Performance and Microstructural Changes in LSM-Based SOFC Cathodes Under Accelerated and Conventional Testing

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17th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting

Pittsburgh, PA • 19–21 July 2016

CASE SCHOOL OF ENGINEERING

CASE WESTERN RESERVE UNIVERSITY

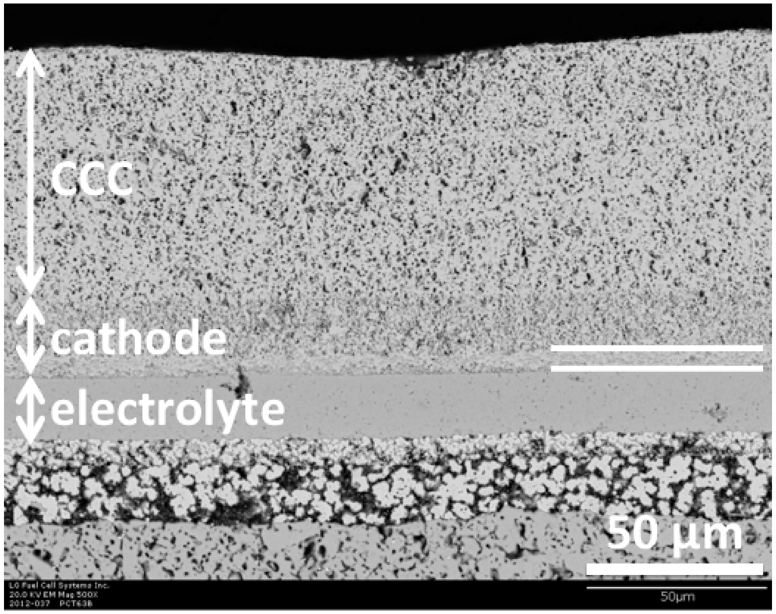
Outline

- Project objectives and approach
- Accelerated vs. long-term conventional testing
- LSM compositions: role of A-site deficiency
    - Durability testing
    - Cathode microstructural changes
    - ASR and TPB density vs. time
- Summary & conclusions
- Ongoing & future work

Background observations: long-term conventional testing

- 15kh, 860 °C:

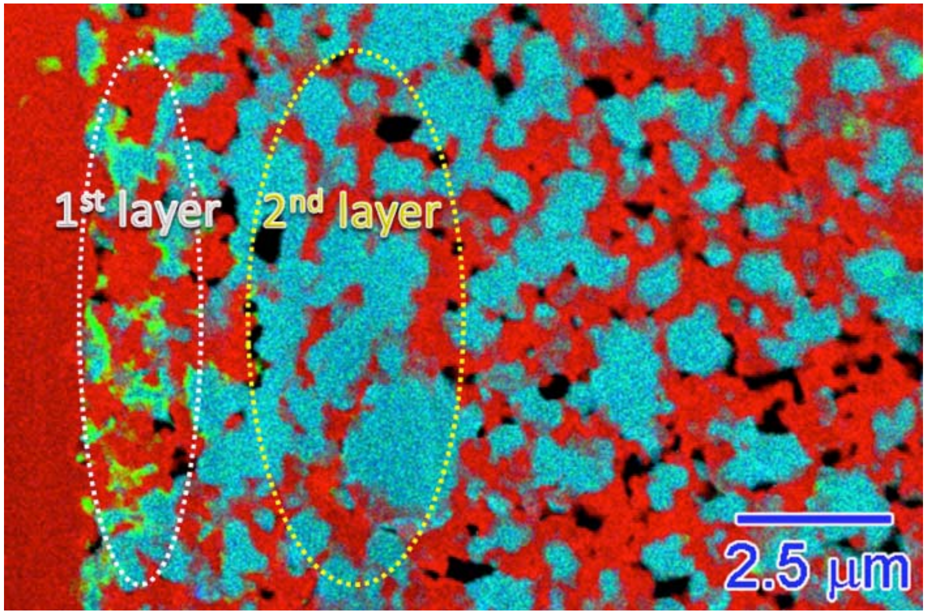
Cathode densification layer



Densified layer (between two white lines) is ~5 µm thick (SEM image, courtesy of LGFCS)

(CCC: cathode current collector)

Segregation of Mn oxides*

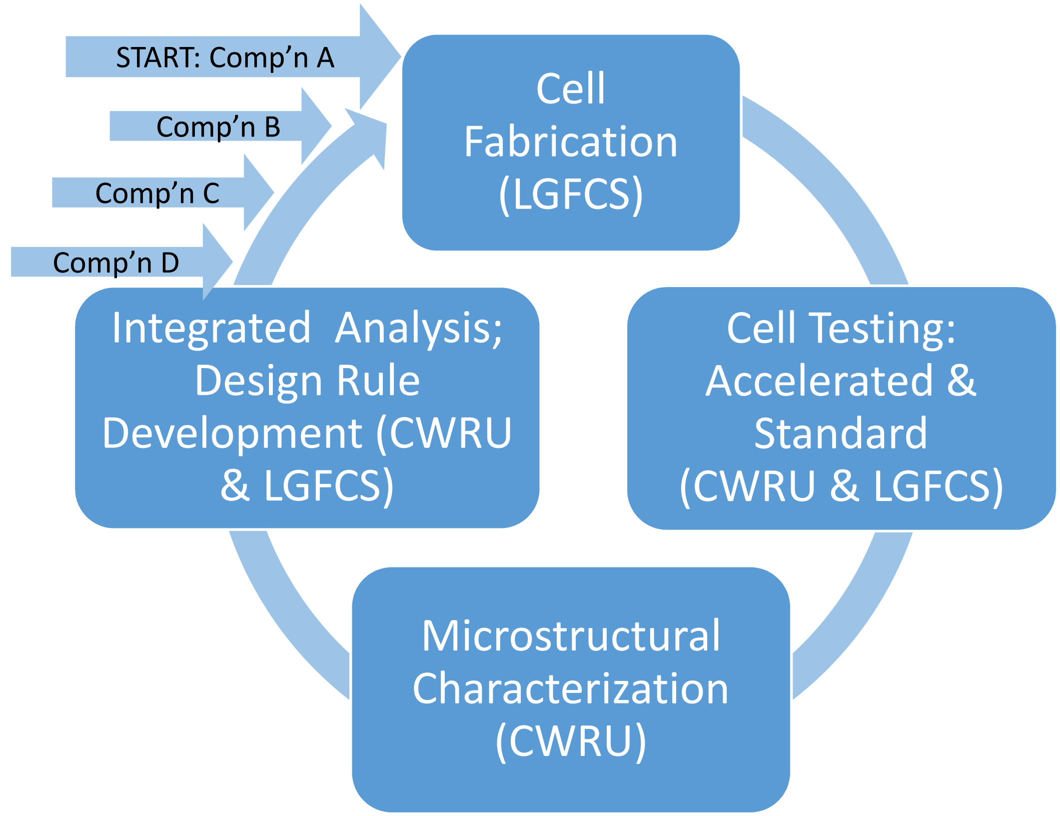


TEM image with EDXS mapping (LSM: blue; zirconia red; MnOx green)
Total of first layer + second layer: 5 µm

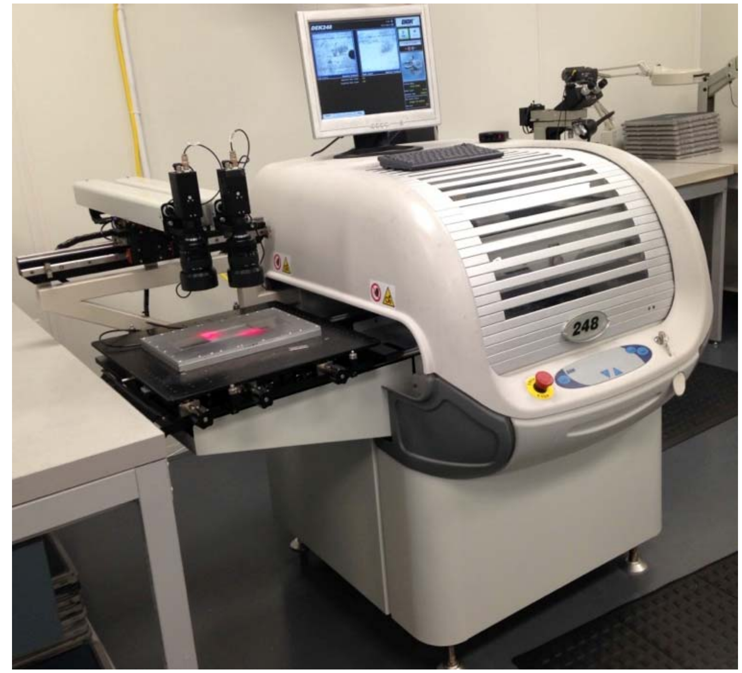
*) H.-J. Wang, M. R. De Guire, G. Agnew, R. Goettler, Z. Liu, Z. Xing, A. Heuer, *Met. Mater. Trans. E*, **1** [3] 263-271 (2014). DOI: 10.1007/s40553-014-0026-5.

Project Objectives and Approach

- Implement an accelerated testing protocol to *replicate long-term microstructural changes* in *shorter times*
- Understand *microstructural basis of long-term performance loss* in LSM-based SOFC cathodes
- *4 cycles* of cathode formulation, testing, and analysis in *3 years*
- Develop strategies for *optimizing LSM-based cathodes* for improved long-term performance and stability



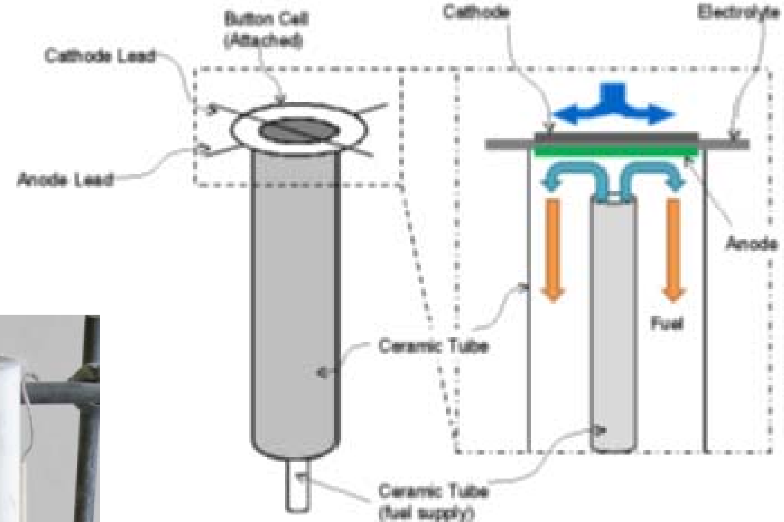
Procedures: button cell specifications



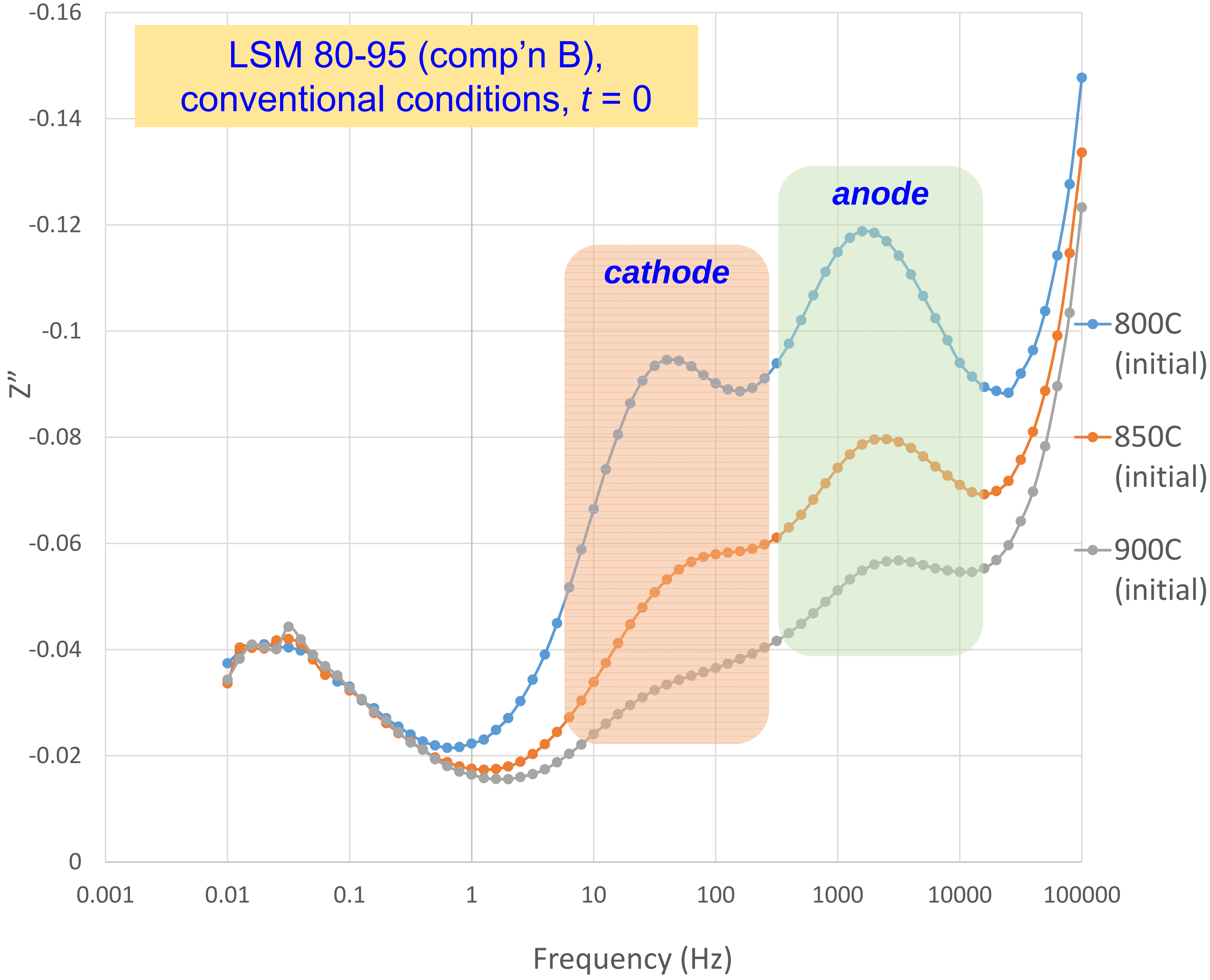
- Fabricated at LGFCS
- Cell details:
  - 8YSZ electrolyte, 32 mm dia.
  - NiO-8YSZ anode (60:40 wt%)
  - Cathodes: A-site deficient LSM + 8YSZ (50:50 wt%)
    - Comp'n A: $(La_{0.85}Sr_{0.15})_{0.90}MnO_{3\pm\delta}$ *(LSM 85-90)*
    - Comp'n B: $(La_{0.80}Sr_{0.15})_{0.95}MnO_{3\pm\delta}$ *(LSM 80-95)*
  - Electrodes: screen printed, 9.5 mm dia., fired separately

Procedures: button cell testing

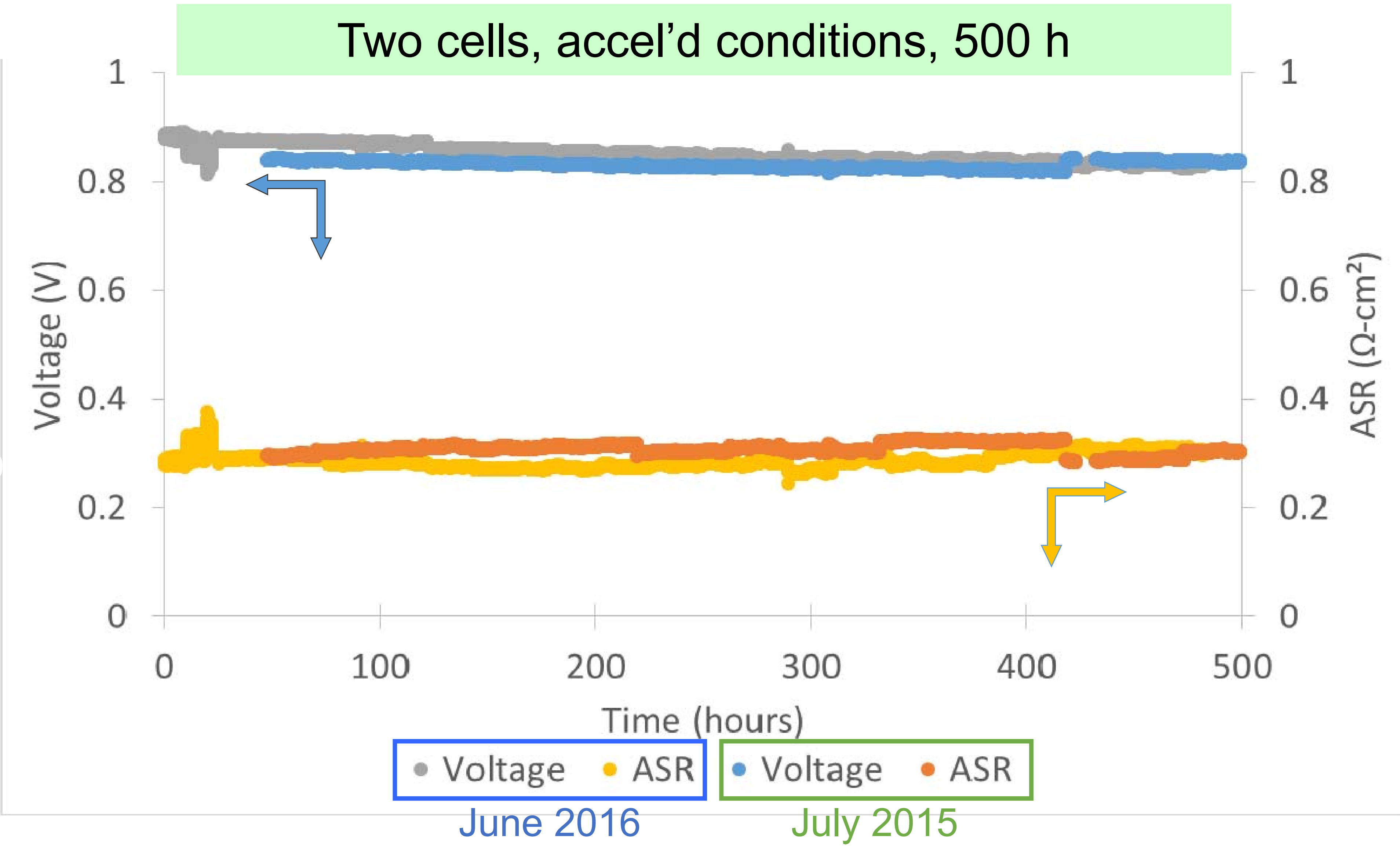
- Pt mesh and wires attached to both electrodes
- Cell sealed to zirconia tube with fired glass paste
- Anode reduction followed by 24-h burn-in at OCV
- Pre-test protocols: details below
- Durability testing
  - H_2, 50 sccm
  - Accelerated tests: 1000 °C, 0.760 A cm^{-2}
  - Conventional tests: 900 °C, 0.380 A cm^{-2}
  - I-V and EIS scans every 24 or 48 h



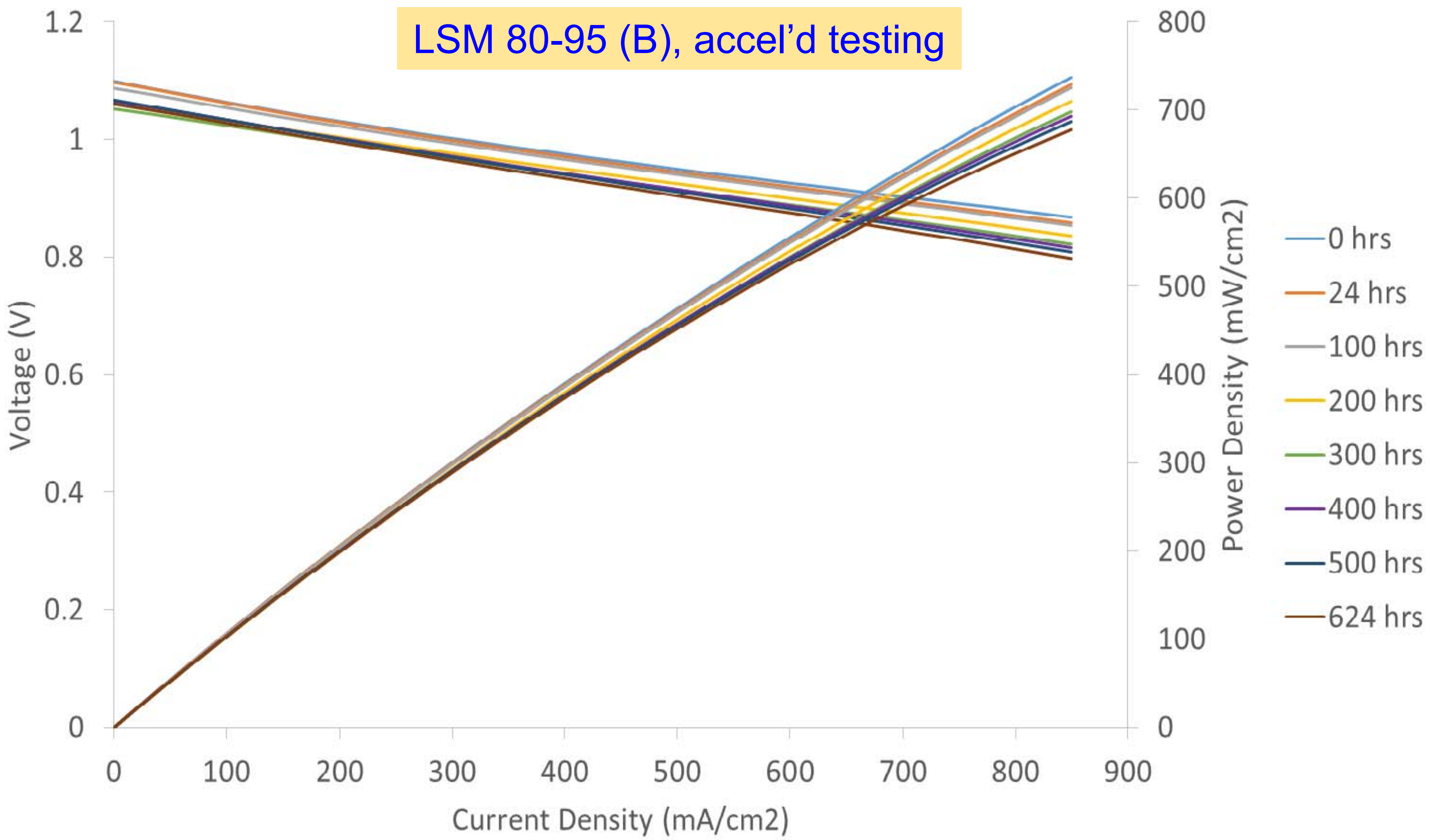
Pre-test protocol: temperature parametric study



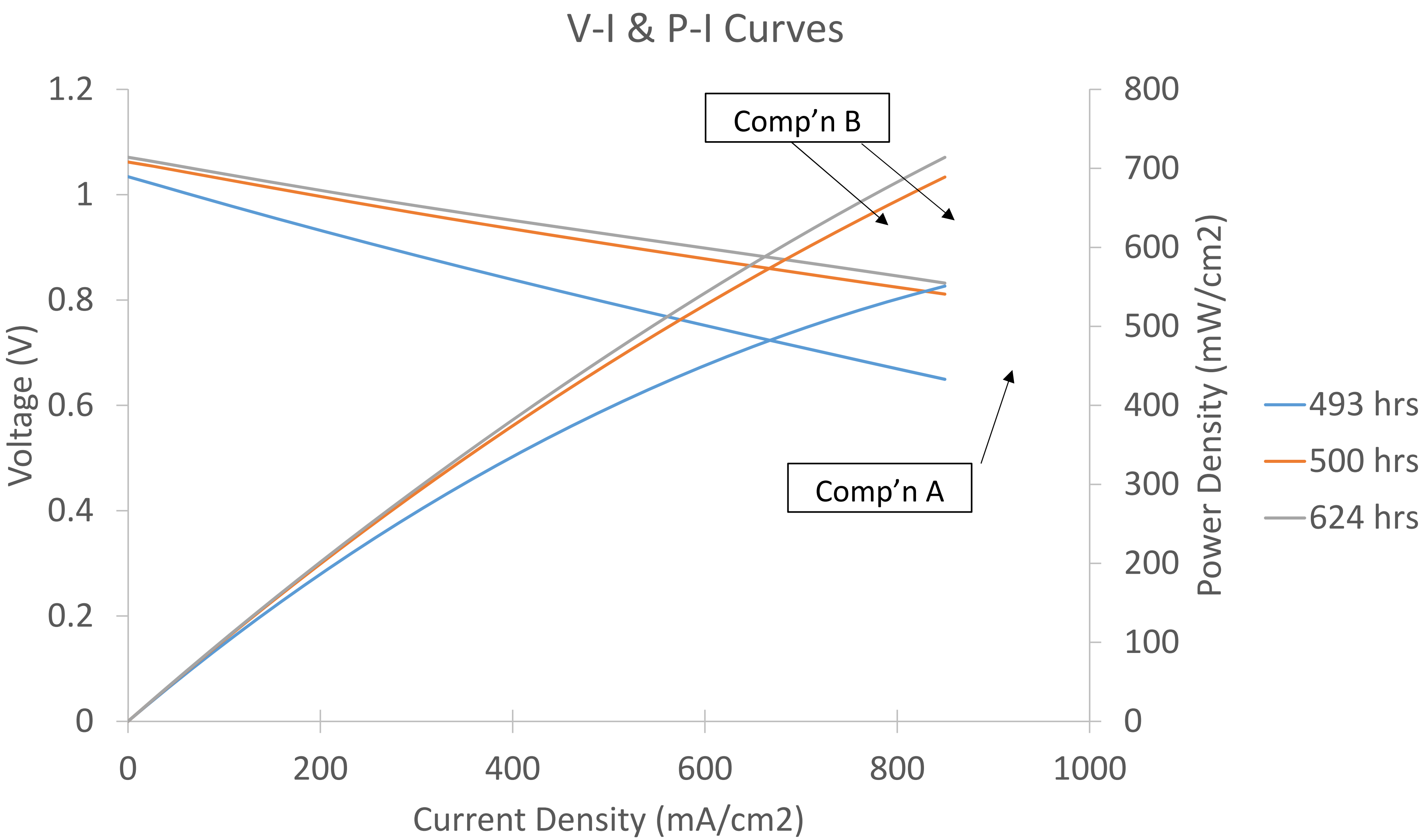
LSM 80-95 (B) durability testing: reproducibility



Representative V-I & P-I sweeps, 0–624 h



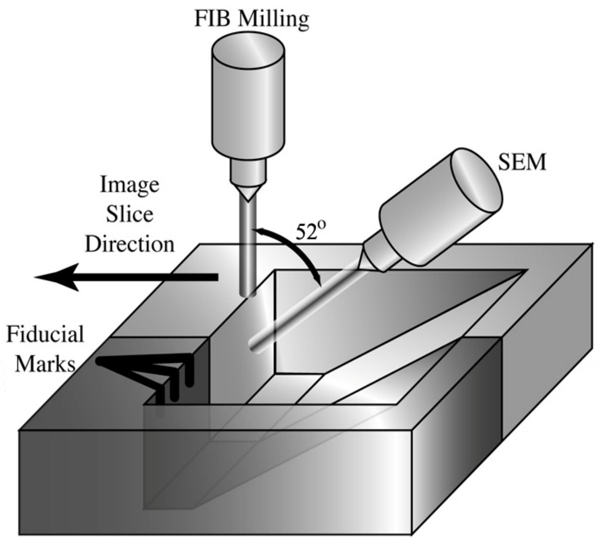
Comparative V-I & P-I sweeps, A vs. B

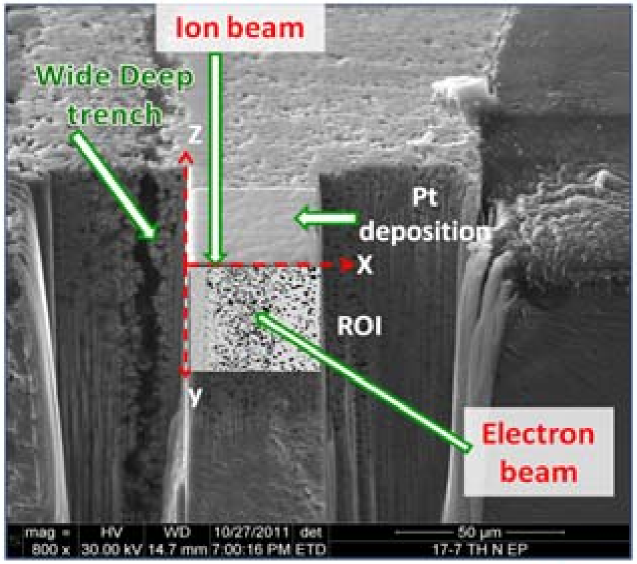


ASR and changes over time: summary

- In durability testing and EIS: *LSM 80-95* (B) had *lower:*
  - Initial ASR
  - Final ASR
  - ΔASR over time (Ω cm^2 kh^{-1})

Procedures: FIB Slice & View for 3DR





each slice
150 nm thick

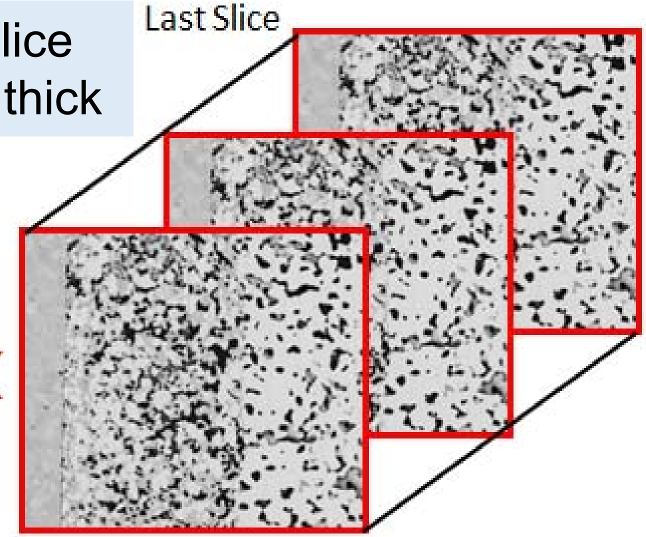
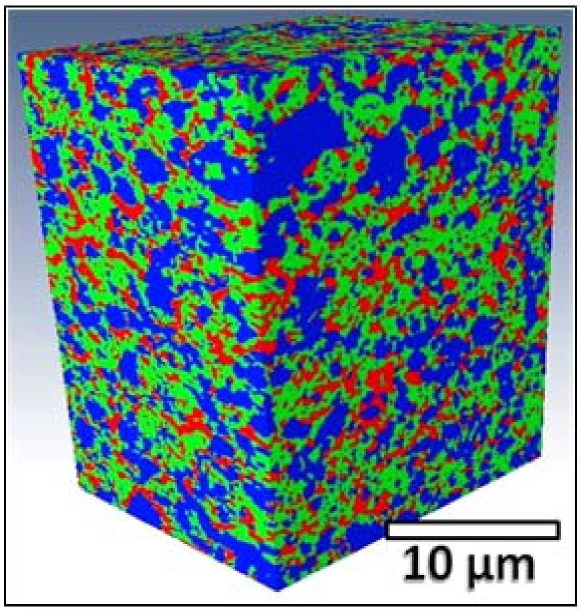


Image resolution:
4096*3536 pixels
Imaging mode:
backscattered
(Immersion detector)



LSM 85-90 (A) microstructural evolution: 3D reconstruction

LSM 85-90 cathode:	as-received	after 200 h accel'd testing	after 493 h accel'd testing
pore size (µm)	0.20	0.34	0.42
pore tortuosity	2	1.7	1.6
normalized pore surface area (μm^{-1})	26	17.4	14.2
total TPB (μm^{-2})	17.1	9.6	5.86
active TPB (μm^{-2})	10.3	8.2	5.13

as *t* ↑

↑
↓
↓
↓
↓

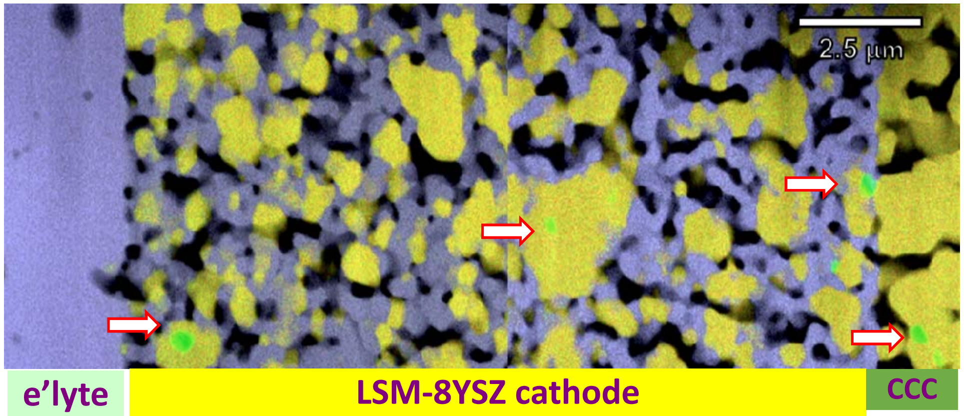
Coarsening of pores, loss of pore area and TPB

Other observations —

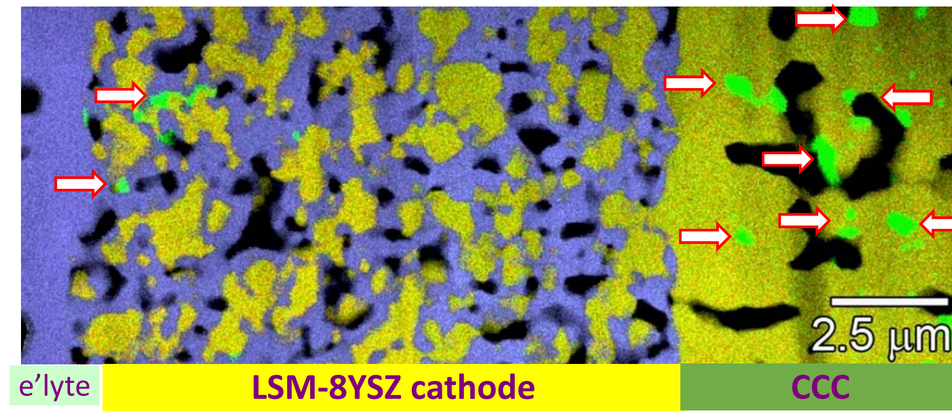
- Phase fraction profiles: flat across cathode
- Densification at cathode-electrolyte interface? Inconclusive

LSM 85-90 (A) microstructural evolution: TEM

as reduced



500 h



MnO_x dispersed across cathode and CCC

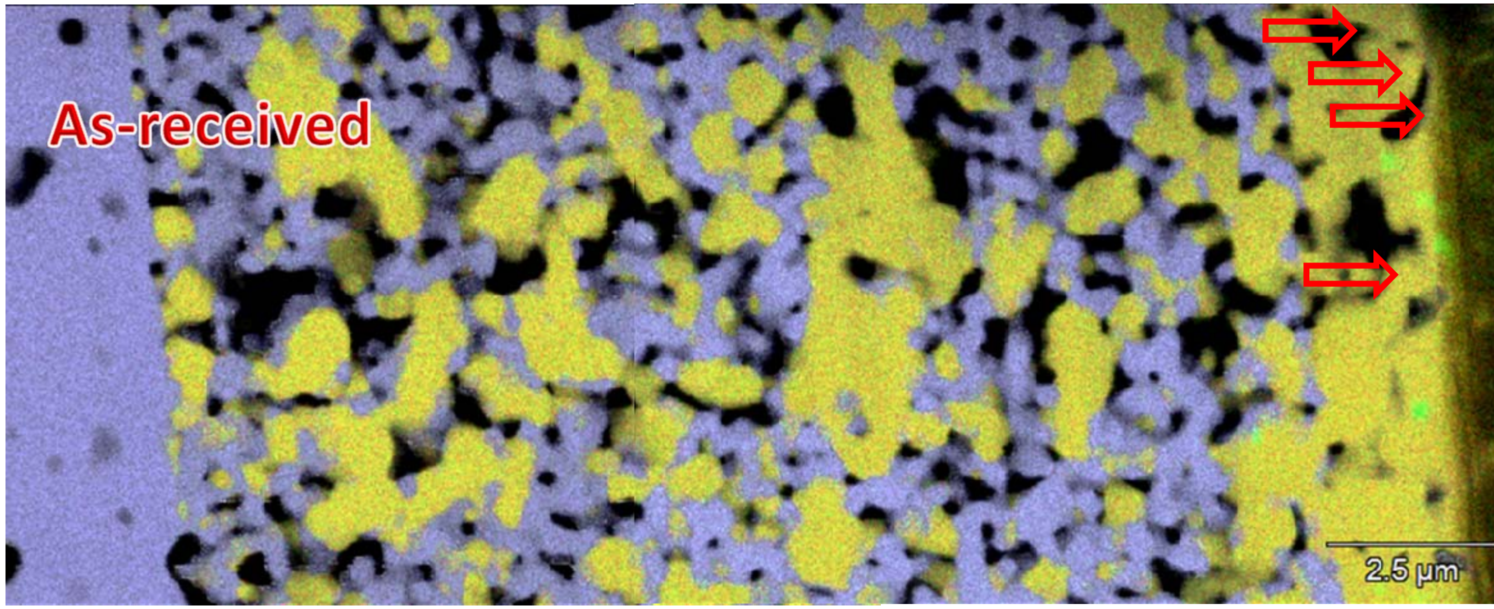
Accumulation of MnO_x at cathode-electrolyte interface

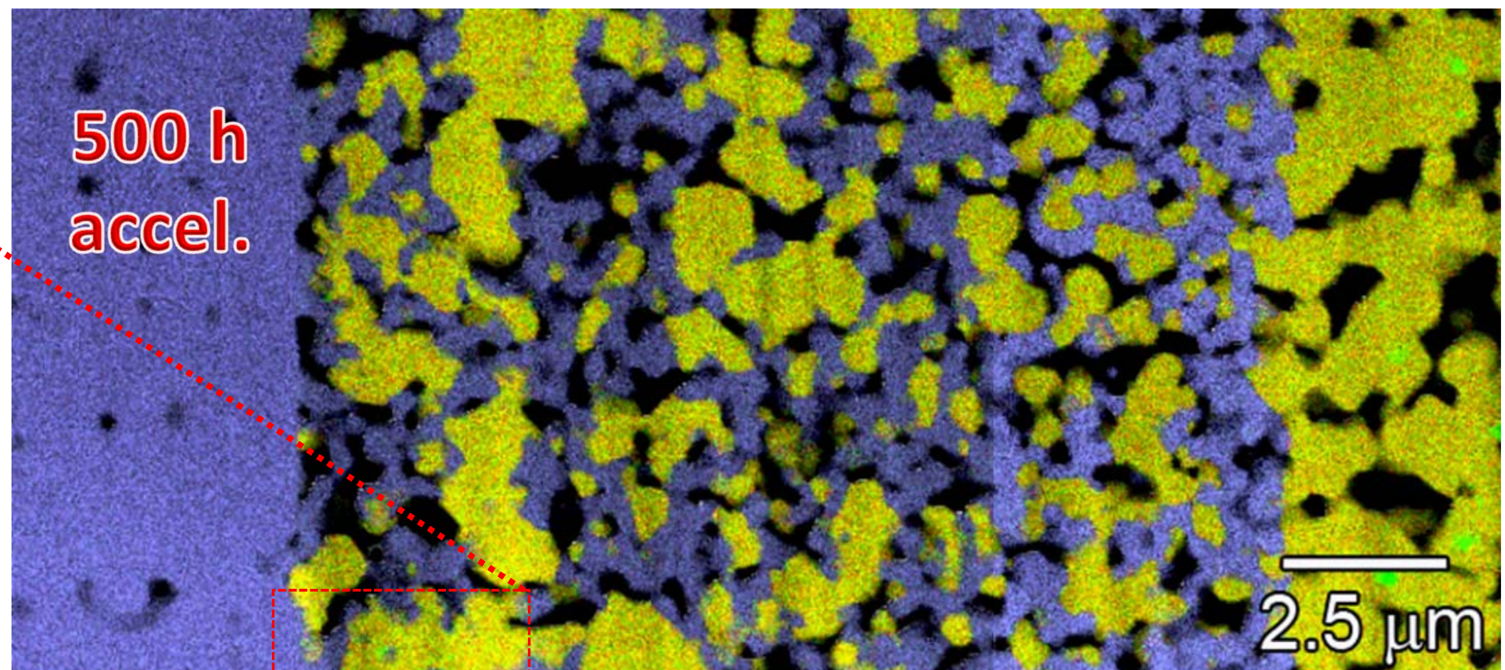
Other observations —

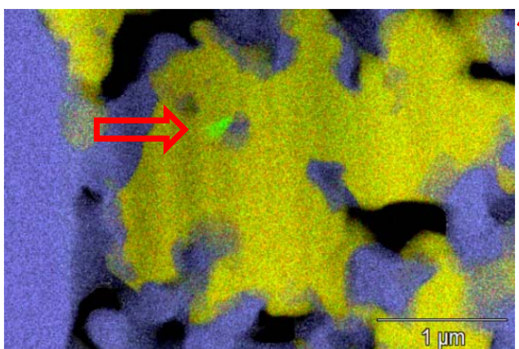
- LSM and YSZ composition profiles: flat across cathode
- Densification at cathode-electrolyte interface? Inconclusive

LSM 80-95 (B) microstructural evolution: TEM

- As received: MnO_x (⇨) only in CCC
- 500 h accel'd testing: occasional small MnO_x grains near electrolyte interface

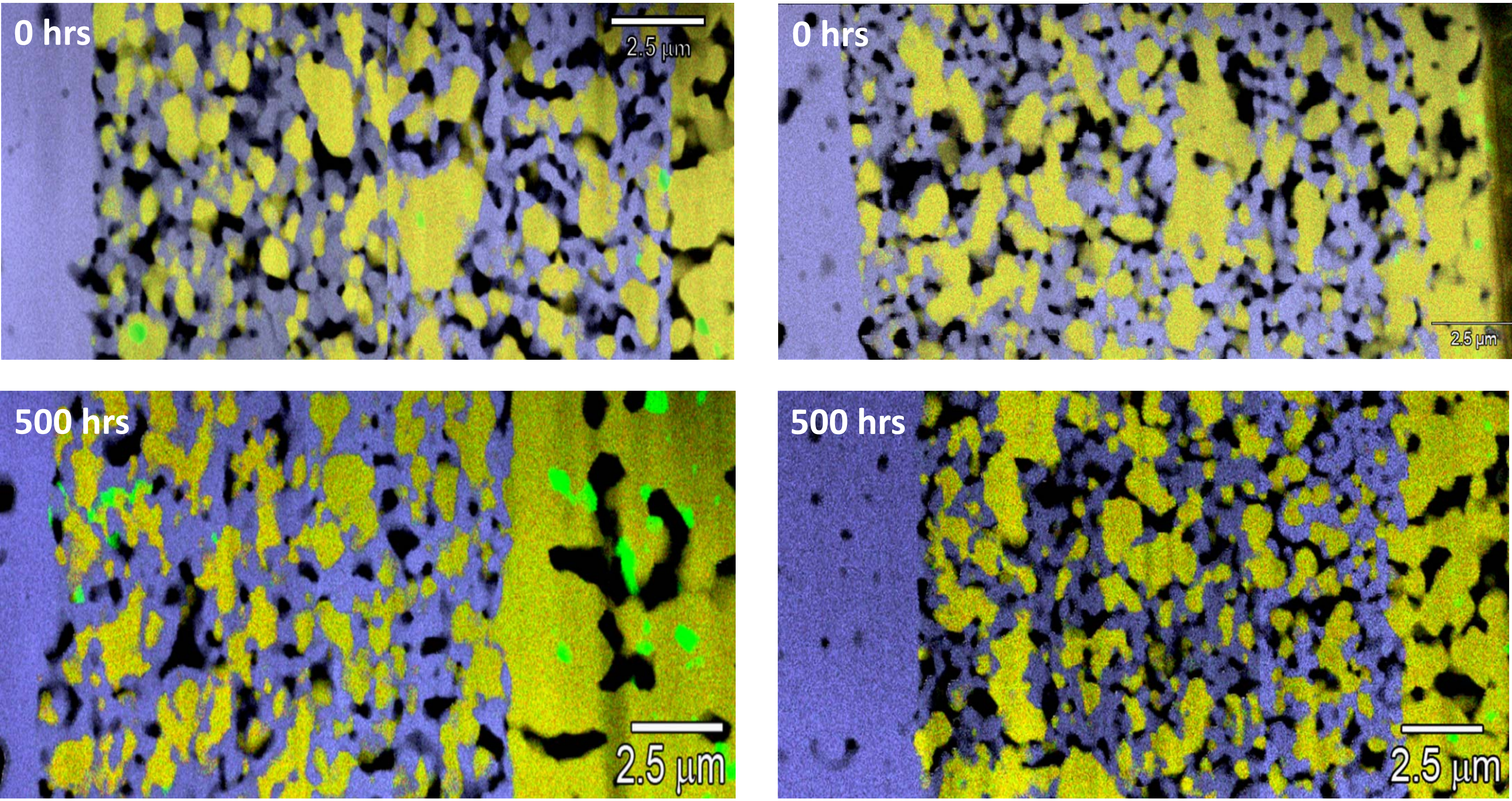






A – B comparison: TEM

LSM 85-90 (A), accel'd | **LSM 80-95 (B), accel'd**



- More MnO_x observed in LSM 85-90 (untested and tested)
- Larger MnO_x particles in LSM 85-90 CCC
- More pores in LSM 80-95 cathode post-testing

A – B comparison: 3D reconstruction

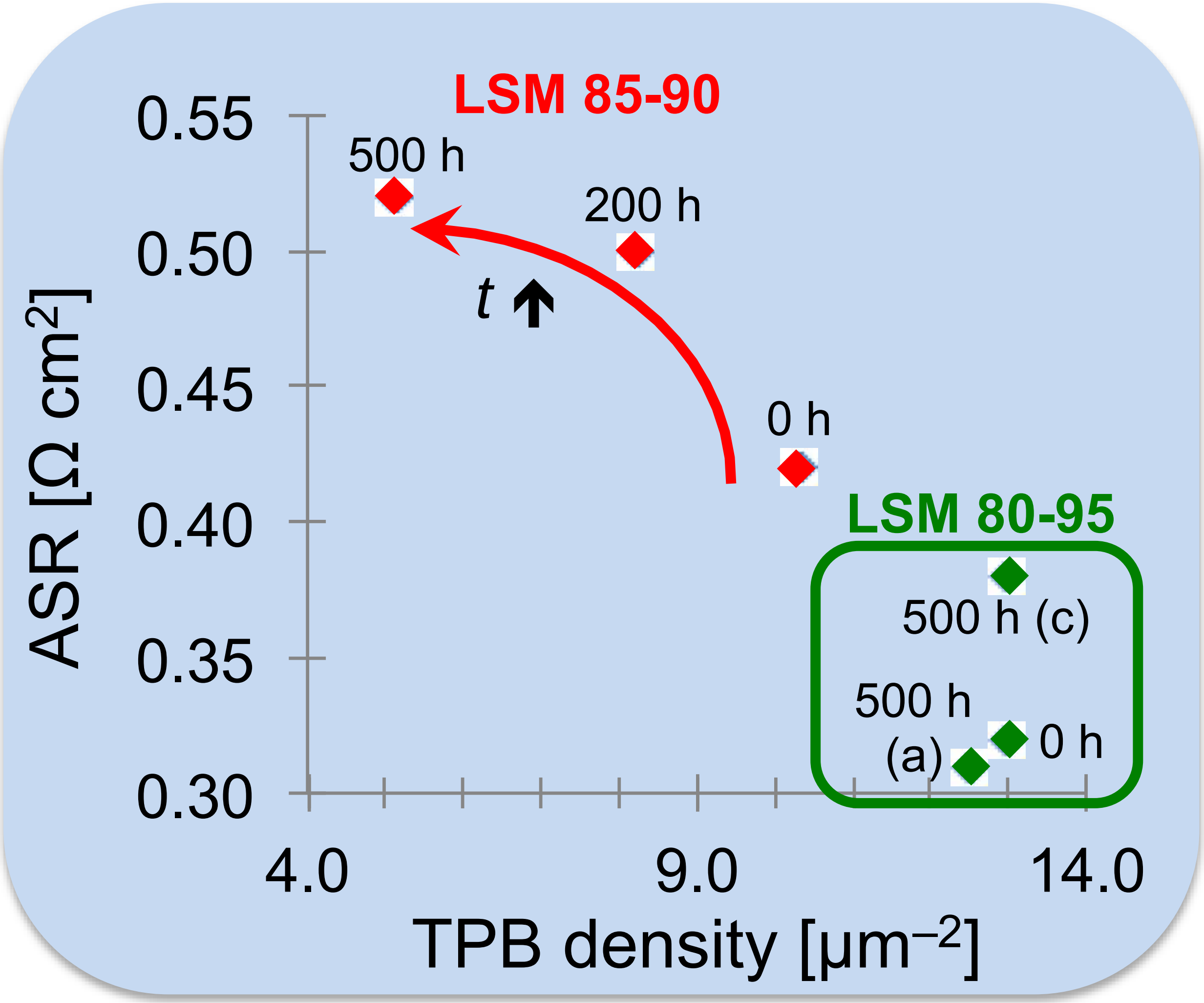
		LSM 85-90 (composition A)			LSM 80-95 (composition B)		
		as received	**500 h conv test**	493 h accel. test	as received	**500 h conv test**	500 h accel'd test
sample volume (μm^3)		4350	3700	4525	6300	5000	5096
volume fraction (%)	porosity	**17**	**21.9**	**18.4**	**29**	**26**	**26**
	YSZ	42	42.6	43.2	33	35.5	35
	LSM	41	35.5	38.4	38	38.5	39
particle diameter (μm)	porosity	**0.2**	**0.4**	**0.42**	**0.46**	**0.45**	**0.38**
	YSZ	0.5	0.5	0.46	0.47	0.42	0.51
	LSM	0.6	0.65	0.6	0.67	0.65	0.7
tortuosity	porosity	2.0	1.65	1.6	1.34	1.4	1.67
	YSZ	1.5	1.47	1.3	1.32	1.65	1.66
	LSM	1.3	1.45	1.4	1.3	1.5	1.44
normalized surface area (μm^{-1})	porosity	26	15.7	14.2	13	13.3	15.9
	YSZ	12	11.5	13	13	14	11.9
	LSM	10	8.9	9.9	8.9	9.3	8.5
Total TPB (μm^{-2})		**17.1**	**11**	**5.9**	**14.5**	**14.2**	**14.8**
Active TPB (μm^{-2})		**10.3**	**9.5**	**5.1**	**13.0**	**13**	**12.5**

In contrast to LSM 85-90 (A), ***LSM 80-95*** (B) shows:

- Pore refinement (!?) and increasing area and tortuosity
- ***Stabler TPB*** (total and active)

A – B comparison: ASR and TPB density

- **LSM 85-90**, as *t* ↑:
  - active TPB density ↓
  - ASR ↑
- **LSM 80-95:**
  - Higher active TPB density
  - Lower ASR
- Overall: inverse correlation between ASR and TPB density



Summary & Conclusions

- During accelerated testing up to 500 h:
  - *LSM 85-90* (A) cathode:
    - Pore coarsening
    - MnO_x segregation at electrolyte-cathode interface
    - Microstructure–performance trend over time:
      - *TPB density* ↓
      - *ASR* ↑
  - *LSM 80-95* (B) cathode:
    - Stabler microstructure
    - Less A-site deficient → *less MnO_x*
    - *Higher TPB, lower ASR* than LSM 85-90
  - Not yet observed:
    - Cathode densification at electrolyte
    - Mn depletion at electrolyte

Inverse TPB – ASR relationship is emerging

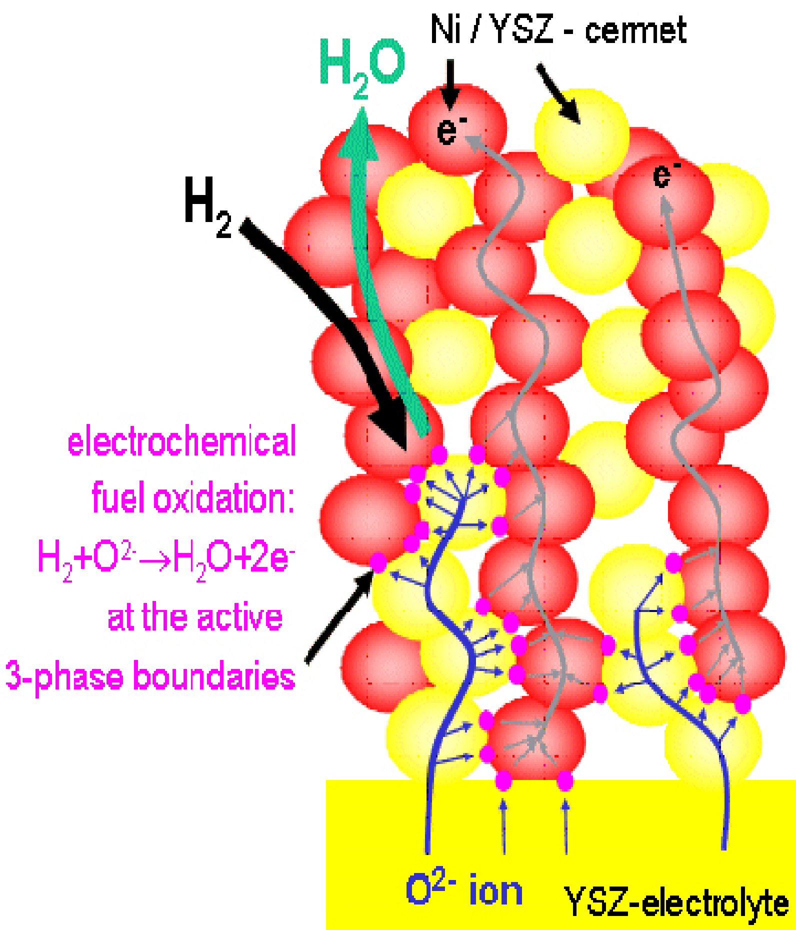
Ongoing & Future Work

- Continue reproducibility studies
- 624-h accelerated test: microstructural analysis underway; look for densification layer
- Thermodynamic studies to predict conditions for MnO_x formation
- MnO_x formation: symptom, or cause, of degradation?
- Continue to explore relationship between TPB and ASR
  - vs. LSM composition
  - Accelerated vs. conventional testing
- Composition C cells fabricated; testing & analysis are underway

Acknowledgments

- Funding: DoE SECA Core Technology Program (DE-FE0023476)
- NETL program manager: Patcharin Burke
- Mirko Antloga, Craig Virnelson (CWRU)

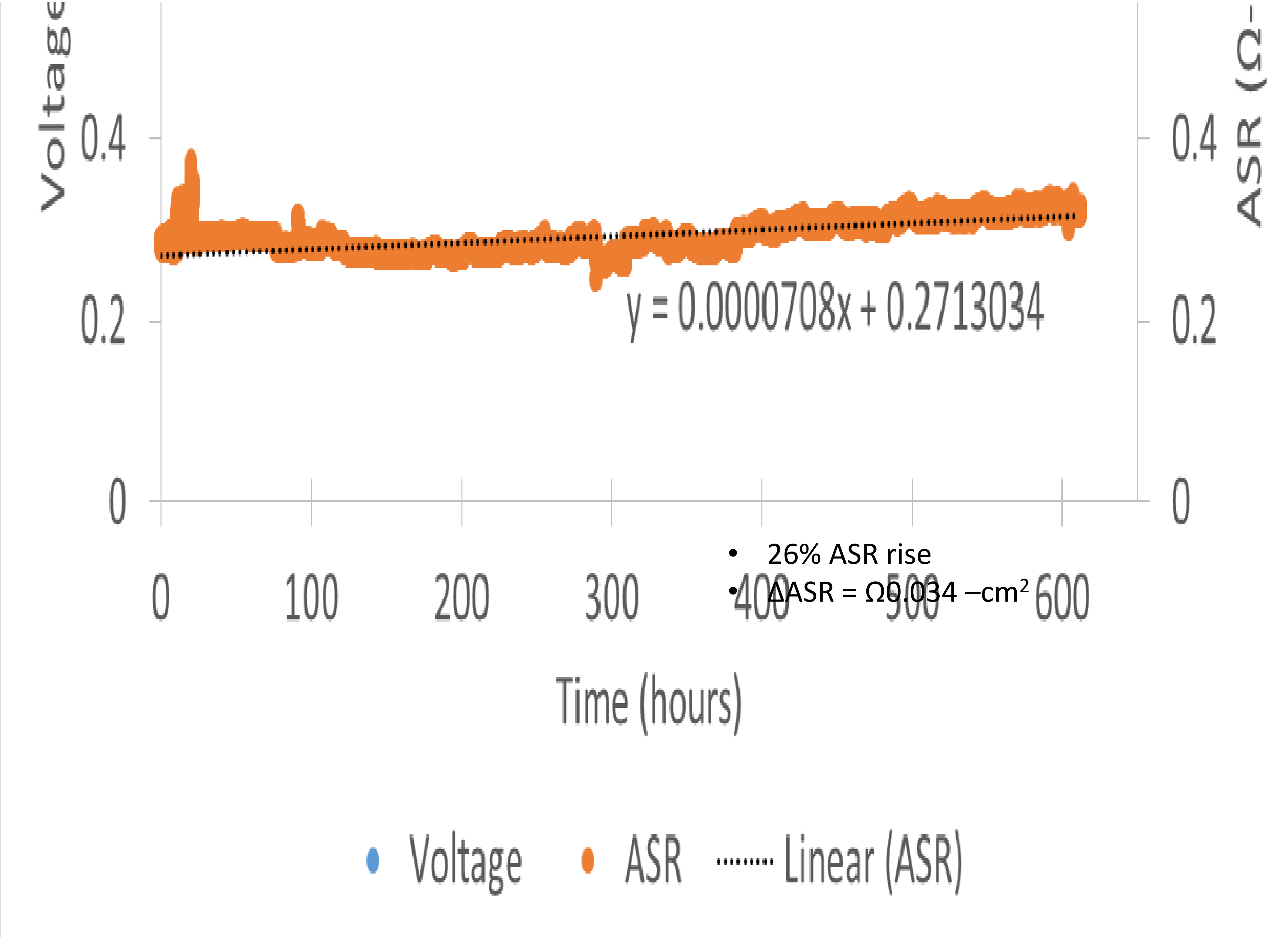
3DR in SOFCs: Triple phase boundaries (TPB)



- YSZ: ***100% ionic*** conductor
- LSM (cathode) and Ni (anode): ***100% electronic*** conductors
- For TPB to be ***active electrochemically,*** it must have ***percolation paths:***
  - ***Ionic conductor*** must connect to ***electrolyte***
  - ***Electronic conductor*** must connect to ***current collector***
  - ***Pore*** must connect to ***external atmosphere***

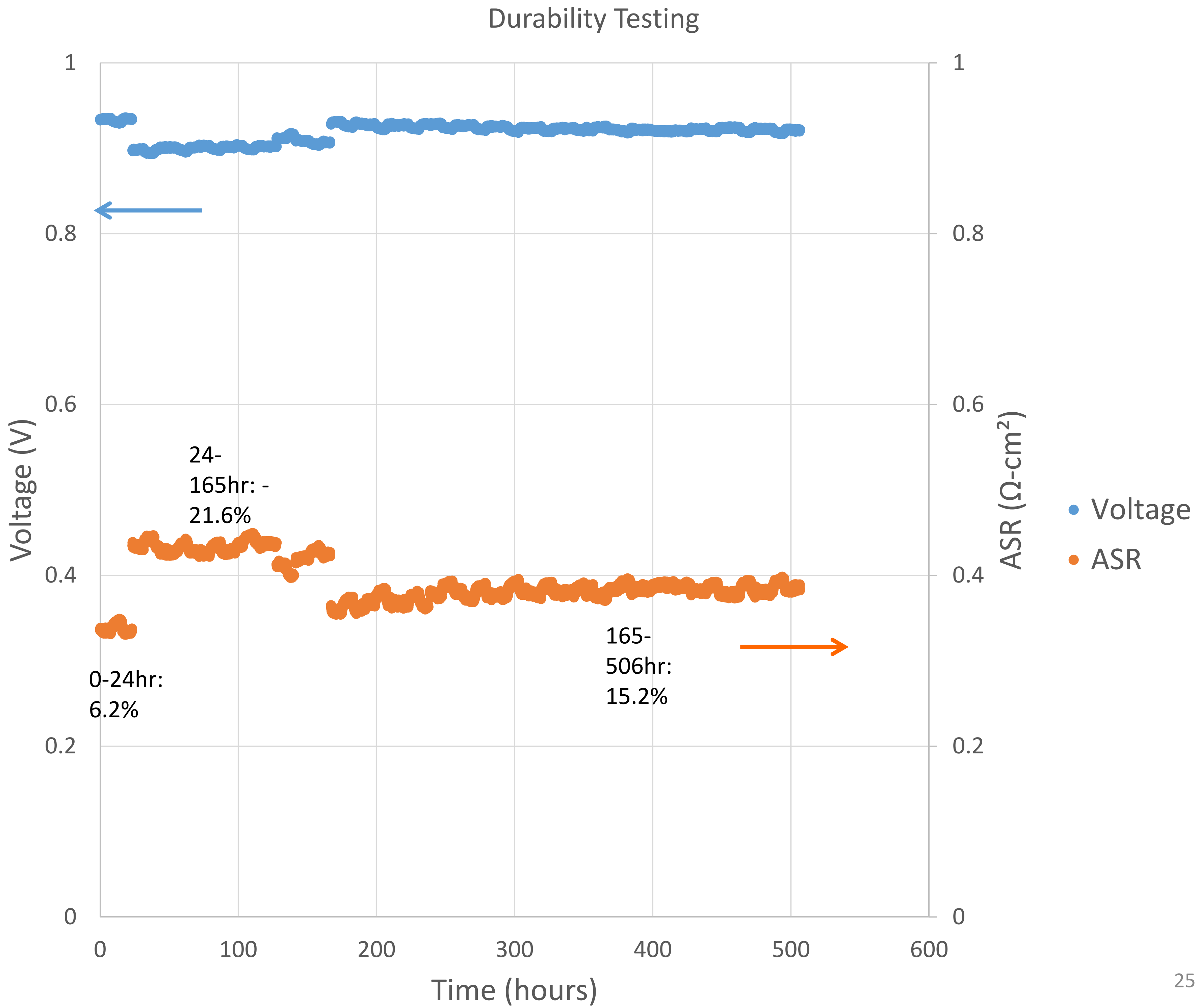
3DR can definitively determine
whether TPB is ***active***, or may be ***inactive***

LSM 80-95 durability testing: 624 h

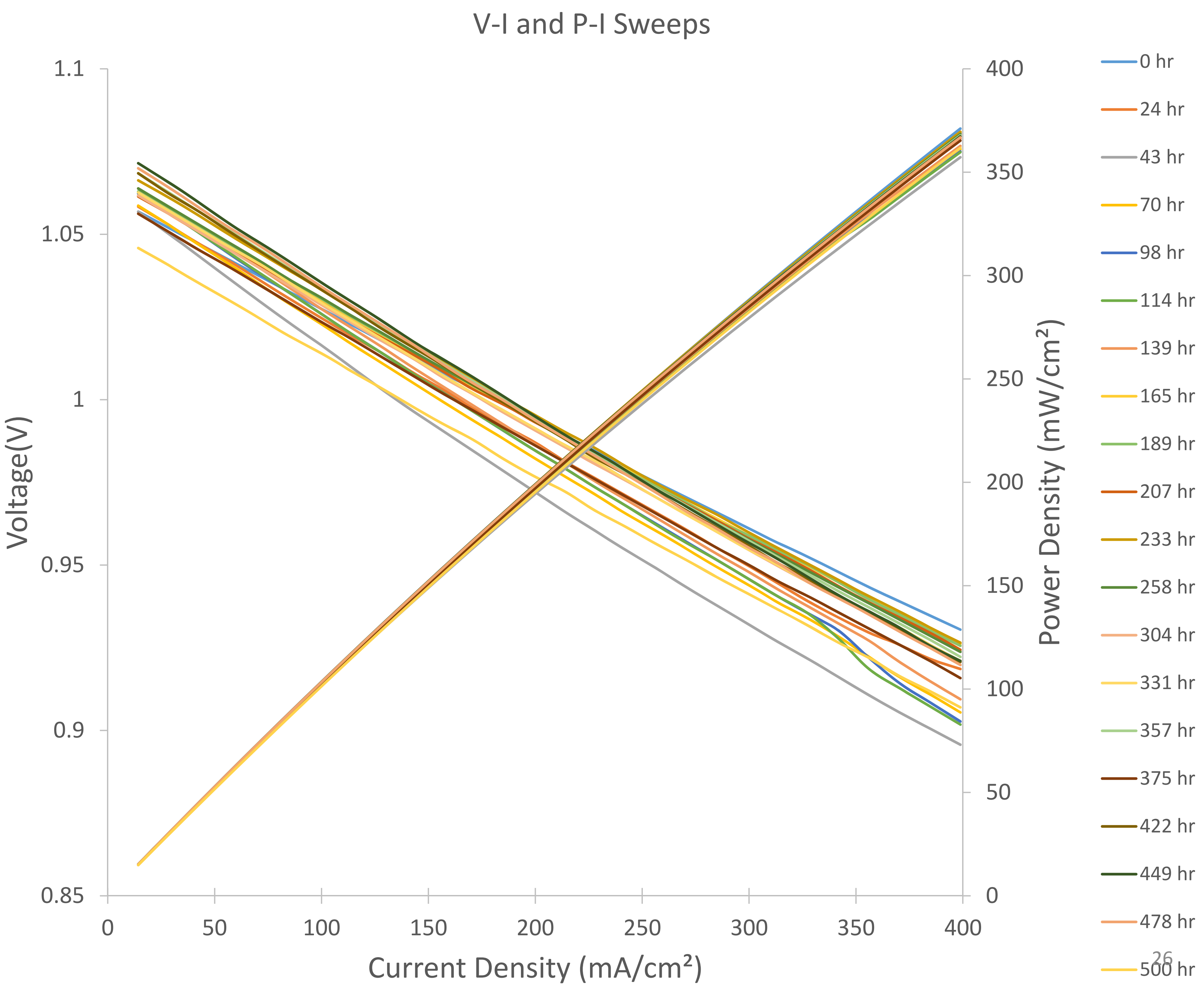


- 26% ASR rise
- ΔASR = Ω0.034 –cm^2

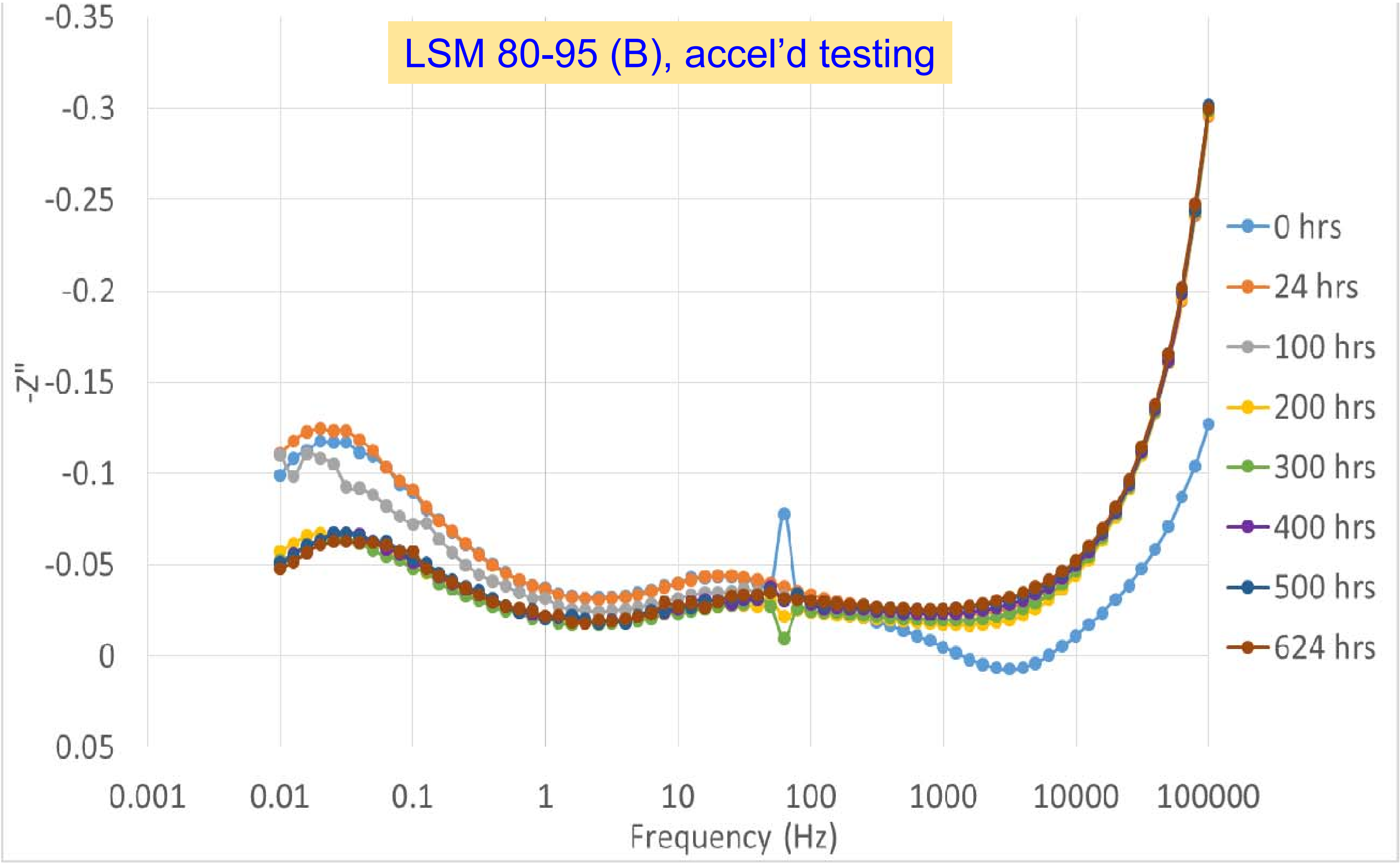
Cathode B: 500-hr Conventional Test



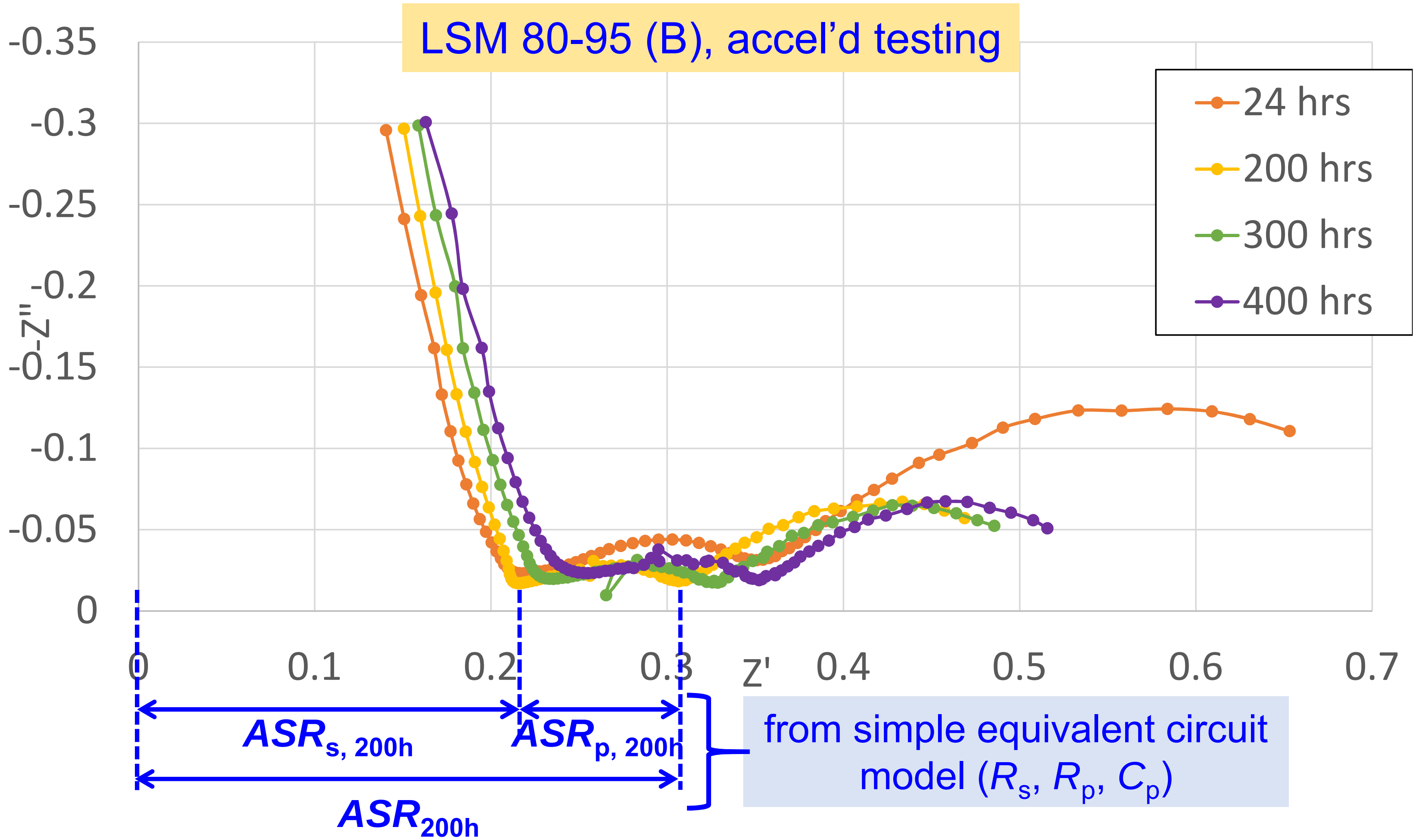
Cathode B: 500-hr Conventional Test



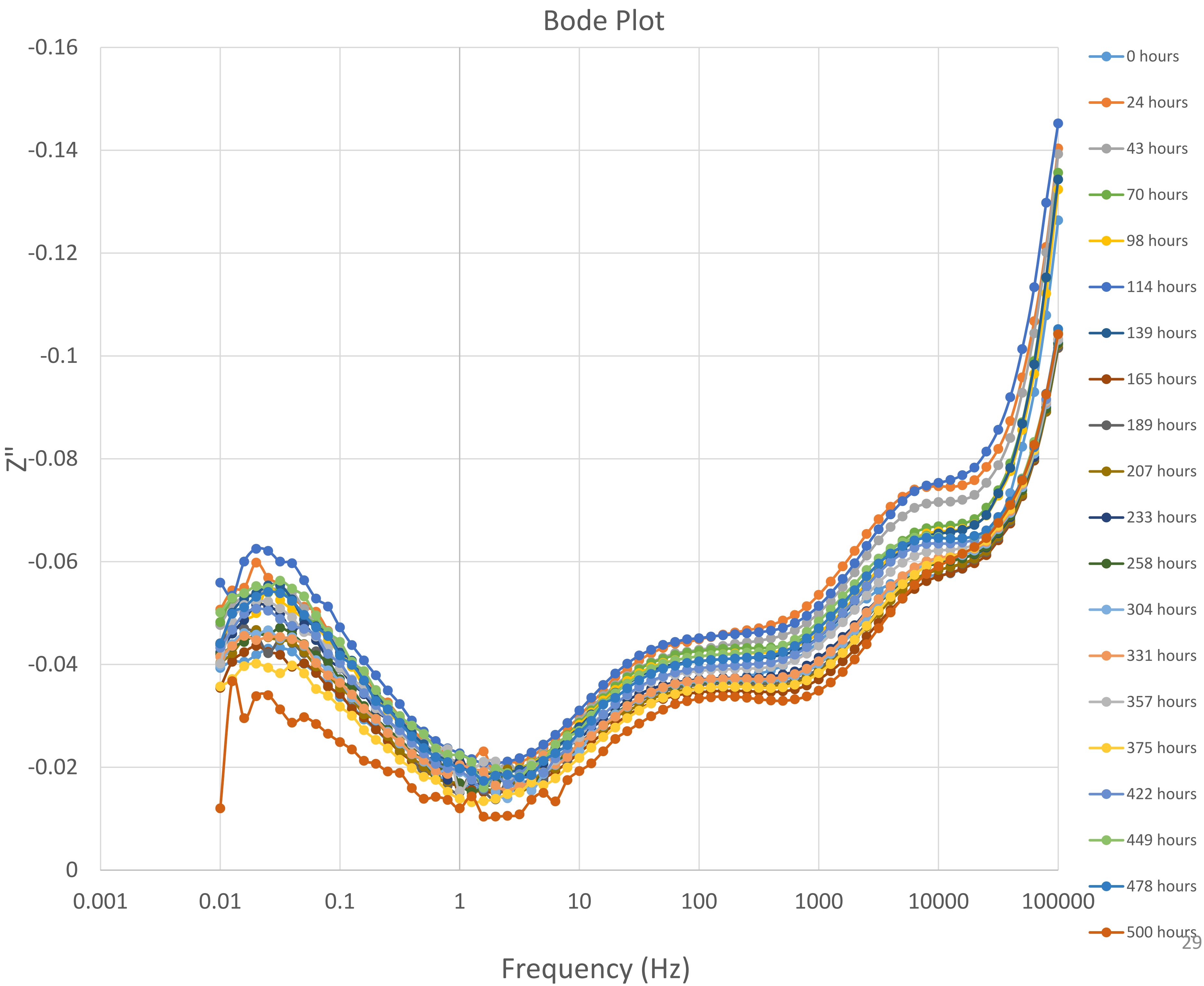
Representative Bode plots, 0–624 h



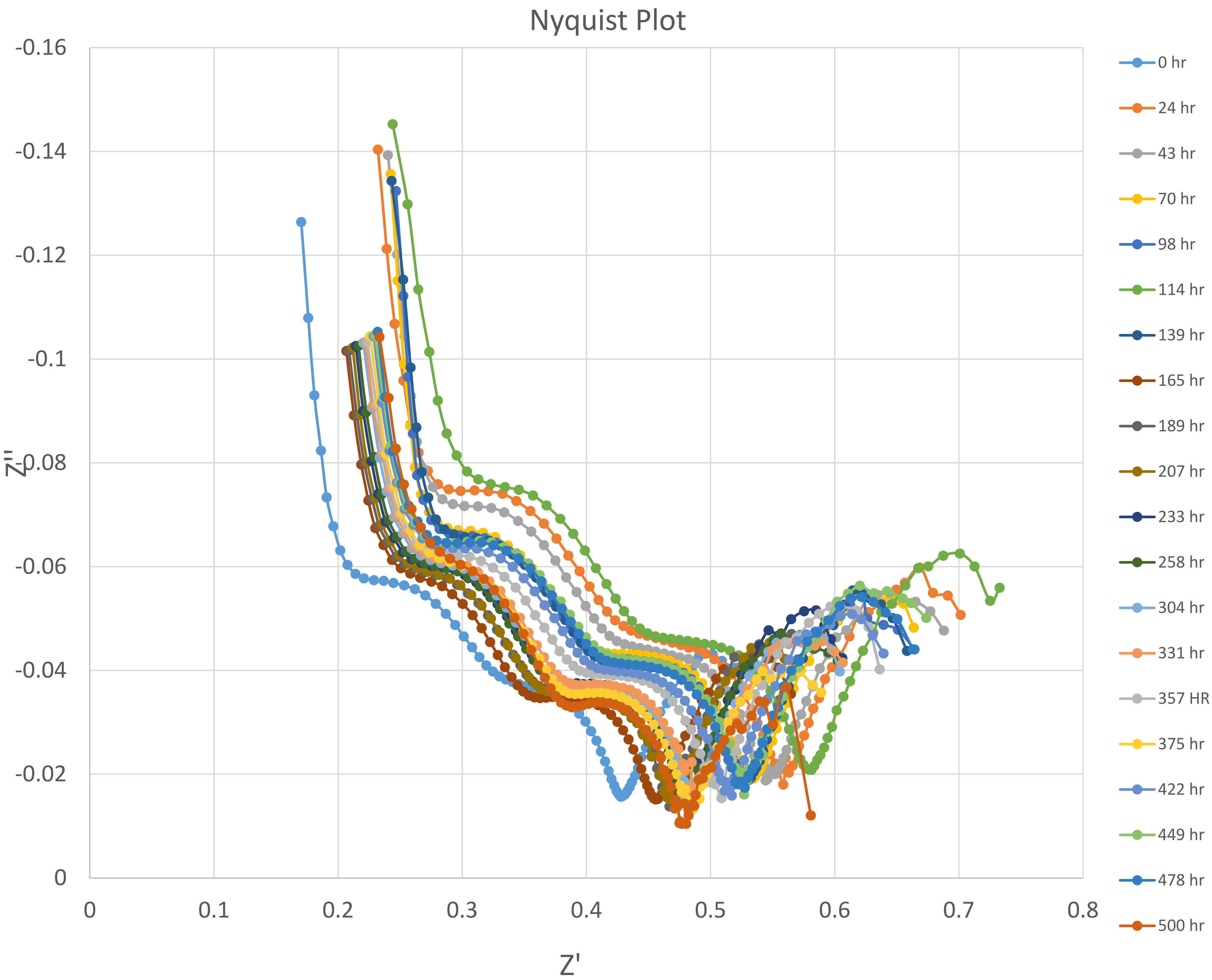
Representative Nyquist plots, 24–400 h

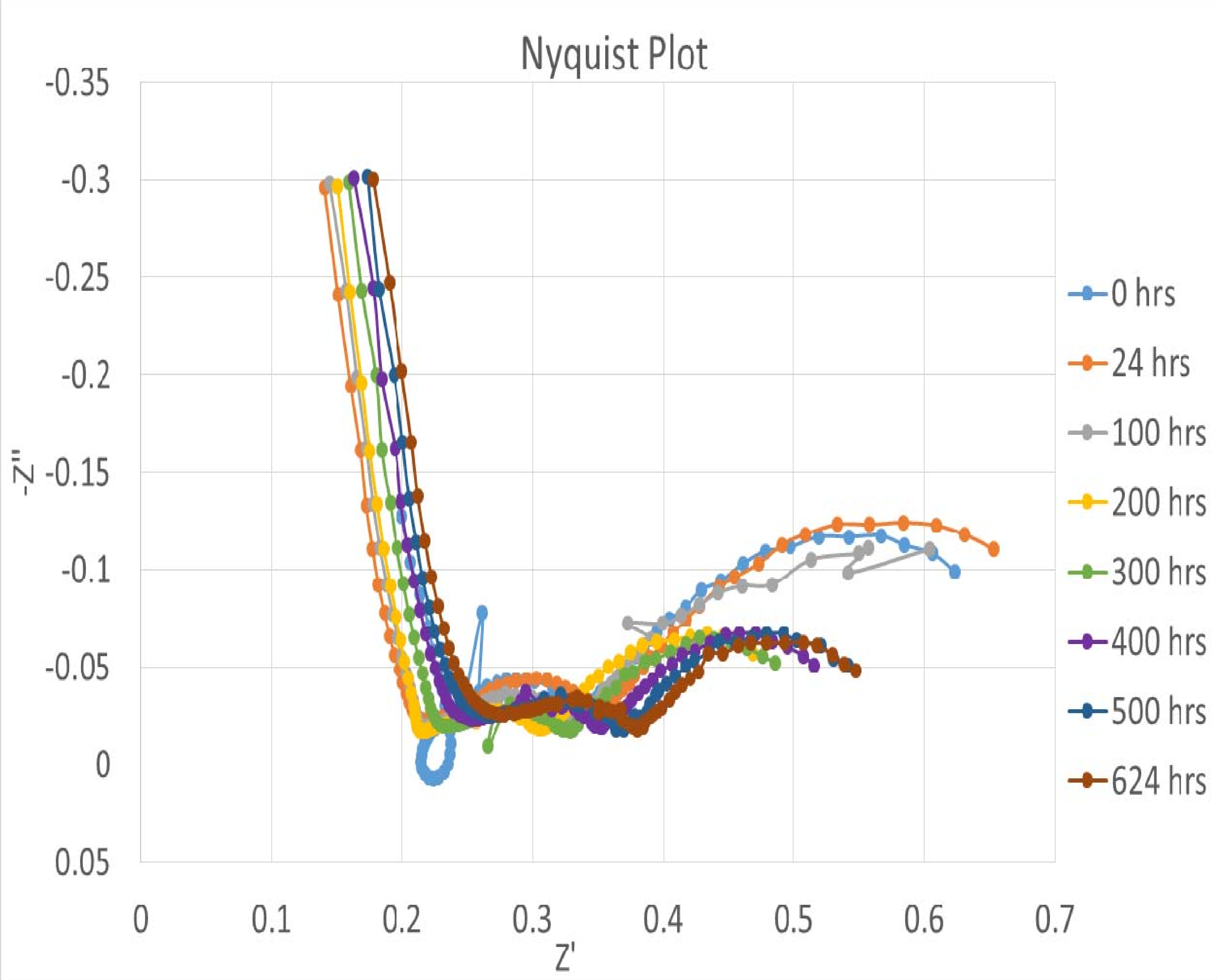


Cathode B: 500-hr Conventional Test



Cathode B: 500-hr Conventional Test




Nyquist Plot
-0.35
-0.3
-0.25
-0.2
-0.15
-0.1
-0.05
0
0.05
-Z''
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Z'
0 hrs
24 hrs
100 hrs
200 hrs
300 hrs
400 hrs
500 hrs
624 hrs

Microstructural studies

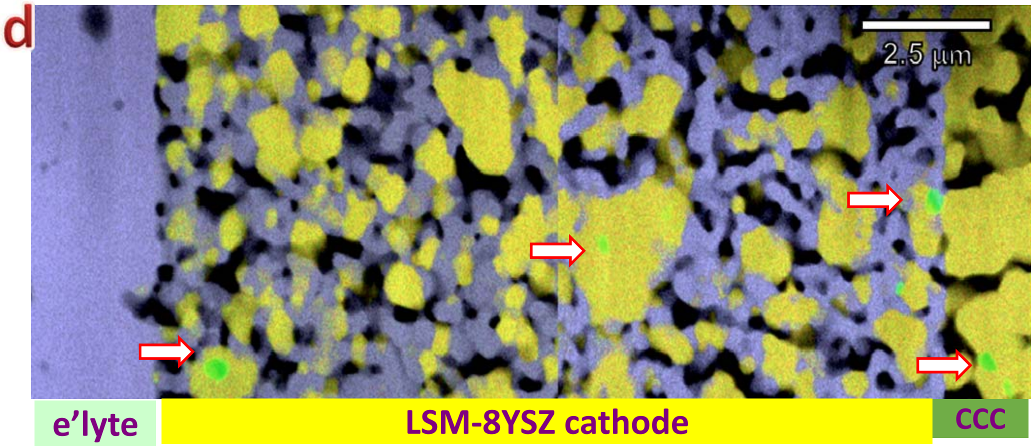
Progress as of 2016-03-08

	GenA button cell		GenB button cell	
	TEM	3D	TEM	3D
As-received	√	√	√	√
72 h accelerated	√	√		
200 h accelerated	√	√		
500 h accelerated	√	√	√	√
500 h conventional	√	√	√	√

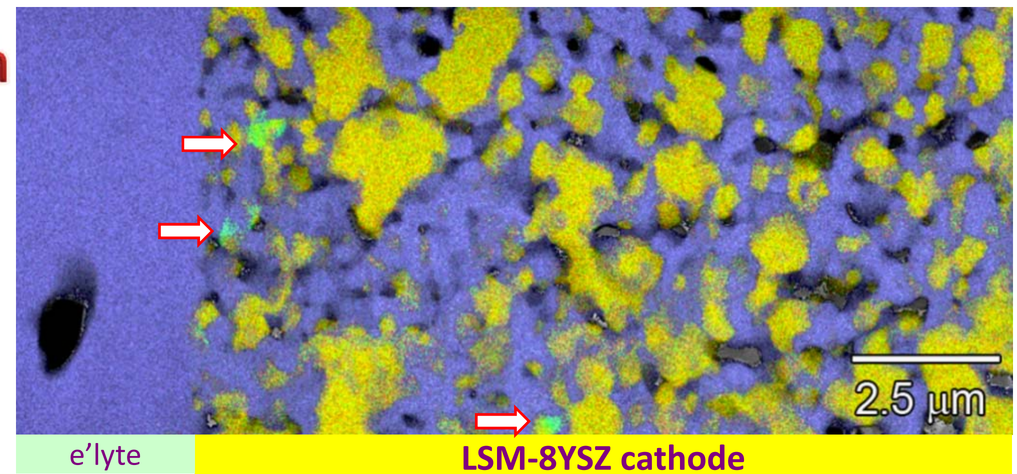
TEM w/EDXS mapping

- As reduced (0 h)
  - MnO_x (red arrows) observed sparingly across entire cathode
- 72 h and 493 h accelerated testing
  - MnO_x near cathode/electrolyte interface
  - MnO_x also observed in LSM cathode current collector (CCC) for 500 h
  - Smaller pores, but no obvious densification layer

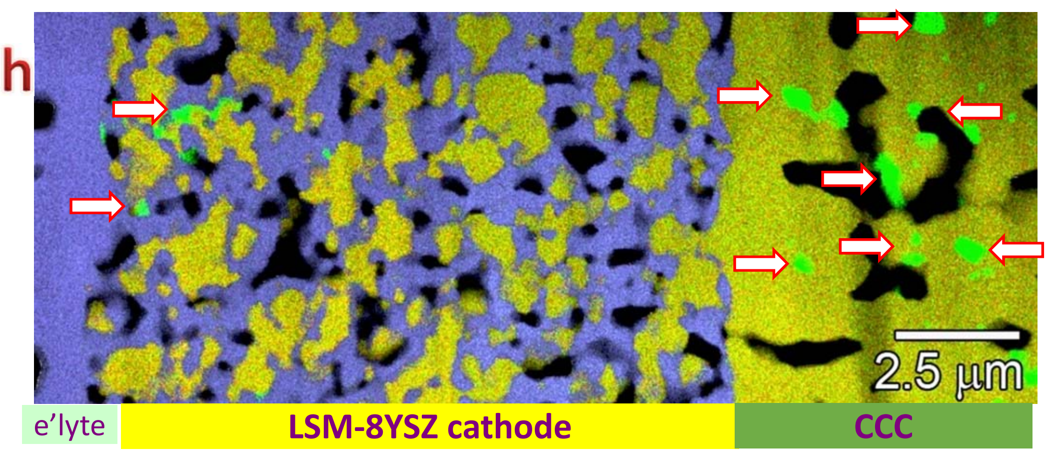
as reduced



72 h

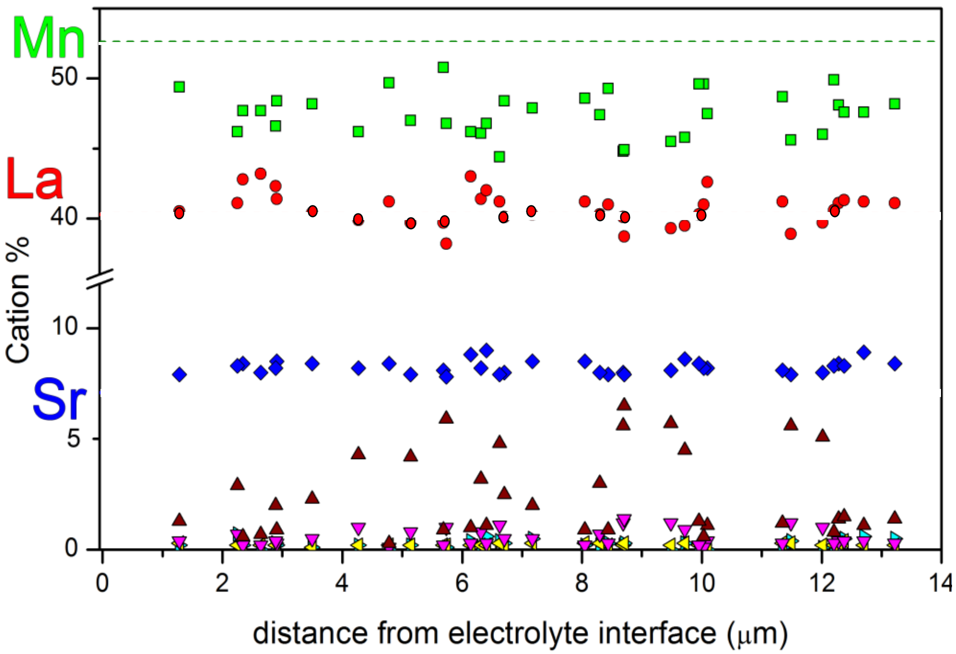


500 h

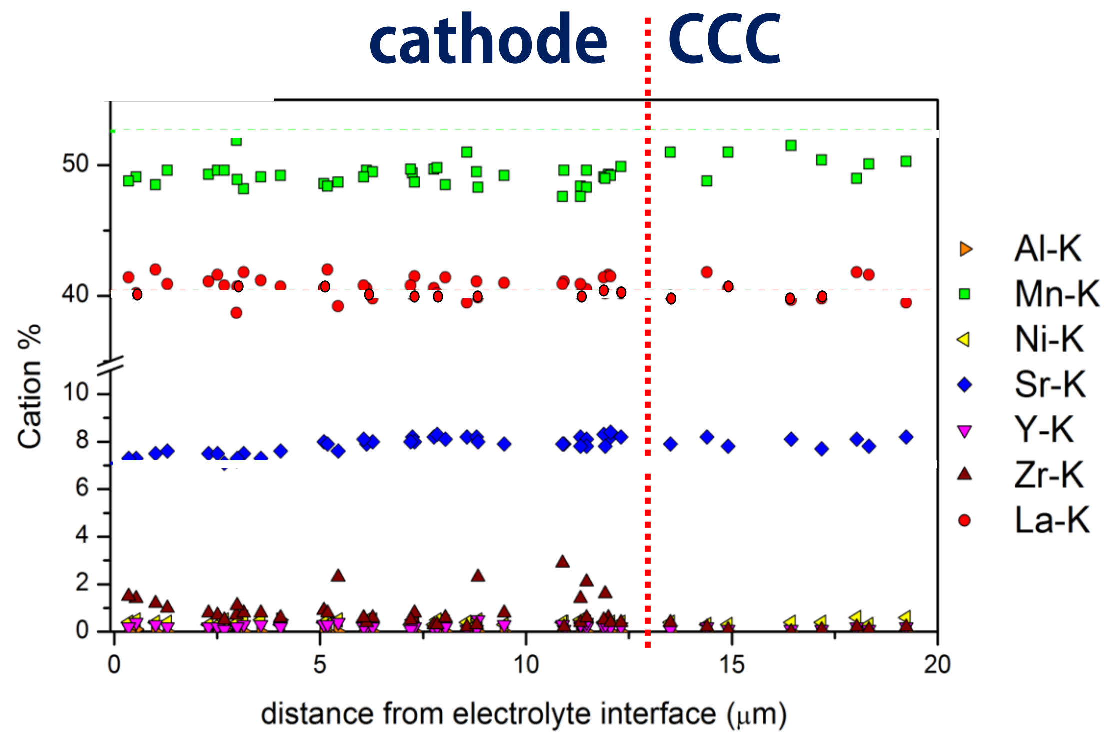


TEM w/EDXS of bulk LSM composition

72 h

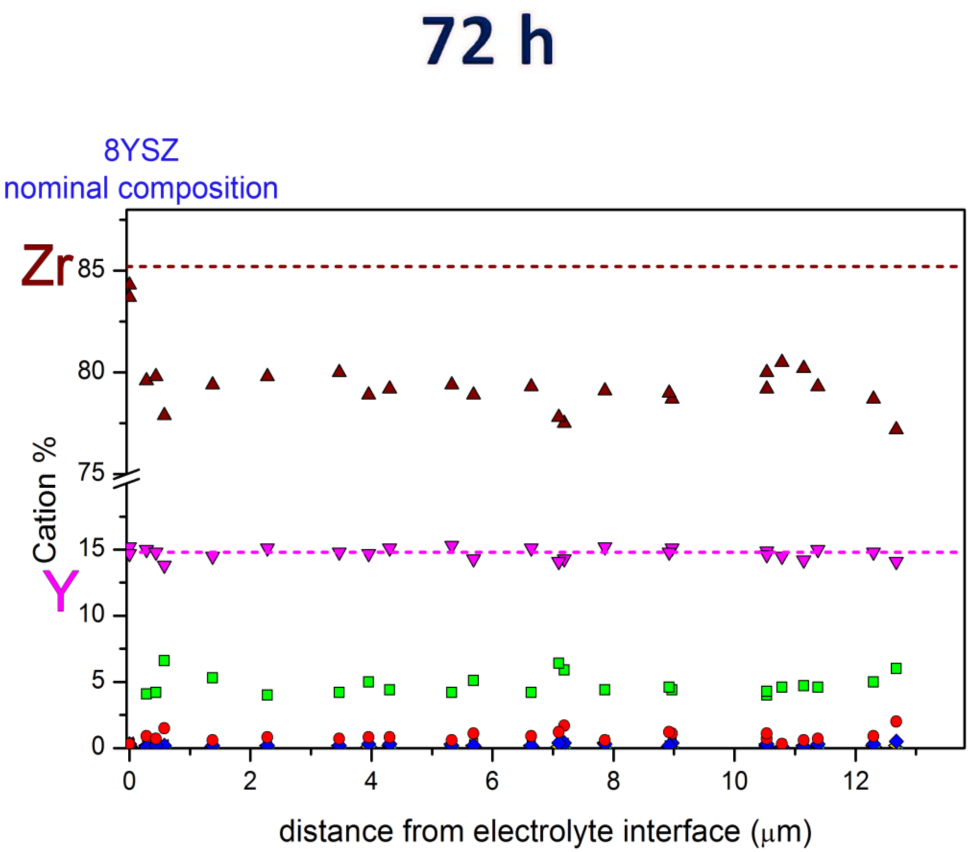


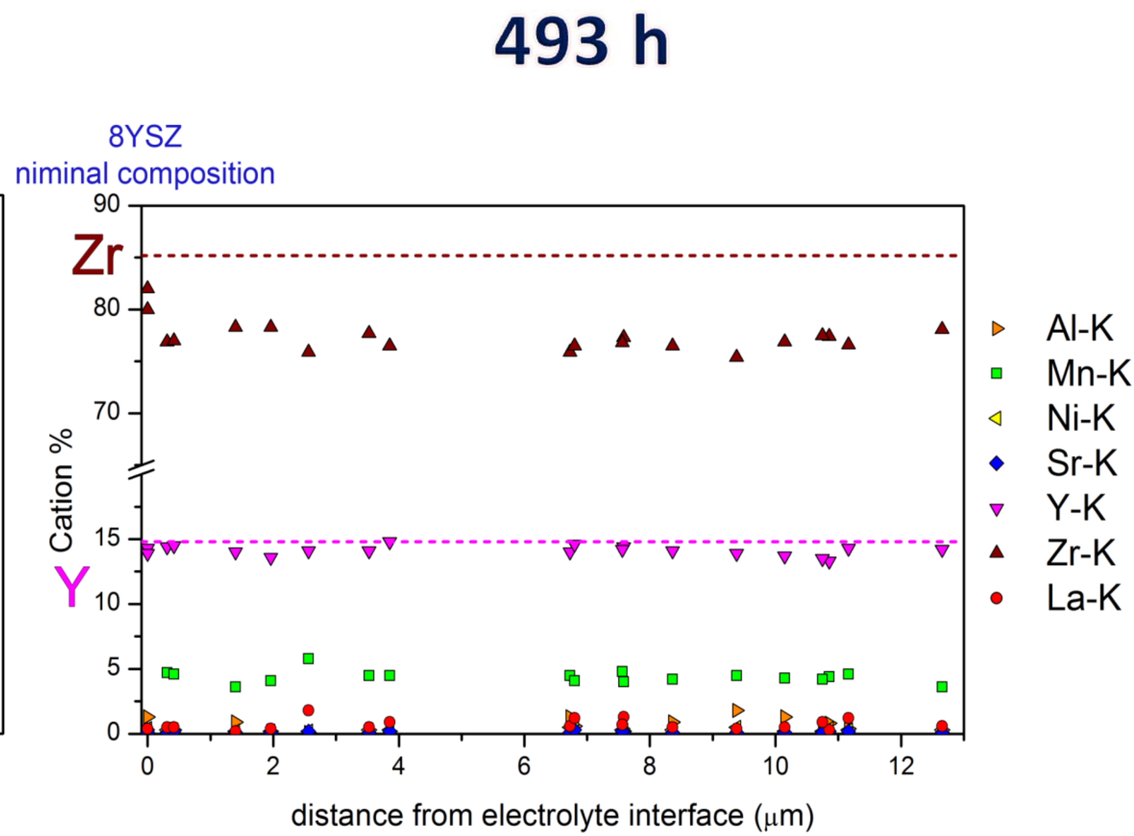
493 h



- **Uniform LSM composition across cathode and CCC**
- **Same composition as in as-reduced cell (not shown)**

TEM w/EDXS of bulk 8YSZ composition





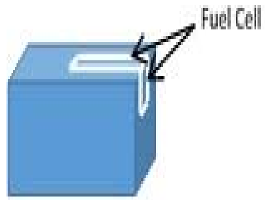
- **Uniform YSZ composition across cathodes**
- **4 – 5 cat% Mn**

1

Overview: 3D Reconstruction Process

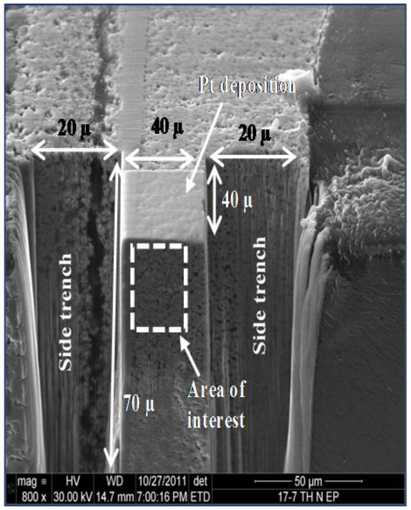
1: Sample Preparation

- Impregnate with epoxy
- Mount with SOFC layers exposed on two sides
- Polish specimen
- Coat with Pd



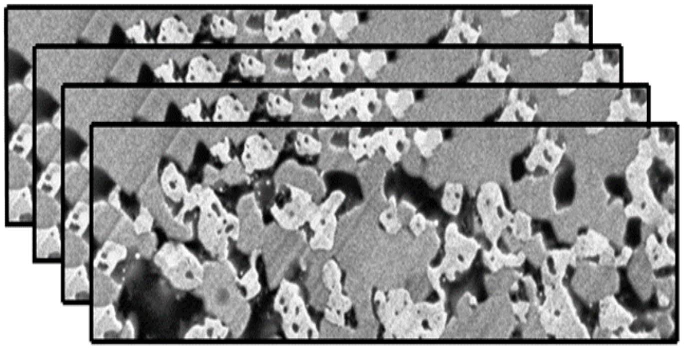
2: Preparing Area of Interest

- Deposit Pt to protect area of interest
- Focused Ga-ion beam (FIB): prepare two side trenches, one front trench



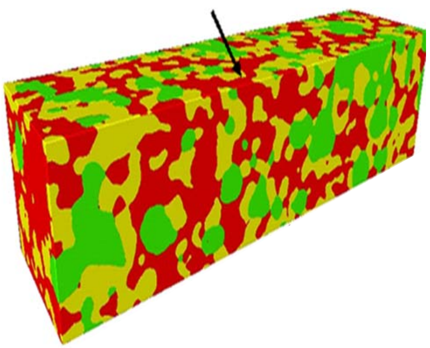
3: Data Collection

- Iteratively "slice and view":
  - FIB sections, 150 nm thick
  - Each section imaged in SEM



4: Data Processing

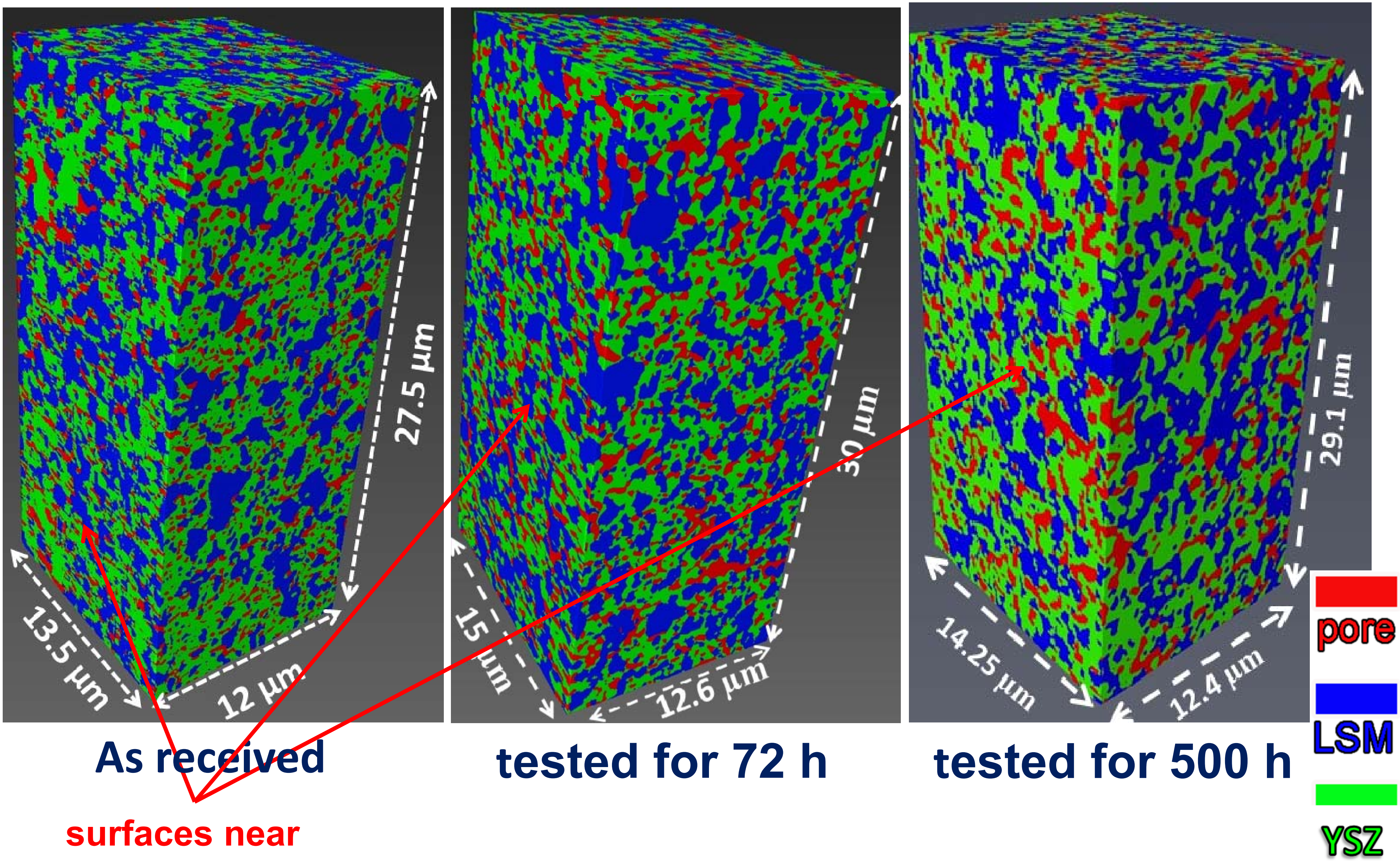
- Phase segmentation
- Synthesize stack of 2D images
- Calculate:
  - volume fractions
  - particle diameters
  - tortuosity
  - triple phase boundary (TPB) density



Slide 36

1 Making steps 1 through 4 appear one at a time could be helpful here. Otherwise the slide is a bit overwhelming at first sight.
Before you leave this slide, you should briefly point out what aspects of your sample preparation were not routine, or for which you deviated from standard practice in ways that improved your analyses.
Mark De Guire, 10/28/2014

3DR of cathode A — accelerated testing



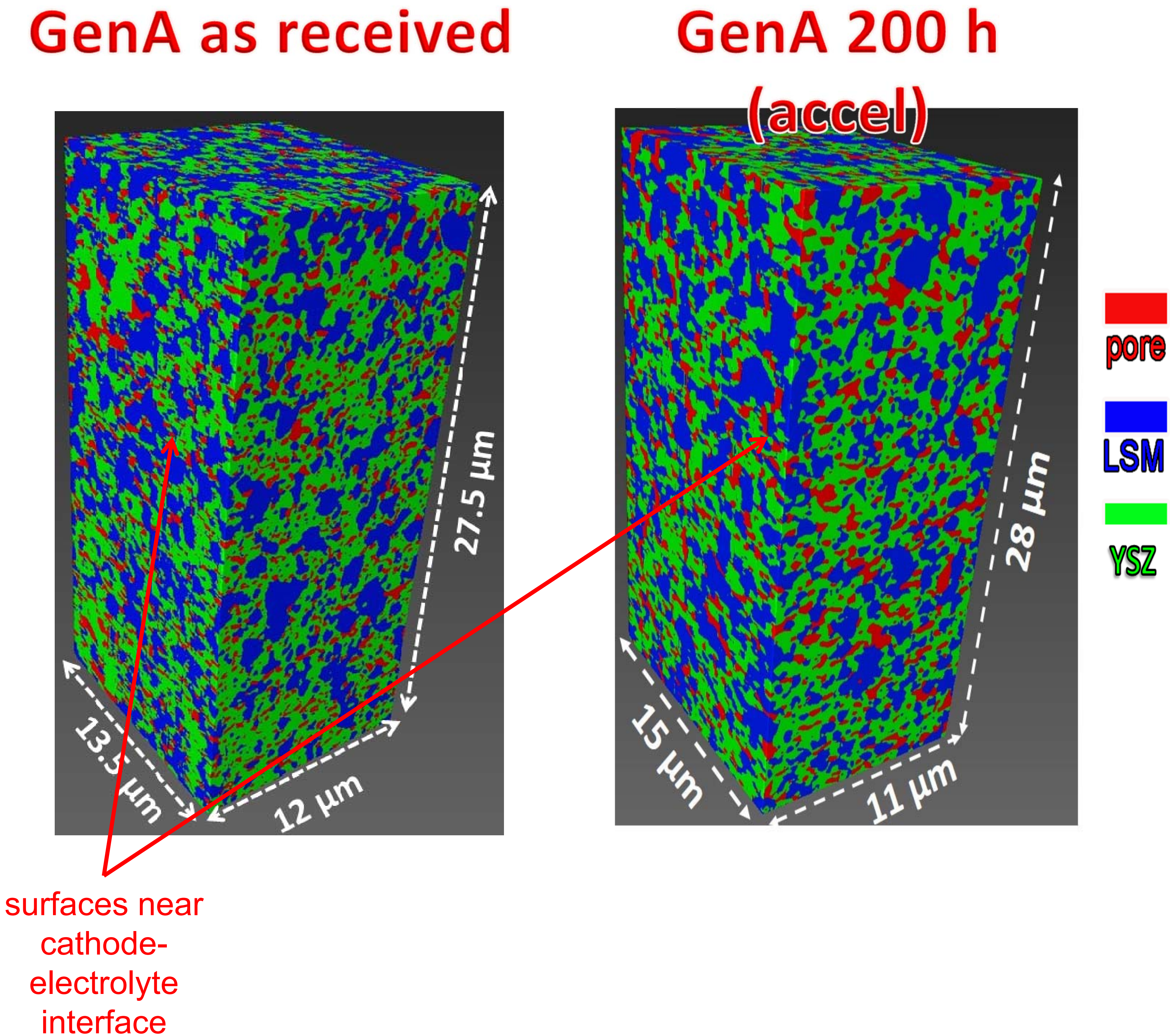
As received

tested for 72 h

tested for 500 h

surfaces near cathode-electrolyte interface

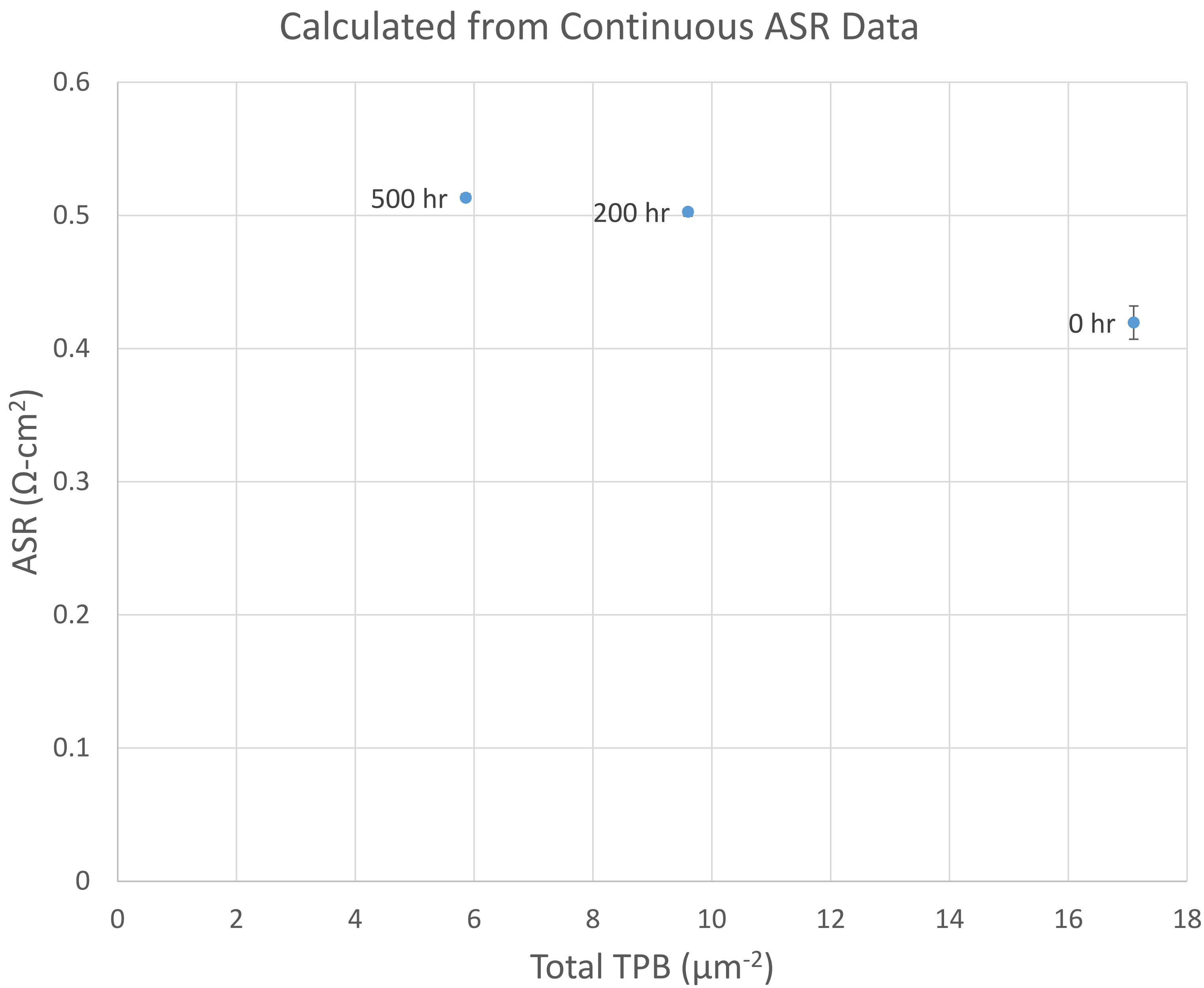
- **No obvious densification layer — consistent with TEM**


GenA as received
GenA 200 h
(accel)
27.5 µm
13.5 µm
12 µm
28 µm
15 µm
11 µm
pore
LSM
YSZ
surfaces near
cathode-
electrolyte
interface

		Gen A		
		as received	**200 h accel.**	**493 h accel.**
sample volume (μm^3)		≈ 4350	≈ 4620	≈ 4525
volume fraction (%)	porosity	17	17	18.4
	YSZ	42	41	43.2
	LSM	41	42	38.4
particle diameter (μm)	porosity	**0.2**	**0.34**	**0.42**
	YSZ	0.5	0.6	0.46
	LSM	0.6	0.7	0.6
tortuosity	porosity	2	1.7	1.6
	YSZ	1.5	1.43	1.3
	LSM	1.3	1.35	1.4
normalized surface area (μm^{-1})	porosity	26	17.4	14.2
	YSZ	12	10	13
	LSM	10	7.6	9.88
Total TPB (μm^{-2})		**17.1**	**9.6**	**5.86**
Active TPB (μm^-		[illegible]	[illegible]	[illegible]

		Gen A		Gen B	
		as reduced	493 h accel.	as received	500 h accel
sample volume (μm^3)		≈ 4350	≈ 4525	≈ 6300	≈ 5096
volume fraction (%)	porosity	**17**	**18.4**	**29**	**26**
	YSZ	42	43.2	33	35
	LSM	41	38.4	38	39
particle diameter (μm)	porosity	**0.2**	**0.42**	**0.46**	**0.38**
	YSZ	0.5	0.46	0.47	0.51
	LSM	0.6	0.6	0.67	0.7
tortuosity	porosity	2	1.6	1.34	1.67
	YSZ	1.5	1.3	1.32	1.66
	LSM	1.3	1.4	1.3	1.44
normalized surface area (μm^{-1})	porosity	26	14.2	13	15.88
	YSZ	12	13	13	11.88
	LSM	10	9.88	8,9	8.5
Total TPB (μm^{-2})		**17.1**	**5.86**	**14.5**	**14.8**
Active TPB (μm^{-2})		**10.3**	**5.13**	**13.0**	**12.5**

Total TPB – ASR relationship



Active TPB – ASR relationship