Effects of Composition and Operating Conditions on the Microstructure and Performance of LSM-Based SOFC Cathodes

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Outline

- $(La_{1-x}Sr_x)_{1-y}MnO_{3\pm\delta}$ (lanthanum strontium manganite, LSM)

  — effect of *Mn excess* (A-site deficiency) on long-term performance

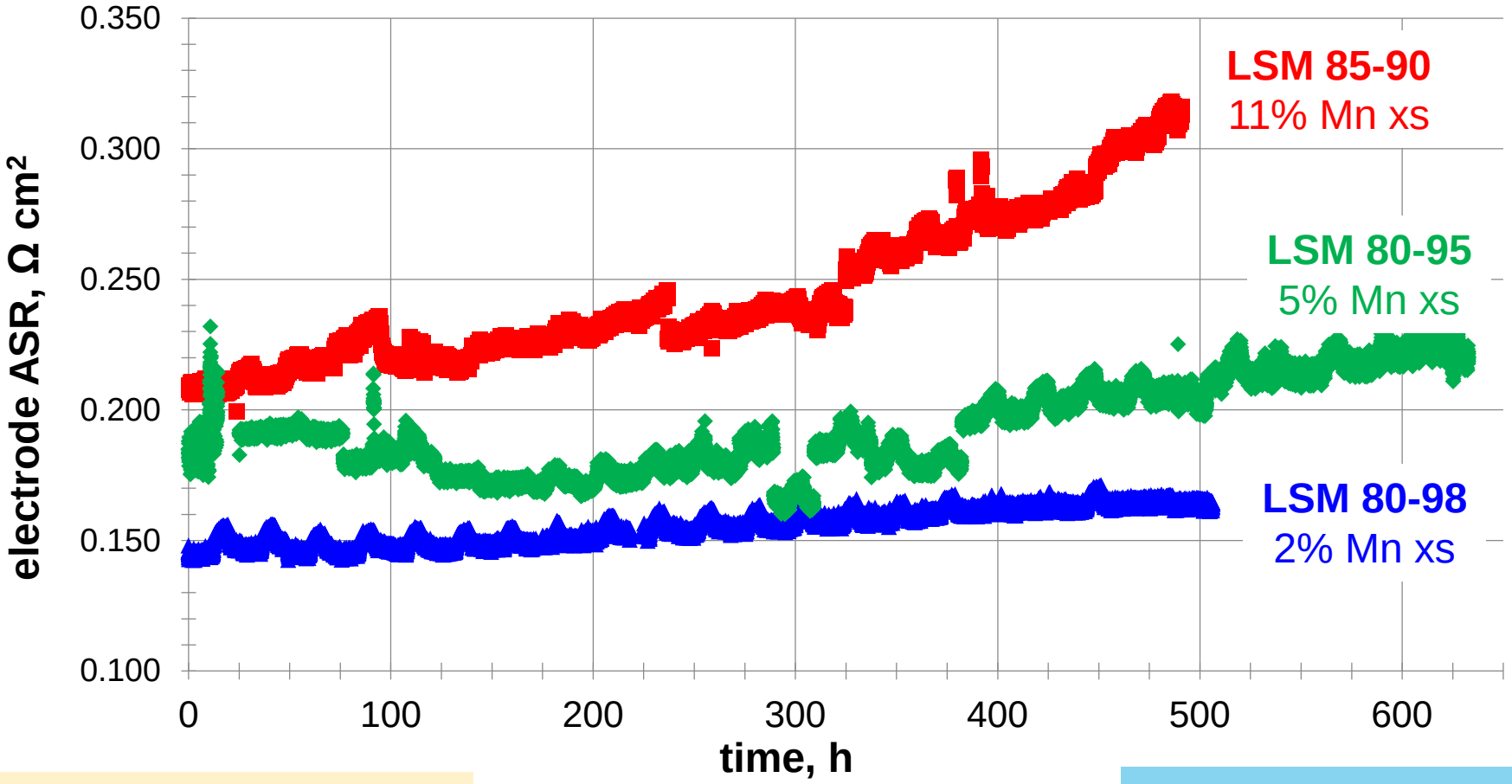
  - Durability testing ⇒ *ASR* (area specific resistance) vs. time
  - Cathode *microstructural* changes
    - *TEM/EDXS* (transmission electron microscopy / energy-dispersive x-ray spectroscopy)
    - *3DR* (3D reconstruction)

- New observations and questions
  - Comparison: long-term conventional testing vs. accelerated testing
  - Mn distribution and its evolution with time — a clue to degradation?

Cell specifications; testing procedures

- Button cells fabricated at LGFCS
  - 8YSZ electrolyte
  - NiO / 8YSZ anode
  - Cathodes: LSM / 8YSZ
    - $(La_{0.85}Sr_{0.15})_{0.90}MnO_{3\pm\delta}$ (LSM 85-90) — *11%* Mn excess
    - $(La_{0.80}Sr_{0.20})_{0.95}MnO_{3\pm\delta}$ (LSM 80-95) — *5%* Mn excess
    - $(La_{0.80}Sr_{0.20})_{0.98}MnO_{3\pm\delta}$ (LSM 80-98) — *2%* Mn excess
- Cell testing
  - Anode: humidified H_2, 50 sccm
  - Cathode: ambient air
  - *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

Electrode ASR (accelerated testing)*



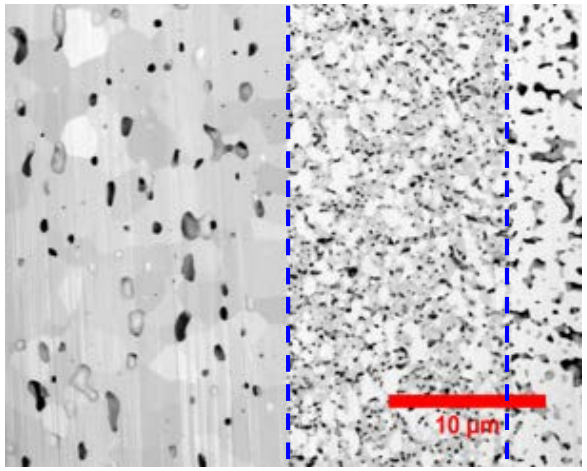
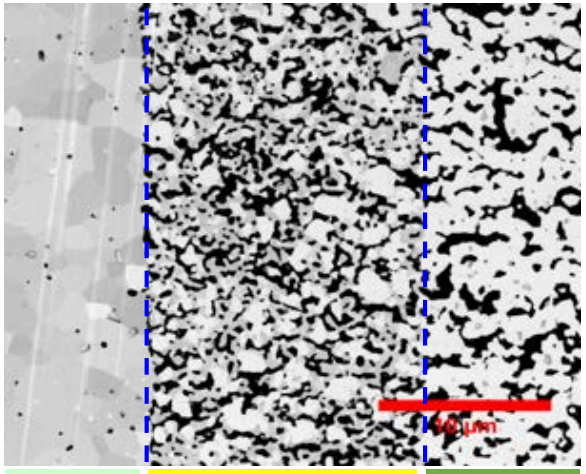
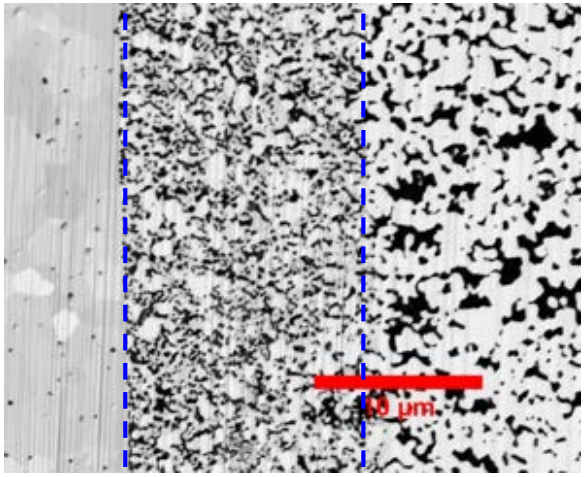
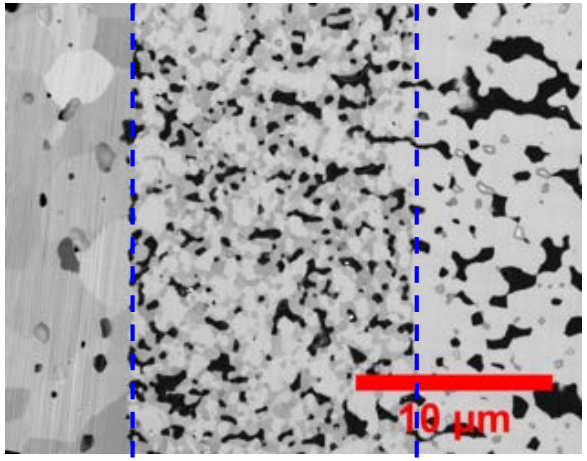
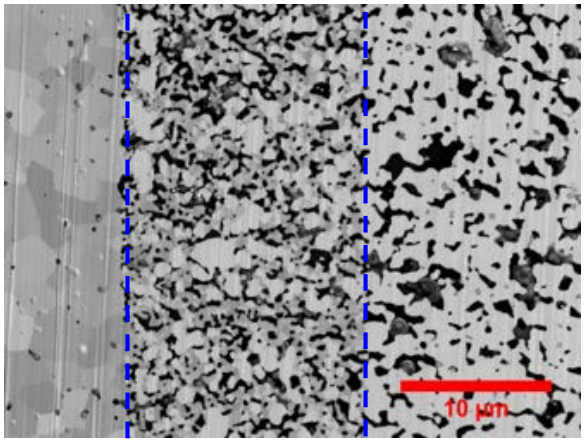
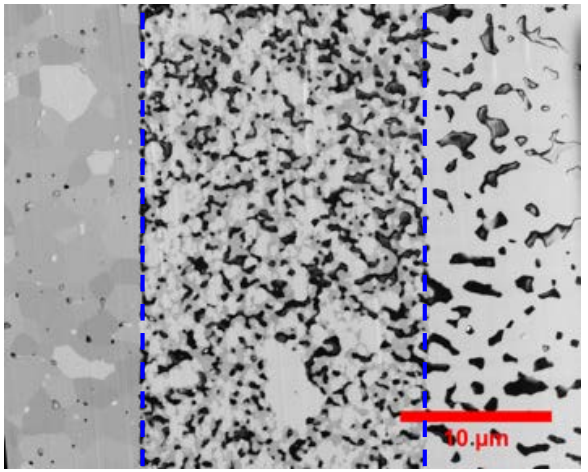
LSM 85-90 (11% Mn xs):
- ***Highest ASR*** overall
- ***Highest rise in ASR***

ASR ↓ as Mn excess ↓

LSM 80-98 (2% Mn xs):
- ***Lowest ASR*** overall
- ***Highest power,*** 500 h

*) total cell DC ASR, minus estimated ASR for 8YSZ substrate @ nominal thickness & DC conductivity

Microstructural change after 500 h accelerated testing

	LSM 85-90 (11% Mn xs)	LSM 80-95 (5% Mn xs)	LSM 80-98 (2% Mn xs)
as received			
500 h, accel'd			

- Coarsening of pores & LSM
- Densification of CCC*

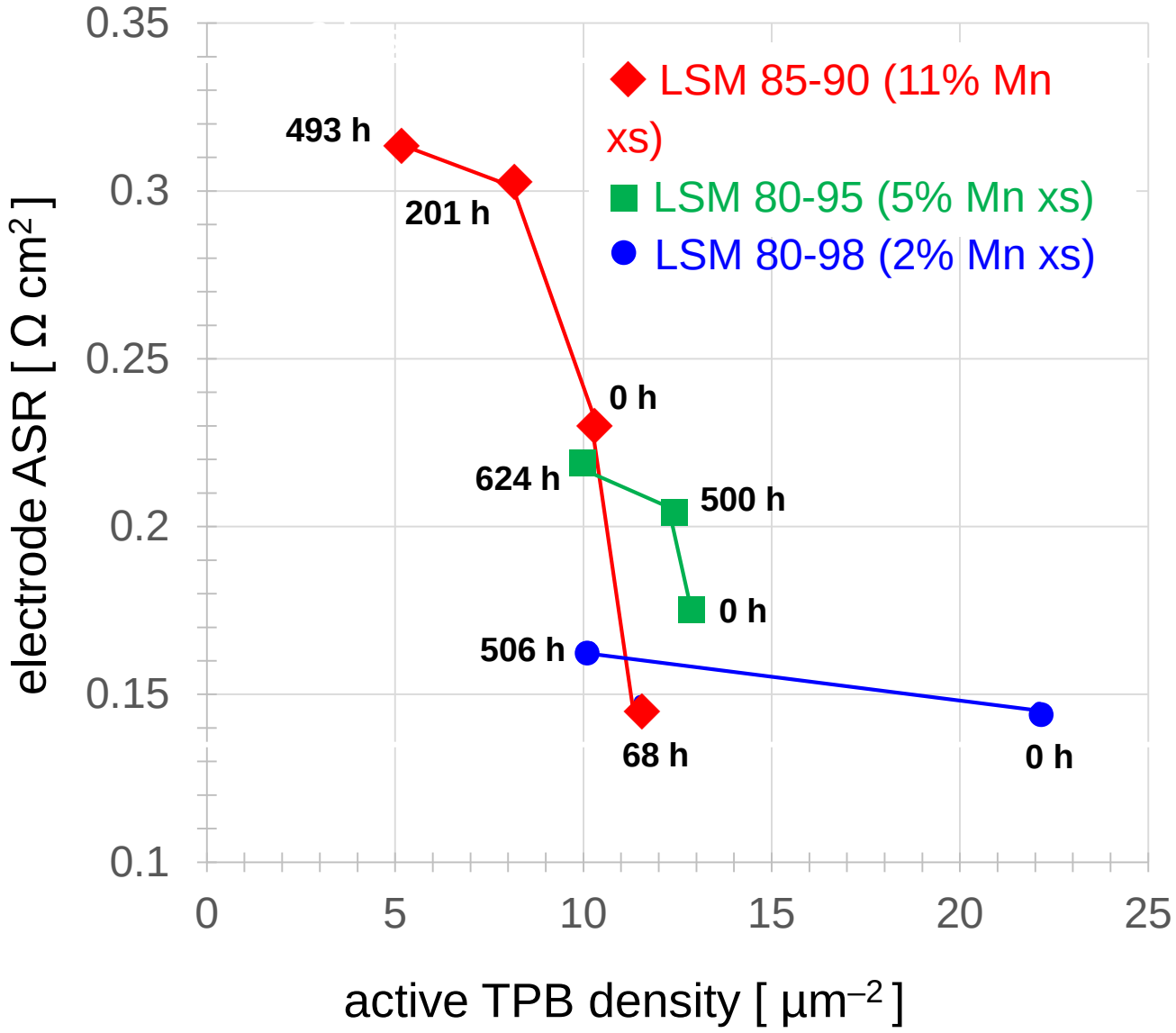
- Highest overall microstructural stability

- Coarsening of pores & LSM
- Densification of CCC*

*) cathode current collector

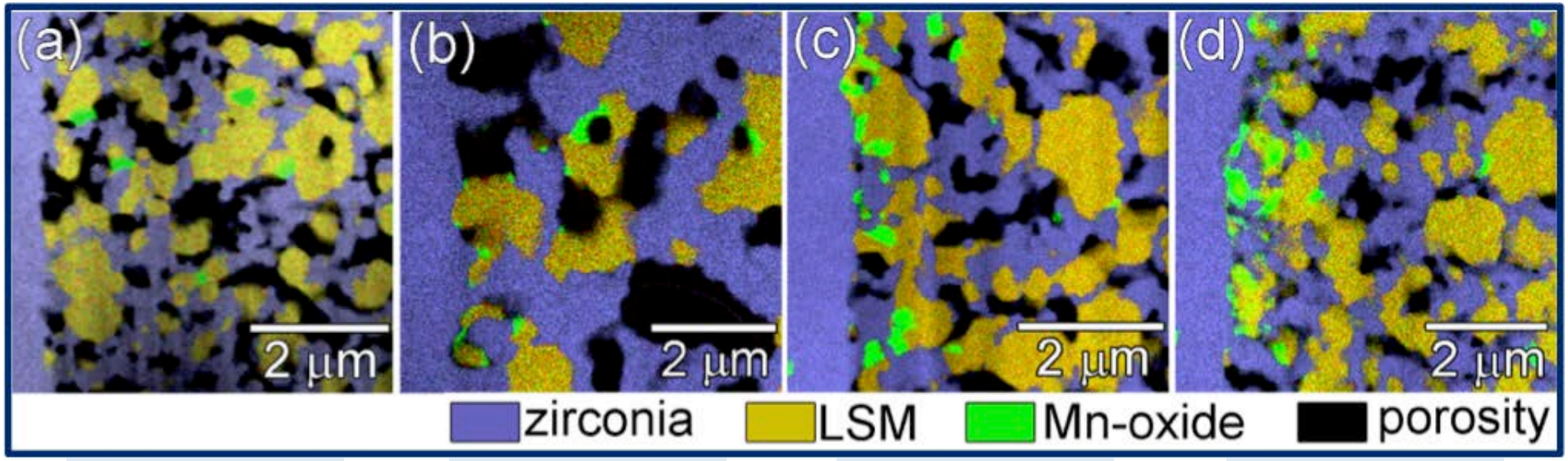
ASR and TPB density: role of Mn excess **(accel'd testing)**

- As Mn excess ↑, ***ASR*** ↓
- As test time ↑:
  - ***Active TPB*** ↓
  - ***Total ASR*** ↑
- Effects on ASR diminish as Mn excess ↓



Prior work, normal conditions: TEM/EDXS

cells tested at 800 °C



as fired | 2 kh | 8 kh | 16 kh

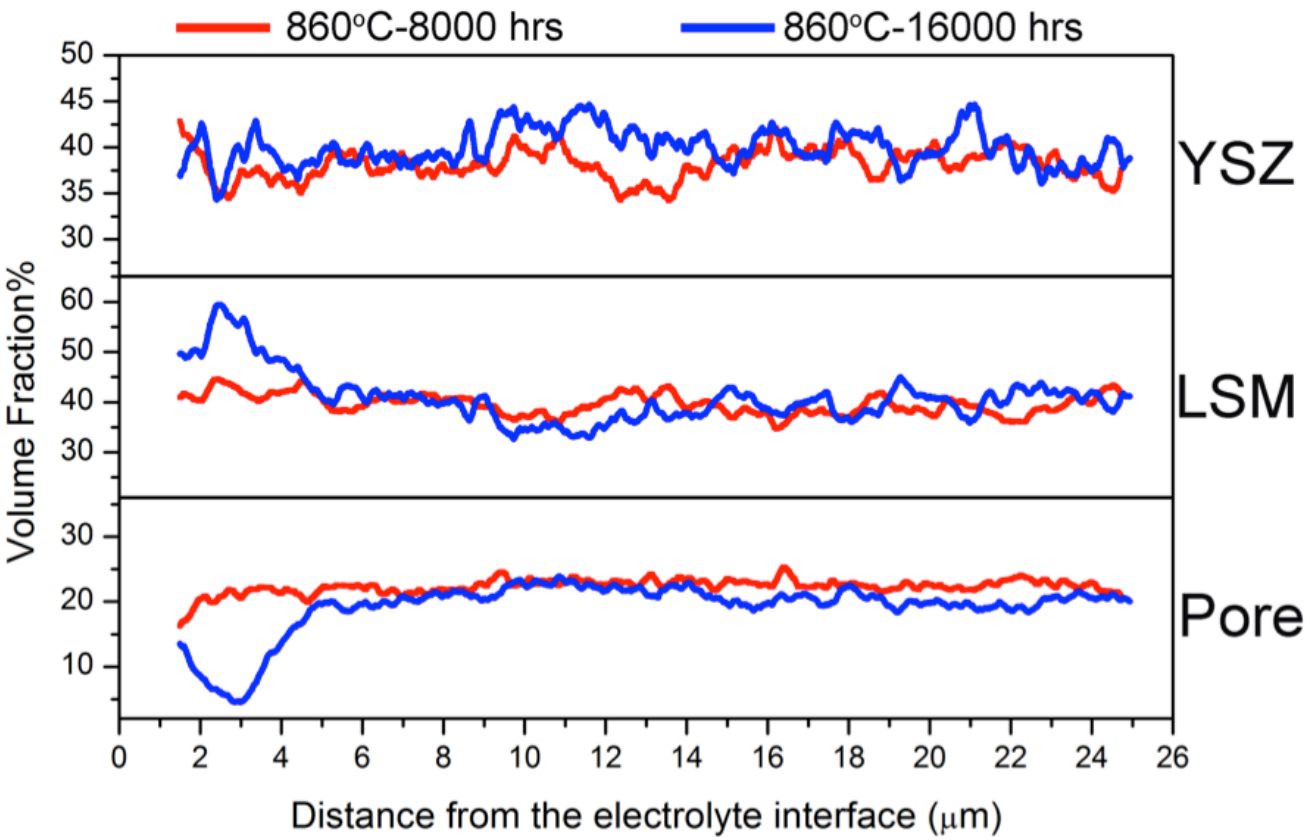
At cathode-electrolyte interface* after extended testing:[1]

- *Reduced porosity*
- *Accumulation of Mn_2O_3 or Mn_3O_4*[2]

*) Left side of each image

1) H.-J. Wang et al., 14th SECA Workshop, Pittsburgh, Pennsylvania, July 2013.
2) H.-J. Wang et al., *Metall. Mater. Transactions E: Materials for Energy Systems* **1** [3] 263-271 (2014).

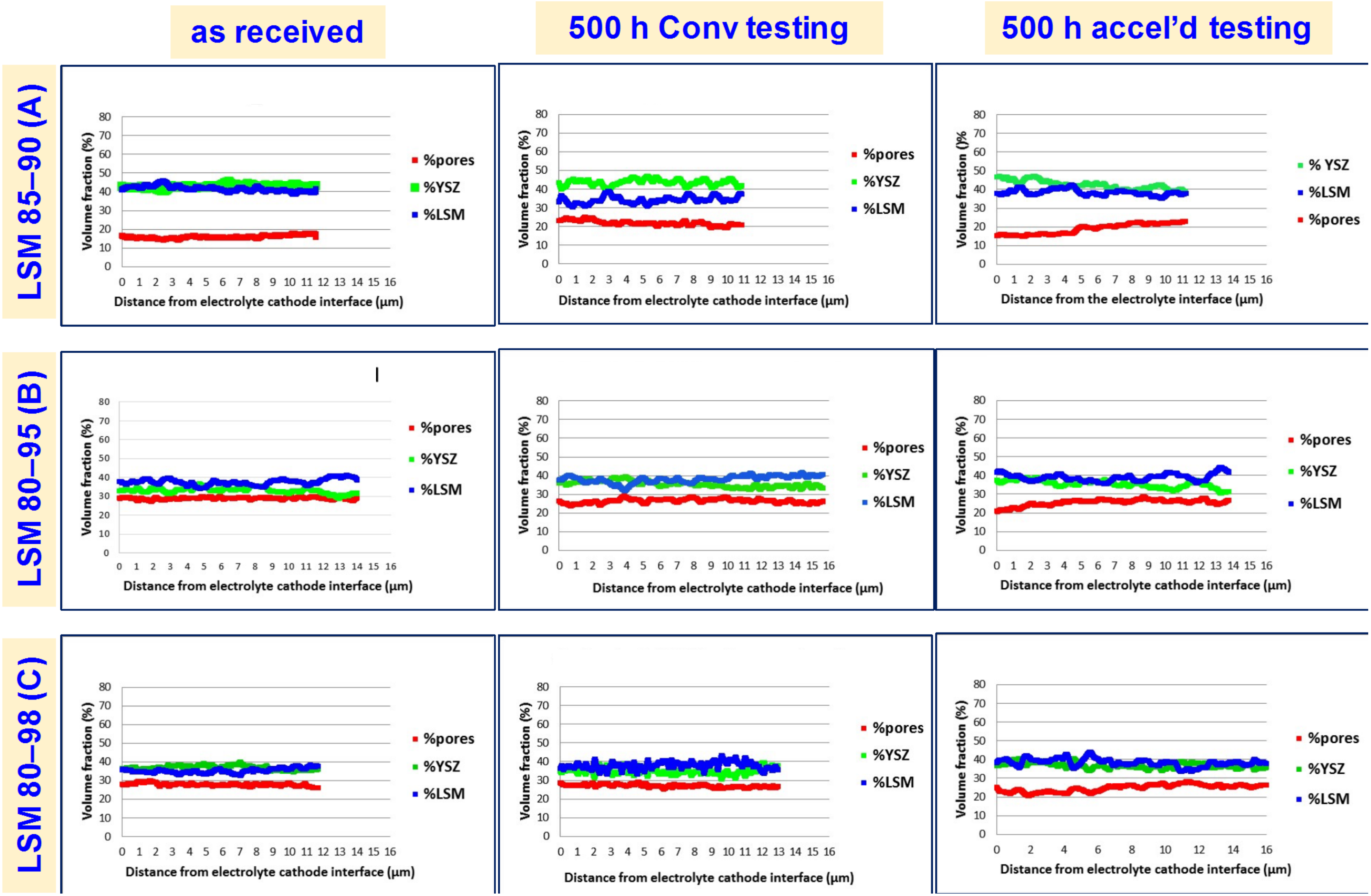
Prior work, normal conditions: 3DR



- ***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

Phase profiles across cathodes



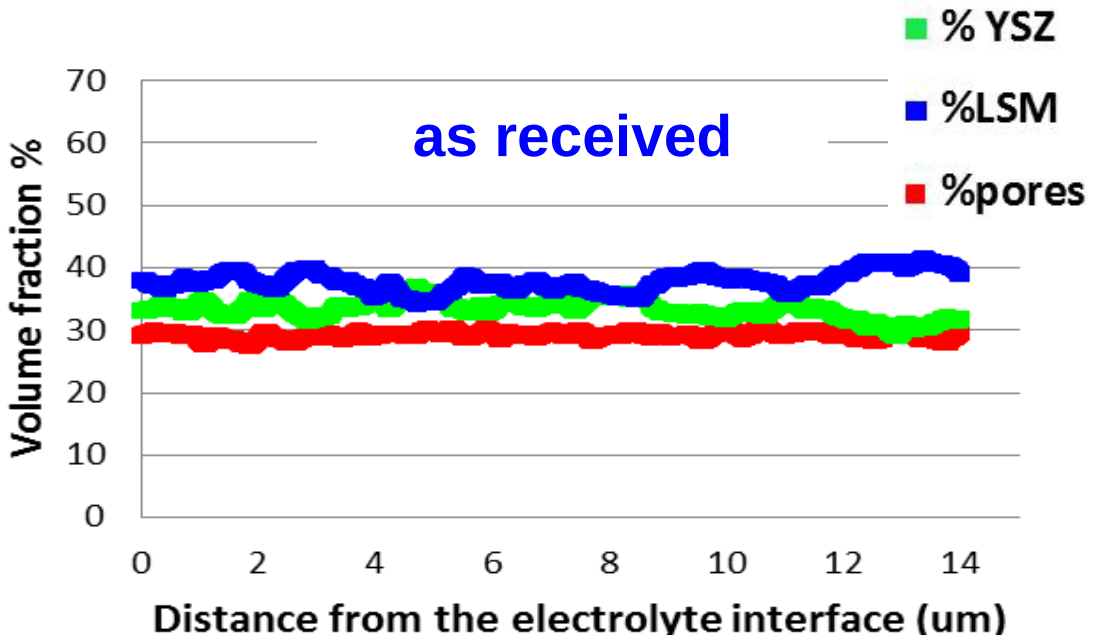
As-received and 500-h conv'l testing:
uniform phase profiles

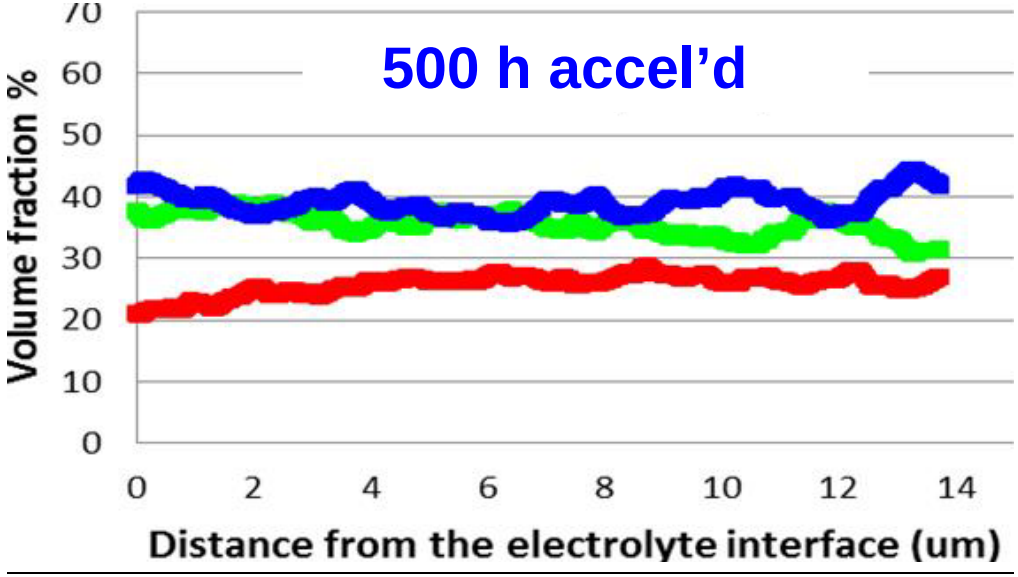
Porosity gradients,
lowest at e'lyte interface

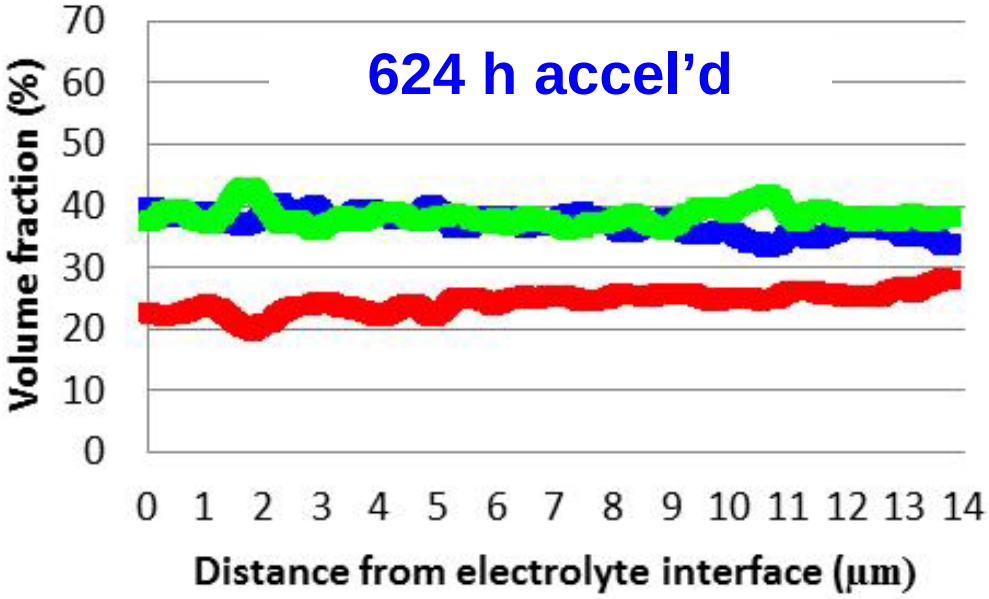
LSM 80-95: phase profiles, 0–624 h accel'd testing

5% Mn excess:

- Develops porosity gradient during operation, …
- … denser at cathode/ electrolyte interface
- Not localized at e'lyte







Microstructural evolution during operation

Normal conditions,
8,000–16,000 h:

- ***Loss of porosity*** at cathode/electrolyte interface

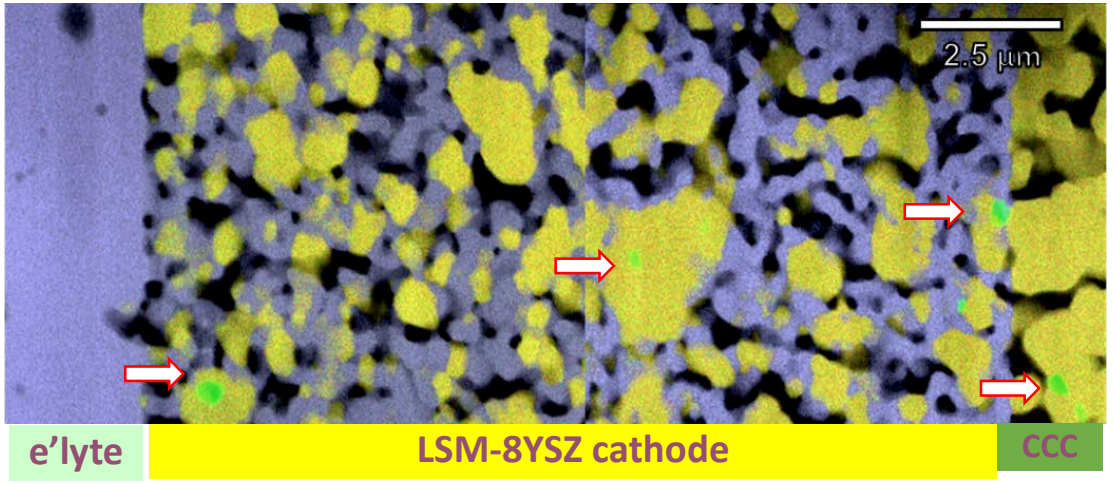
- Mn oxides:
  - localized at cathode/ electrolyte interface
  - increasing with time

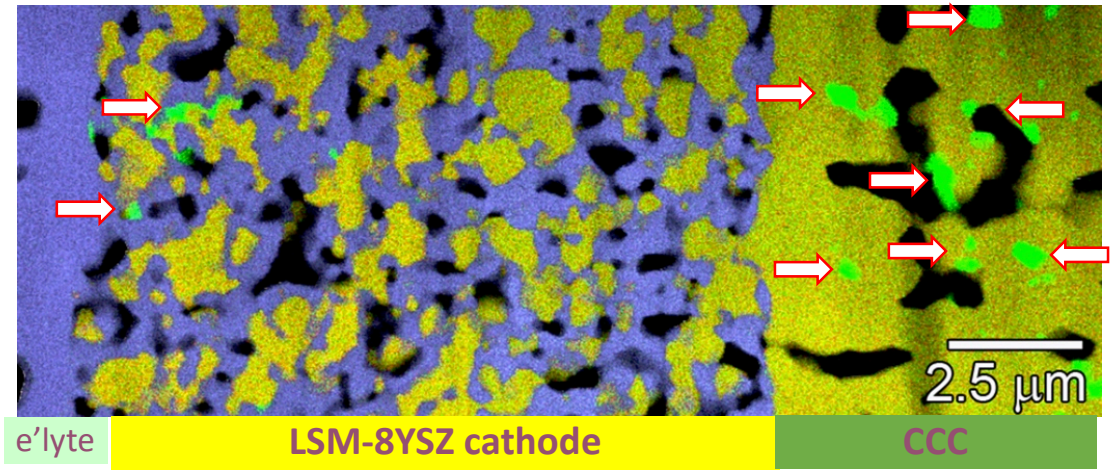
Accelerated conditions,
≤ 624 h:

- ***Porosity gradient,*** lowest at cathode/electrolyte interface

11% Mn excess: TEM w/EDXS, 0–493 h accel'd testing

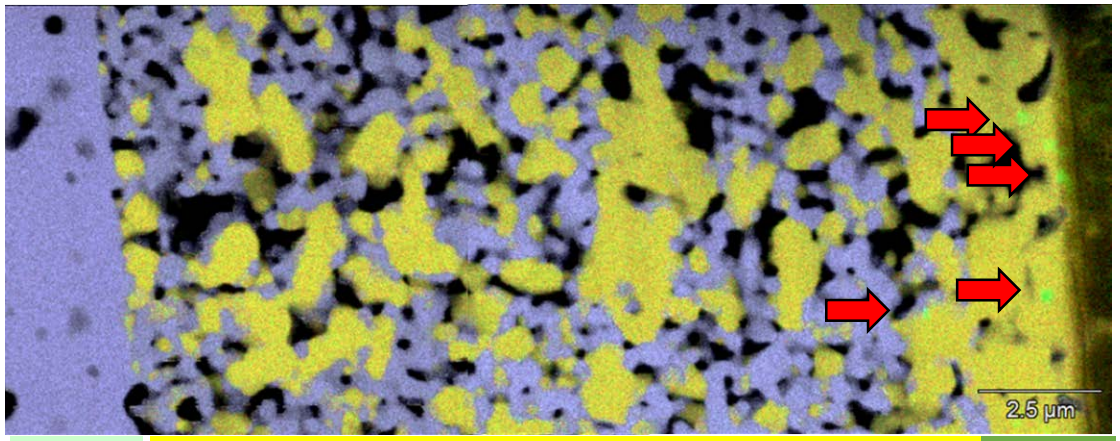
- As received (0 h)
  - MnO_x observed sparingly across entire cathode
- 493 h accelerated testing
  - MnO_x near cathode/ e'lyte interface and in LSM cathode current collector (CCC)



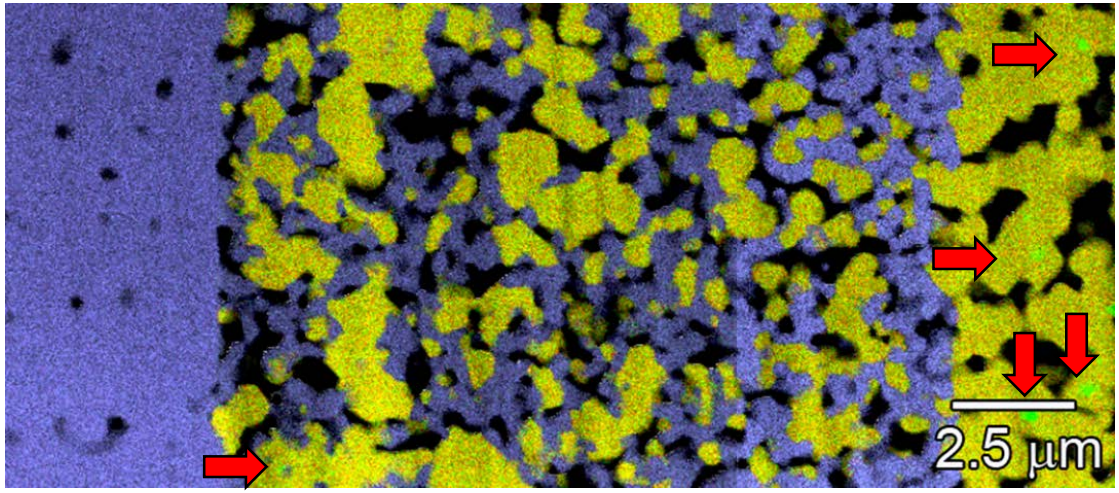


5% Mn excess: TEM w/EDXS, 0–624 h accel'd testing

as received



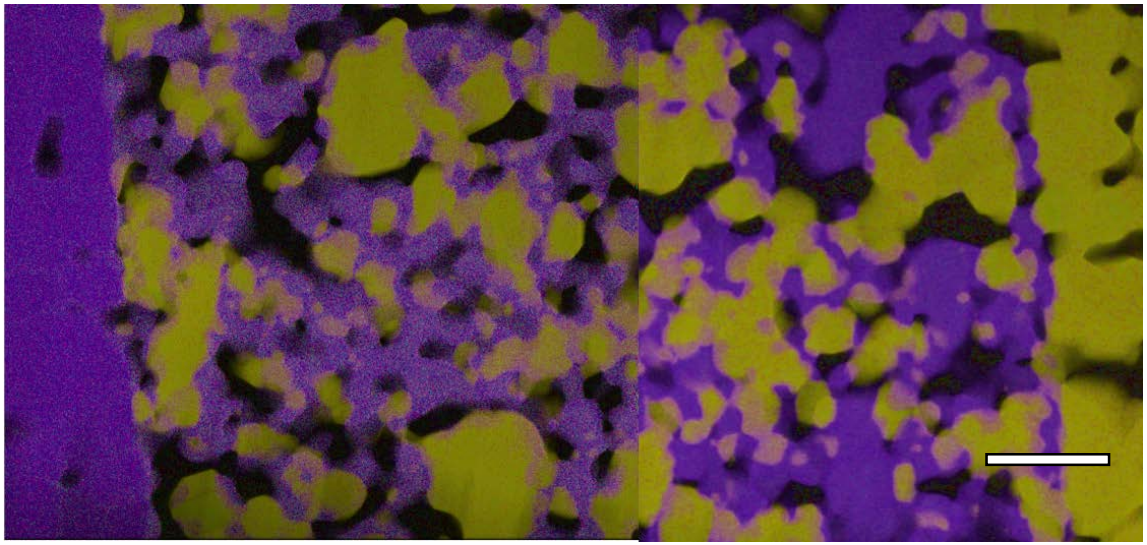
500 h



MnO_x:

- *Rarely seen* in cathode
- *Seen in CCC*

624 h



Not seen at 5% Mn xs:

Densification and MnO_x ***localized*** at cathode/ electrolyte interface

Microstructural evolution during operation

Normal conditions,
8,000–16,000 h:

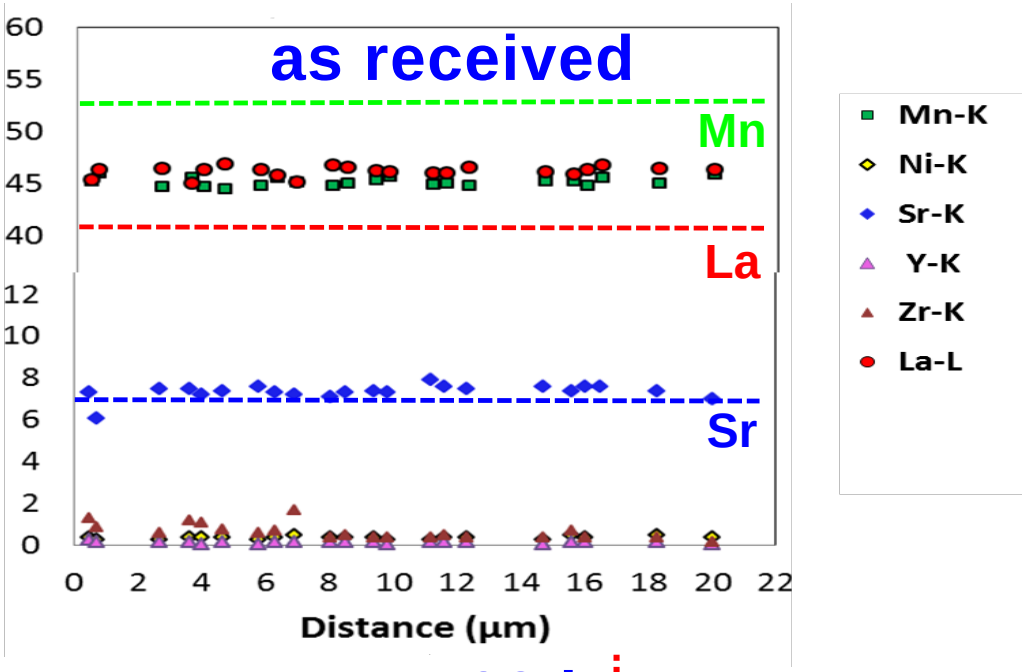
- ***Loss of porosity*** at cathode/electrolyte interface
- Mn oxides:
  - localized at cathode/ electrolyte interface,
  - increasing with time

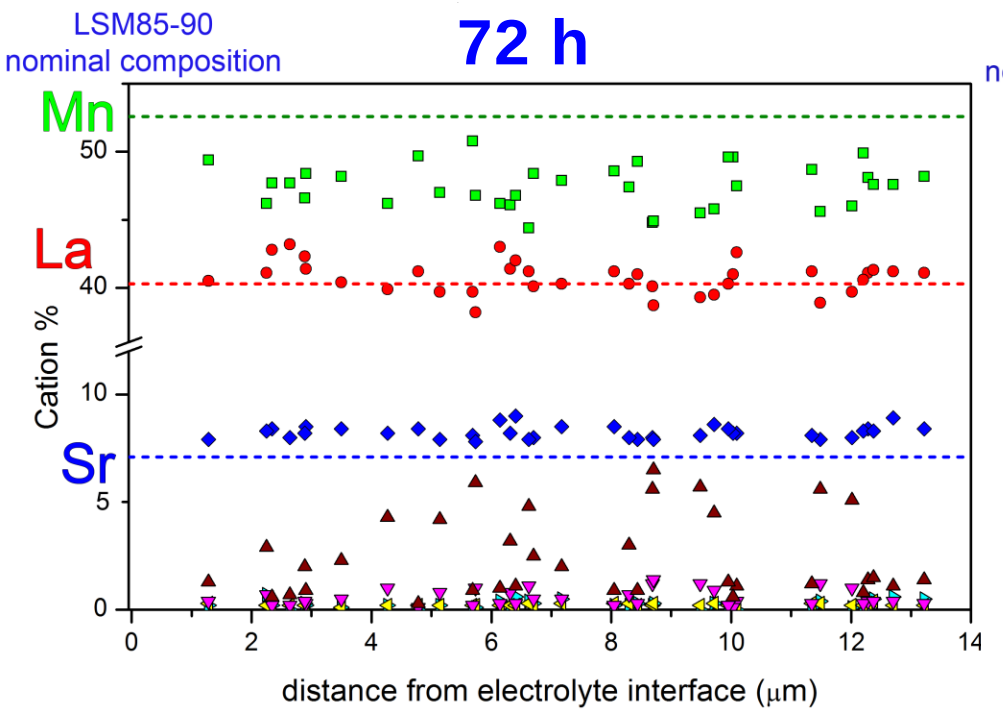
Accelerated conditions,
≤ 624 h:

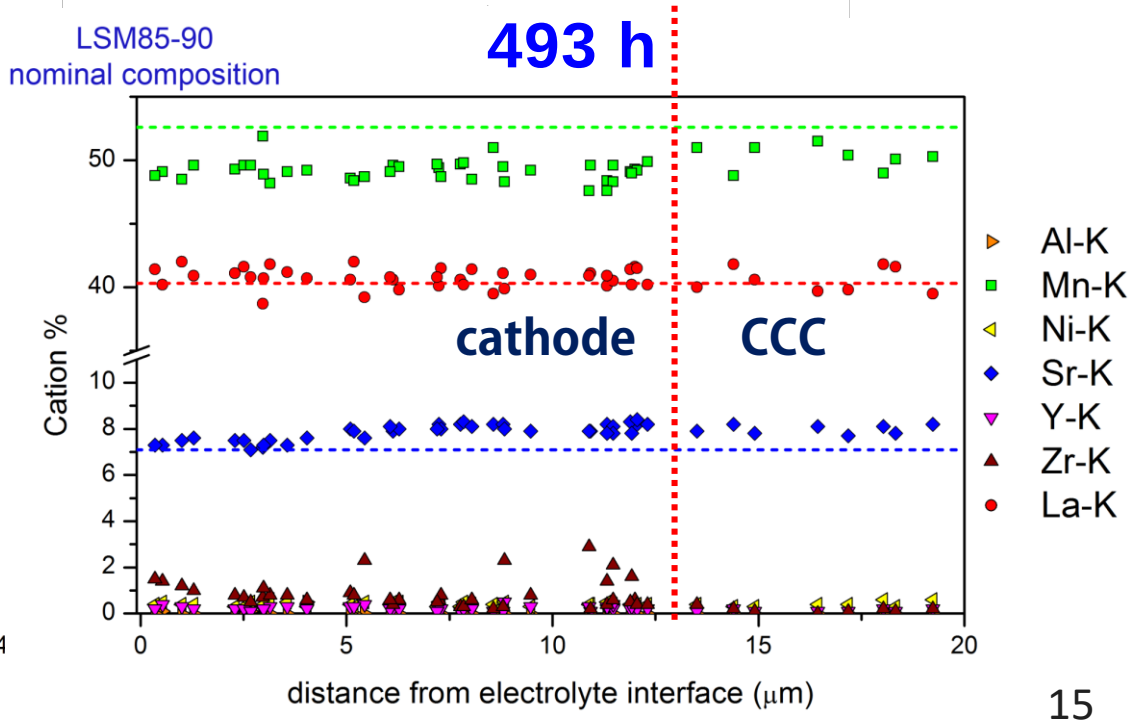
- ***Porosity gradient,*** lowest at cathode/electrolyte interface
- Mn oxides:
  - localized at cathode/ electrolyte interface,
  - for Mn excess ≥11%

11% Mn xs: LSM EDXS profiles, 0–493 h accel'd testing

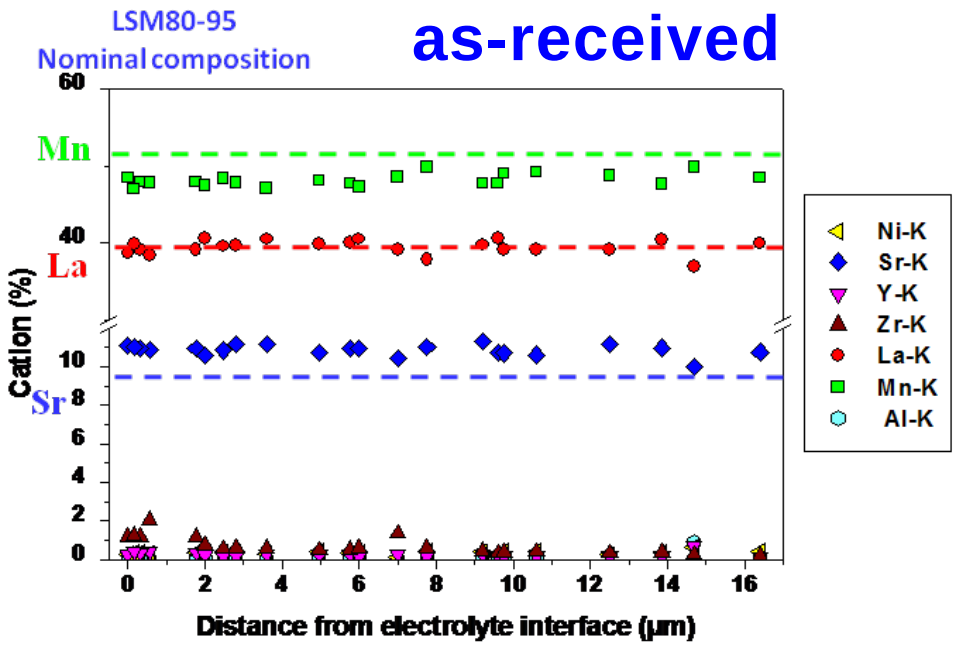
- *[Mn] low* before testing,
- *… approached nominal composition* during operation

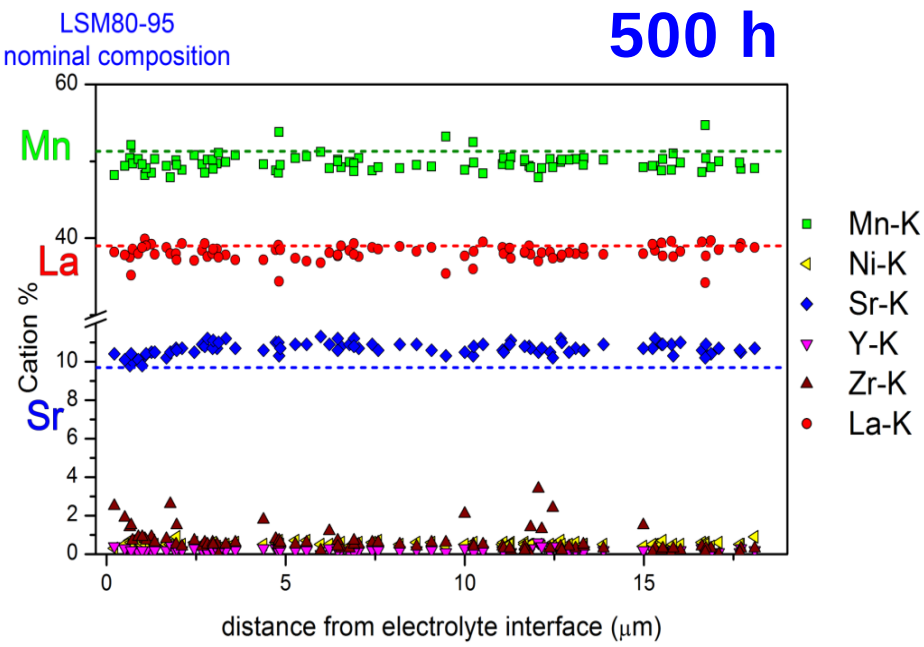


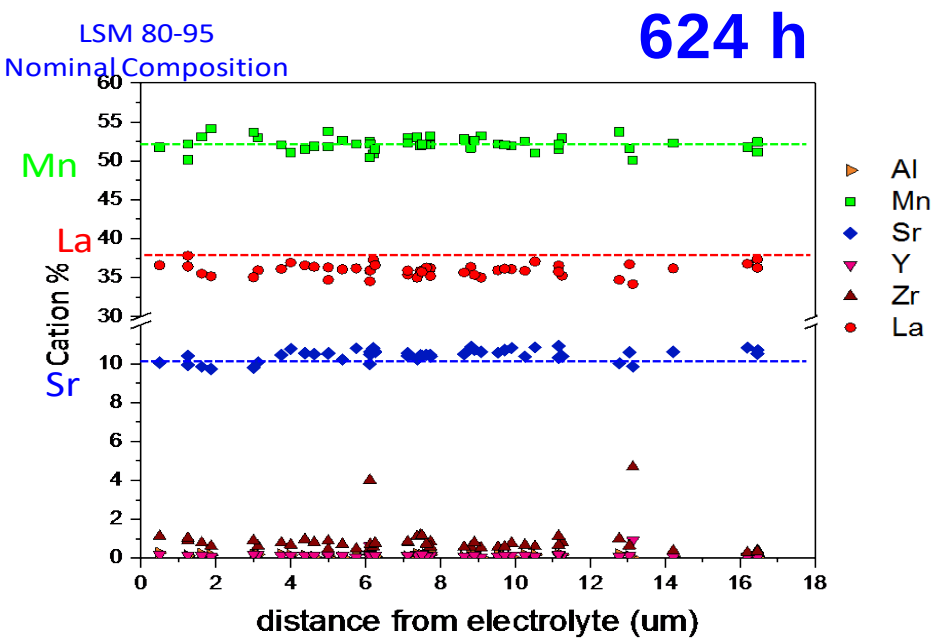




5% Mn excess: LSM EDXS profiles, 0–624 h accel'd testing



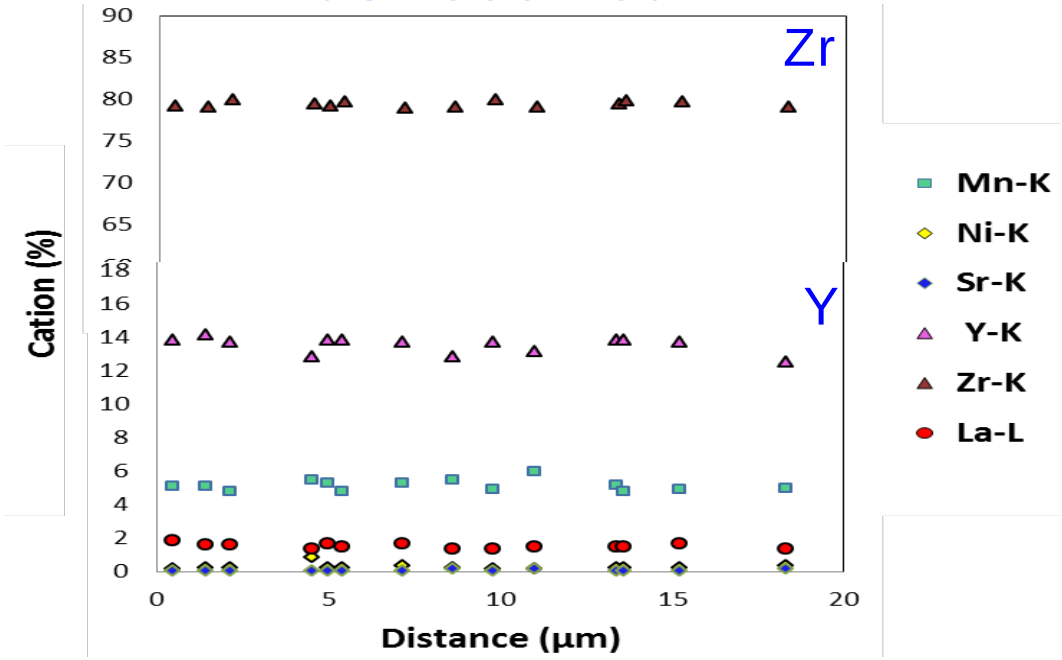




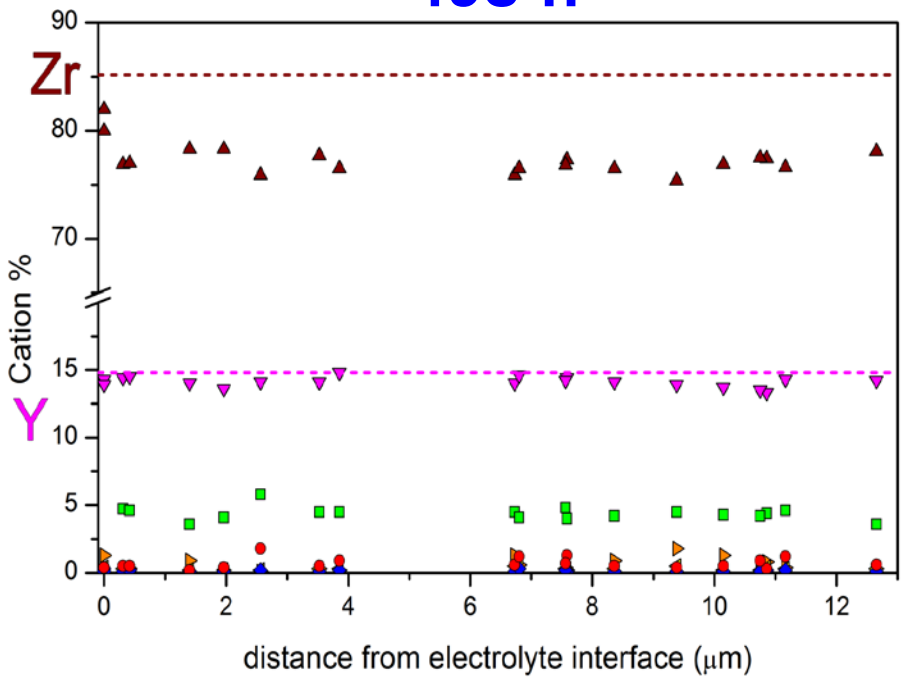
cation %	as received	500 h	624 h
Mn	**48**	**50**	**52**
La	40	38	36
Sr	11	11	11

11% Mn excess, 8YSZ EDXS profiles, 0–493 h accel'd testing

as received



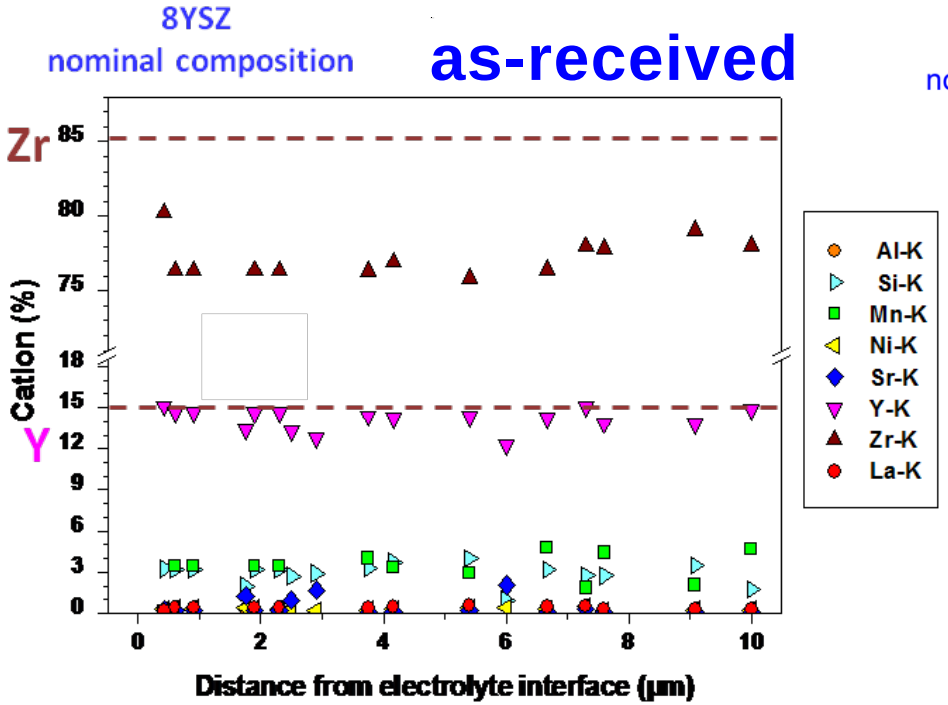
493 h

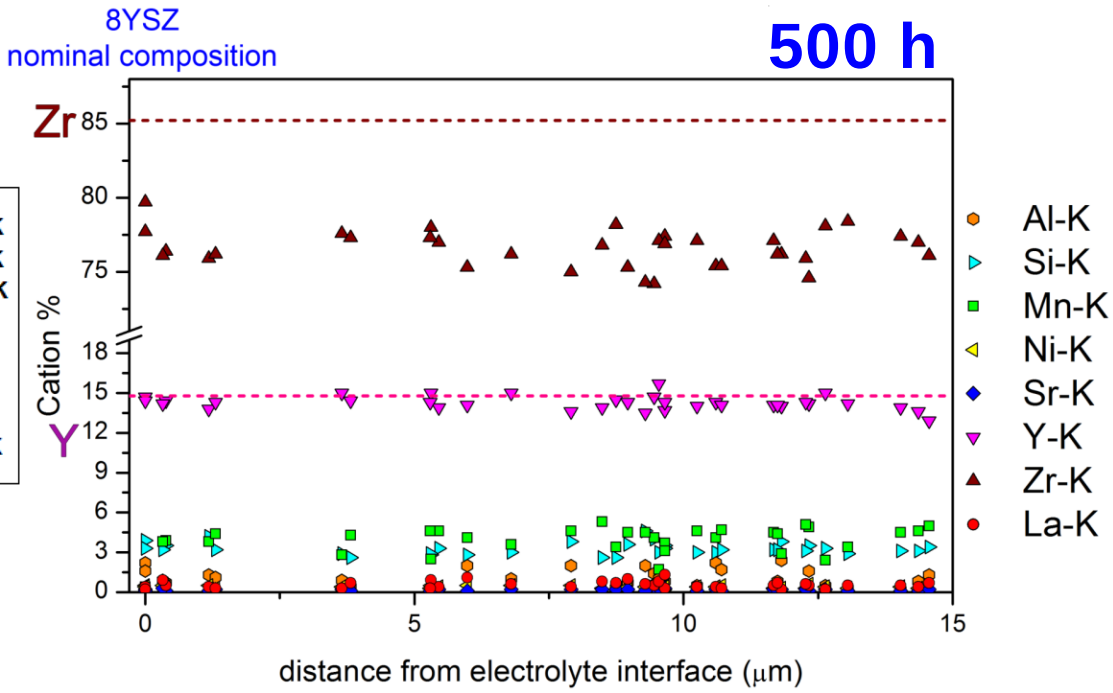


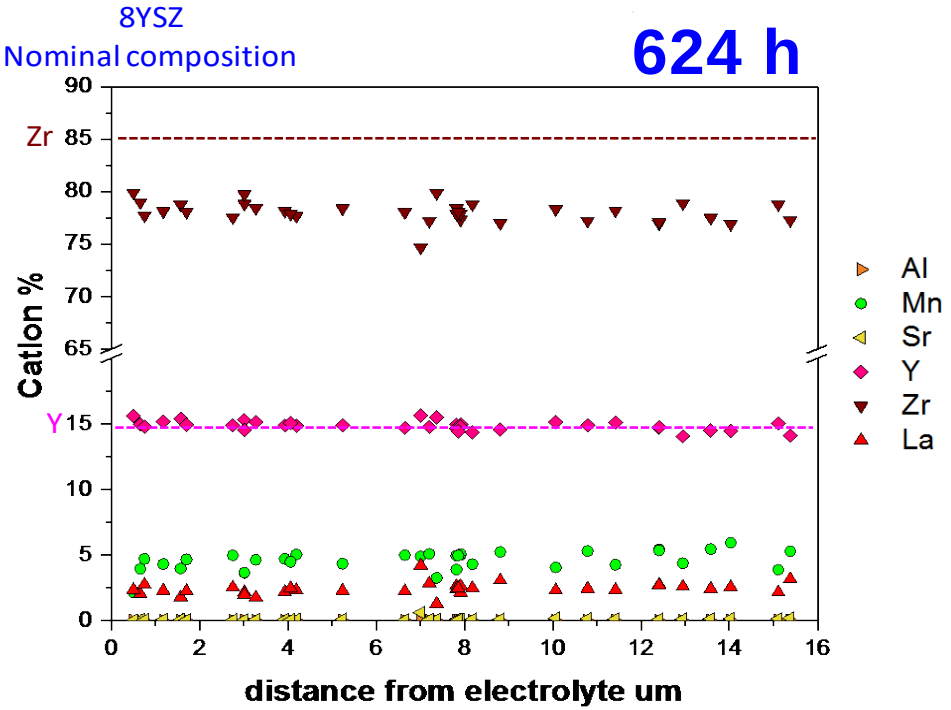
- Uniform YSZ composition across cathodes
- Little change after 493 h

cation %	as received	493 h
Zr-K	79.0	77.0
Y	13.5	14.1
Mn	5.2	4.4

5% Mn excess, 8YSZ EDXS profiles, 0–624 h accel'd testing





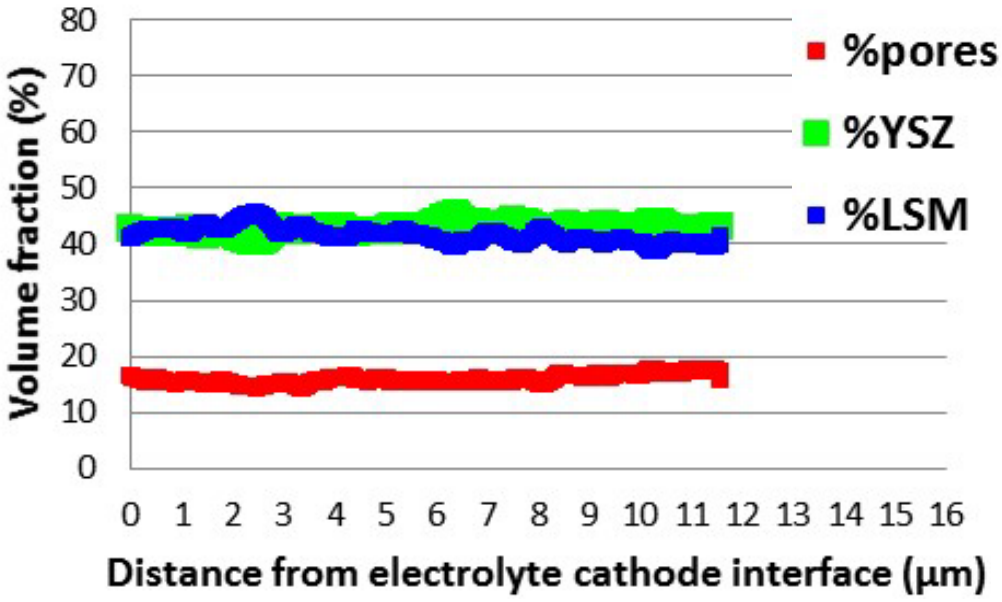


cation %	as received	500 h	624 h
Y	14	14	15
Zr	76	76	77.5
Mn	**4.3**	**4**	**4.7**

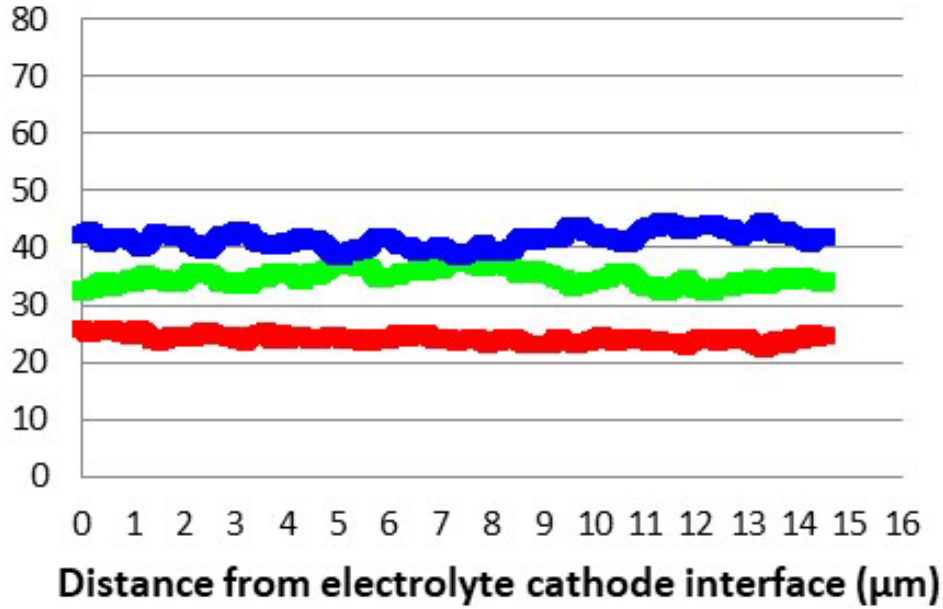
If Mn is "going back into the LSM" during operation, it is not leaving the YSZ

LSM 85-90 / 8YSZ (11% Mn excess) — as received

200–µm electrolyte



100–µm electrolyte



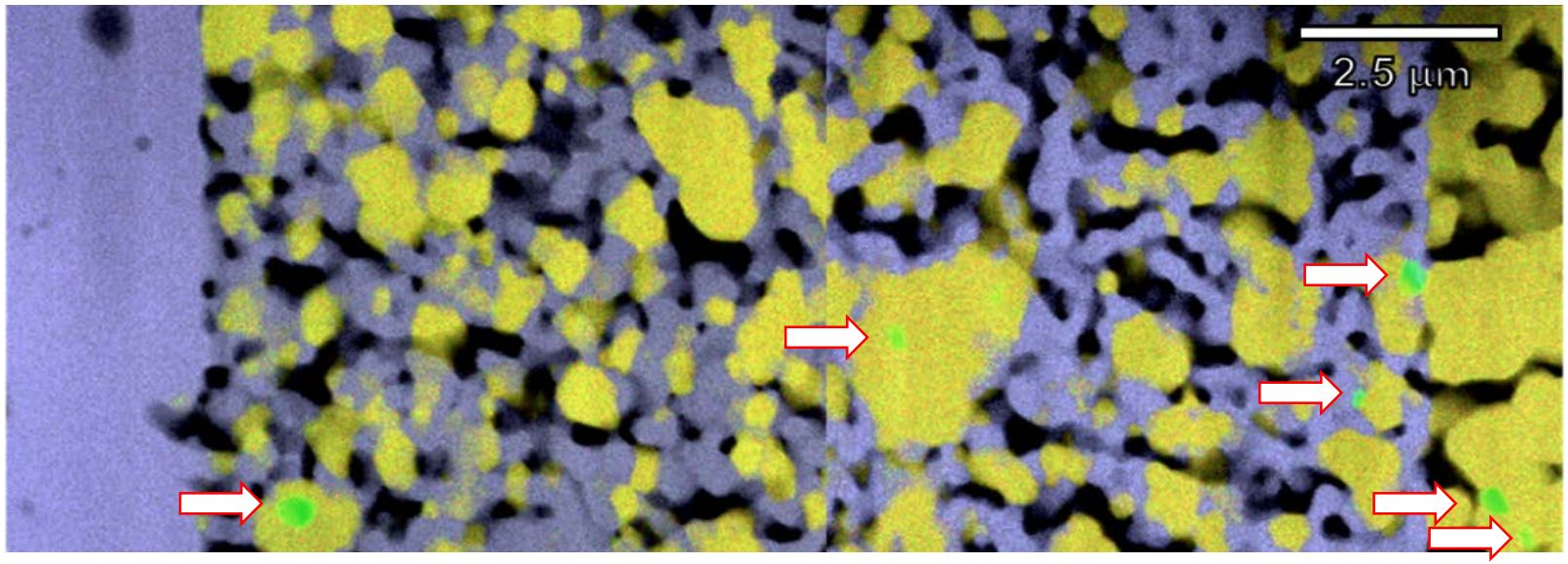
Significantly ***lower porosity***

Porosity still ***lower than other*** cathodes

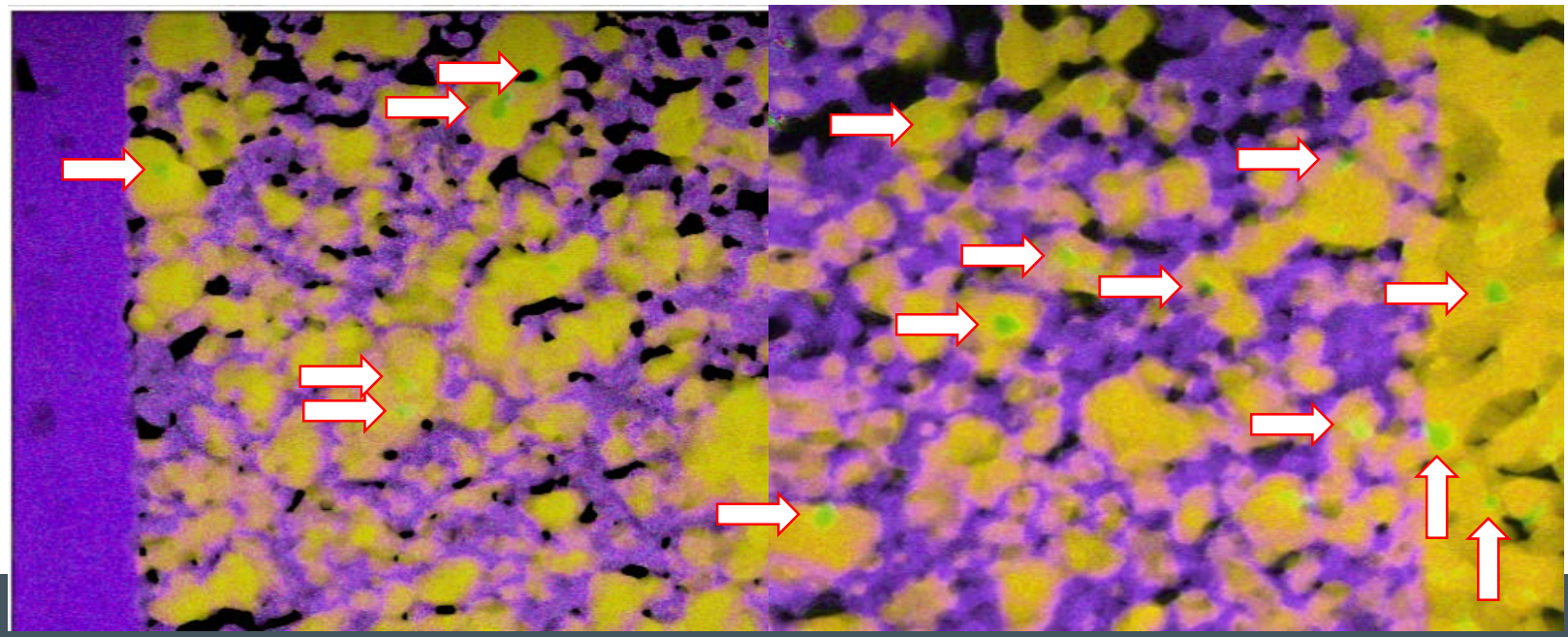
No gradients in phase fractions — typical of all as-received cathodes

LSM 85-90 / 8YSZ (11% Mn excess) — as received

200-µm electrolyte: larger MnO_x particles



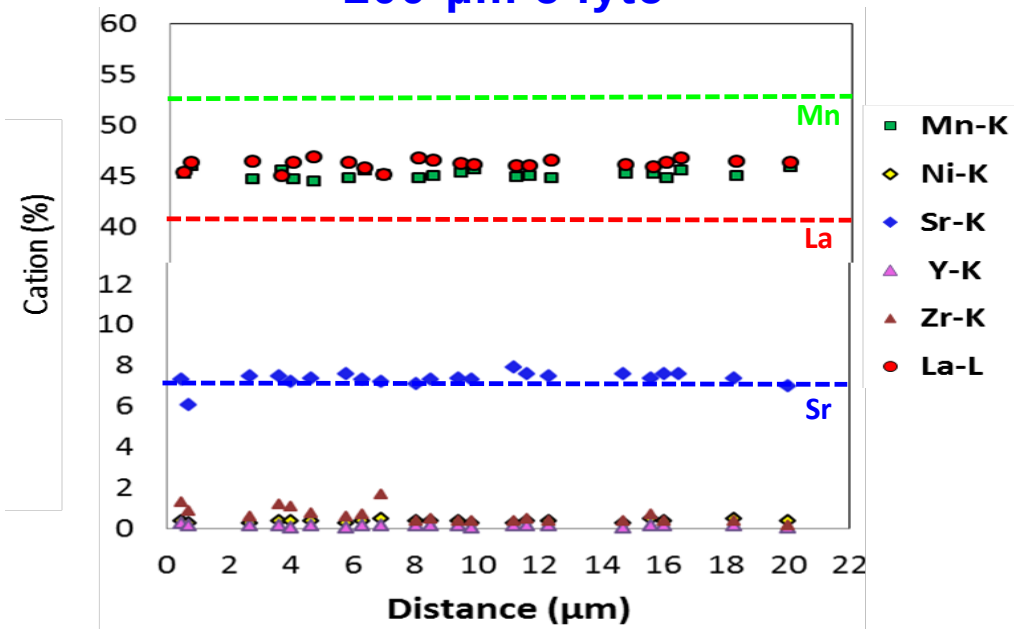
100-µm electrolyte: more MnO_x particles



LSM 85-90 / 8YSZ (11% Mn excess) — as received

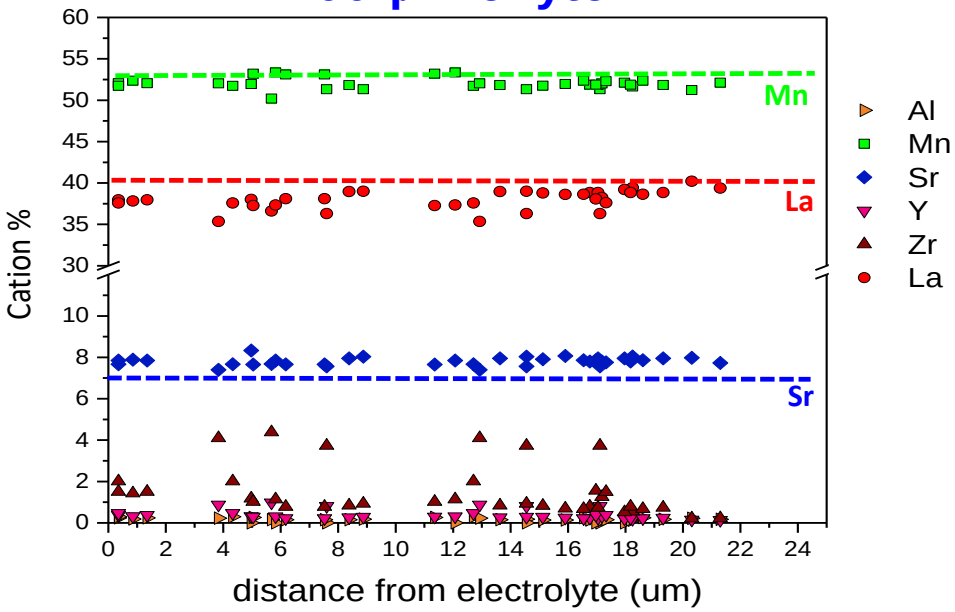
LSM 85-90
nom. comp'n

200-µm e'lyte



LSM 85-90
nom. comp'n

100-µm e'lyte



Summary: cathode microstructures, as received (3DR)

as received		LSM 85-90 (100-µm e'lyte)	LSM 80-95	LSM 80-98	Cathode D
sample volume (µm^3)		5,400	6,300	4,100	6,840
volume fraction (%)	porosity	**23**	**29**	**28**	**31**
	YSZ	35	33	37	34
	LSM	41	38	35	35
Total TPB (µm^{-2})		**20.6**	**14**	**22**	**18.4**
Active TPB (µm^{-2})		**19.4**	**13**	**20**	**17**

Testing of LSM 85-90 cathodes on 100-µm electrolytes: ***in progress***
porosity is low;
TPB density is relatively high;
many small Mn oxide particles;
Net effect on ASR: ***TBD***

Summary

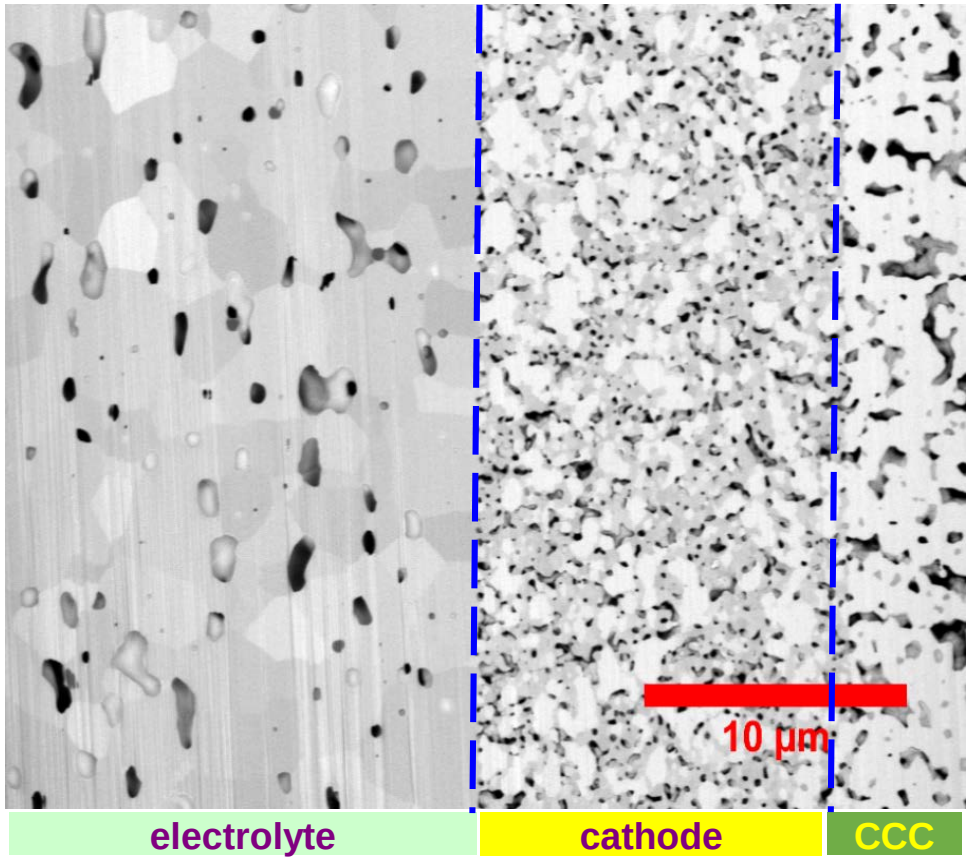
- ***ASR decreases with Mn excess*** (A-site deficiency) from 11% to 2% — ***why?***
- ***Mn oxides: not predictive*** of ASR or degradation rate
  - A local probe of p_{O_2}?
  - A reservoir for Mn?
- Effects of densification at cathode/CCC interface?
- ***Mn distribution*** and its evolution with time — a clue to degradation?
- Analysis of EIS results — in progress
- ***Role of p_{O_2}*** — focus of new project

Acknowledgments

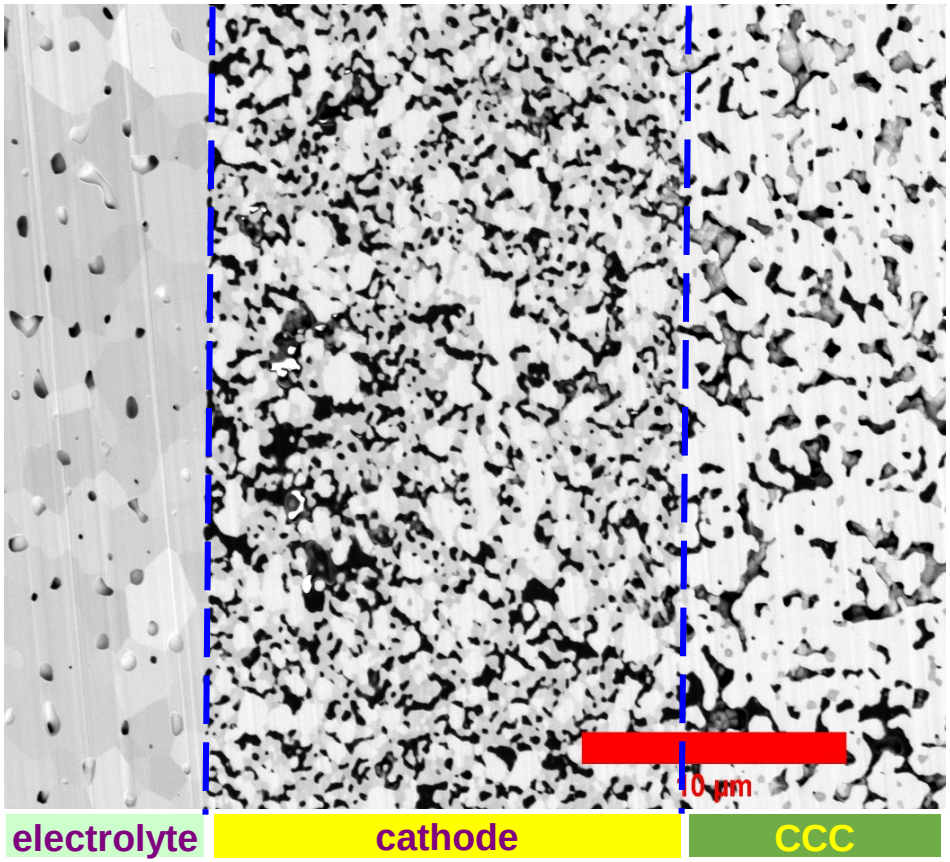
- Funding: DoE SOFC Core Technology Program (DE-FE0023476)
- Program managers: Dr. Shailesh Vora, Dr. Patcharin Burke (NETL)
- Mirko Antloga (CWRU)

- For 2018, prior results not previously presented:
  - Conventional test results
  - Trends in R_p, R_s, R_{tot} (EIS vs. durability testing)
  - R_p, R_s, R_{tot} vs. time (CeCe's thesis) — compare to ASR from durability testing?
  - Does higher $R_{electrolyte}$ (thicker; same material) have more effect on ASR and degradation rate than just the higher resistance itself?

LSM 85-90 / 8YSZ (11% Mn excess) — as received

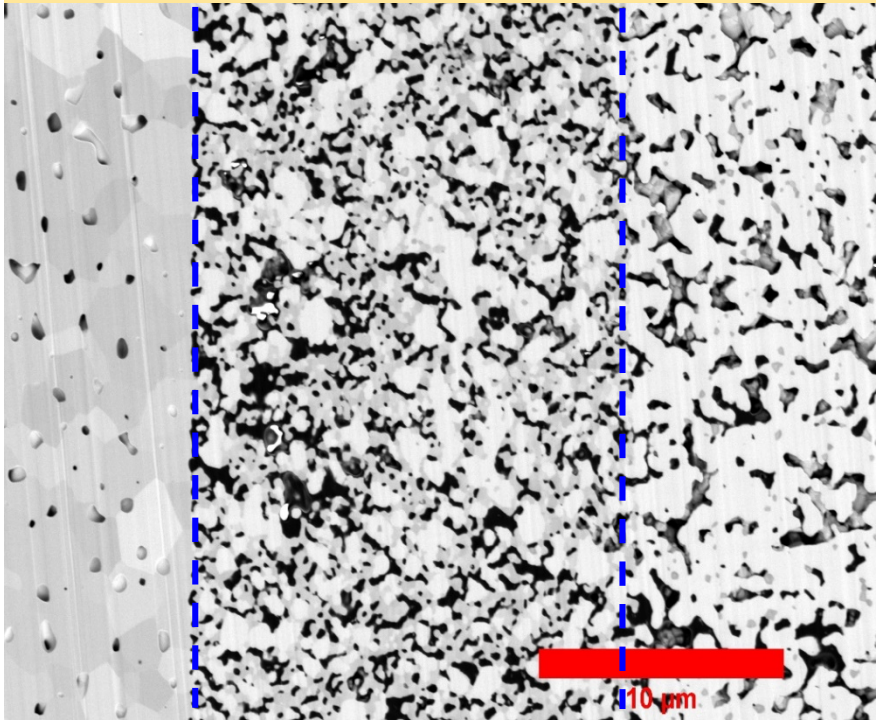


200–µm electrolyte
lower porosity, smaller pores

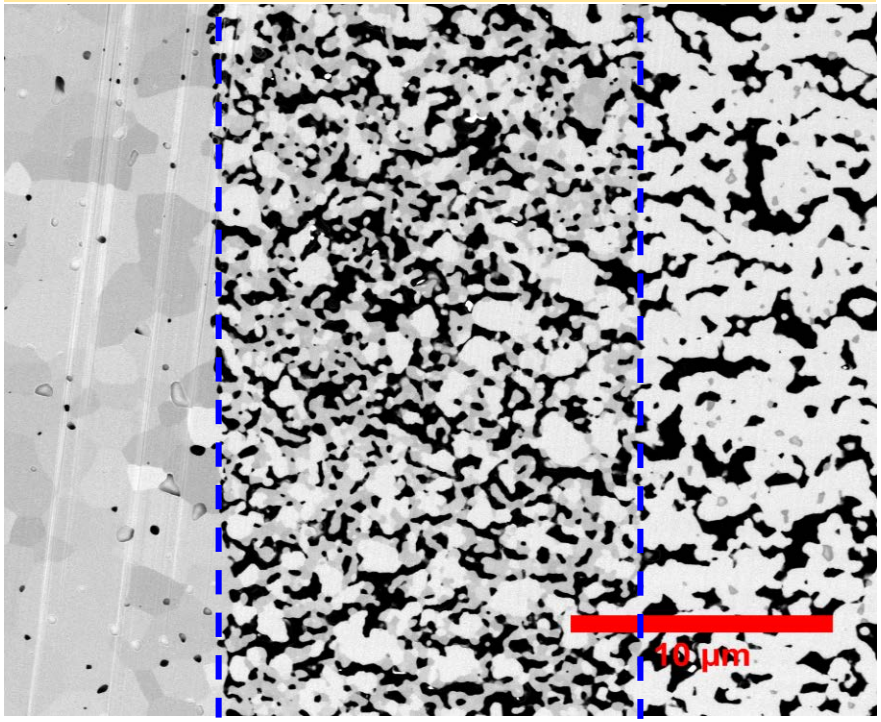


100–µm electrolyte
more & larger pores

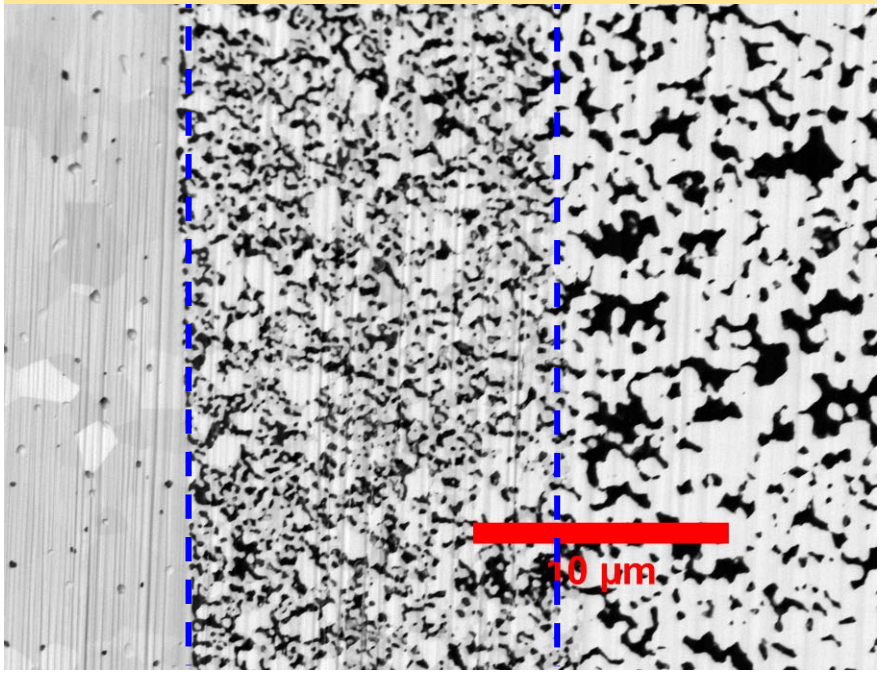
LSM 85-90 (A) (thin e'lyte)



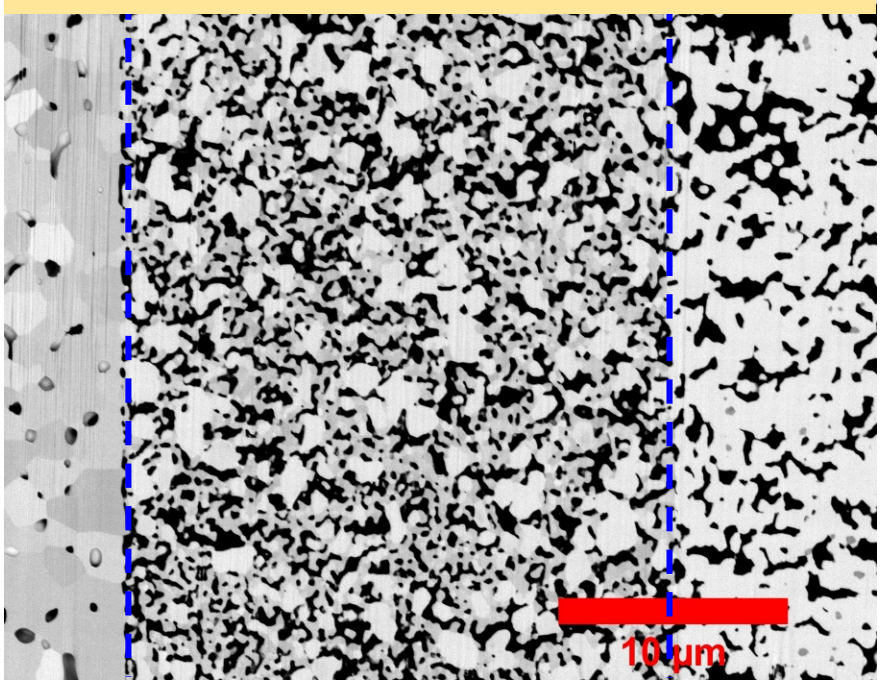
LSM 80-95 (B)

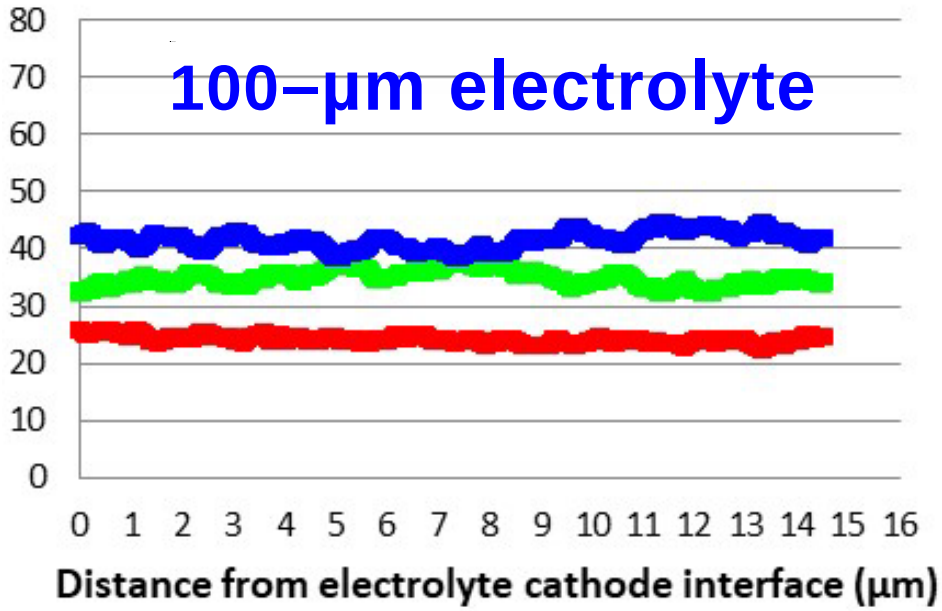


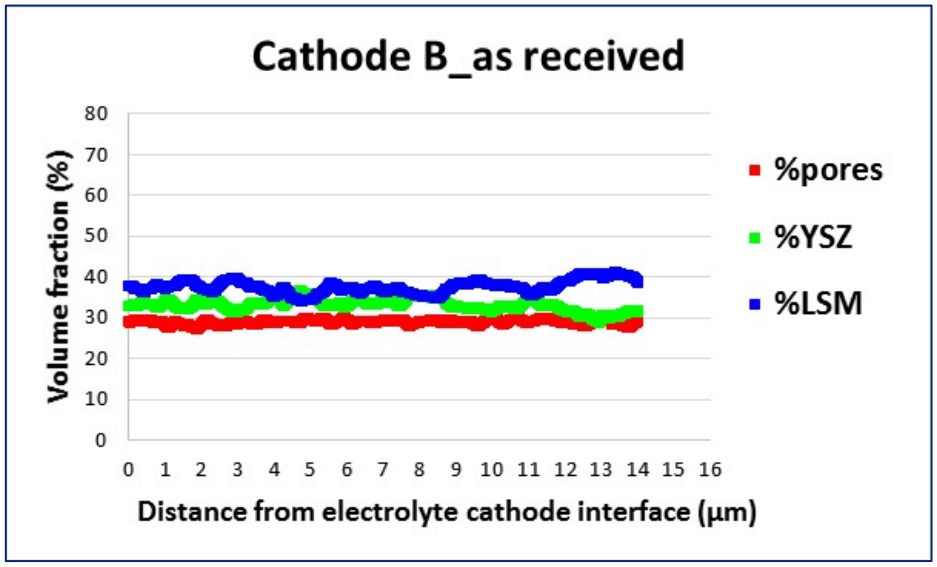
LSM 80-98 (C)

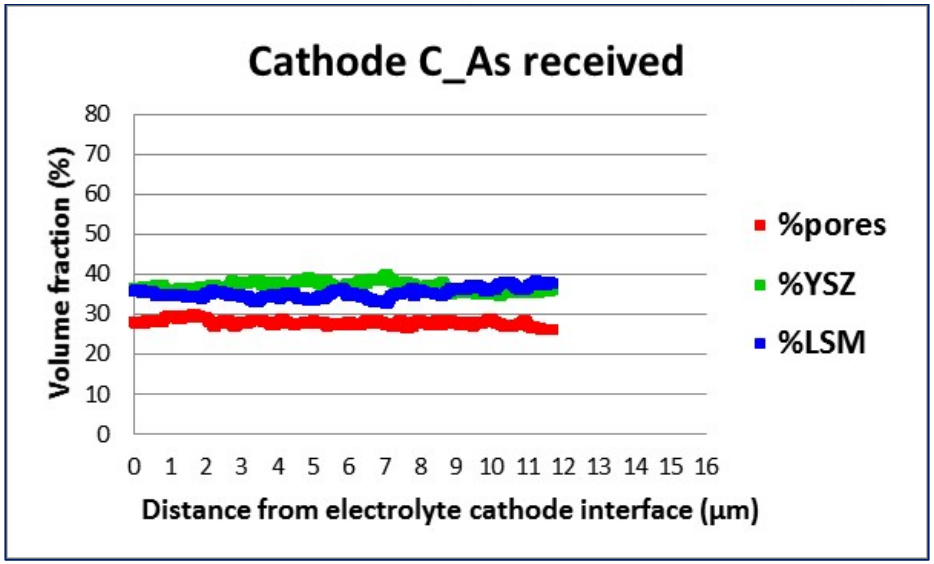


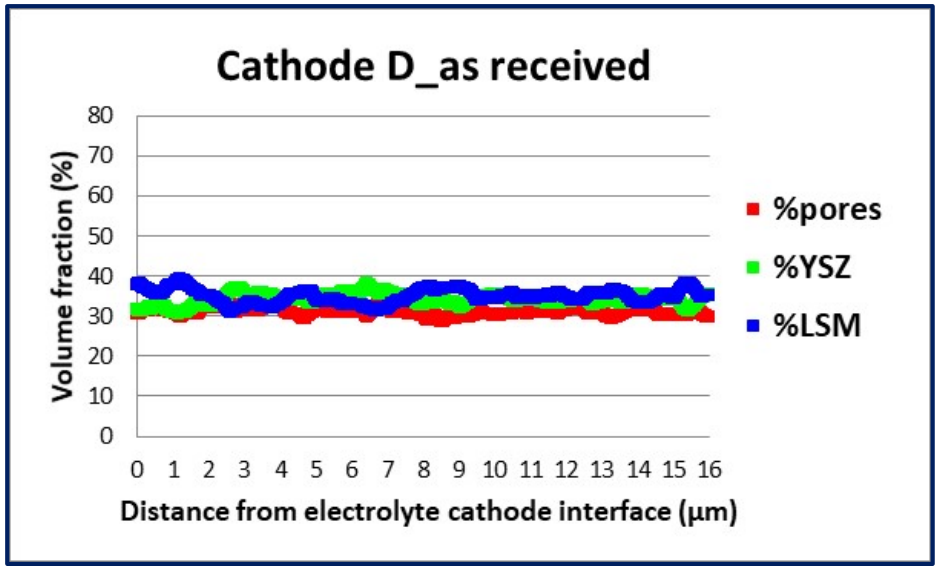
Cathode D







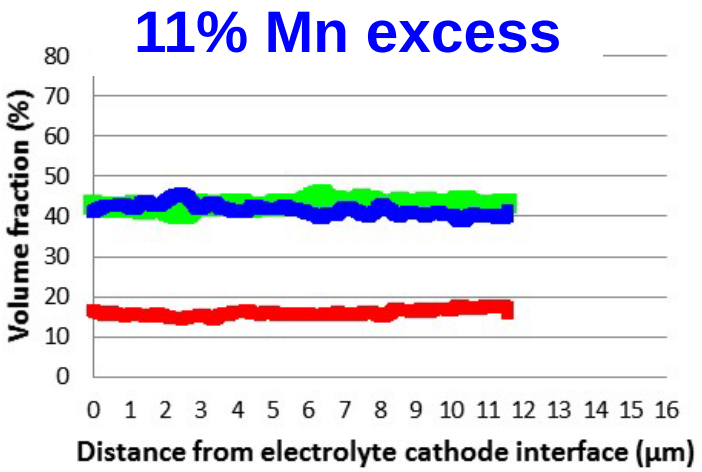


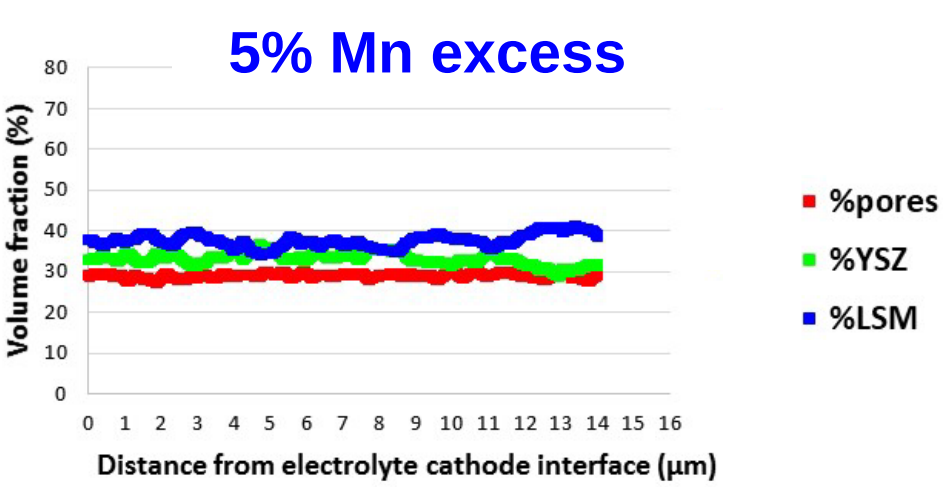


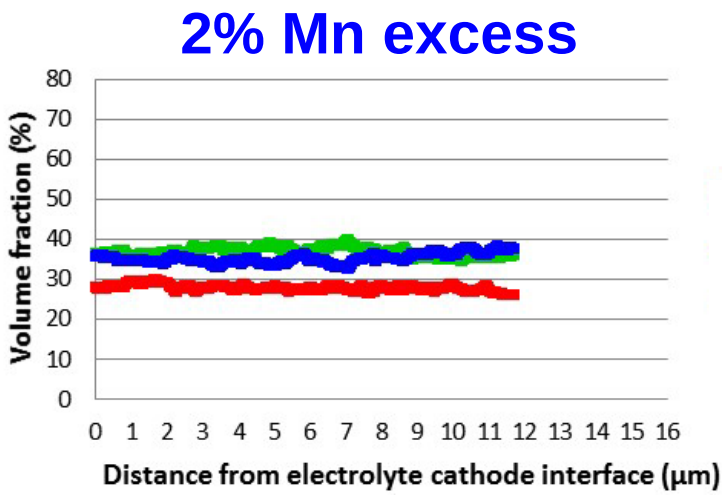
Vol%	LSM 85-90 (thin)	LSM 80-95 (B)	LSM 80-98 (C)	Cathode D
porosity	23	29	28	31
YSZ	35	33	37	34
LSM	41	38	35	35

Phase profiles, as received (3DR)

All cells showed uniform phase profiles as received

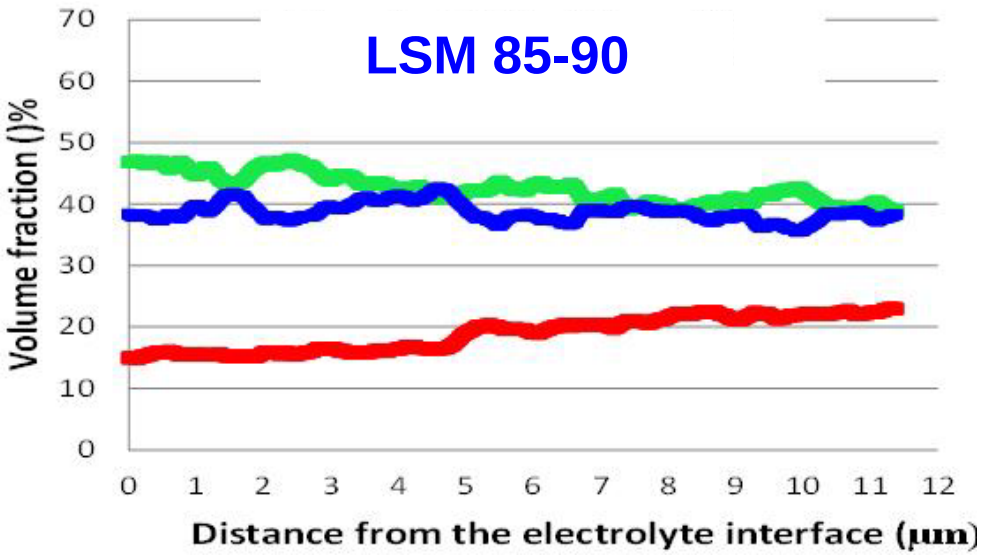


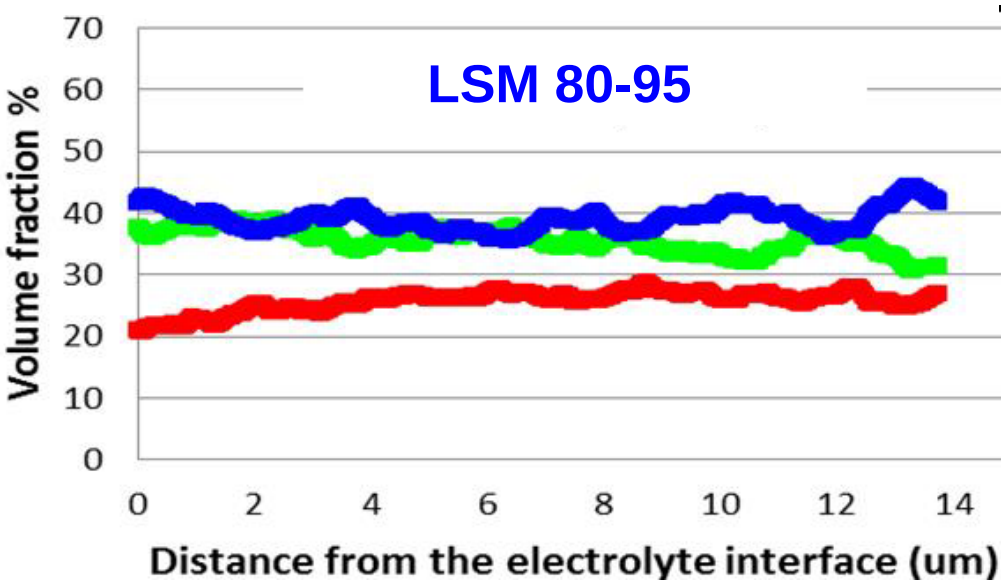


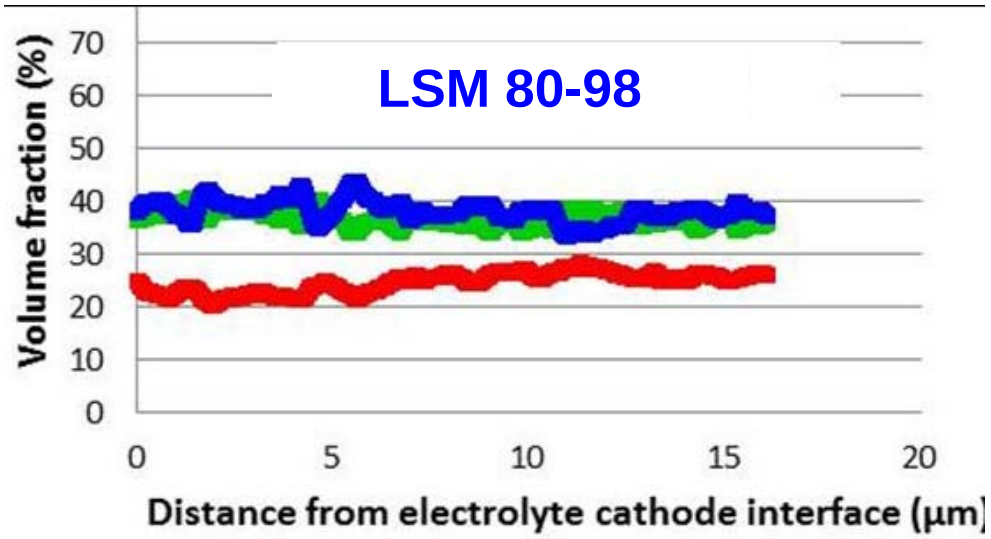


Vol%	LSM 85-90	LSM 80-95	LSM 80-98	Cathode D
porosity	17	29	28	31
YSZ	41	33	37	34
LSM	41	38	35	35

Phase profiles across cathode after 500 h accel'd testing (3DR)







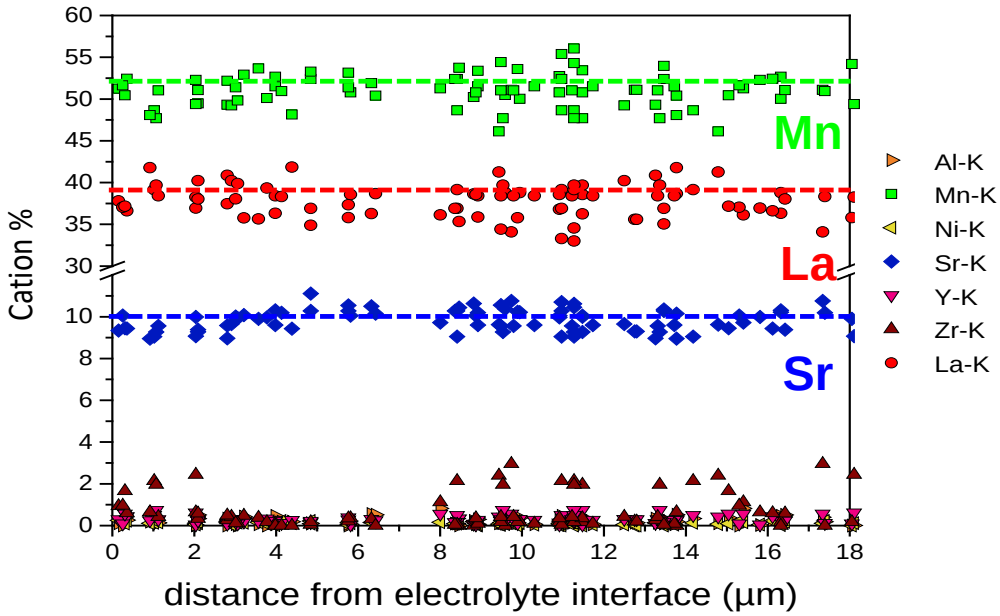
All three cathodes developed slight *porosity gradients* after 500 h of accelerated testing, with *lowest porosity at cathode-electrolyte interface*

3D calculation: comparison Gen A, B and C

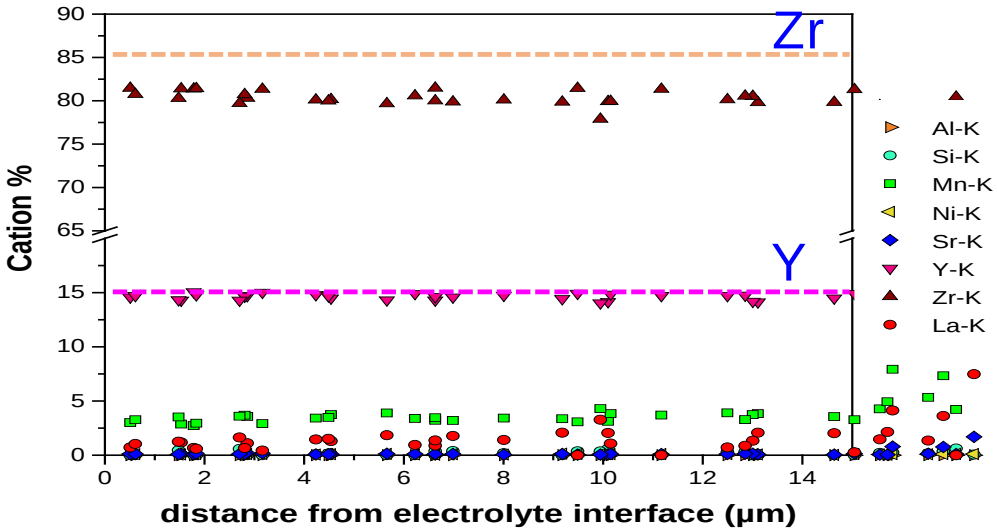
		Gen A		Gen B			Gen C	
		As reduced	493 h accel test	As received	500h Accel test	624 hrs Accel test	As received	500h Accel test
sample volume (μm^3)		4350	4525	6300	5096	4550	4100	5012
volume fraction (%)	porosity	**17**	**18**	**29**	**25**	**25**	**28**	**25**
	YSZ	41	43	33	35	37	37	37
	LSM	41	38	38	40	38	35	38
particle diameter (µm)	porosity	**0.2**	**0.42**	**0.4**	**0.5**	**0.5**	**0.3**	**0.4**
	YSZ	0.5	0.46	0.5	0.5	0.5	0.3	0.5
	LSM	**0.6**	**0.6**	**0.6**	**0.7**	**0.7**	**0.5**	**0.7**
tortuosity	porosity	2.0	1.6	1.5	1.7	1.4	1.7	1.7
	YSZ	1.5	1.3	1.6	1.7	1.5	1.8	1.8
	LSM	1.3	1.4	1.4	1.4	1.4	1.6	1.6
normalized surface area (μm^{-1})	porosity	26	14	16	13	13	21	14
	YSZ	12	13	13	12	11	18	13
	LSM	10	9.9	9	8	8	13	8
Total TPB (μm^{-2})		**17**	**5.9**	**14**	**15**	**11**	**22**	**11**
Active TPB (μm^{-2})		**10**	**5.1**	**13**	**13**	**10**	**20**	**10**

LSM 80-98 & 8YSZ EDXS profiles, 500 h accel'd testing

LSM profiles



8YSZ profiles

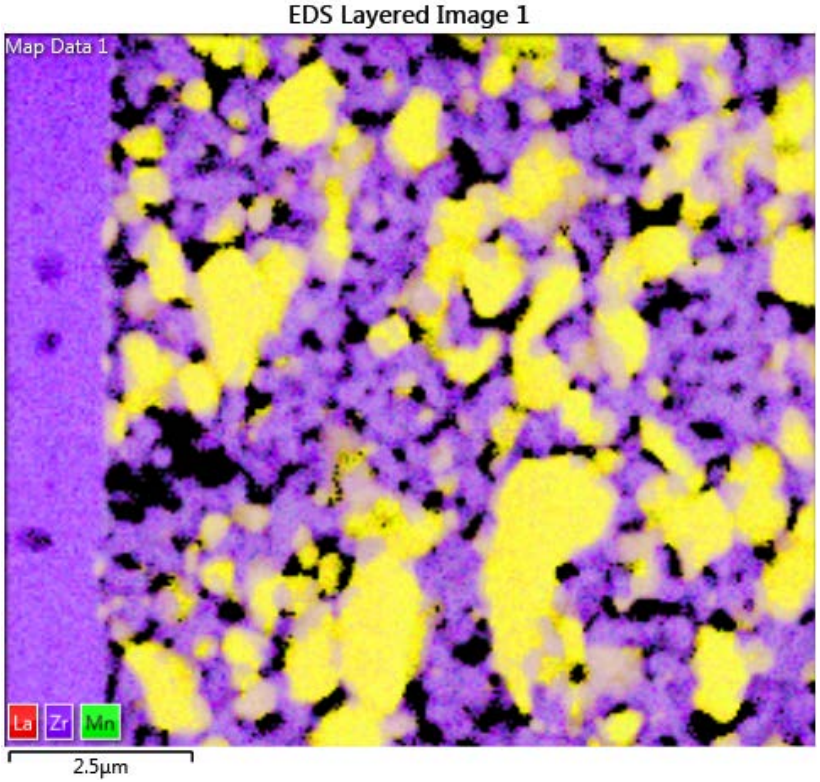


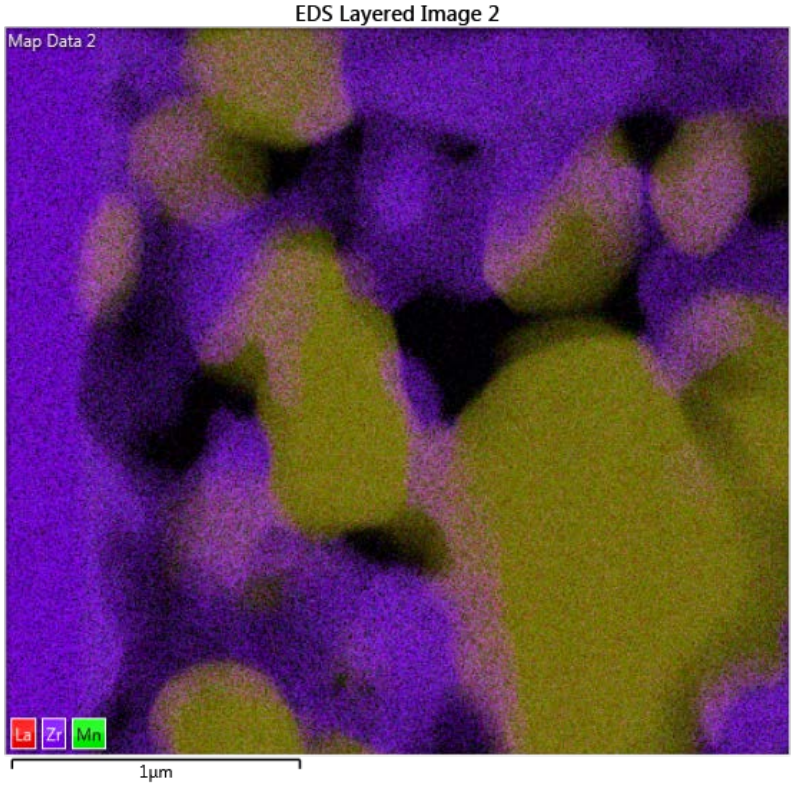
Likewise at 2% Mn excess:

- Mn level in LSM matches nominal composition after 500 h accel'd testing
- If Mn is "going back into the LSM" during operation, it is not leaving the YSZ

Cathode D, as rec'd: microstructure near e'lyte

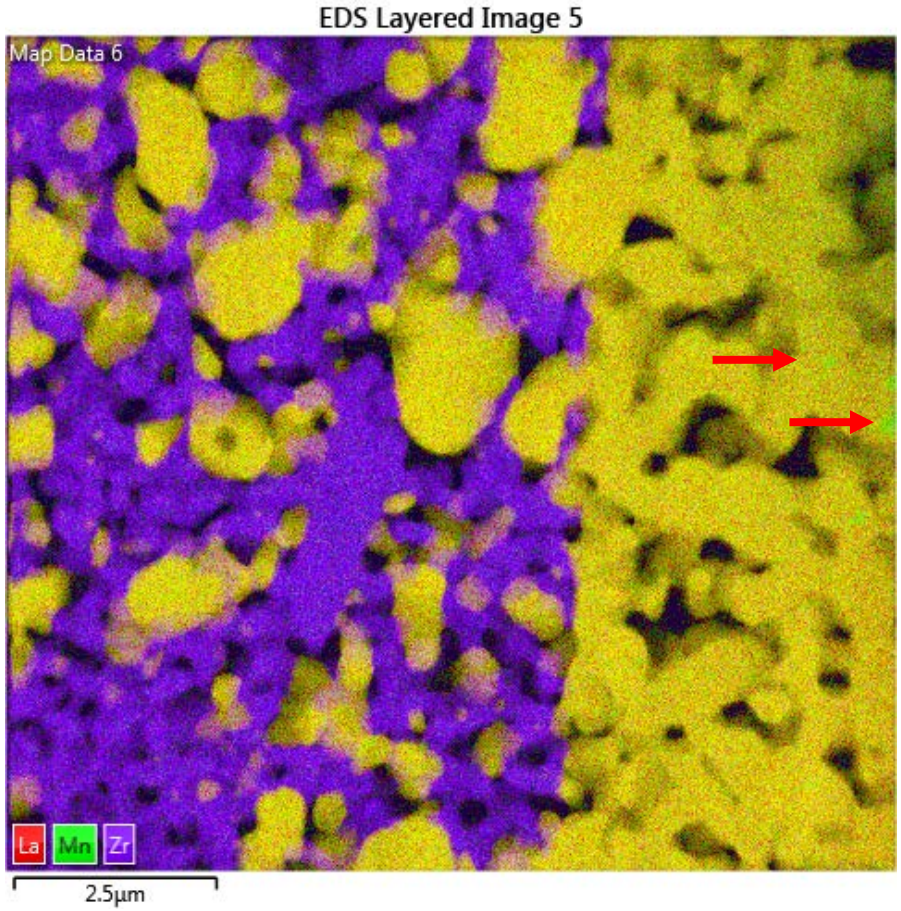
- Uniform microstructure across cathode
  - No gradients in phase fractions
  - LSM matches nominal composition
  - YSZ contains 4–5 cat% Mn (typical)
- No MnO_x observed near electrolyte nor inside cathode



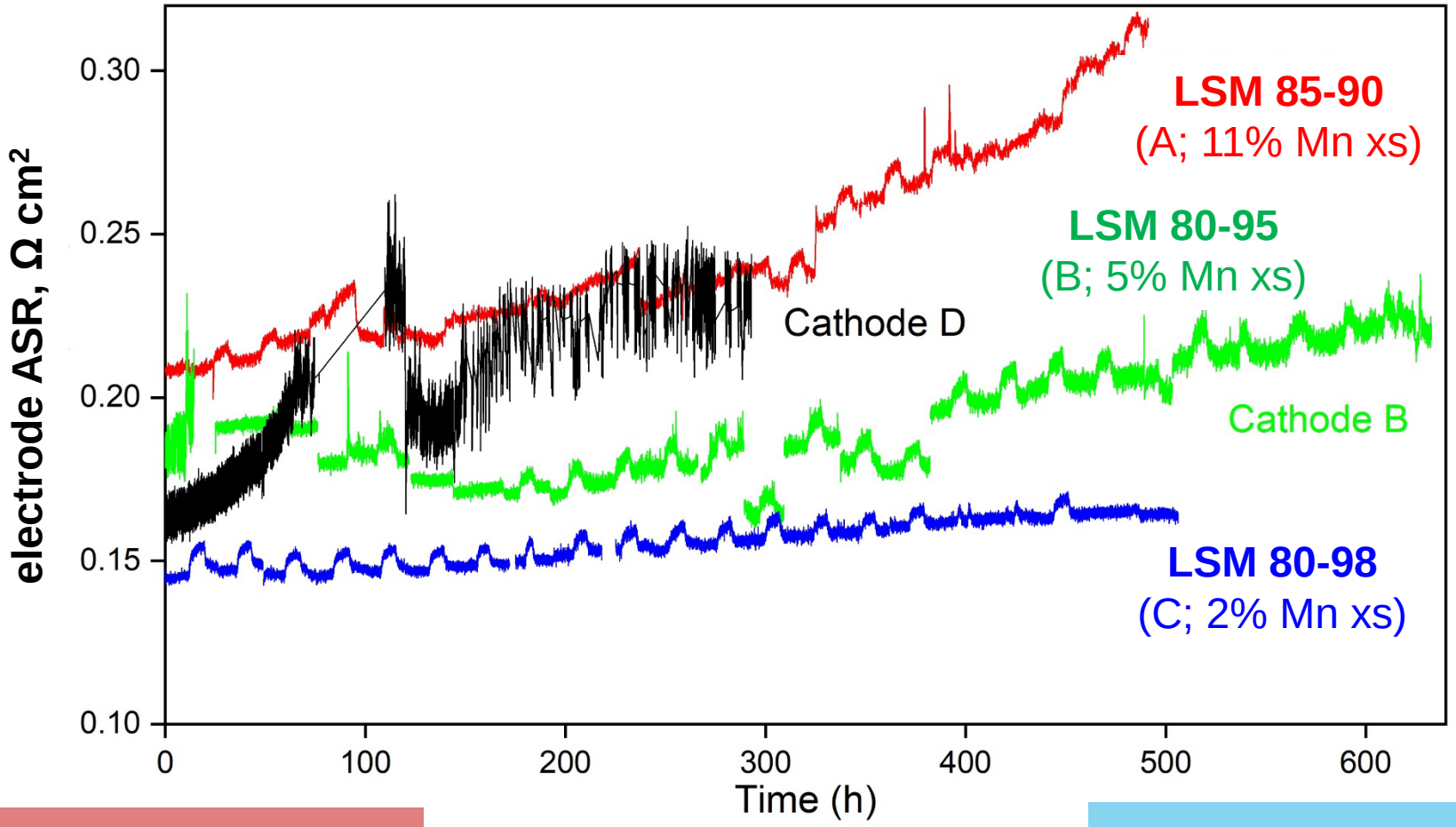


Cathode D, as rec'd: microstructure near CCC

- MnO_x not seen inside the cathode nor near CCC interface
- MnO_x is observed inside the CCC (red arrows)



A – B – C – D comparison: Electrode ASR* **(accel'd testing)**



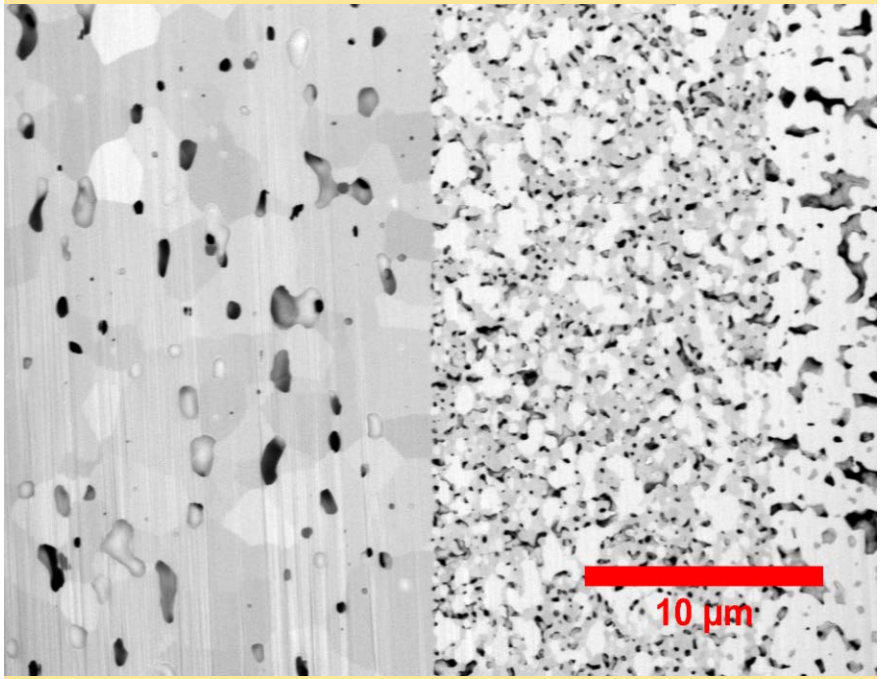
LSM 85-90 (11% Mn xs):
- ***Highest ASR*** overall
- ***Highest rise in ASR***

ASR ↓ as Mn excess ↓
(A → B → C)

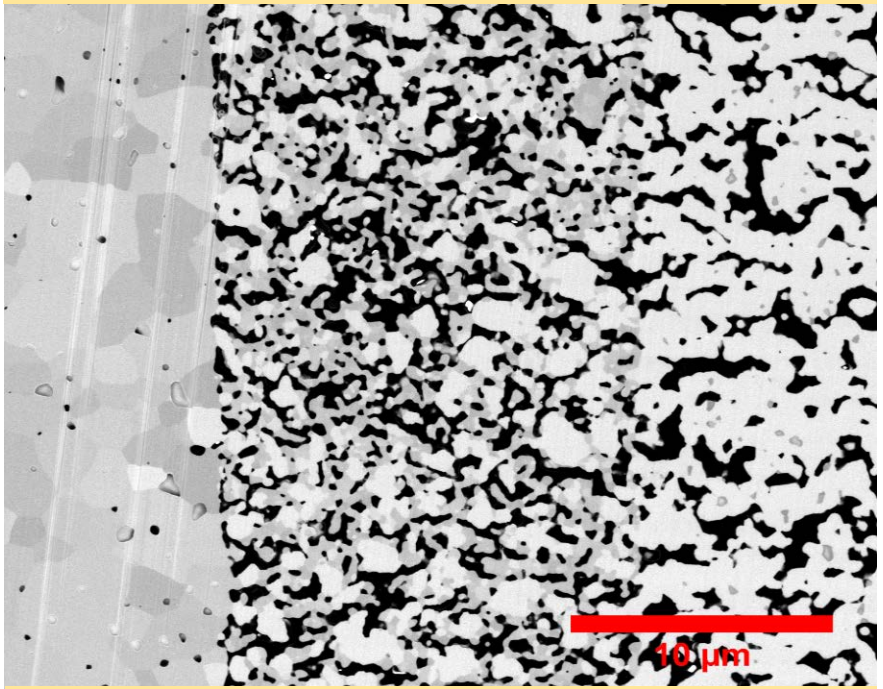
LSM 80-98 (2% Mn xs):
- ***Lowest ASR*** overall
- ***Highest power,*** 500 h

*) total cell DC ASR, minus estimated ASR for 8YSZ substrate @ nominal thickness & DC conductivity

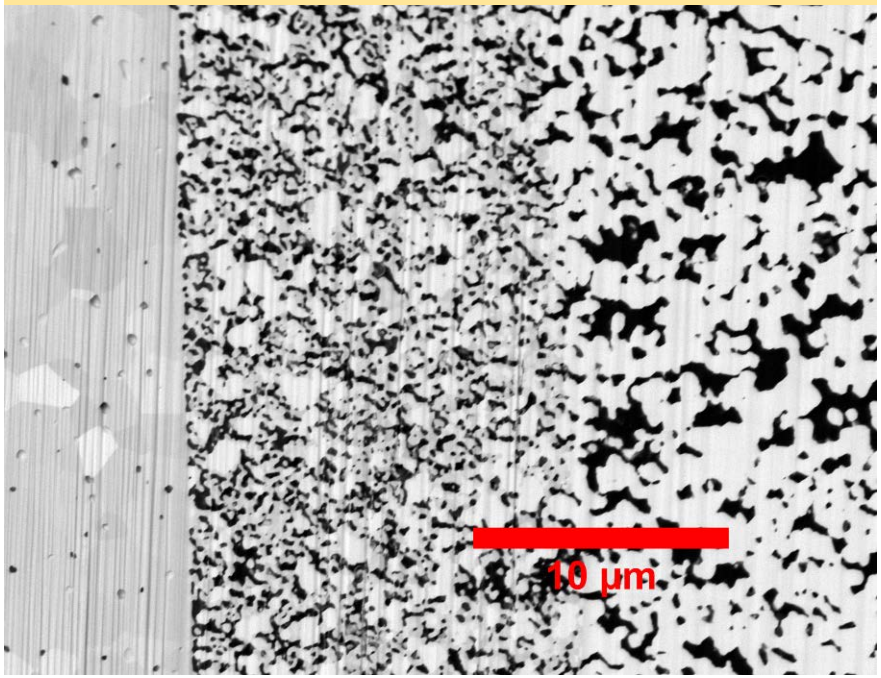
Cathode A: LSM85-90



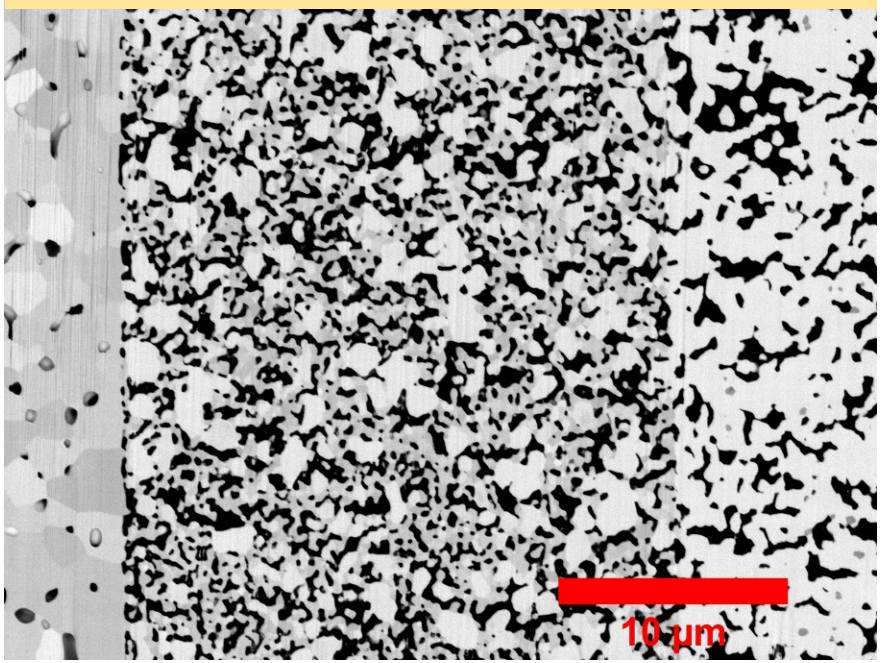
Cathode B: LSM80-95



Cathode C: LSM80-98



Cathode D



LSM 85-90 / 8YSZ (A) — as received

LSM 85–90 (A), as rec'd		**200–μm electrolyte**	**100–μm electrolyte**
sample volume (μm³)		4,350	5,400
volume fraction (%)	***porosity***	**17**	**23**
	YSZ	41	35
	LSM	41	41
particle diameter (μm)	***porosity***	**0.2**	**0.3**
	YSZ	0.5	0.4
	LSM	0.6	0.6
tortuosity	porosity	2.0	1.6
	YSZ	1.5	1.6
	LSM	1.3	1.4
normalized surface area (μm^{-1})	porosity	26	21
	YSZ	12	10
	LSM	10	9.5
total TPB (μm^{-2})		**17.1**	**20.6**
active TPB (μm^{-2})		**10.3**	**19.4**

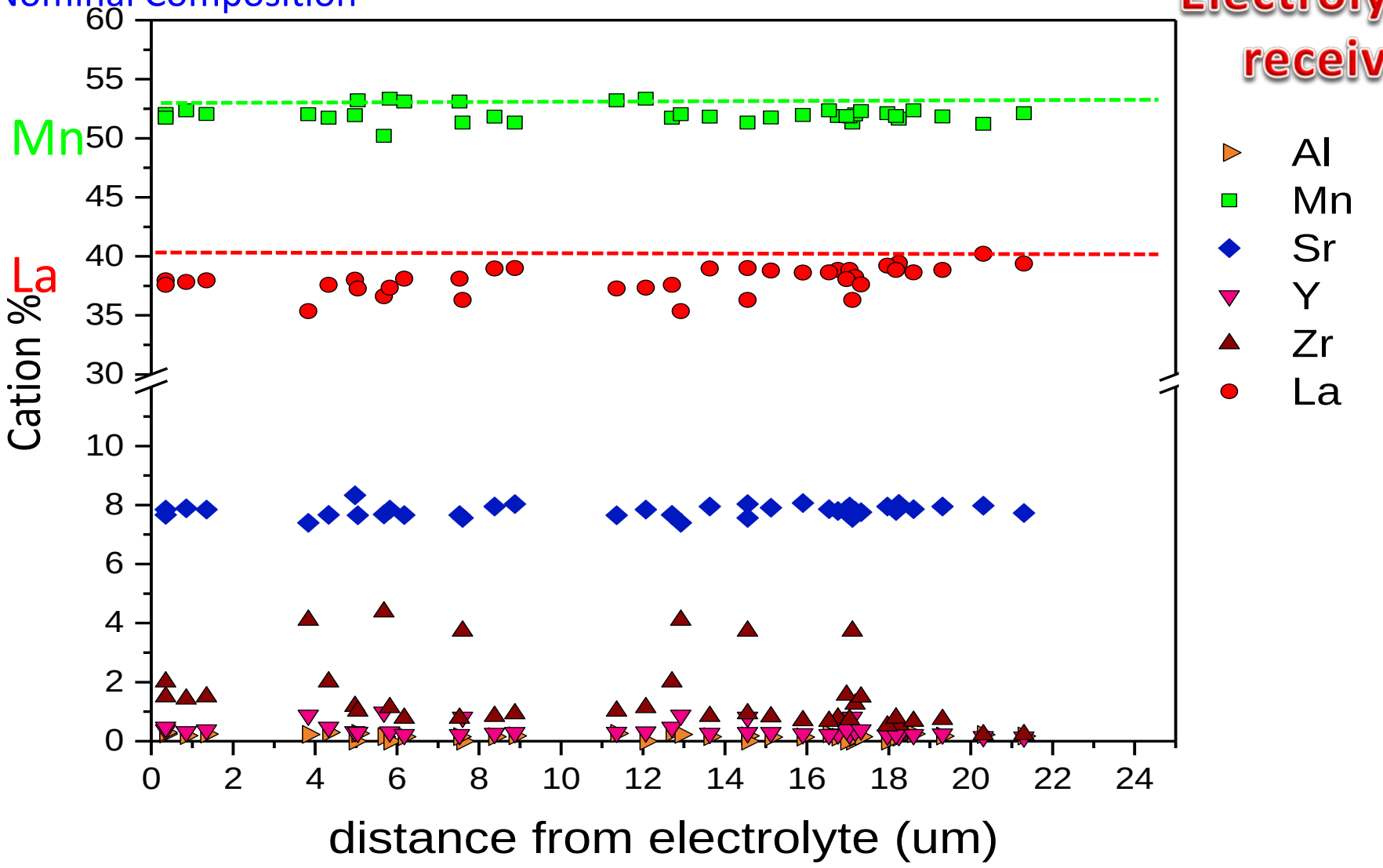
Summary: cathode microstructures, as received (3DR)

as received		LSM 85-90 (A) (200-μm e'lyte)	LSM 80-95 (B)	LSM 80-98 (C)	Cathode D
sample volume (μm³)		4,350	6,300	4,100	6,840
volume fraction (%)	porosity	**17**	**29**	**28**	**31**
	YSZ	41	33	37	34
	LSM	41	38	35	35
particle diameter (μm)	porosity	**0.2**	**0.4**	**0.3**	**0.4**
	YSZ	0.5	0.5	0.3	0.3
	LSM	0.6	0.6	0.5	0.6
tortuosity	porosity	2.0	1.5	1.7	1.5
	YSZ	1.5	1.6	1.8	1.7
	LSM	1.3	1.4	1.6	1.4
normalized surface area (μm^{-1})	porosity	26	16	21	16
	YSZ	12	13	18	17
	LSM	10	9	13	9
Total TPB (μm^{-2})		**17**	**14**	**22**	**18.4**
Active TPB (μm^{-2})		**10**	**13**	**20**	**17**

Bulk LSM particle composition profile

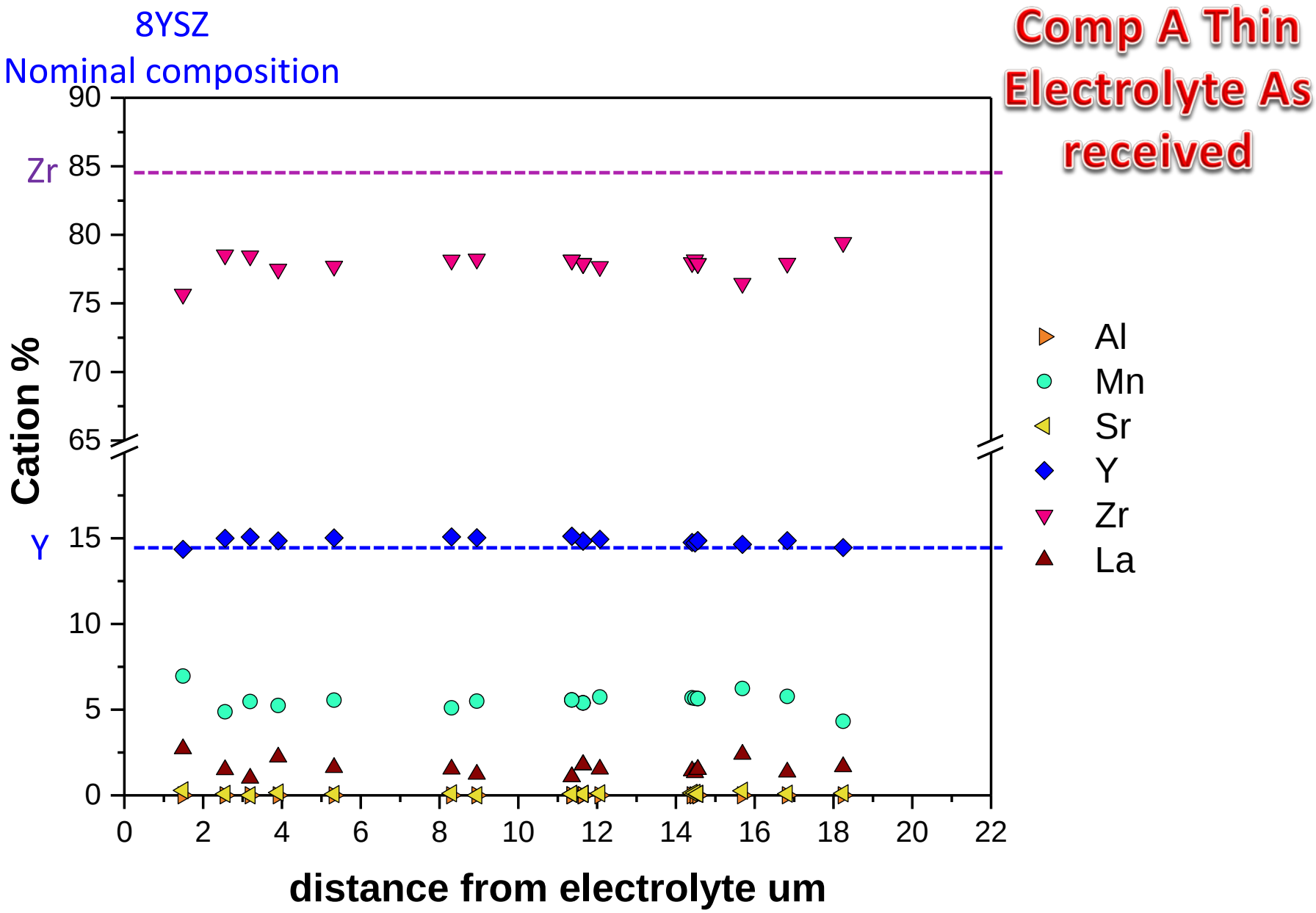
LSM 85-90
Nominal Composition

Comp A Thin Electrolyte As received



- Uniform LSM composition across the cathode composition A Thin electrolyte (as received)

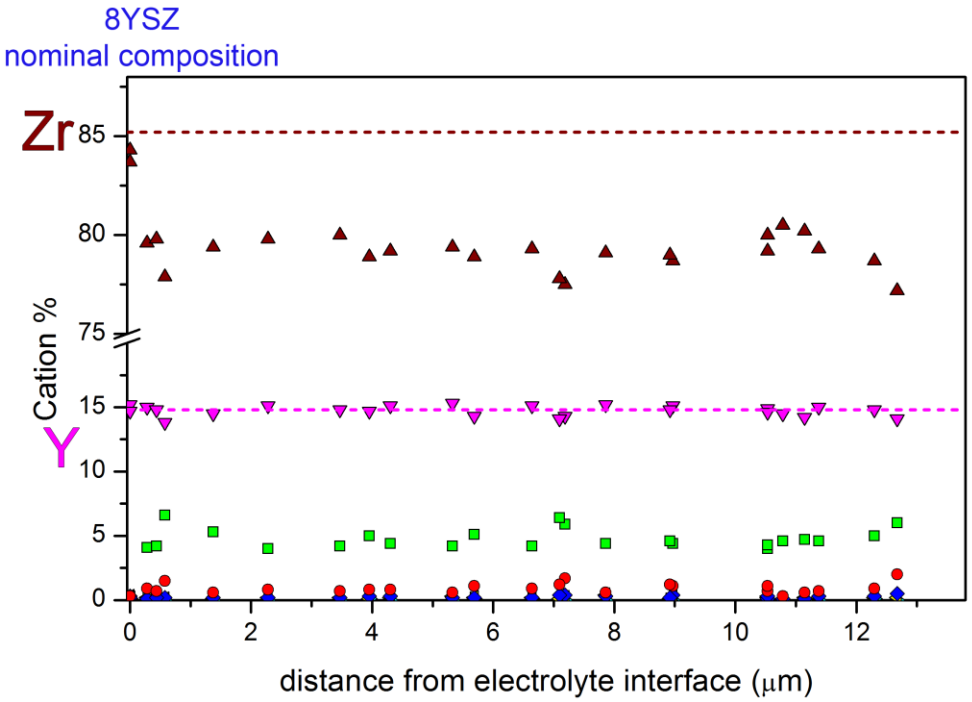
Bulk 8YSZ particle composition profile



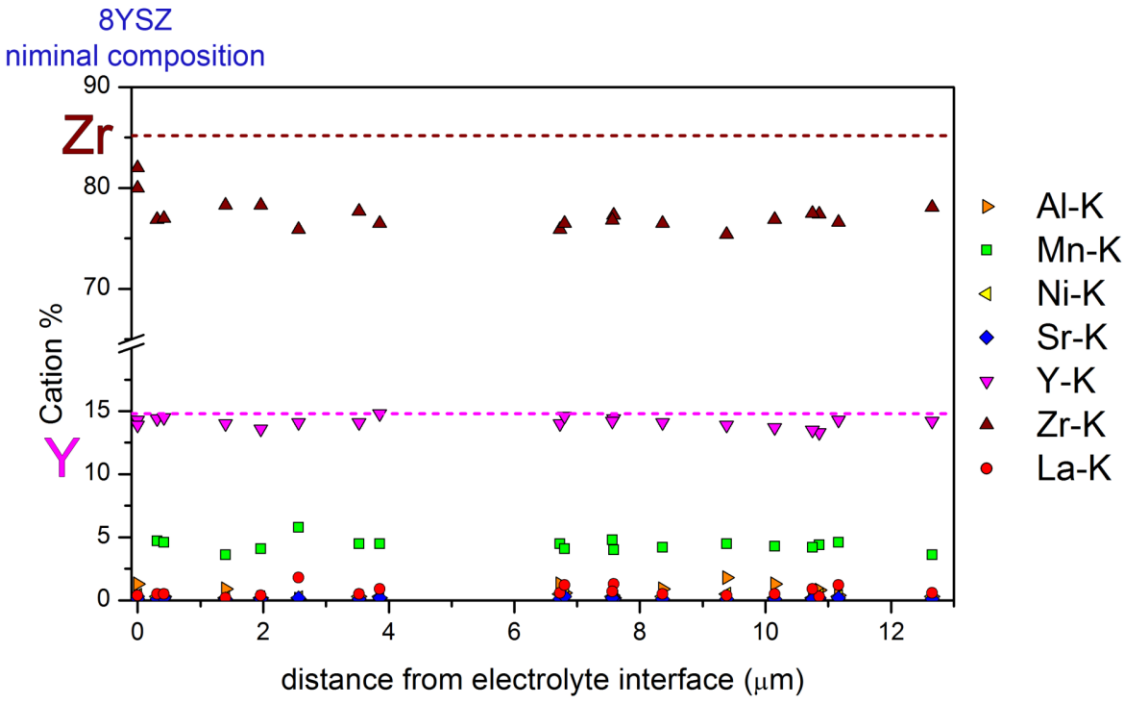
- Uniform 8YSZ composition across the cathode composition C
- ~4.5 cat% Mn dissolved in 8YSZ

TEM w/EDXS of bulk 8YSZ composition

72 h



493 h

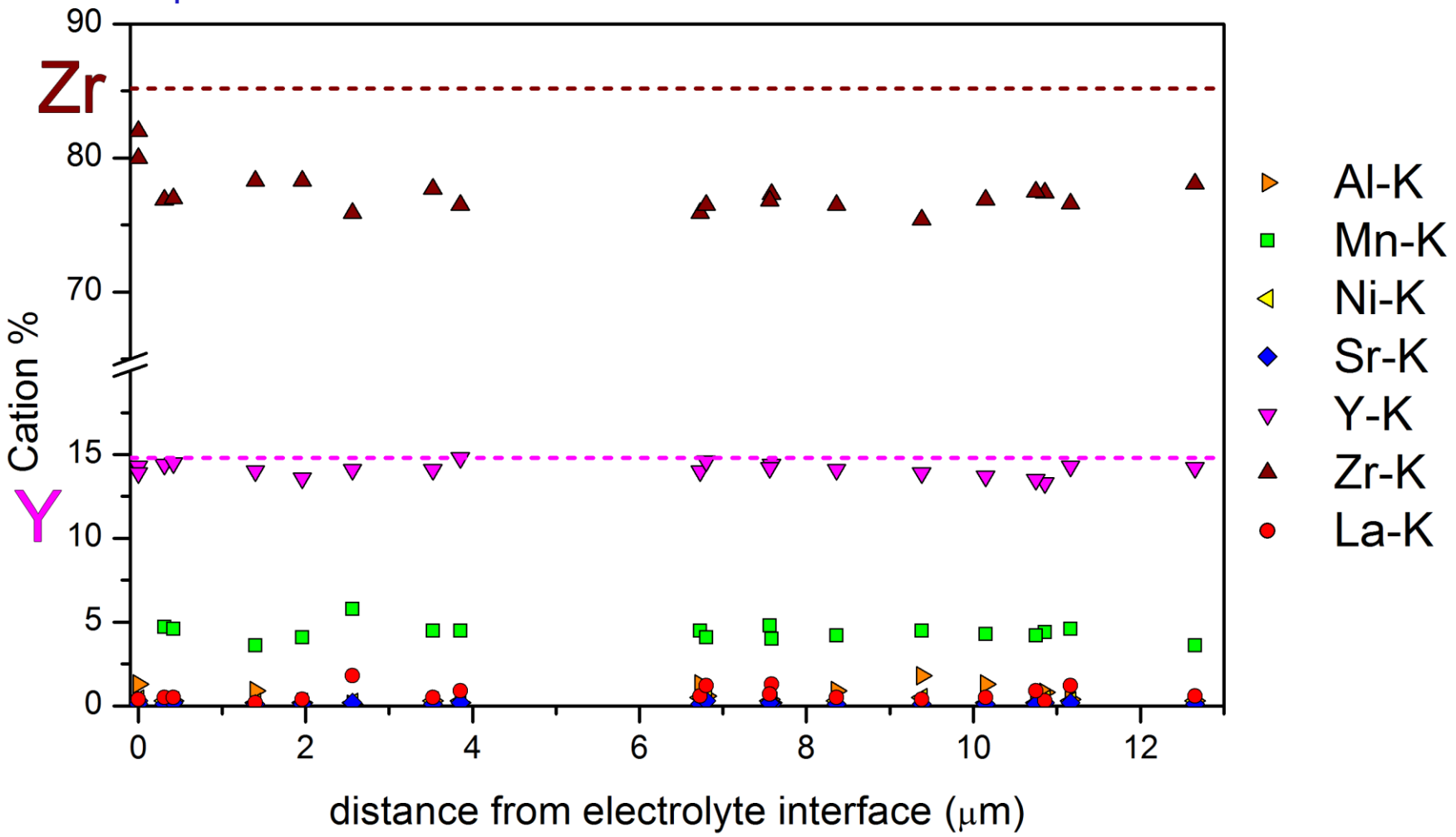


- **Uniform YSZ composition across cathodes**
- **4 – 5 cat% Mn**

Bulk 8YSZ particle composition profile

8YSZ

niminal composition

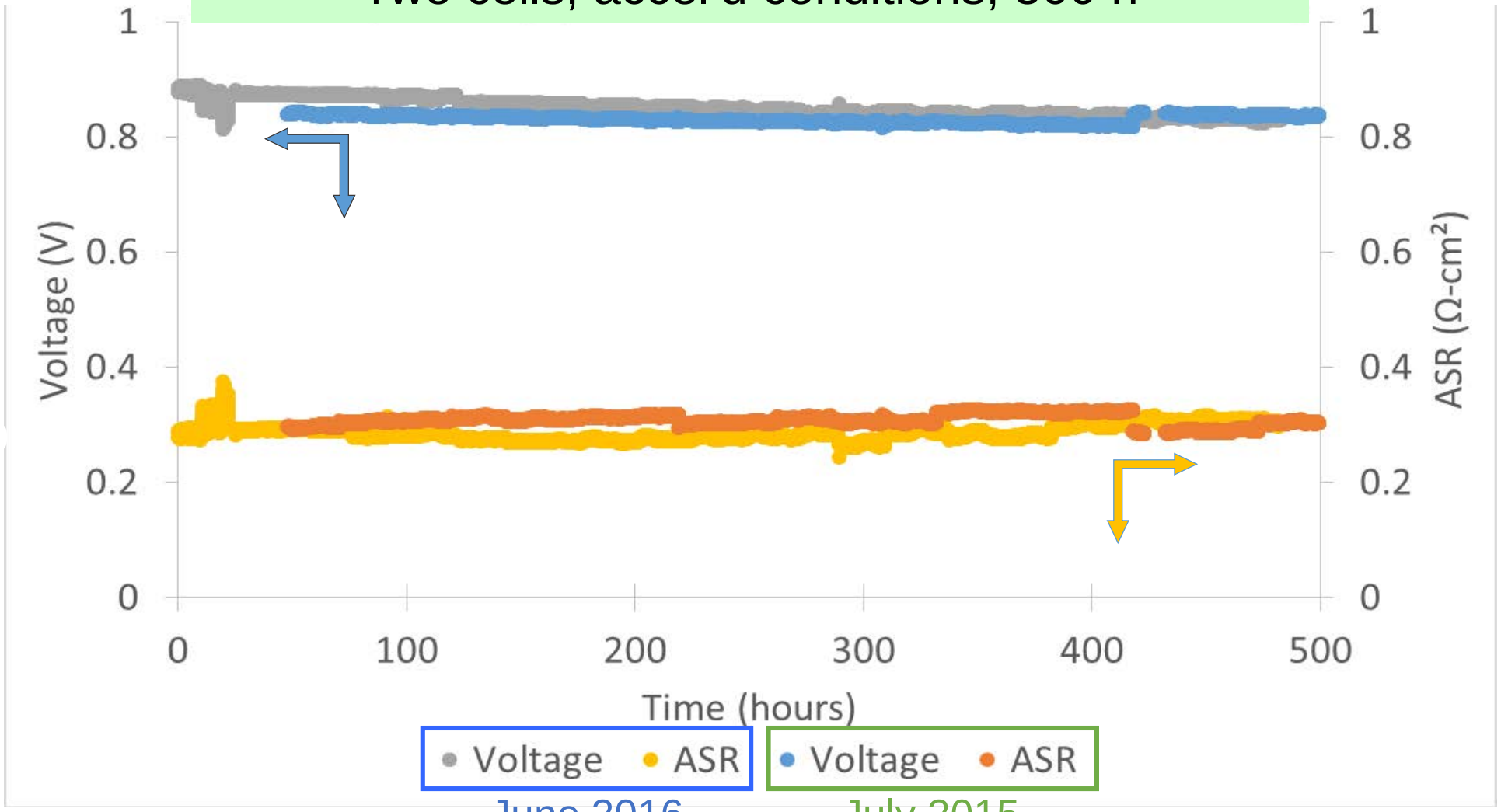


	Al	Si	Mn	Ni	Sr	Y	Zr	La
Cation %	0.6	2.8	4.4	0.3	0.1	14.1	77.0	0.7

~4.4 cation % Mn is found to dissolve in the 8YSZ

LSM 80-95 (B) durability testing: reproducibility

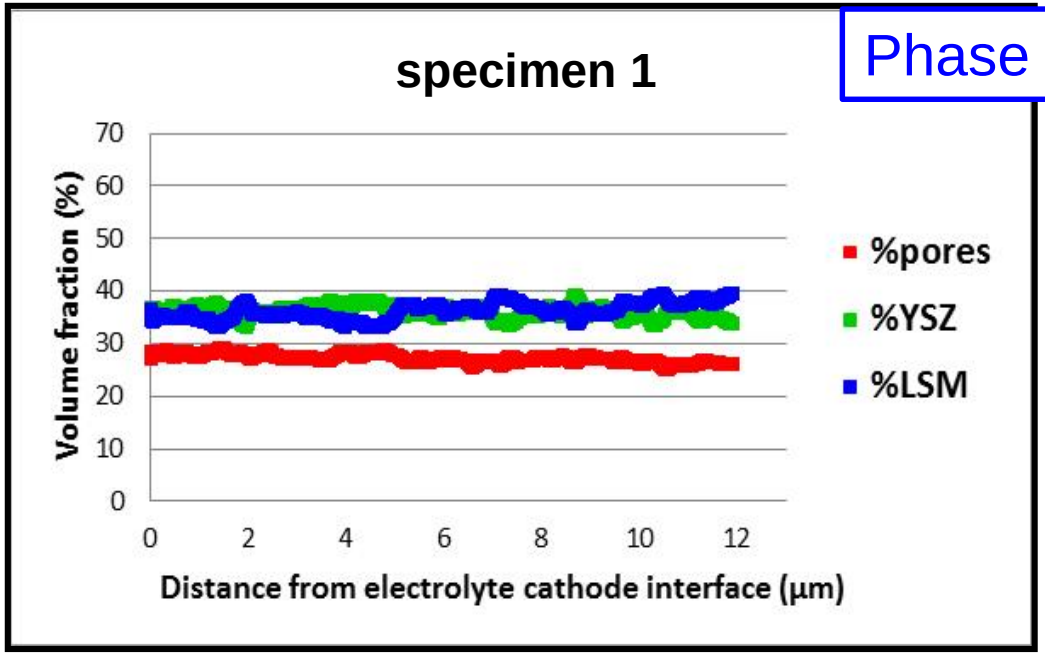
Two cells, accel'd conditions, 500 h

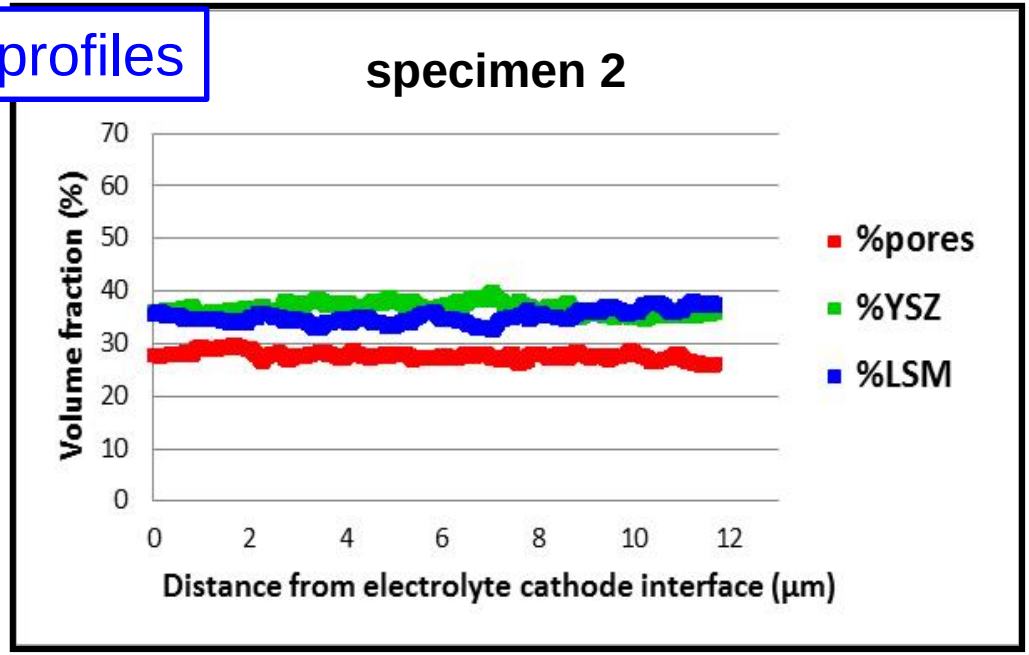


Reproducibility of 3D reconstruction data

LSM 80-98 (C) as received, two specimens

Phase profiles





Phase fractions & TPB

	specimen 1	specimen 2
porosity	**27** vol%	**28** vol%
YSZ	**36** vol%	**37** vol%
LSM	**37** vol%	**36** vol%
total TPB	**27.4** μm^{-2}	**21.7** μm^{-2}
active TPB	**24.2** μm^{-2}	**20.0** μm^{-2}

standard deviations

avg. microstructural params.: **0–5%**

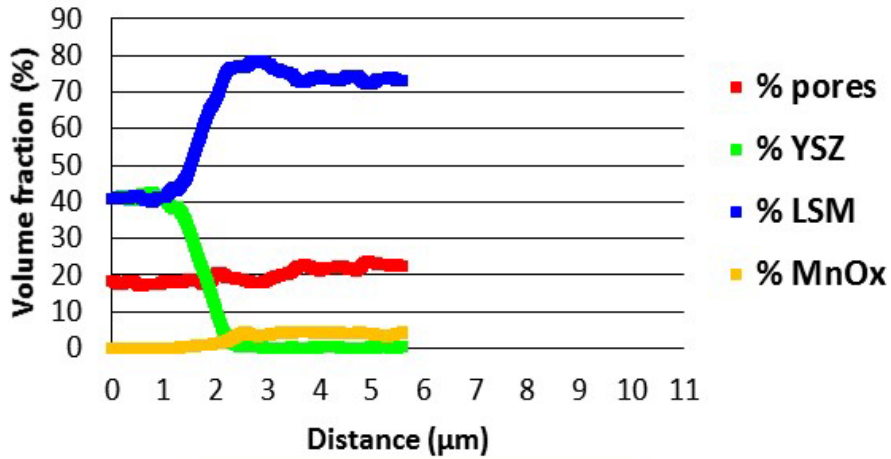
TPB: **~15%**

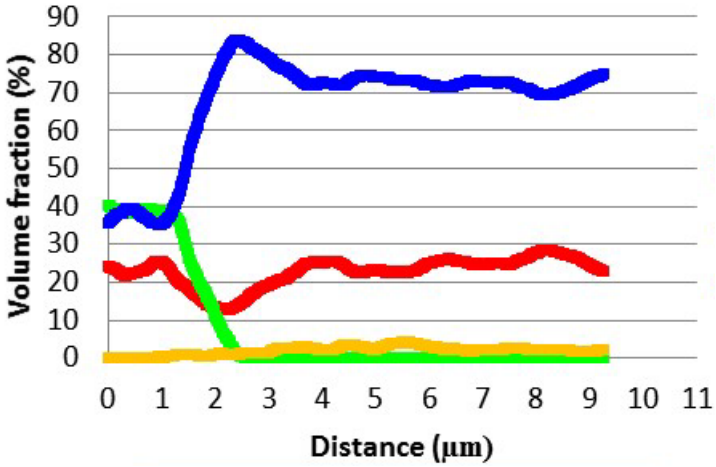
Phase profiles at cathode/CCC interface (3DR)

as received

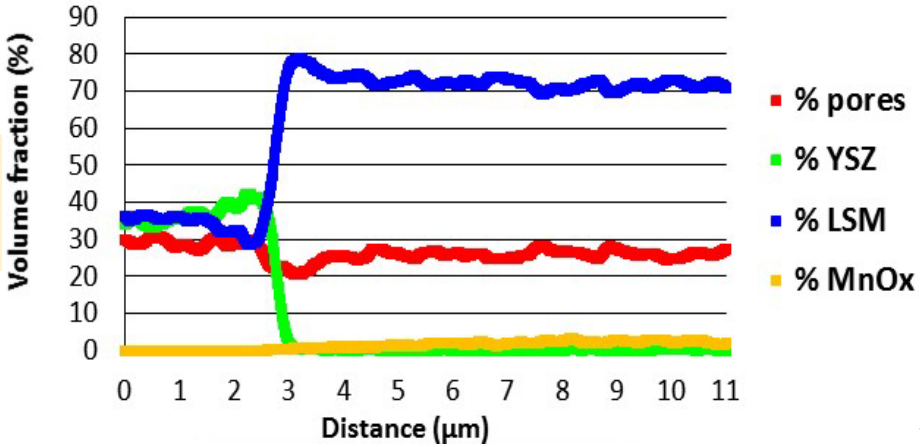
500 h accel'd testing

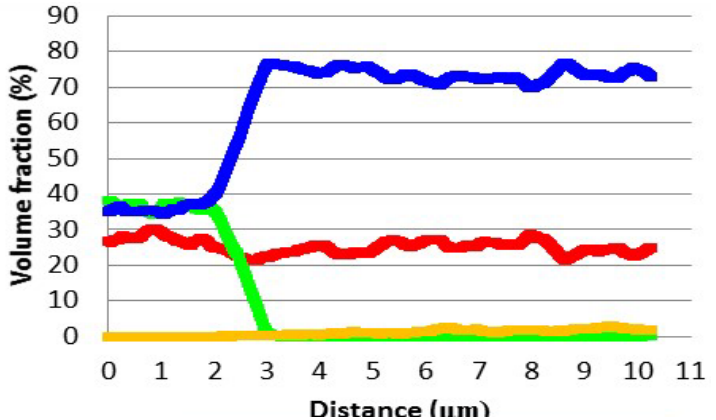
LSM 85-90
11% Mn xs



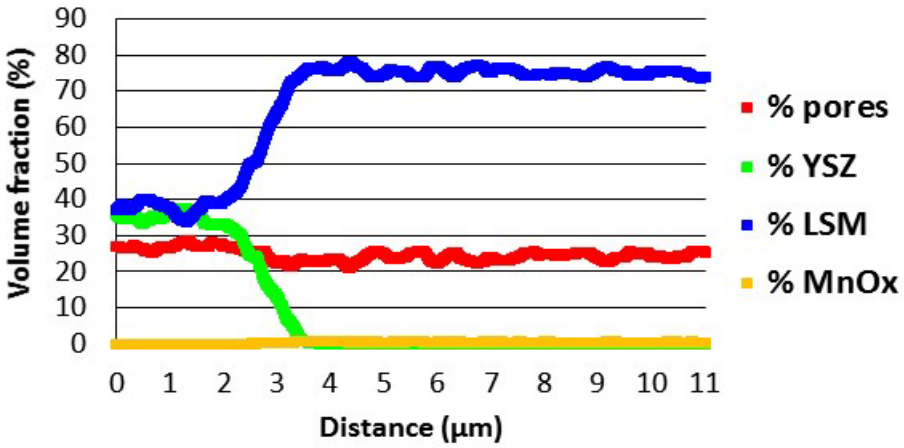


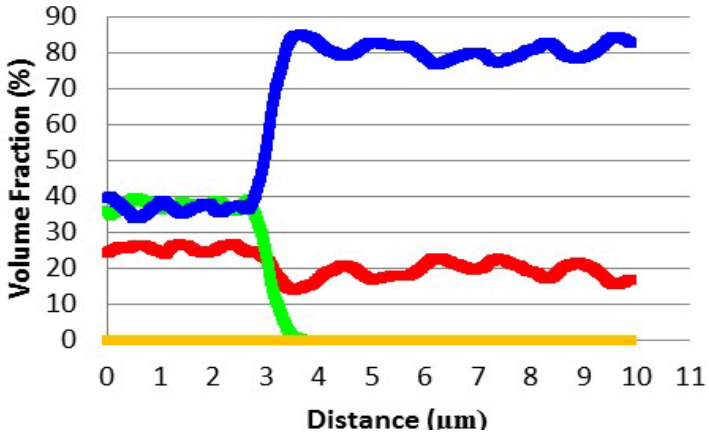
LSM 80-95
5% Mn xs



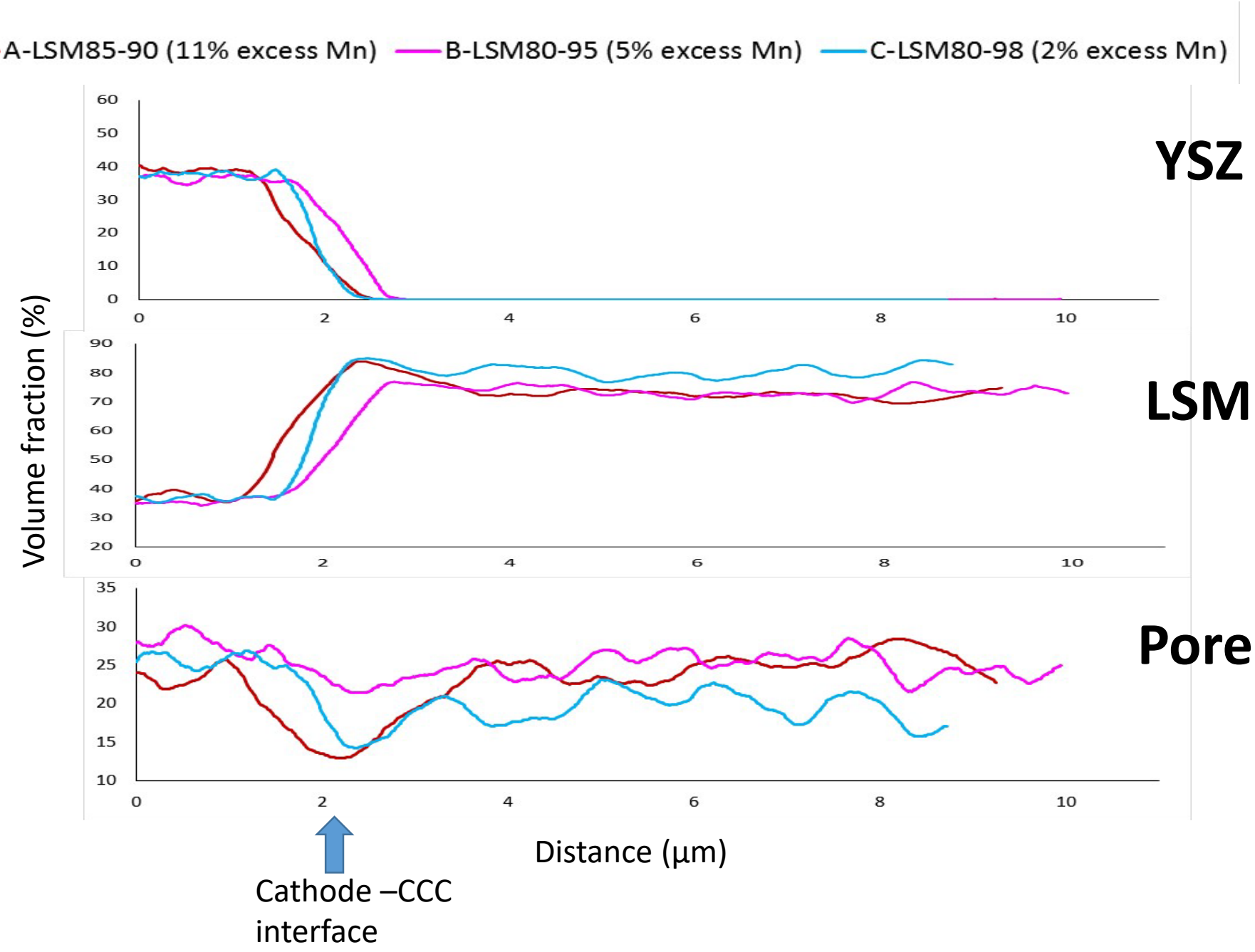


LSM 80-98
2% Mn xs





A – B – C comparison: cathode-CCC interface (500 h accel'd testing)



In LSM 85-90 (A) and LSM 80-98 (C), at cathode-CCC interface:

- *Densification* (bottom plot)

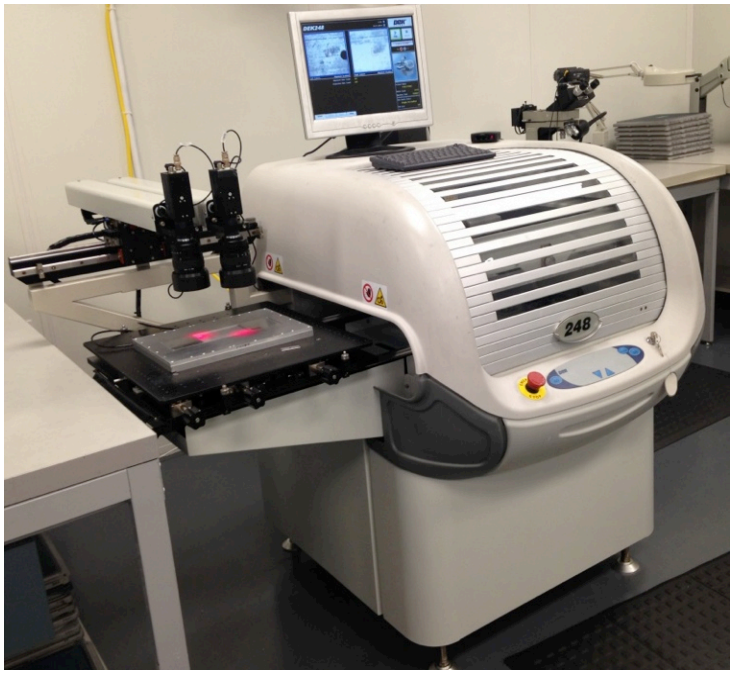
A – B – C comparison: porosity and TPB density

	LSM 85-90; 11% Mn xs		LSM 80-95; 5% Mn xs			LSM 80-98; 2% Mn xs	
	as rec'd	493h accel	as rec'd	500h accel	624h accel	as rec'd	500h accel
sample volume, μm^3	4350	4525	6300	5096	4550	4100	5012
porosity, volume %	**17**	**18**	**29**	**25**	**25**	**28**	**25**
pore diameter, µm	**0.23**	**0.42**	**0.38**	**0.5**	**0.46**	**0.28**	**0.44**
pore surface area, μm^{-1}	26	14	16	13	13	21	14
total TPB, μm^{-2}	**17.1**	**5.9**	**14.5**	**14.8**	**11**	**21.7**	**11.1**
active TPB, μm^{-2}	**10.3**	**5.1**	**13.0**	**12.5**	**10**	**20.0**	**10.2**

Vs. LSM 85-90 (A) and 80-98 (C), ***LSM 80-95*** (B) shows:

- ***Less pore coarsening*** and loss of pore area
- ***Stabler TPB*** (total and active)

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)*
    - Comp'n C: $(La_{0.80}Sr_{0.15})_{0.98}MnO_{3\pm\delta}$ *(LSM 80-98)*
  - Electrodes: screen printed, 9.5 mm dia., fired separately

Our observed trend in electrode ASR vs. A/B ratio
is opposite of electrical conductivity predicted by defect chemistry modeling.

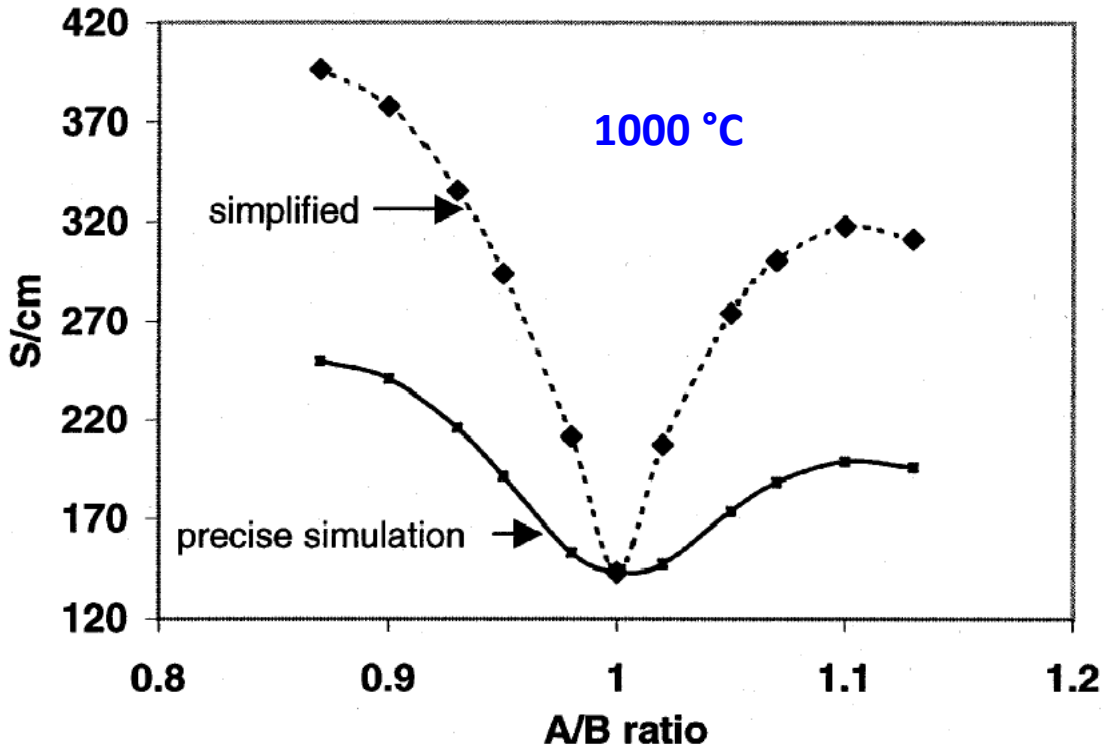
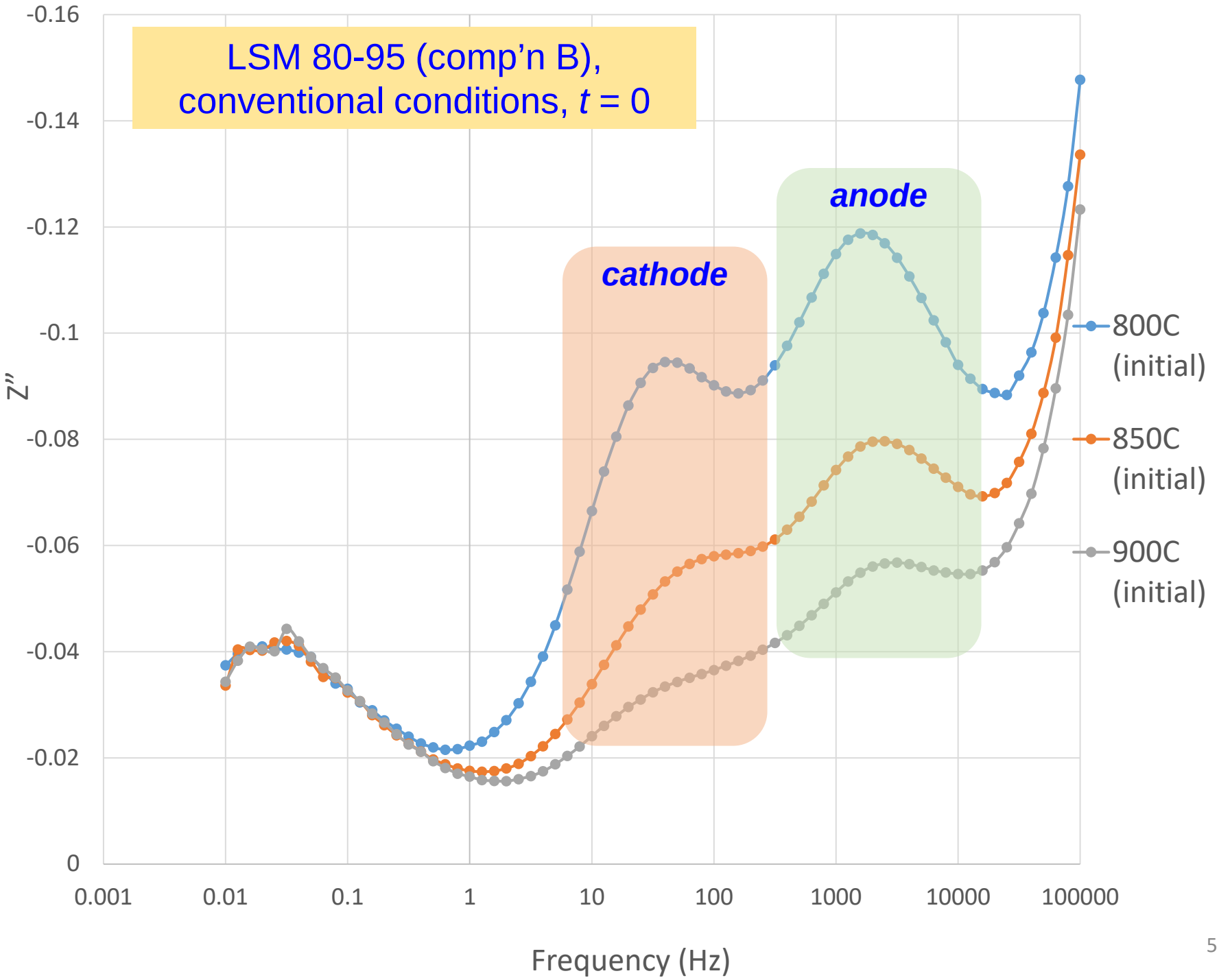


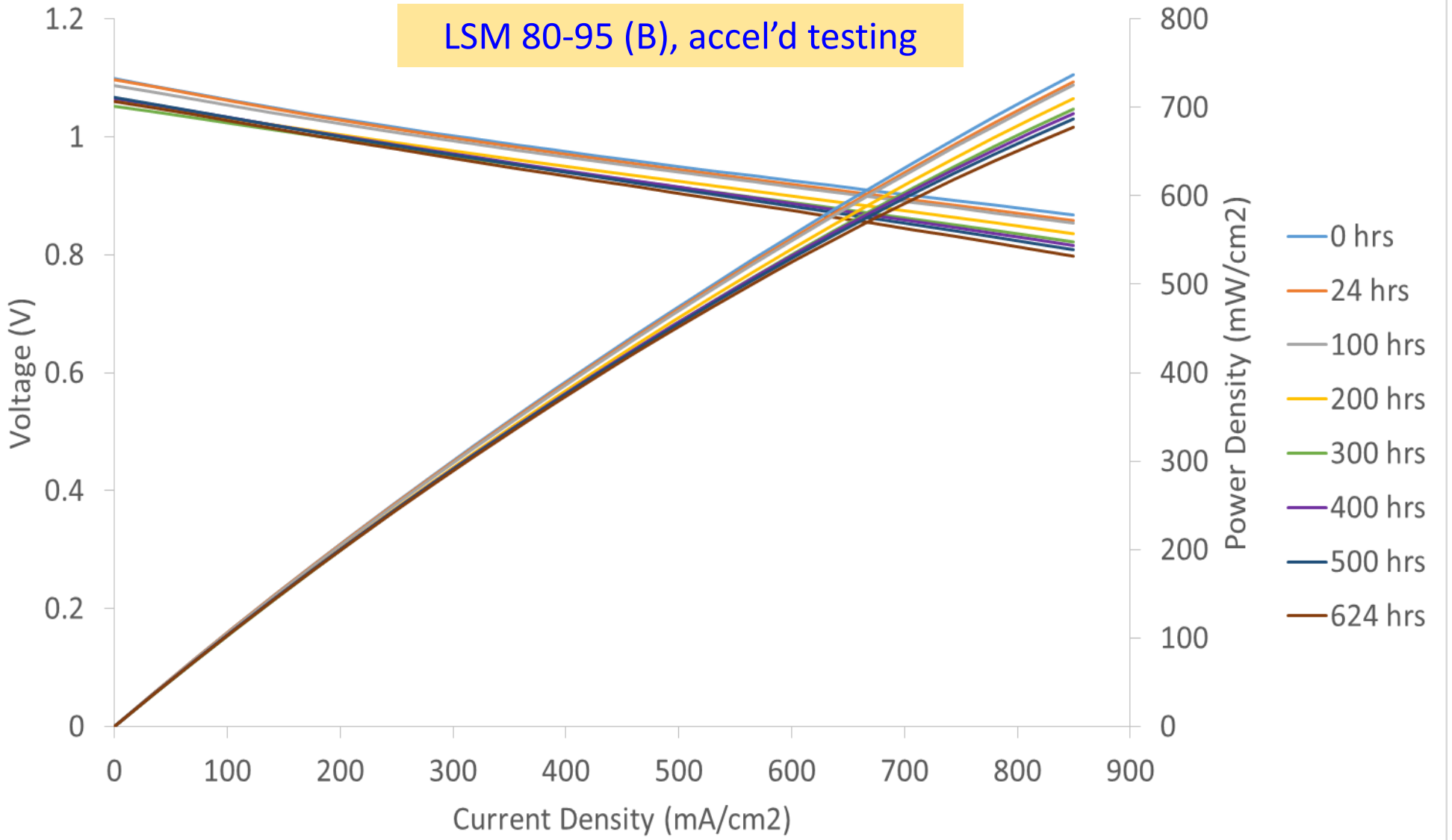
Fig. 8. Variation of total conductivity of 10% Sr doped LSM, small polaron model. Same equilibrium constants as in Fig. 7. The conductivity, predicted from Eqs. (20) and (21), based on simplifications, are shown for comparison.

F.W. Poulsen, *Solid State Ionics* **129** (2000) pp. 145 –162

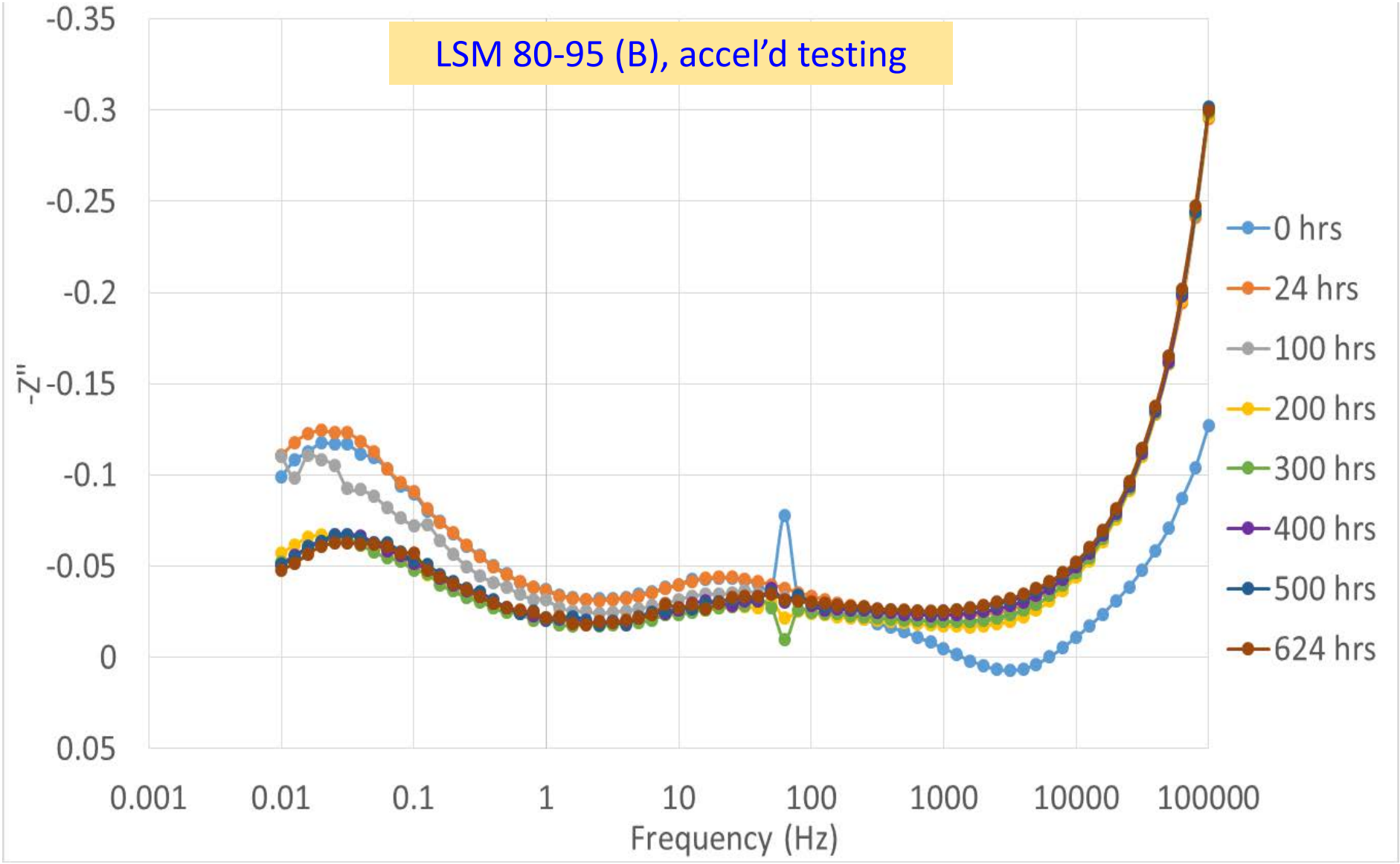
Pre-test protocol: temperature parametric study



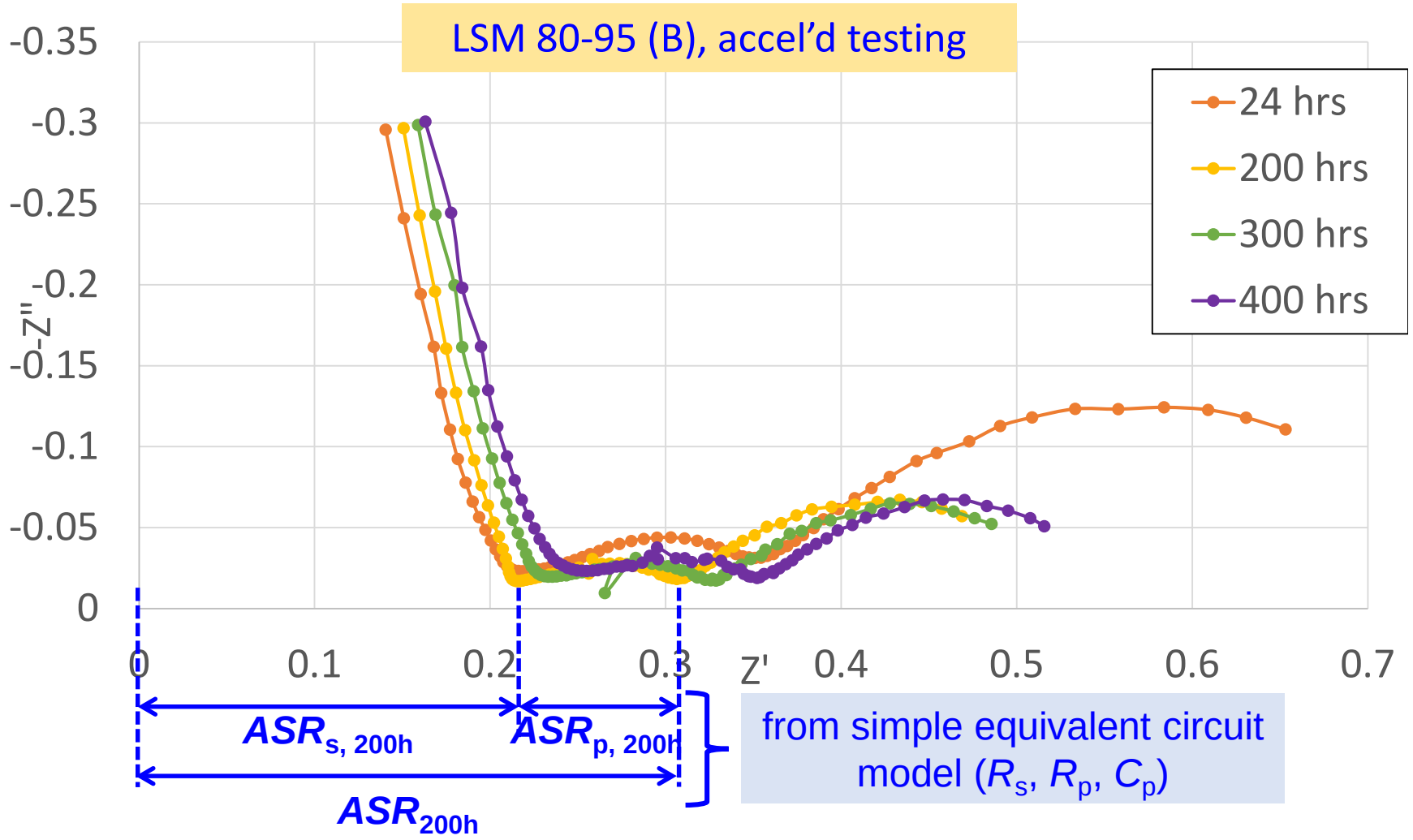
Representative V-I & P-I sweeps, 0–624 h



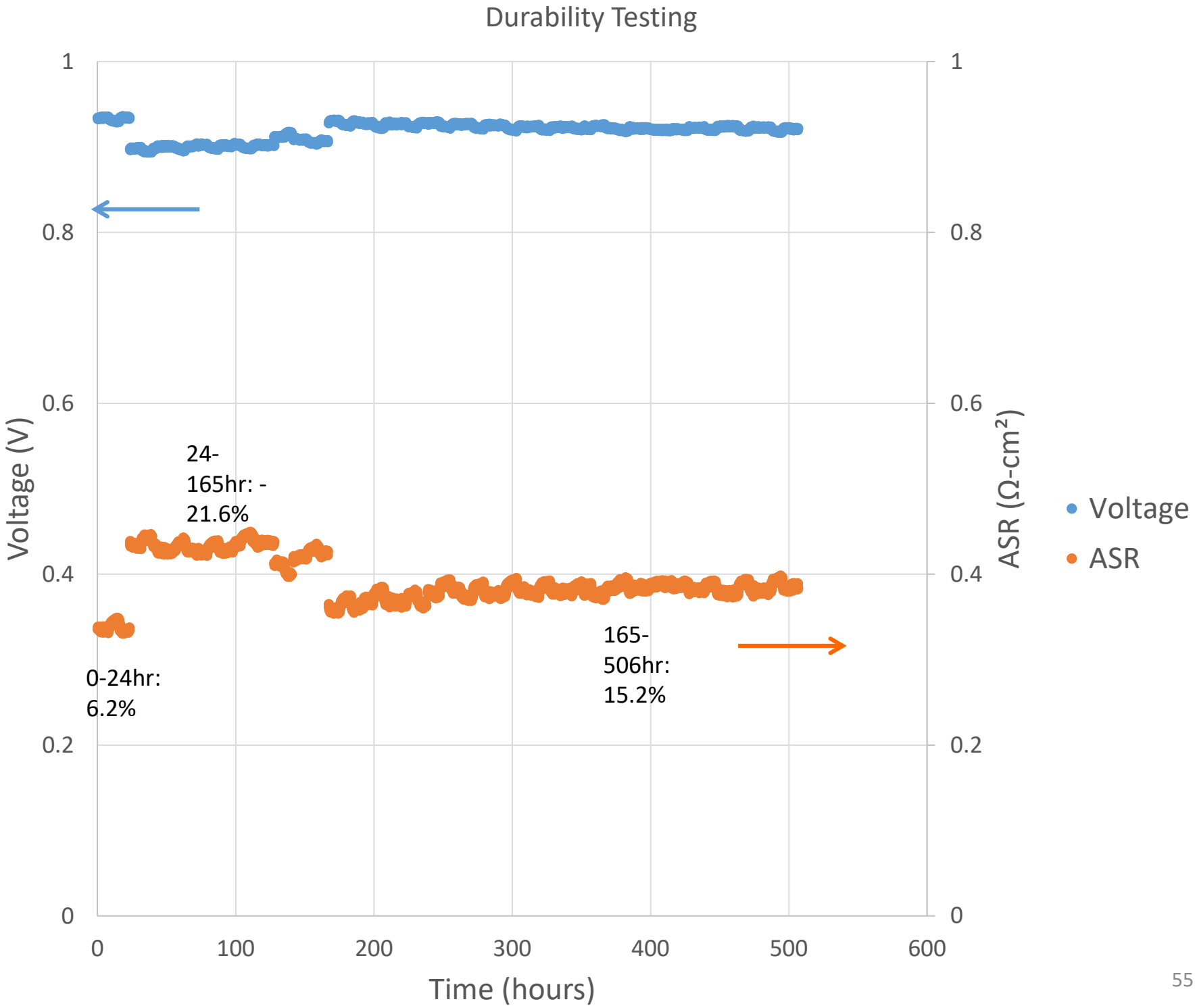
Representative Bode plots, 0–624 h



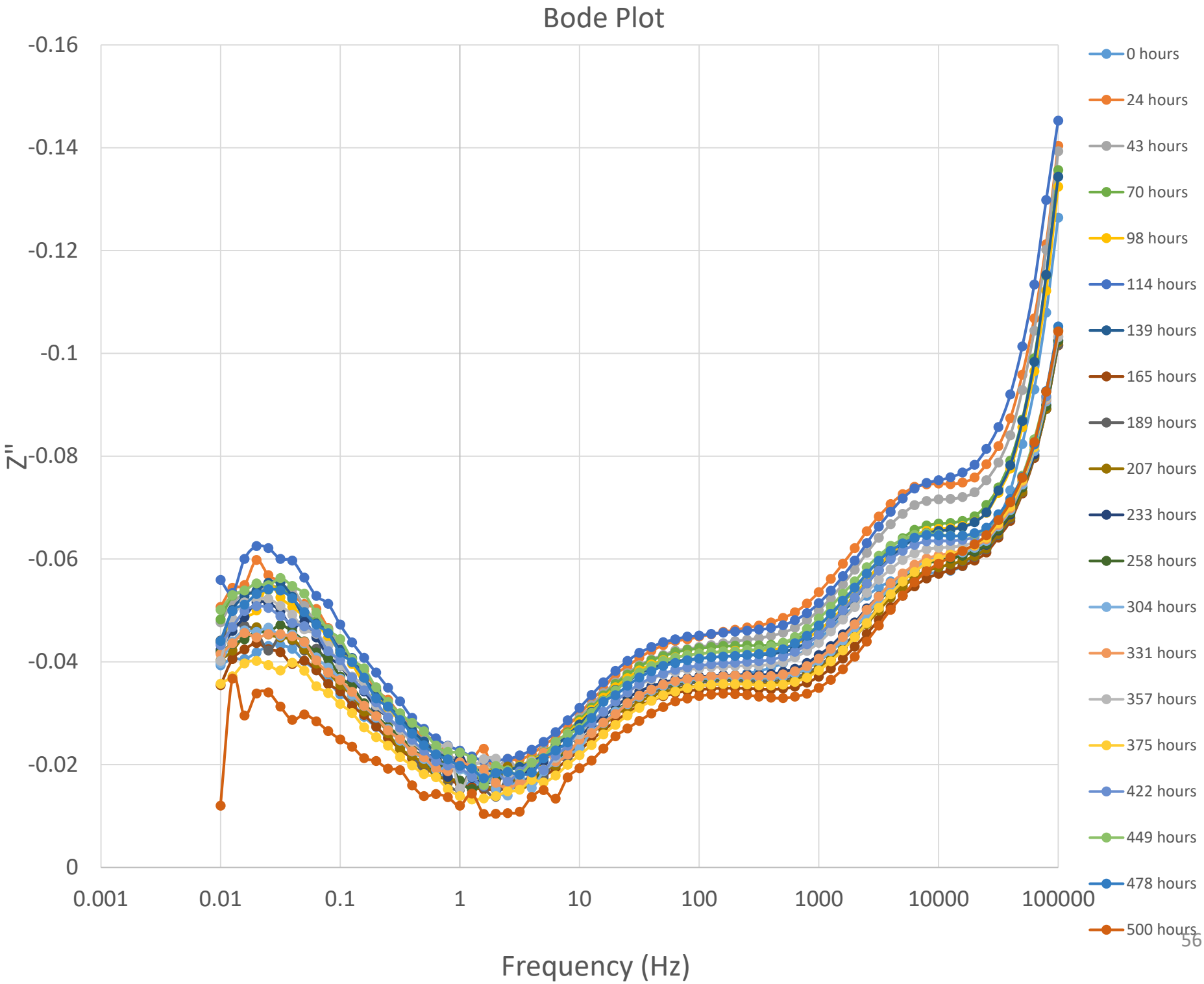
Representative Nyquist plots, 24–400 h



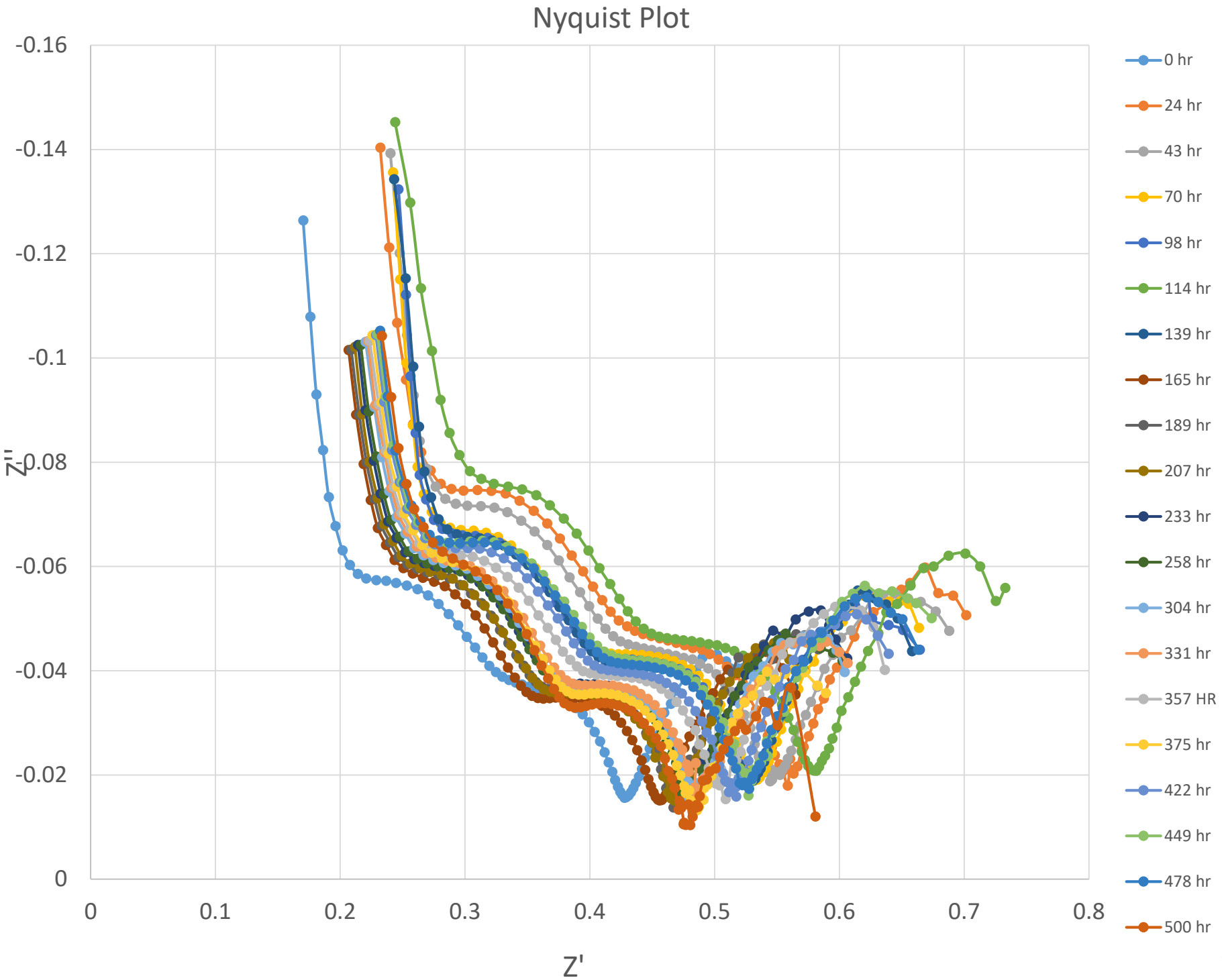
Cathode B: 500-hr Conventional Test



Cathode B: 500-hr Conventional Test



Cathode B: 500-hr Conventional Test



Reproducibility of 3DR (cathode C, as received)

		specimen 1	specimen 2			
Sample Volume (μm^3)		4350	4100			
Cathode composition		C (LSM80-98 / 8YSZ)				
Test condition		As received		Average	Std. dev'n	% dev'n
Volume Fraction (%)	Porosity	27.3	27.9	27.6	0.37	1.4%
	YSZ	36.1	36.8	36.5	0.52	1.4%
	LSM	36.6	35.3	35.9	0.90	2.5%
Particle Diameter (µm)	Porosity	0.26	0.28	0.27	0.01	5.2%
	YSZ	0.32	0.32	0.32	0.00	0.00%
	LSM	0.49	0.46	0.48	0.02	4.5%
Tortuosity	Porosity	1.66	1.77	1.72	0.08	4.5%
	YSZ	1.93	1.86	1.90	0.05	2.6%
	LSM	1.73	1.64	1.69	0.06	3.8%
Normalized Surface Area (μm^{-1})	Porosity	23.0	21.3	22.1	1.21	5.5%
	YSZ	18.6	18.5	18.6	0.08	0.46%
	LSM	12.3	13.1	12.7	0.54	4.2%
Total TPB (μm^{-2})		**27.4**	**21.7**	**24.6**	**4.0**	**16%**
Active TPB (μm^{-2})		**24.2**	**20.0**	**22.1**	**3.0**	**14%**
Active TPB (%)		88.3	92.1	90.0	2.6	3.0%

Use Δ instead of std. dev.?

Average microstructural parameters: *std. dev'ns <5%*
TPB (total & active): *std. dev'ns* ***≤ 4*** *μm^{-2}, ~15%*

		Gen A		
		as received	**200 h**	**493 h**
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^{-2})		**10.3**	**8.2**	**5.13**

A – B comparison: 3DR

		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 – C comparison: 3DR

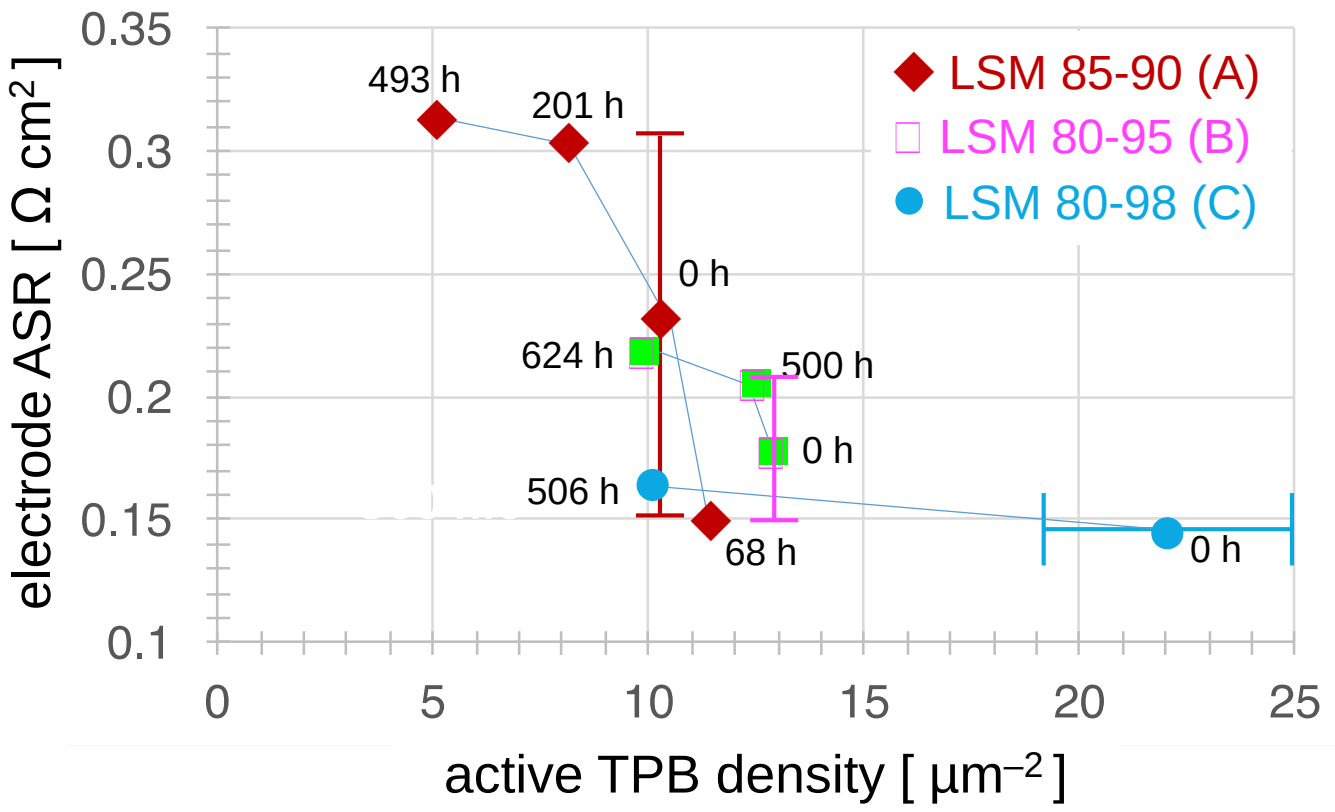
		Gen A		Gen B			Gen C	
		As received	493h Accel test	As received	500h Accel test	624 hrs Accel test	As received	500h Accel test
sample volume (μm^3)		4350	4525	6300	5096	4550	4100	5012
volume fraction (%)	porosity	**17**	**18**	**29**	**25**	**25**	**28**	**25**
	YSZ	41	43	33	35	37	37	37
	LSM	41	38	38	40	38	35	38
particle diameter (μm)	porosity	**0.23**	**0.42**	**0.38**	**0.5**	**0.46**	**0.28**	**0.44**
	YSZ	0.52	0.46	0.45	0.5	0.51	0.32	0.46
	LSM	**0.59**	**0.61**	**0.65**	**0.7**	**0.72**	**0.26**	**0.71**
normalized surface area (μm^{-1})	porosity	26	14	16	13	13	21	14
	YSZ	12	13	13	12	11	18	13
	LSM	10	10	9	8	8	13	8
Total TPB (μm^{-2})		**17.1**	**5.9**	**14.5**	**14.8**	**11**	**21.7**	**11.1**
Active TPB (μm^{-2})		**10.3**	**5.1**	**13.0**	**12.5**	**10**	**20.0**	**10.2**

Vs. LSM 85-90 (A) and 80-98 (C), ***LSM 80-95*** (B) shows:

- ***Less pore coarsening*** and loss of pore area
- ***Stabler TPB*** (total and active)

A – B – C comparison: ASR and TPB density

- As Mn excess ↓, ***ASR*** ↓ (**A** → **B** → **C**)
- As test *t* ↑:
  - ***Active TPB*** ↓
  - ***Total ASR*** ↑
  - Effects diminish as Mn excess ↓ (**A** → **B** → **C**)



reproducibility:
ASR [Ω cm²], 0 h: ± 0.08 (A); ± 0.03 (B)
active TPB density [µm⁻²], 0 h: ± 3.0 (C)