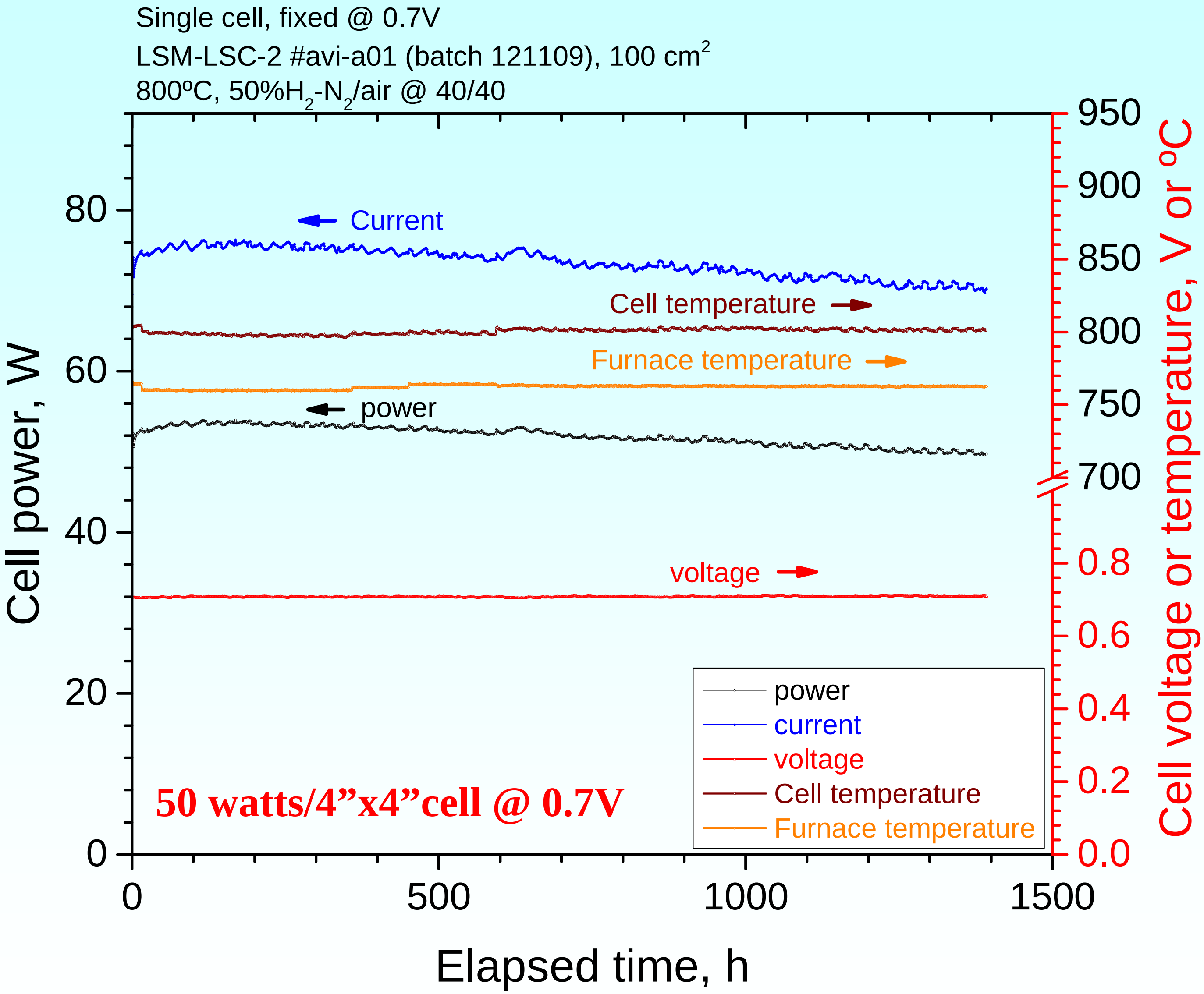
Long-term Test of a Single Cell w/ SSC Infiltration



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

- Cell temperature adjusted to 800ºC
- Dilute fuel w/ fixed 40% utilizations
- Under a constant current of 50 A (0.5A/cm^2)
- Cell voltage ~ 0.78 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/cm^2-hr

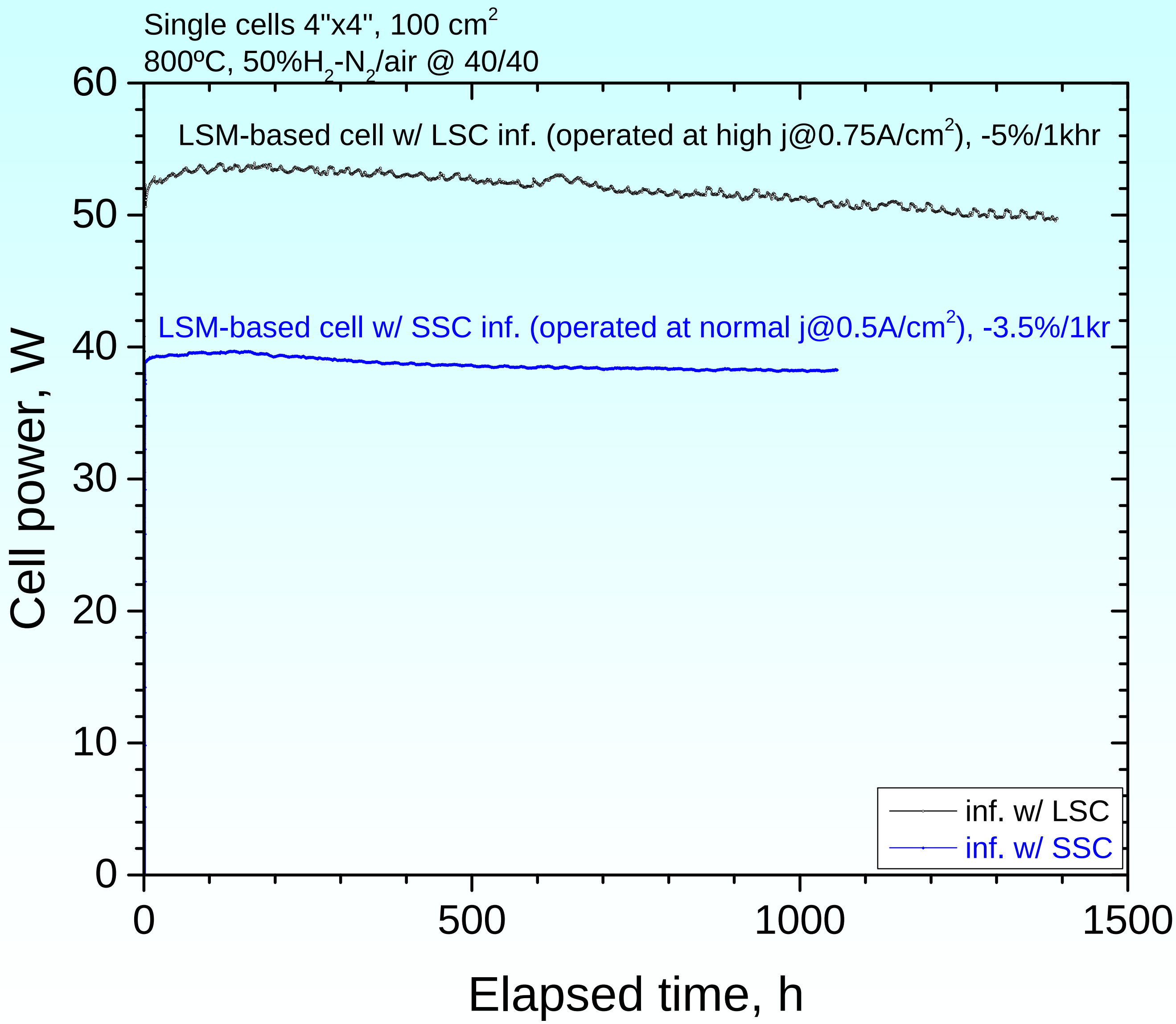
Long-term Test of a Single Cell w/ LSC Infiltration



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

- TC to monitor cell cathode T (800ºC)
- Furnace T was 760ºC
- Dilute H_2 fuel w/ fixed 40% utilizations
- Under a C.V.@0.7V
- Cell current 75~71A (0.75~0.71 A/cm^2)
- Power improved by ~ +12%/1khr during initial 200-hr test
- > 14,00-hr test (on-going), p degradation rate: -5%/1khr, or -0.028 mW/cm^2-hr

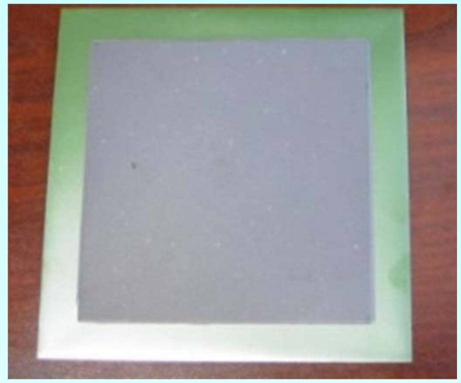
Cell Operating Condition Effect on Degradation



- Effects of cell operating conditions on cell life
- Higher performance had higher degradation rate
- "sweet spot" operating conditions? (need "Hurricane Model" for prediction)

Scale-up Ability

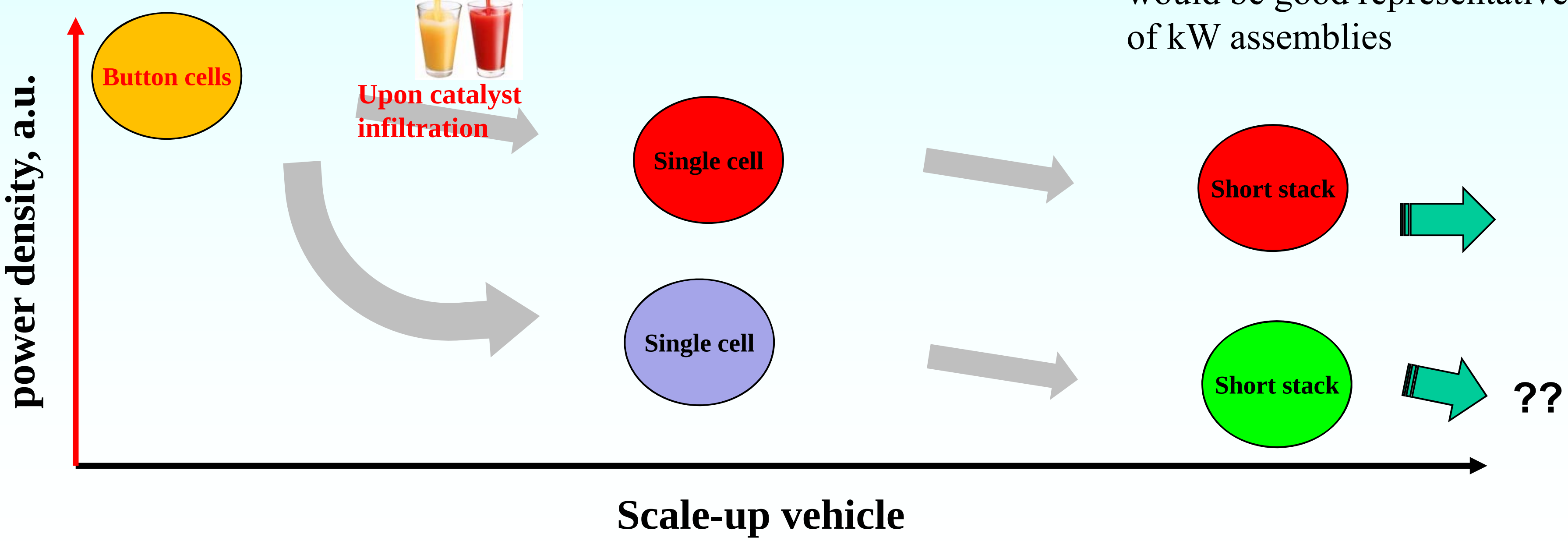
2.8 W/cell (1.4W/cm^2)



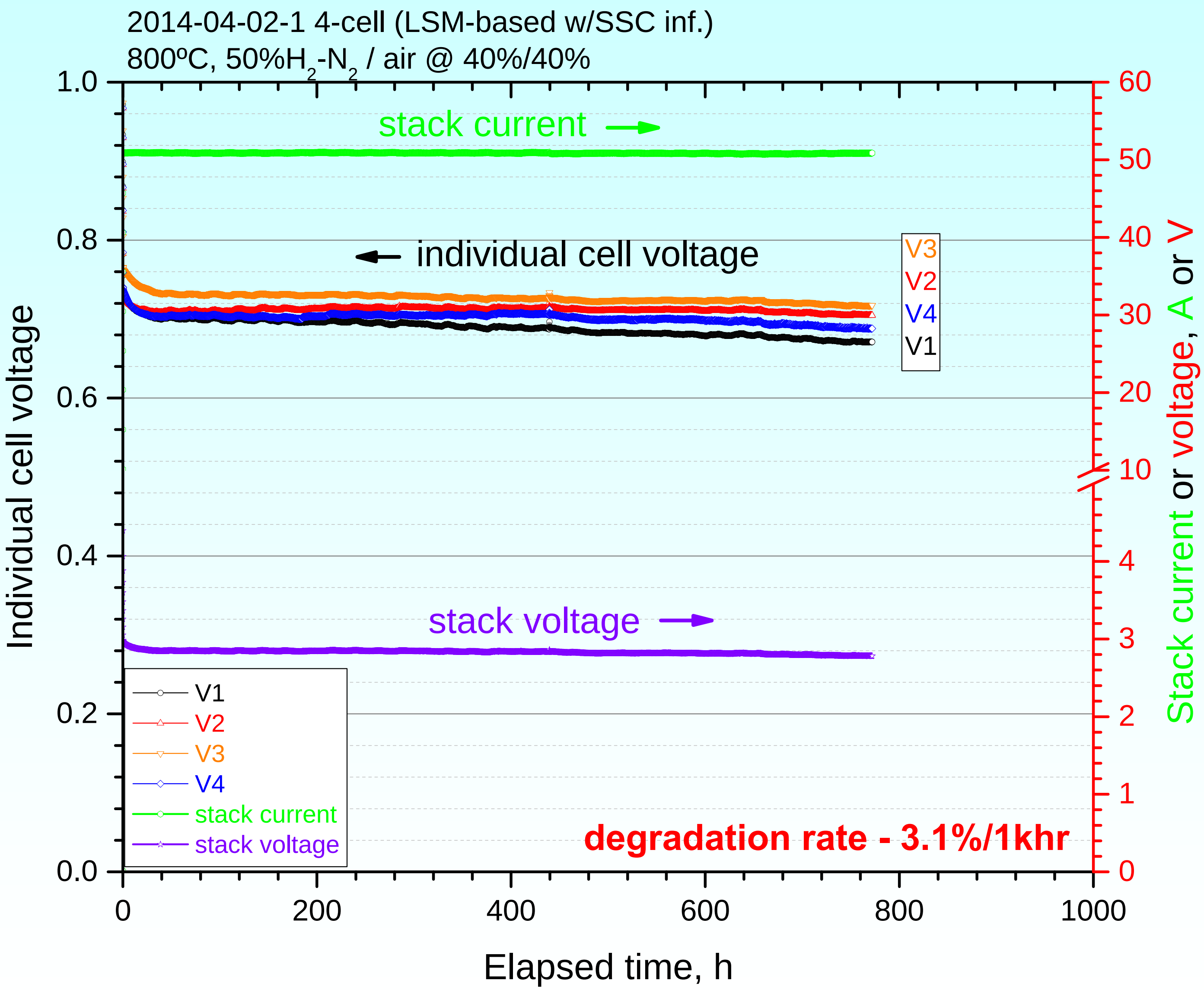
50 W/cell (0.5 W/cm^2)

145 W/4-cell stack (0.36 W/cm^2)

Short stacks (3~10 cells) would be good representative of kW assemblies



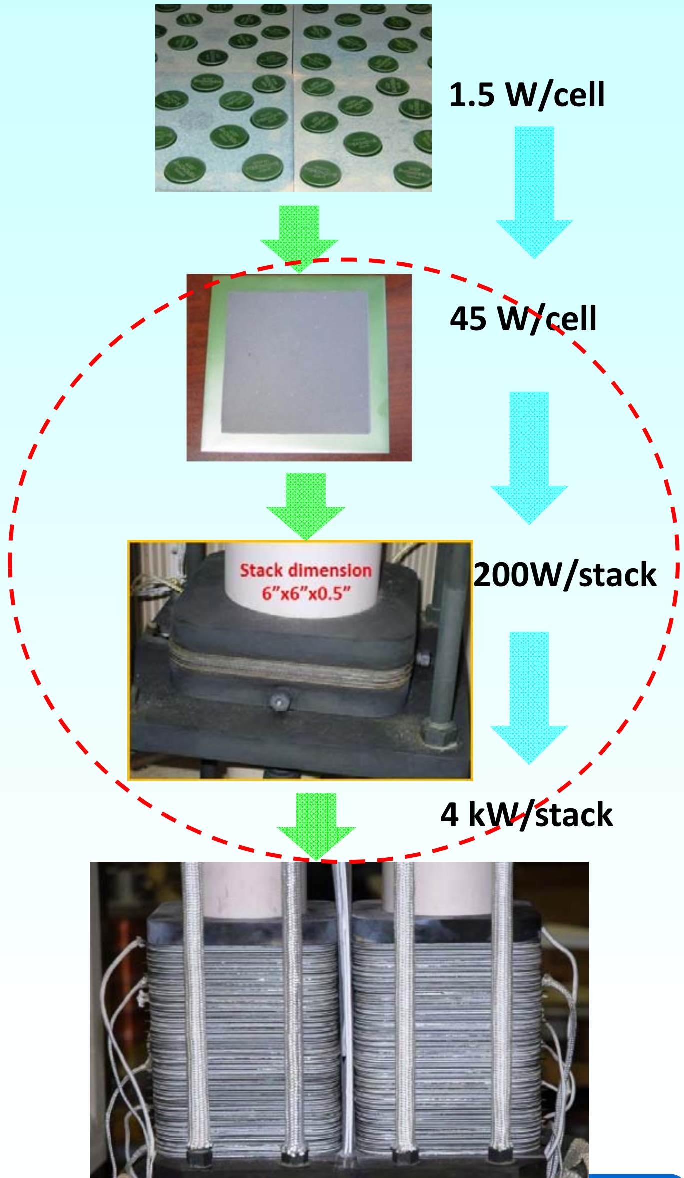
Short Stack Validation



- All four cells were infiltrated w/ SSC
- Top/bottom cell had relatively lower performance than middle cells
- Overall stack performance improvement > 30% after infiltration
- Degradation rate ~ -3.1%/1khr

Summary/Future Work

- Infiltration of a nano-sized electrocatalyst can be 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. However, certain protocols have to be developed for implementing infiltration process on scalable cells;
- Continue to perfect the VPIT processes
  - Explore other catalyst effects under various operating conditions
  - Optimize catalyst structure
  - Identify the electrode degradation attributions
  - Perform techno-economic evaluation
- Evaluate scale-up cells (100 cm^2) and stacks (200W class) for proof-of-concept demonstration (built-on MSRI's standard SOFC products/ platforms)



Acknowledgement

- This material is based upon work supported by the Department of Energy SBIR Phase II Program under Award No. # DE-SC0006374
- Phase II Project Manager Joseph Stoffa, Briggs White, Shailesh Vora, and the entire NETL SECA program management team

Thank you!