Long-Term Degradation of LSM-Based SOFC Cathodes: Use of a Proven Accelerated Test Regimen

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Outline

- Project objectives
- Background findings under normal and accelerated operation
- Procedures
- Microstructure analysis after accelerated cell testing
  - Transmission electron microscopy (TEM) with energy-dispersive x-ray spectroscopy (EDXS) — 0 & 493 h
  - 3-dimensional reconstruction (3DR) — 0 & 72 h
- Performance under accelerated testing — 0, 72, & 493 h
  - V–I, P-I
  - area specific resistance (ASR) vs. time
- Conclusions & summary

Project Objectives

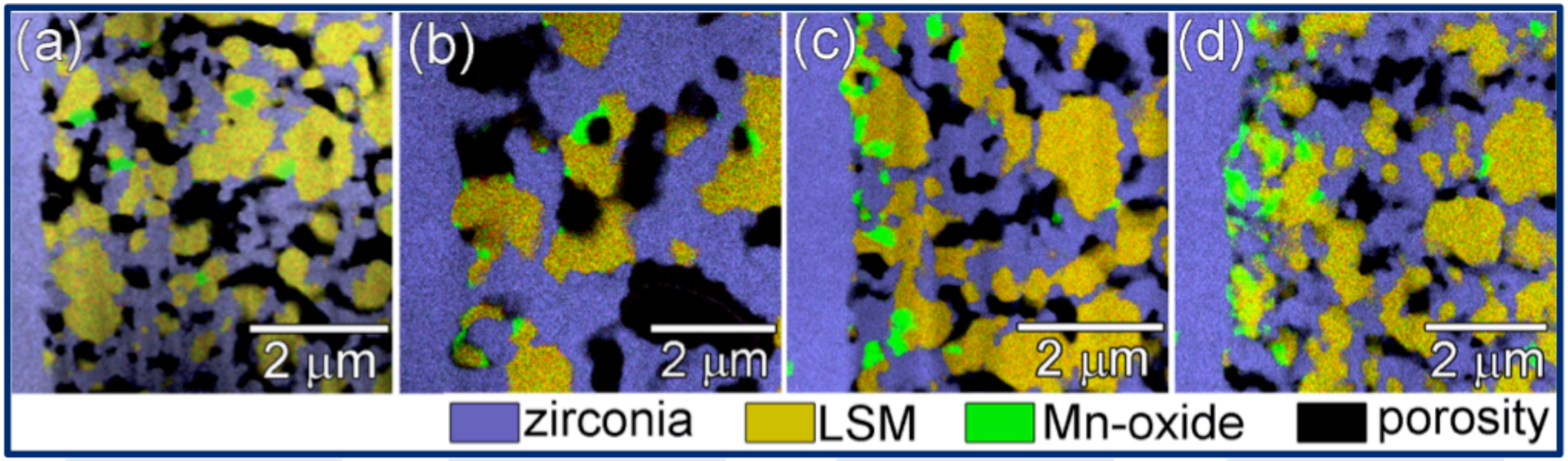
- **Overall objectives:**
  - Understand ***microstructural basis of long-term performance loss*** in SOFC cathodes based on lanthanum strontium manganite (LSM)
  - Develop strategies for ***optimizing LSM-based cathodes*** that achieve improved long-term performance while exhibiting microstructural and chemical stability ***for commercial fuel cell systems***

Project Objectives

- Implement an accelerated testing protocol that …
  - … subjects SOFCs to ***performance-limiting conditions*** more quickly
  - … replicates ***long-term microstructural changes*** in much shorter times
- ***Benefits:***
  - Testing/characterization cycles taking ***months, not years***
  - ***Design rules*** to guide refinements in cathode formulations

Prior work, normal conditions: TEM/EDXS

cells tested at 800 °C



as fired | 2 kh | 8 kh | 16 kh

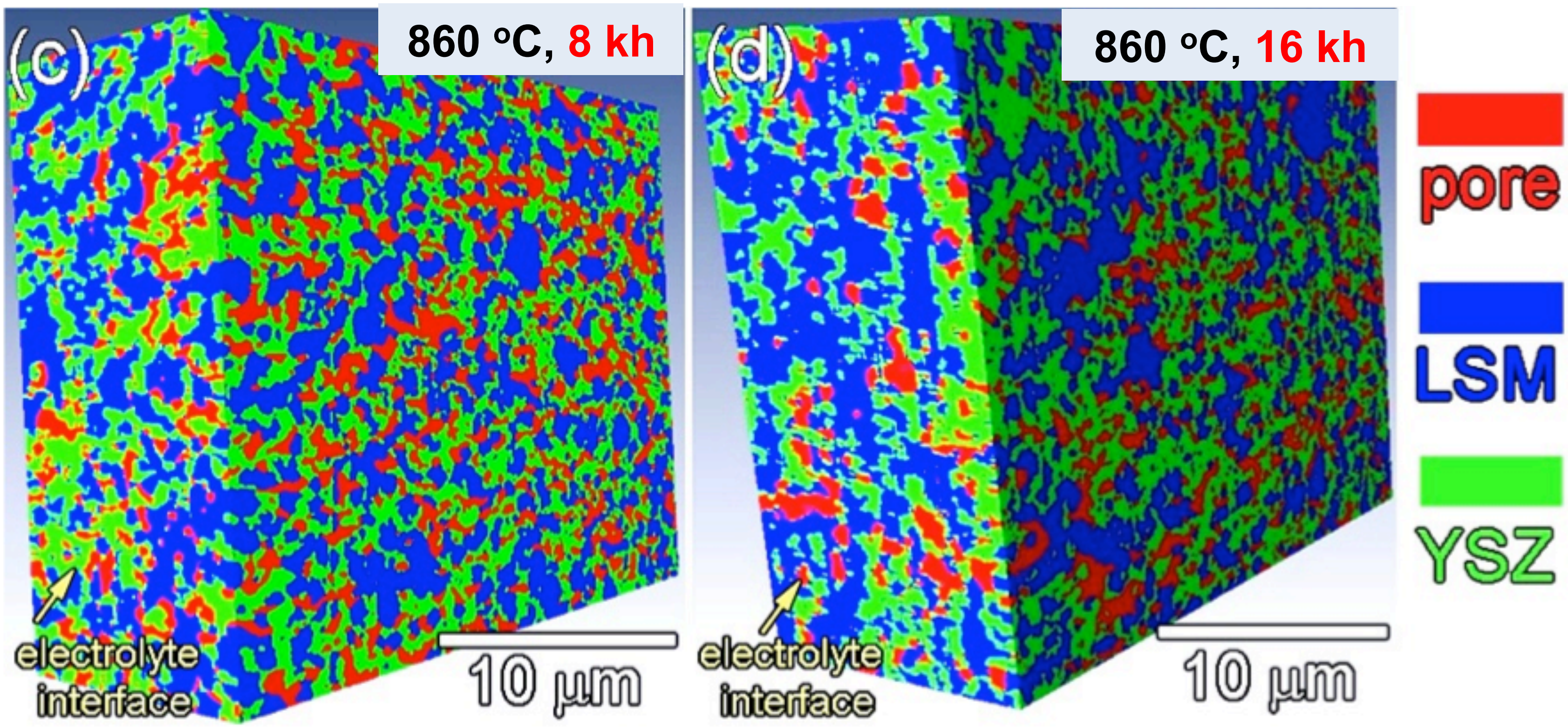
At cathode-electrolyte interface* after extended testing:

- Reduced porosity
- Accumulation of MnO_x

*) Left edge of each image

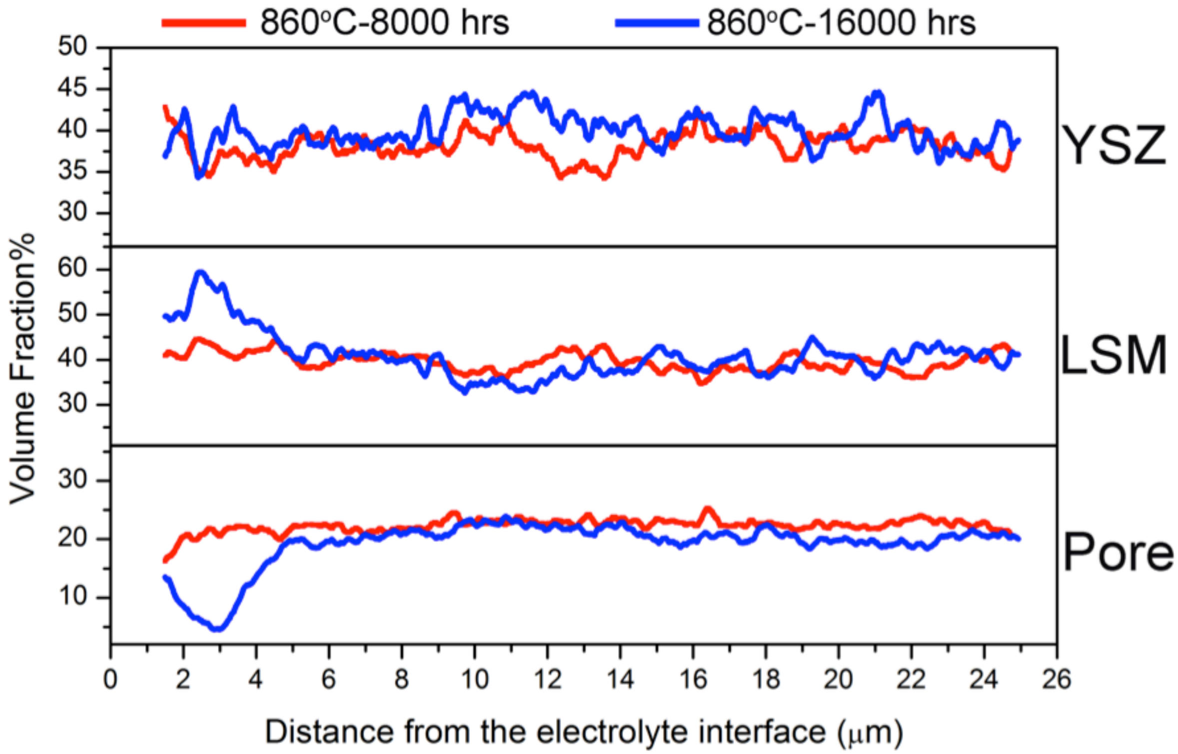
Ref.: H.-J. Wang et al., 14th SECA Workshop, Pittsburgh, Pennsylvania, July 2013

Prior work, normal conditions: 3DR



- 3D reconstruction (3DR) allows direct determination of:
  - Phase fractions and profiles
  - Tortuosity
  - Triple-phase boundary density (active and inactive)

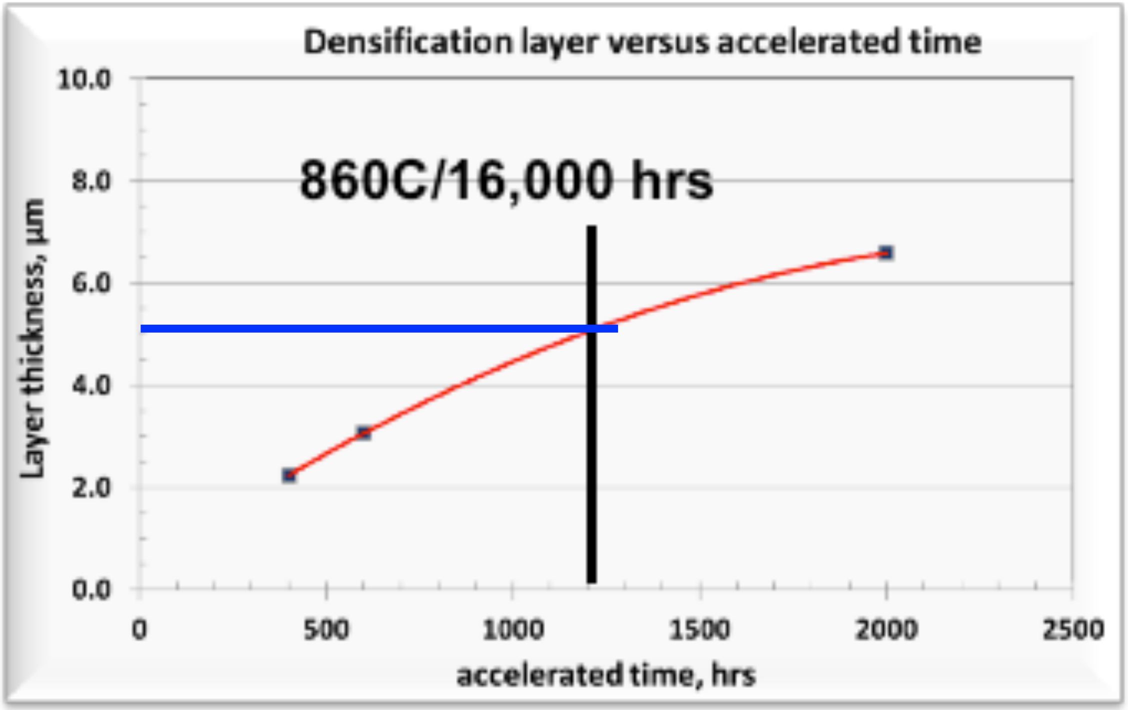
Prior work, normal conditions: 3DR



- ***Cathode densification*** near cathode-electrolyte interface
- Evident after ***16 kh/860 °C,*** but not after 8 kh/860 °C

Ref.: H.-J. Wang et al., 14th SECA Workshop, Pittsburgh, Pennsylvania, July 2013

Prior work, accelerated conditions: SEM



Thickness of densified cathode layer vs. duration of accelerated testing

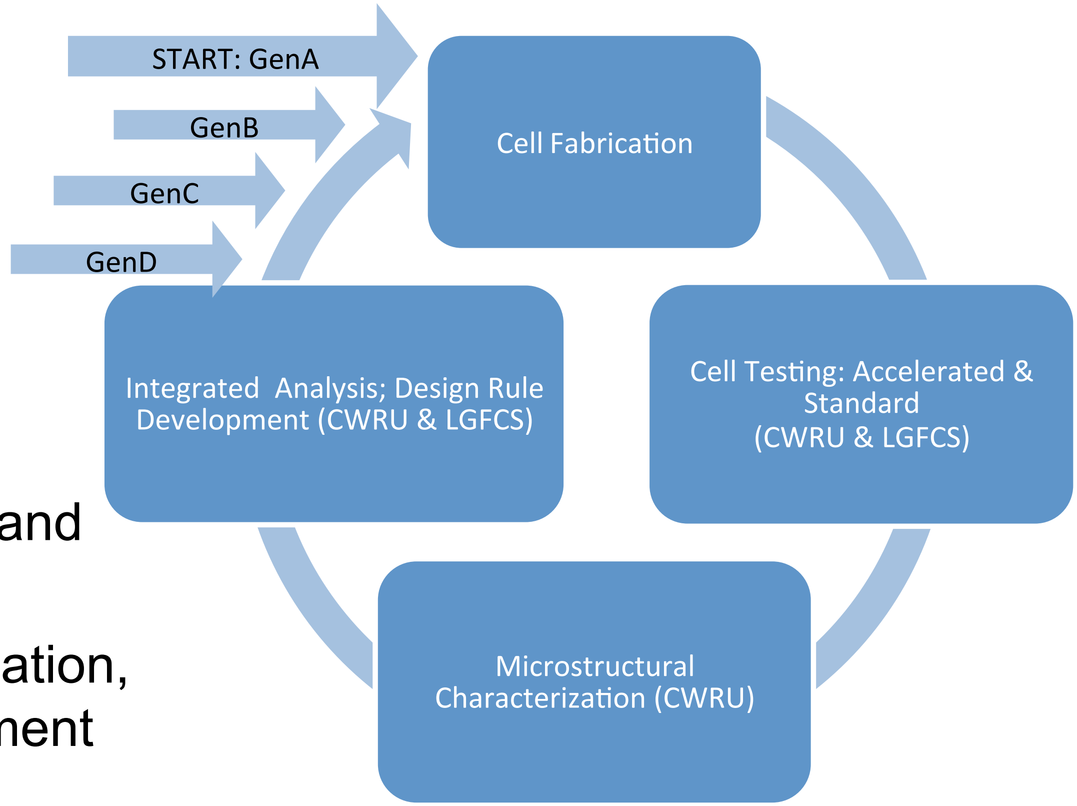
860 ^{o}C, 16 kh, normal conditions
OR
1.2 kh, accelerated conditions

→

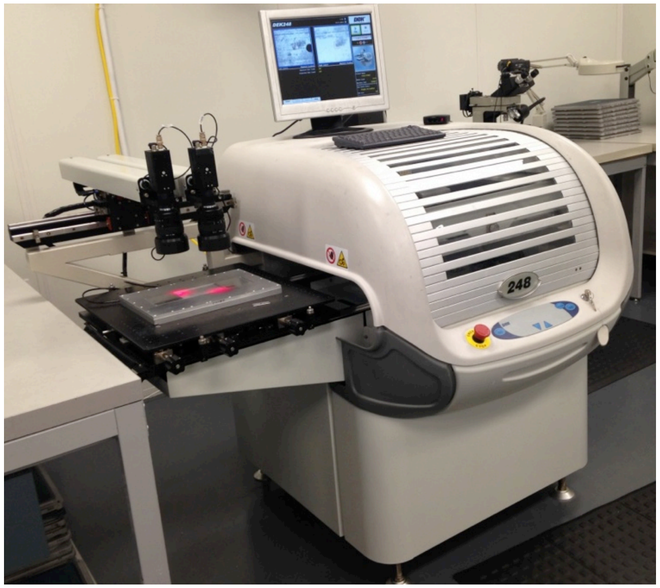
5 µm densification layer

Technical Approach

- ***Button cells*** fabricated
- Cell testing at CWRU using LGFCS's ***accelerated cathode test protocol***
- ***Microstructural characterization*** at CWRU
- ***Collaborative analysis*** and development of design rules
- ***4 cycles*** of cathode formulation, testing, analysis, and refinement ***in 3 years***



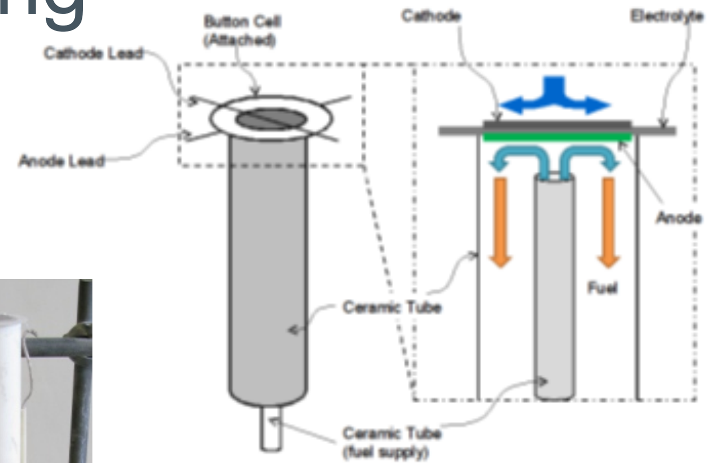
Procedures: button cell specifications



- Cell materials:
  - 8YSZ electrolyte (NexTech)
  - NiO-8YSZ anode (60:40 wt%)
  - Cathode:
    - A-site deficient LSM
    - LSM:8YSZ (50:50 wt%)
- Cell structure and processing
  - Electrolyte: 32 mm dia., 200 µm thick
  - Electrodes: screen printed, 9.5 mm dia., fired separately

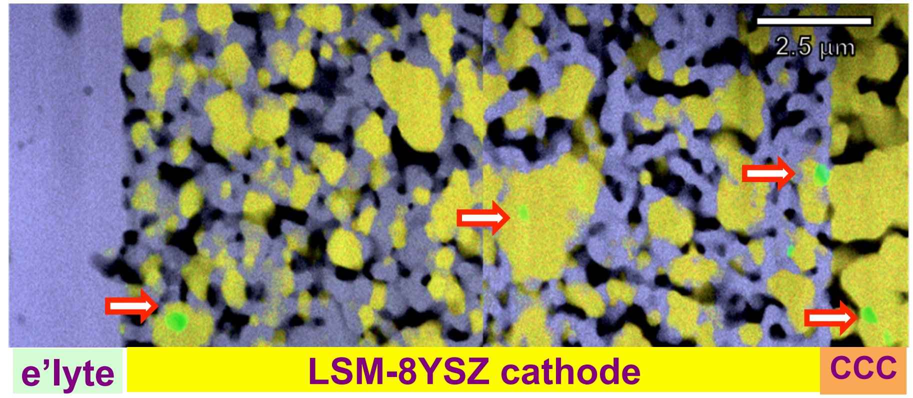
Procedures: button cell testing

- Pt mesh and wires attached to both electrodes
- Cell sealed to zirconia tube with fired glass paste
- Anode reduction followed by 24-h burn-in at OCV
- Hydrogen fuel
- All tests run at constant temperature, anode & cathode atmospheres, & current density
- I-V and EIS scans every 24 or 48 h

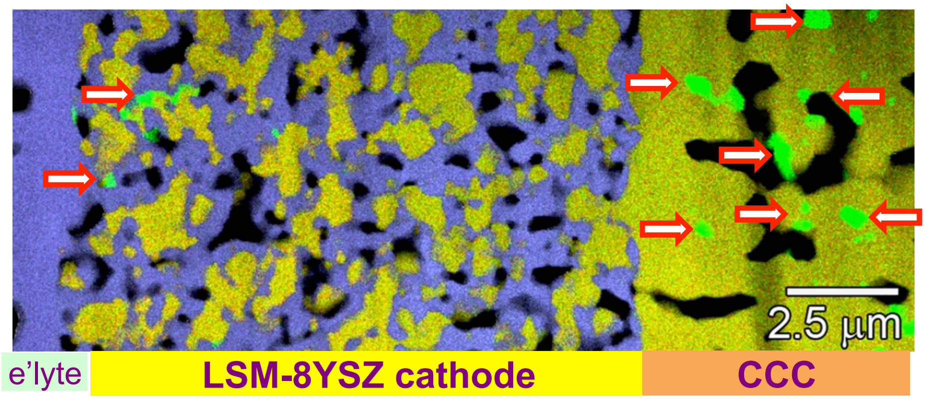


Results: TEM w/EDXS mapping

- As reduced (0 h)
  - MnO_x observed sparingly across entire cathode



- 493 h accelerated testing
  - MnO_x near cathode/e'lyte interface & in LSM cathode current collector (CCC)
  - No obvious densification layer (3DR in progress)



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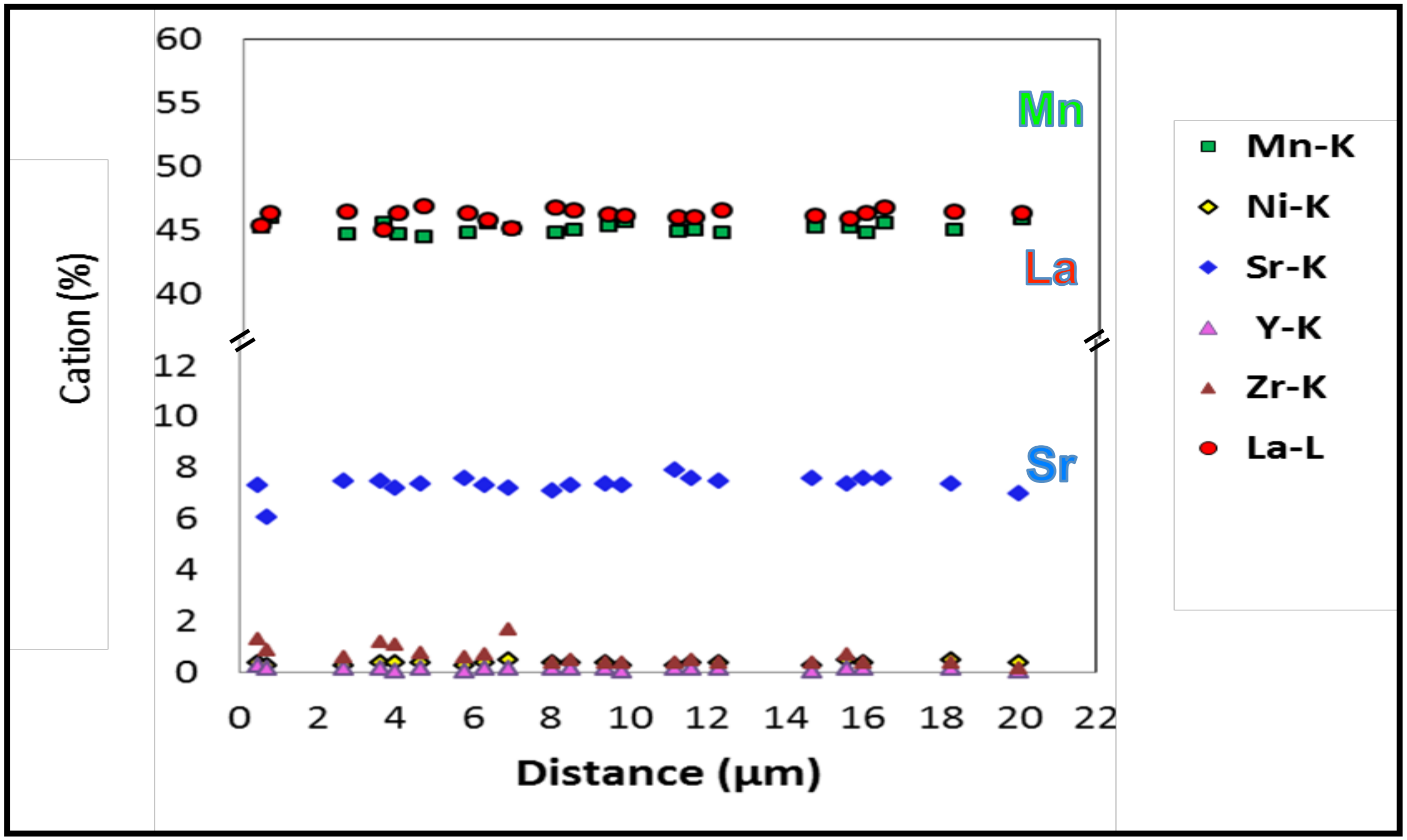
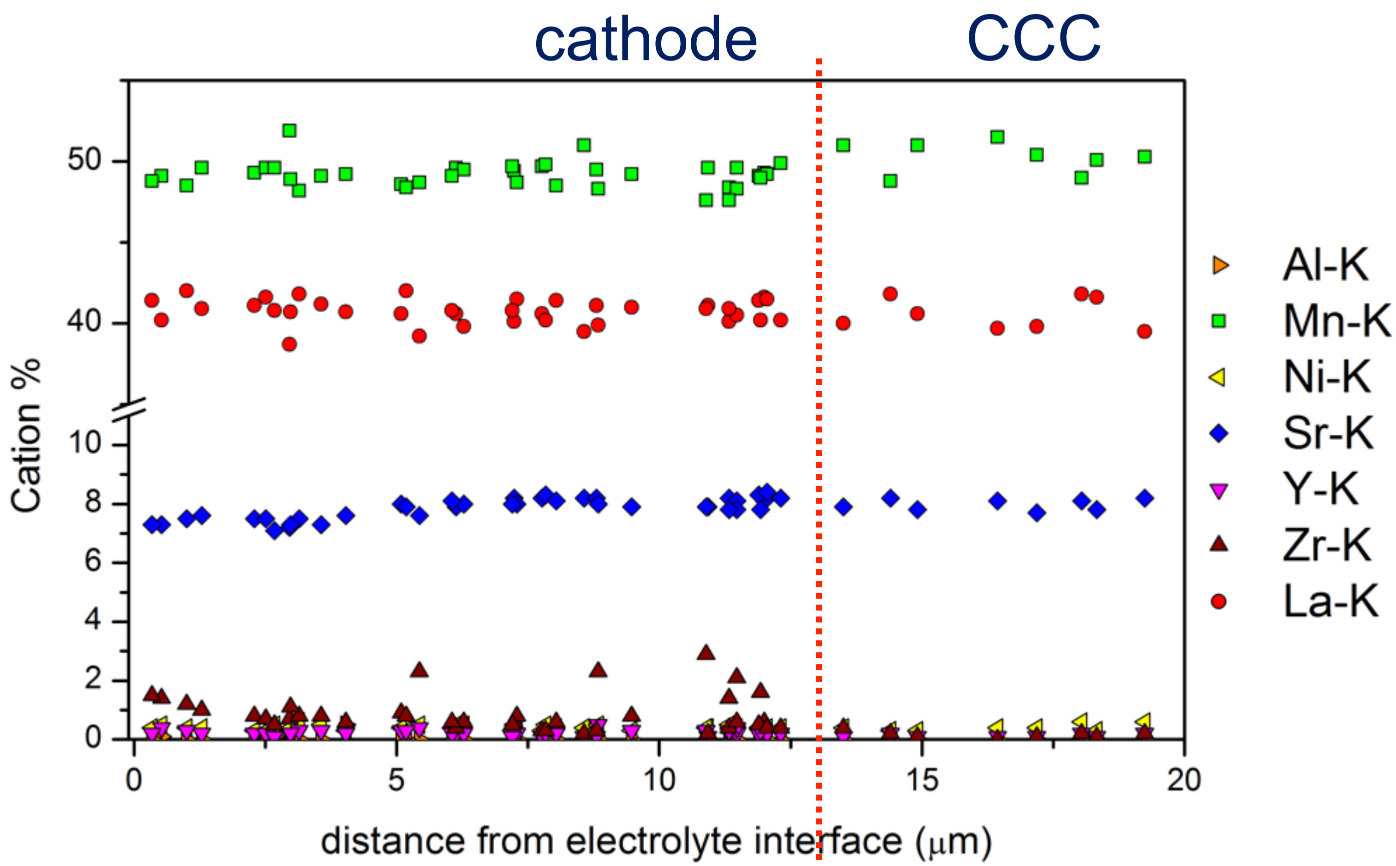
As-reduced cell: LSM profiles (EDXS)



Uniform LSM composition across cathode, pre-testing

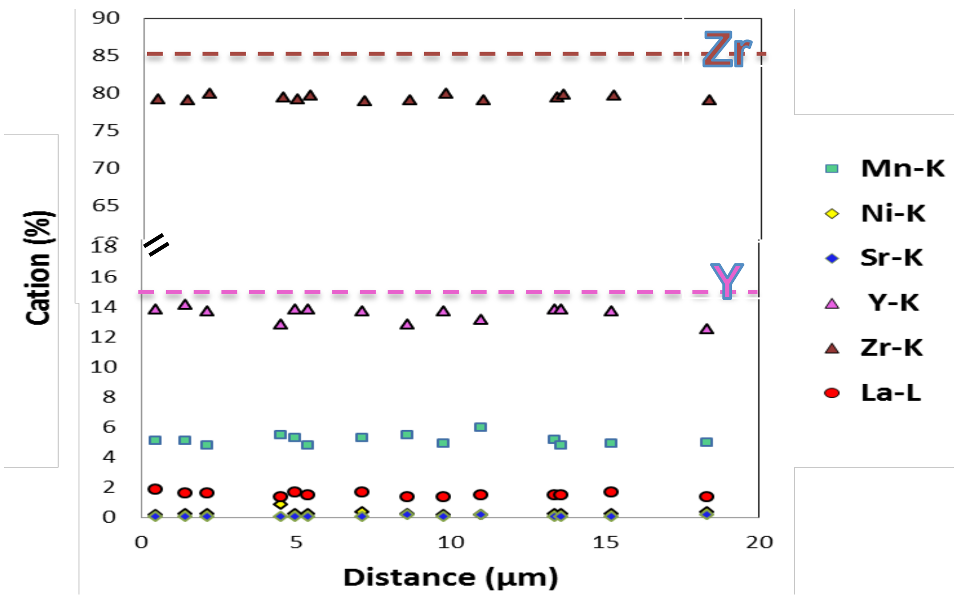
Accelerated testing, 493 h: LSM profiles (EDXS)



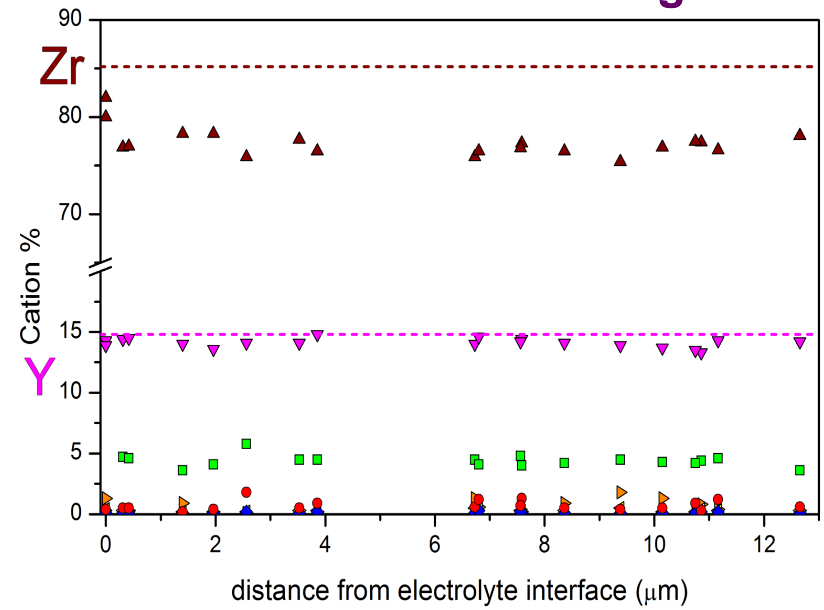
- **Bulk LSM composition is quite homogeneous across cathode and CCC**

YSZ profiles (EDXS)

As reduced (0 h)



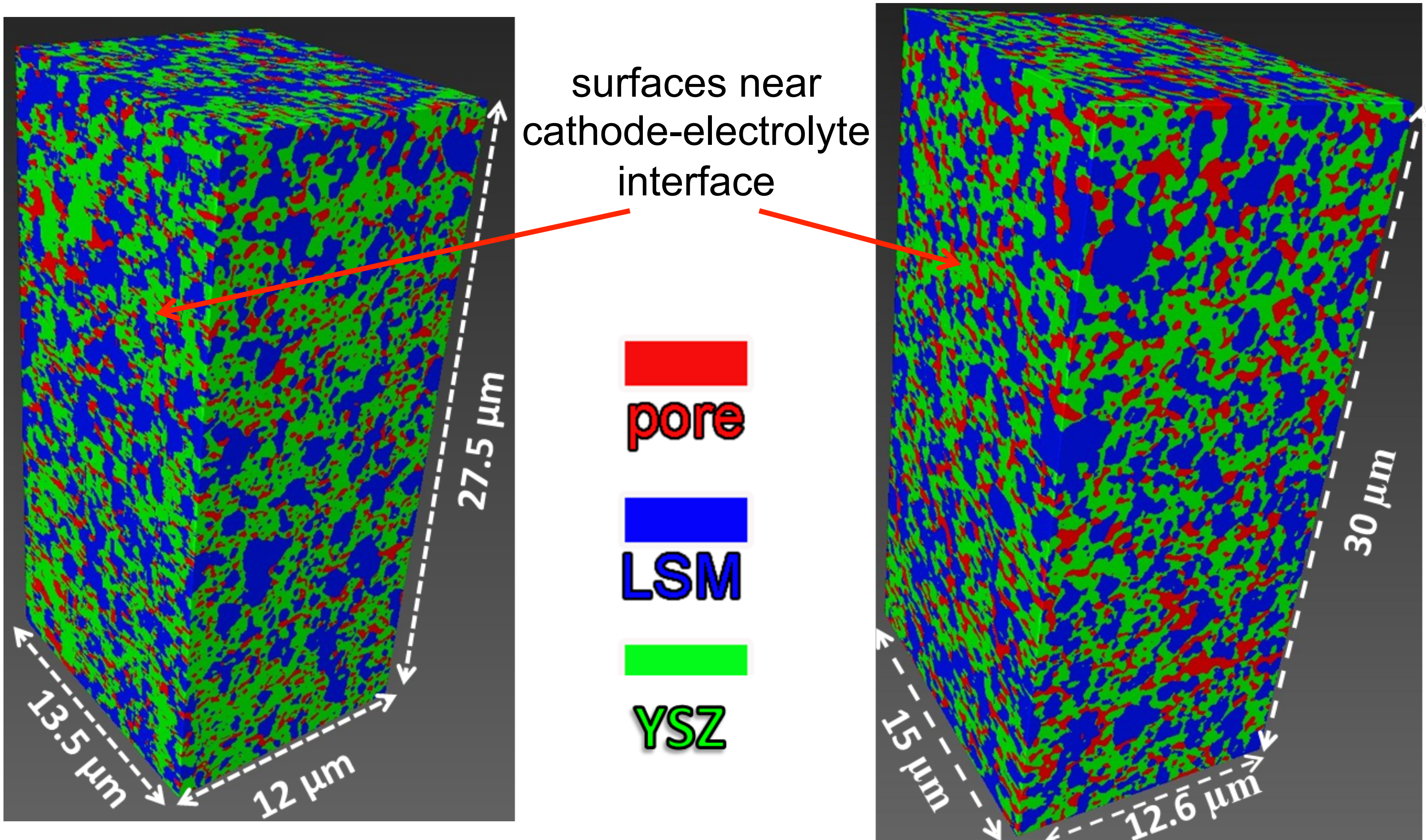
493 h accel'd testing



- Uniform YSZ composition across cathodes
- Little change after 493 h
- 4–5 cat% Mn in YSZ

	Y	Mn	Ni	Sr-K	Zr-K	La-L
0 h (cat%)	13.5	5.15	0.2	0.02	79	1.5
493 h (cat%)	14.1	4.4	0.3	0.1	77.0	0.7

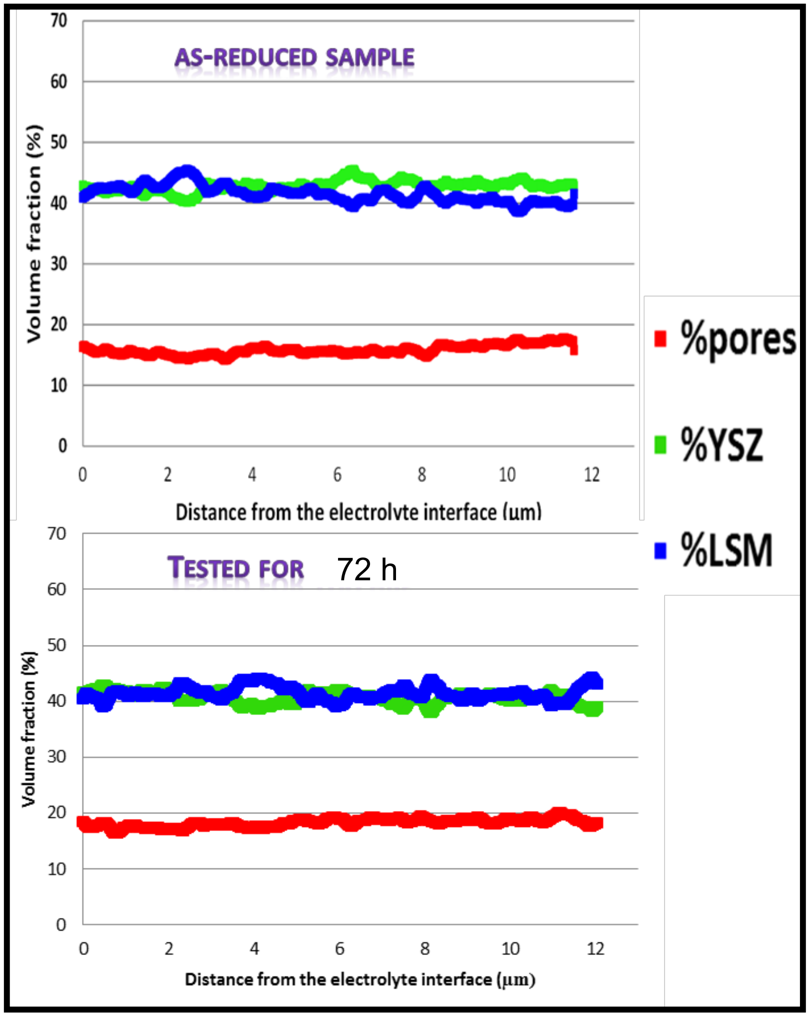
3DR: 0 vs. 72 h of accelerated testing



As reduced

tested for 72 h

Phase profiles: 0 vs. 72 h accelerated testing



As reduced	
porosity	17 vol%
YSZ	42 vol%
LSM	41 vol%

Tested for 72 hrs	
porosity	18 vol%
YSZ	41 vol%
LSM	41 vol%

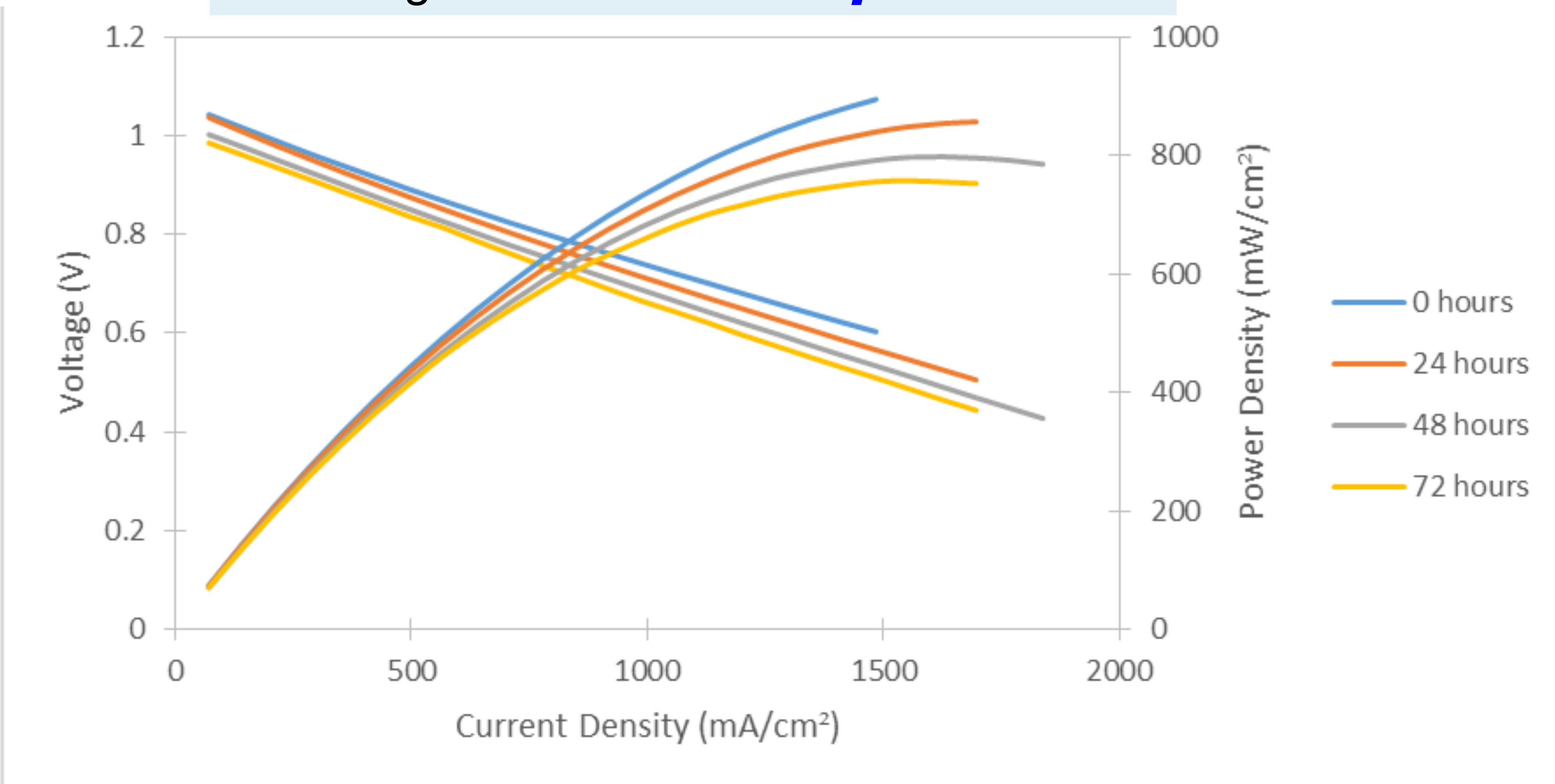
No significant changes in phase fractions or profiles after 72 h testing

Summary of 3DR data: 0 vs 72 h testing

		Button cell, as reduced	Button cell, tested for 72 h
sample volume (μm^3)		≈ 4350	≈ 5670
volume fraction (%)	porosity	17	18
	YSZ	42	41
	LSM	41	41
particle diameter (μm)	porosity	0.2	0.4
	YSZ	0.5	0.5
	LSM	0.6	0.7
tortuosity	porosity	2	1.8
	YSZ	1.45	1.5
	LSM	1.3	1.4
normalized surface area (μm^{-1})	porosity	26	15
	YSZ	12	11.8
	LSM	10	8.6
Total TPB (μm^{-2})		17.11	12.53
Active TPB (μm^{-2})		10.25	11.45

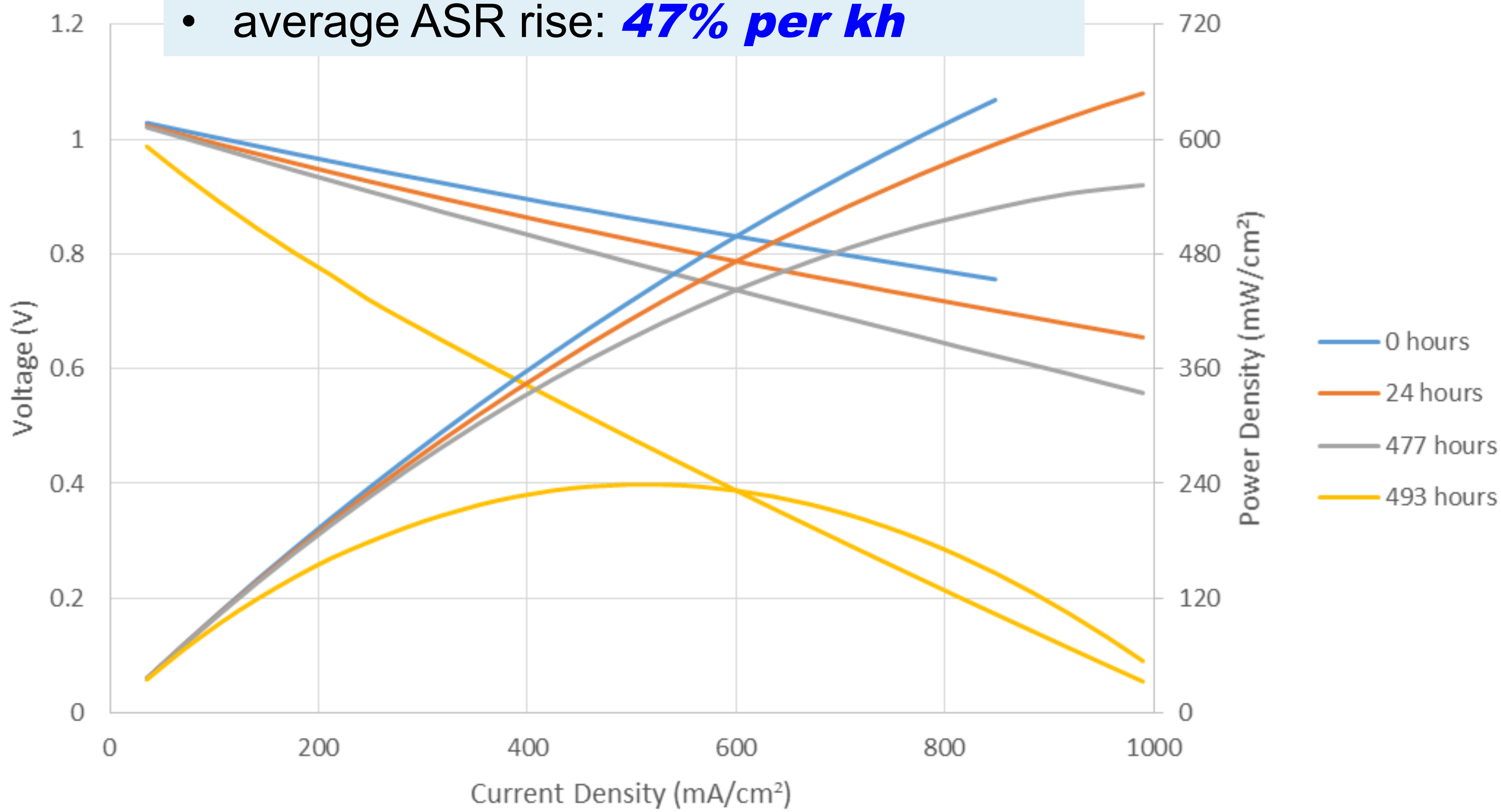
Accelerated testing, 72 h: V-I and P-I plots

- 72 h: ***0.75 W/cm²*** at ***1.6 A/cm²***
- average ASR rise: ***104% per kh***



Accelerated testing, 493 h: V-I and P-I plots

- 477 h: ***0.55 W/cm²*** at ***1.0 A/cm²***
- average ASR rise: ***47% per kh***



Ongoing and future work

- 3DR of 500-h specimen — look for changes in pore size and distribution
- TEM/EDS of 72-h specimen — early changes in MnO_x?
- Additional testing of 1st cathode composition
  - 200-h accelerated test
  - 500-h test, ***normal*** conditions
- Analysis of EIS results (all tested cells)
- 2nd cathode composition selected; cells fabricated
  - Testing to begin later this month

Conclusions

Accelerated testing protocol ➔ much higher rise in ASR (50–100% per kh) than normal operation (goal: ≤1%/kh).

- 72 h:
  - coarsening of pores
  - lower total TPB density
  - no obvious changes in phase fractions or profiles
- 493 h:
  - MnO_x at cathode-electrolyte interface and in CCC
  - No obvious densification layer (3DR in progress)

Conclusions: prior vs. current results

Similarities:

- Microstructural stability of the YSZ phase
- Solubility of Mn in 8YSZ
- MnO_x at cathode-e'lyte interface and CCC at long times

Differences:

- No obvious densification layer after 493 h (3DR in progress)
- High uniformity of LSM composition across cathode

Pending:

- 3DR of 493-h specimen: trends in …
  - TPB density • densification layer
- Testing button cells under normal conditions

Summary

- Microstructural changes in LSM cathodes: culprits, or coincidence?
  - Densification layer
  - MnO_x formation, distribution
  - TPB density
  - Compositional changes in LSM, YSZ
- Unique opportunity to generate several cycles of cathode optimization in relatively short times:
  - Accelerated testing
  - Microstructural analysis
  - Integrated analysis and design rules

— relevant to long-term, commercial SOFC application

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