Performance and Microstructural Changes in LSM-Based SOFC Cathodes

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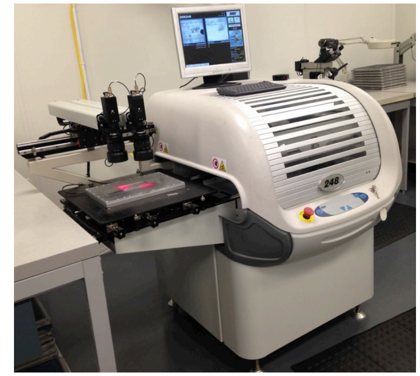
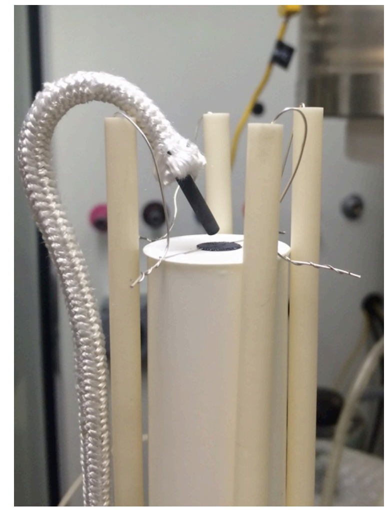
Outline

- $(La_{1-x}Sr_x)_{1-y}MnO_{3\pm\delta}$ (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*** (transmission electron microscopy):
      - Phase composition gradients
      - MnO_x formation
    - ***3DR*** (3D reconstruction):
      - ***TPB*** (three-phase boundary) density (total & active)
      - ***Densification*** at cathode–CCC interface
      - ***Porosity*** gradients
- Summary & conclusions

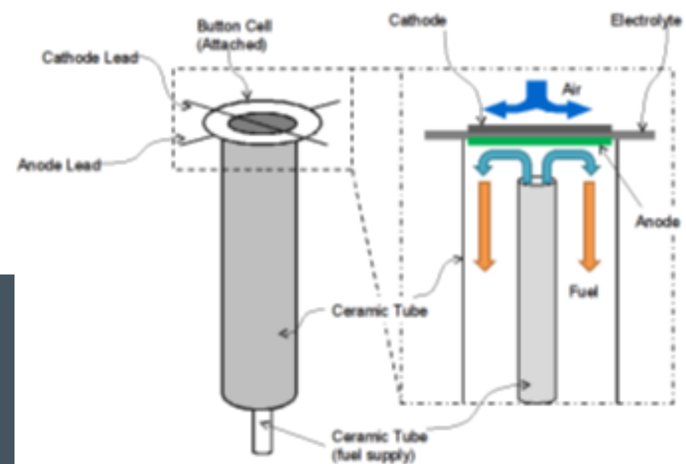
Cell specifications; testing procedures



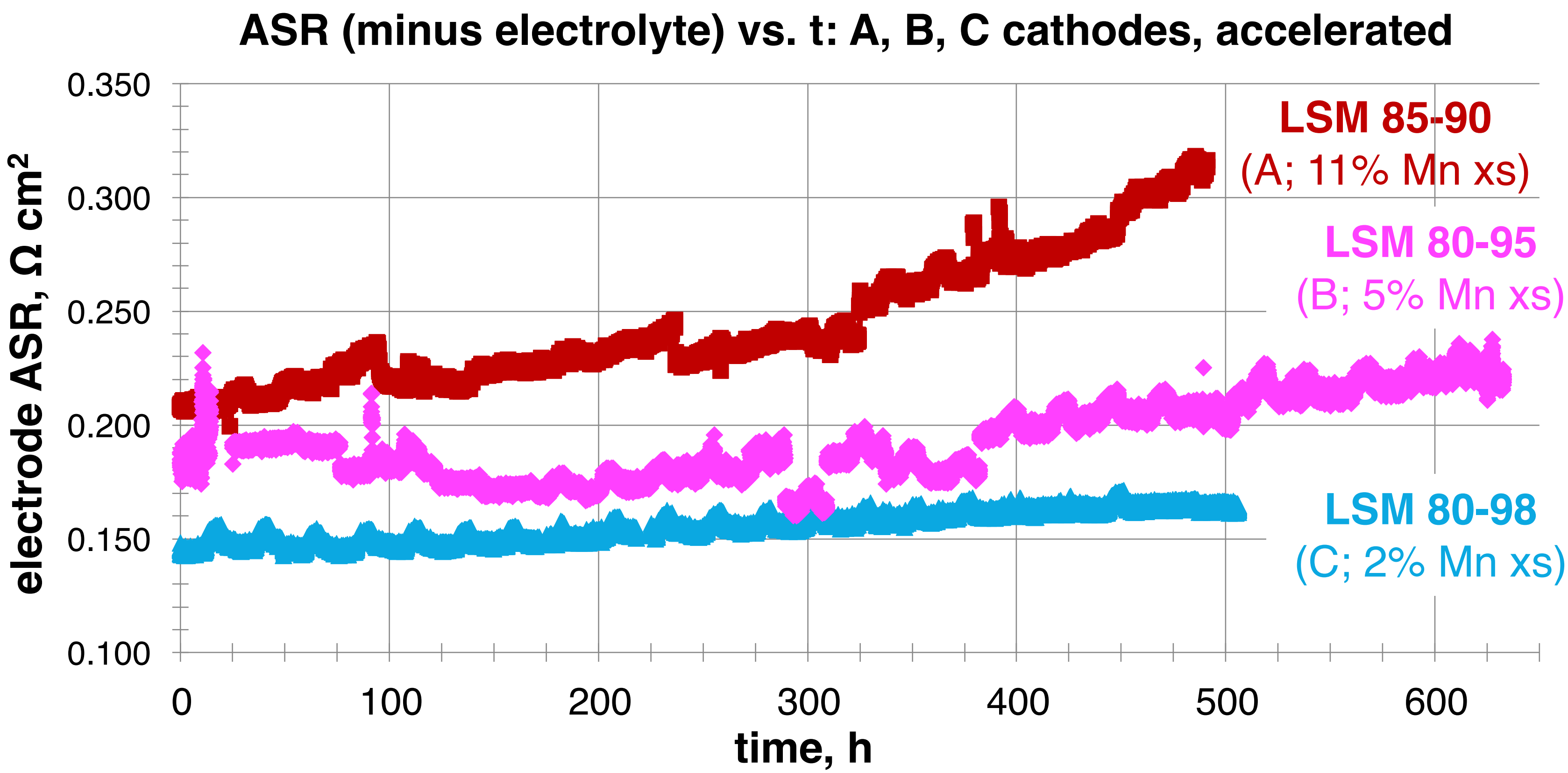
- Button cells fabricated at LGFCS
  - 8YSZ electrolyte
  - NiO / 8YSZ anode
  - Cathodes: LSM / 8YSZ
    - A: $(La_{\mathbf{0.85}}Sr_{0.15})_{\mathbf{0.90}}MnO_{3\pm\delta}$ (LSM 85-90) — ***11%*** Mn excess
    - B: $(La_{\mathbf{0.80}}Sr_{0.15})_{\mathbf{0.95}}MnO_{3\pm\delta}$ (LSM 80-95) — ***5%*** Mn excess
    - C: $(La_{\mathbf{0.80}}Sr_{0.15})_{\mathbf{0.98}}MnO_{3\pm\delta}$ (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



A – B – C comparison: Electrode ASR* (accelerated testing)



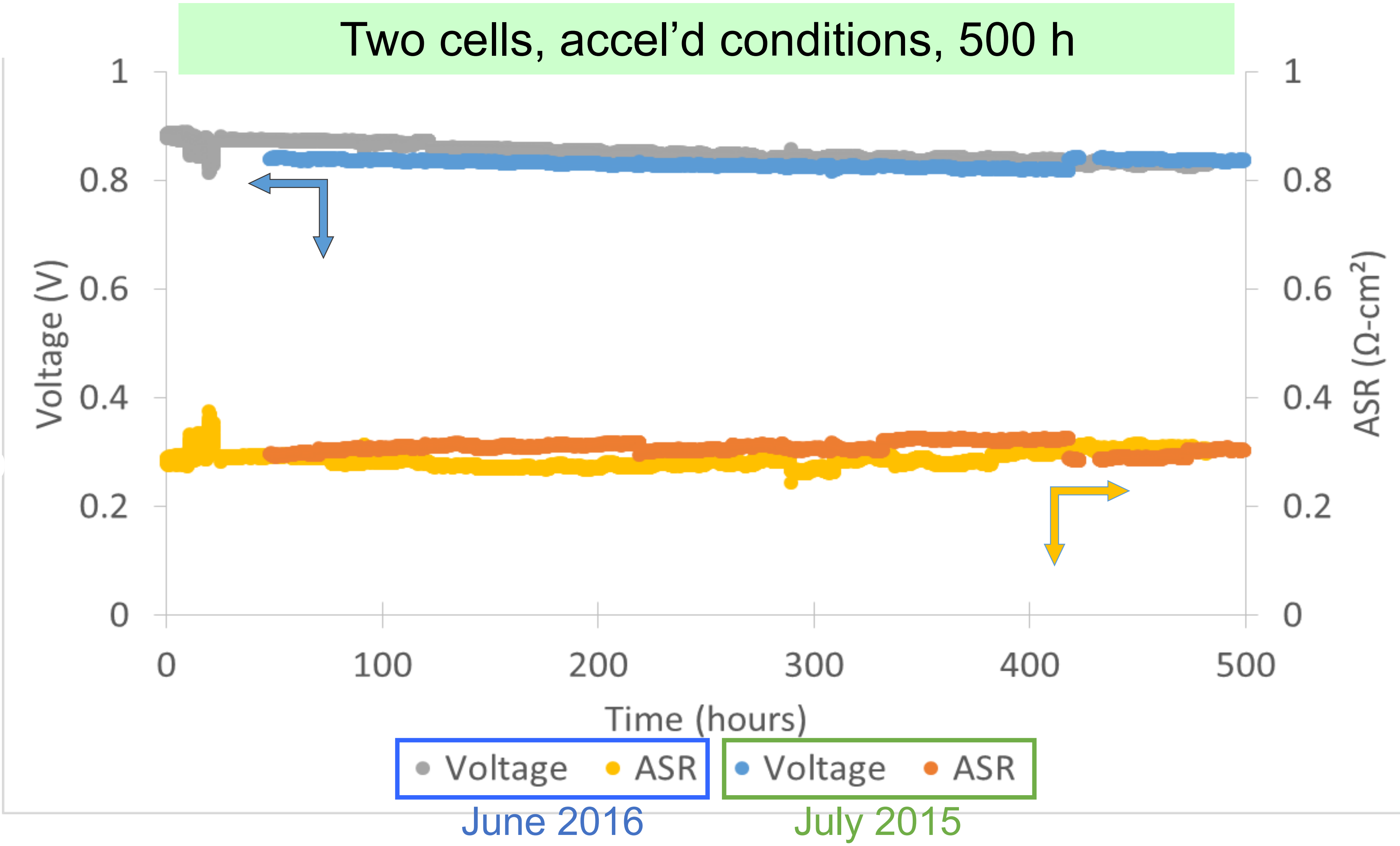
LSM 85-90 *(11% Mn xs):*
- ***Highest ASR*** overall
- ***Highest rise in ASR***

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

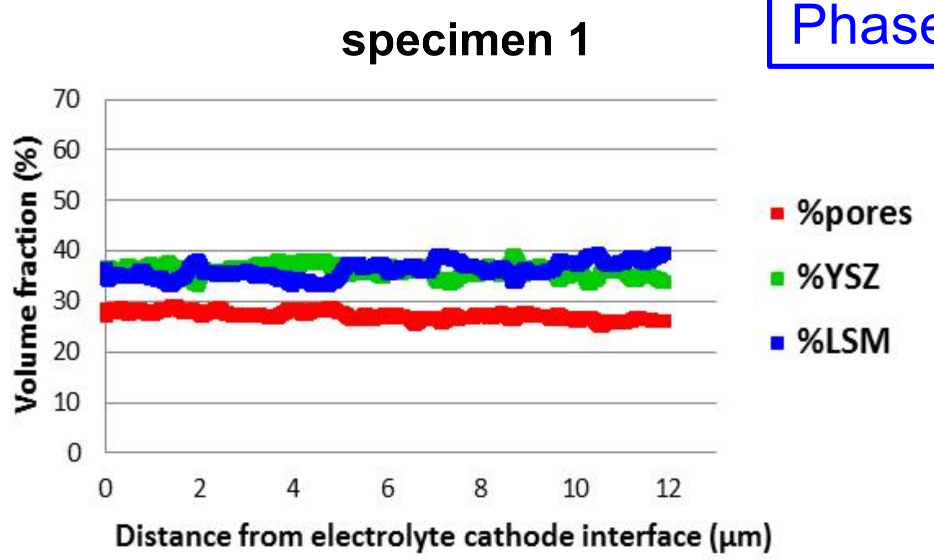
LSM 80-95 (B) durability testing: reproducibility

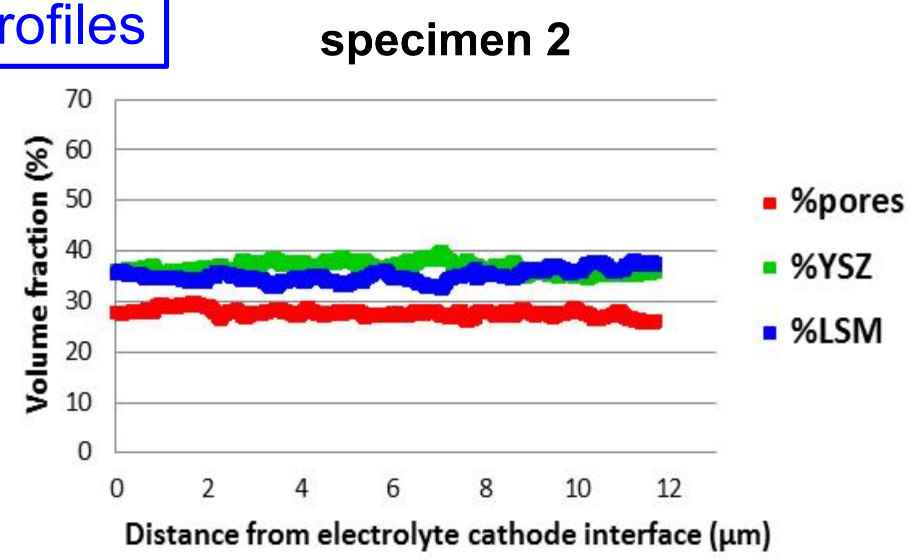


Reproducibility of 3D reconstruction data

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

Phase profiles





Phase fractions & TPB

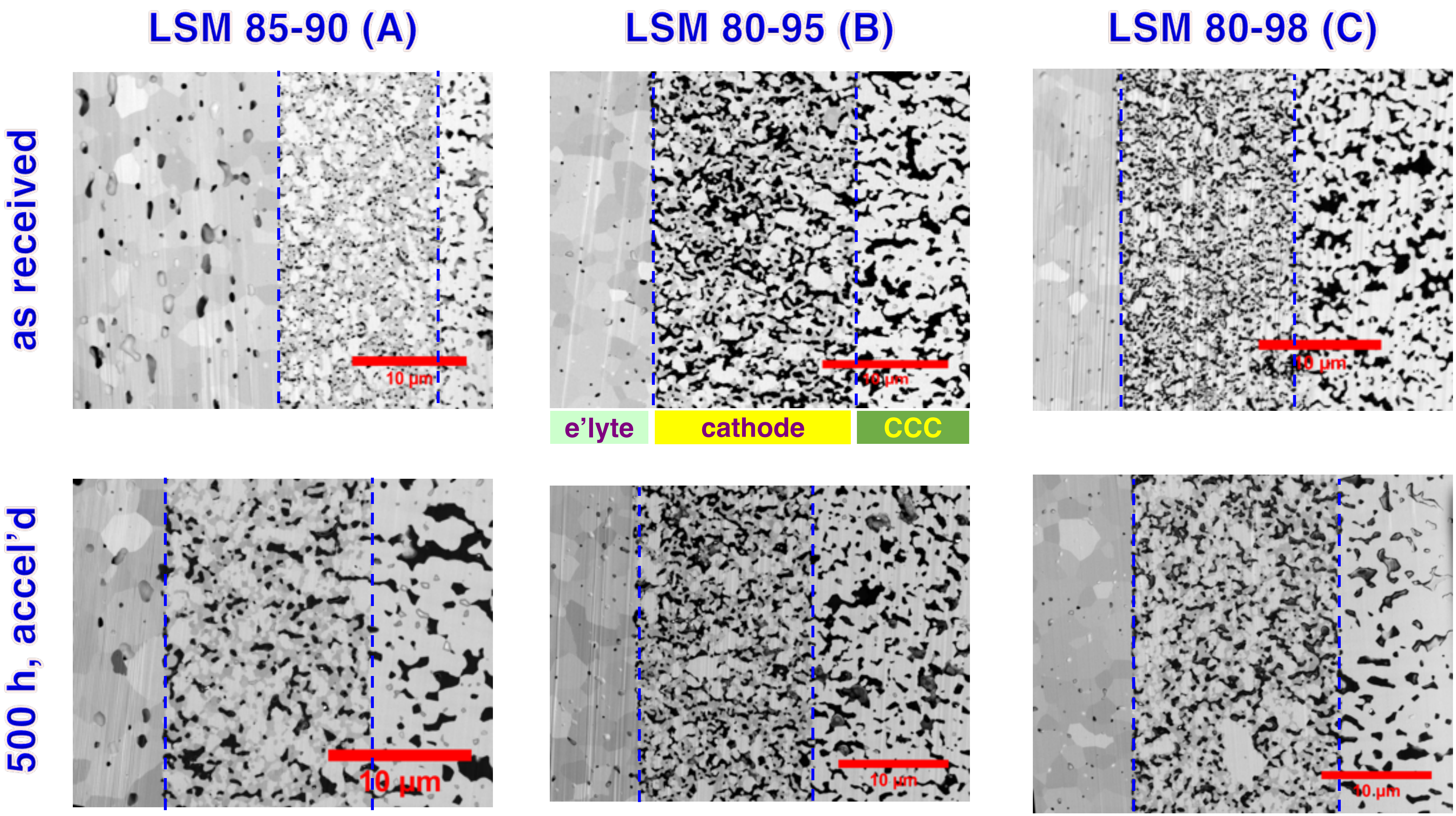
	specimen 1	specimen 2
porosity	**27** vol%	**28** vol%
YSZ	**36** vol%	**37** vol%
LSM	**37** vol%	**36** vol%
total TPB	**27.4** μm^{-2}	**21.7** μm^{-2}
active TPB	**24.2** μm^{-2}	**20.0** μm^{-2}

standard deviations

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

TPB: **~15%**

Microstructural change after 500 h accelerated testing

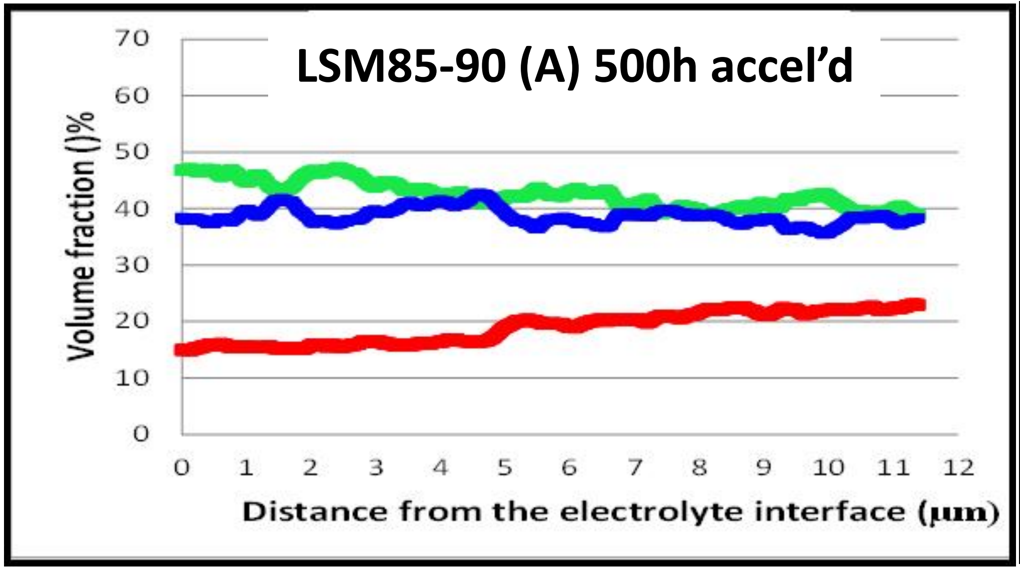


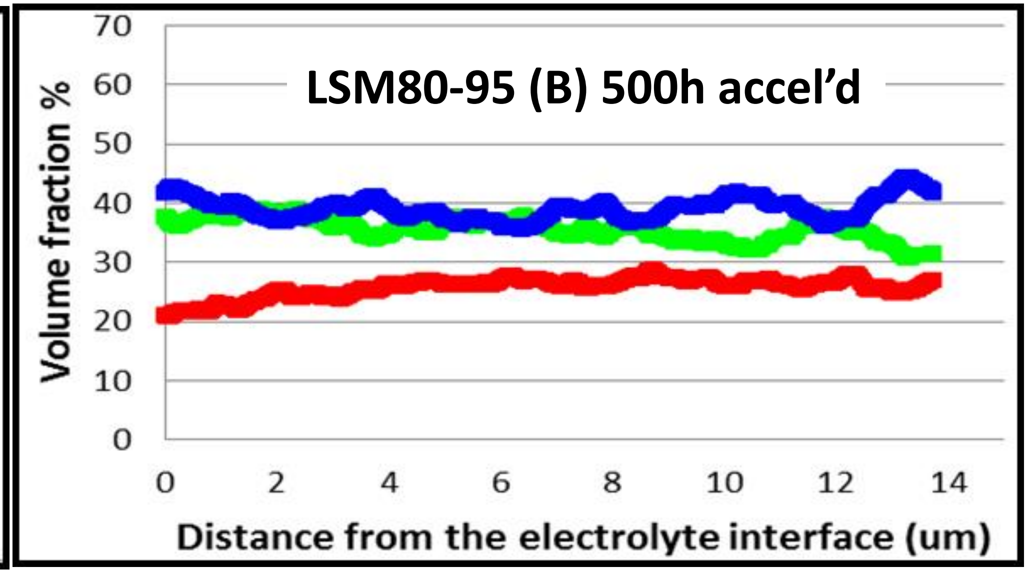
- Coarsening of pores & LSM
- Densification of CCC

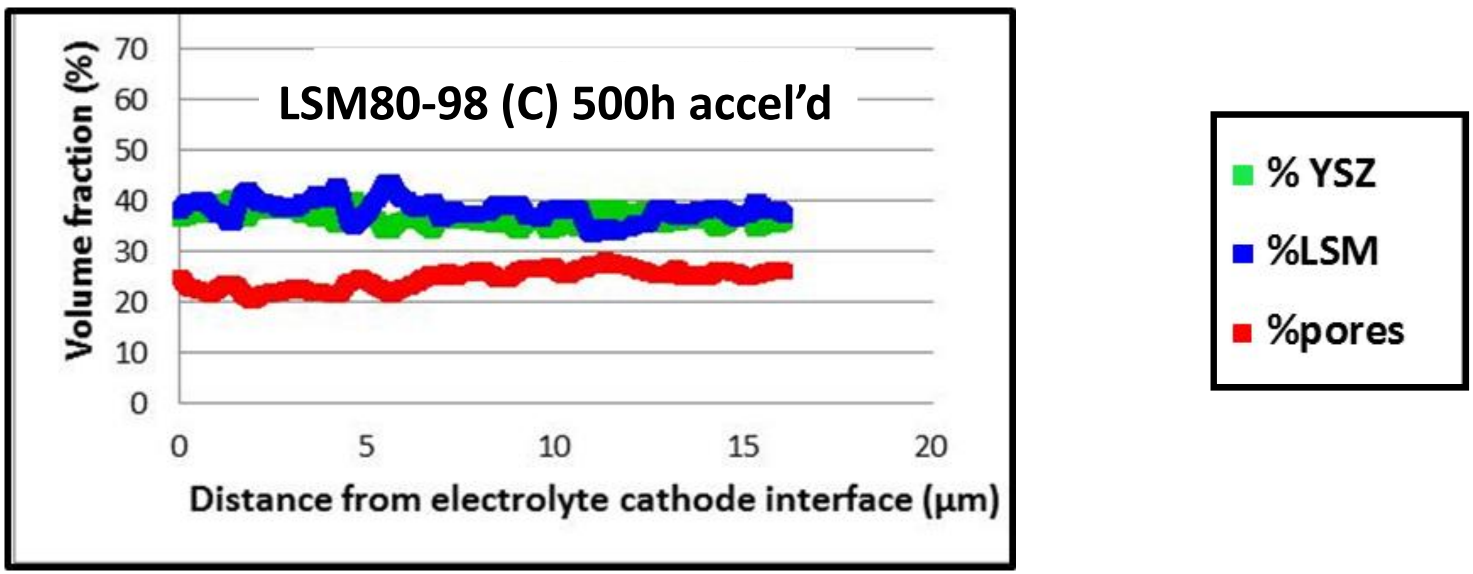
- Highest overall microstructural stability

- Coarsening of pores & LSM
- Densification of CCC

A – B – C comparison: Phase profiles across cathode (3DR)







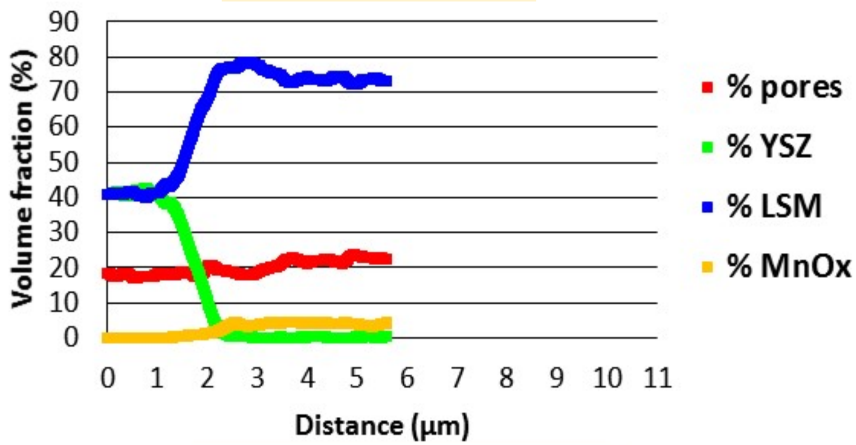
All three cathodes developed slight ***porosity gradients*** after 500 h of accelerated testing, with ***lowest porosity at cathode-electrolyte interface***

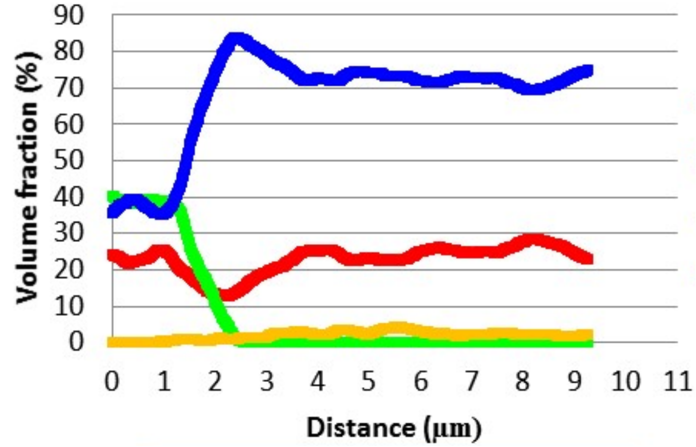
A – B – C comparison: Phase profiles at cathode/CCC interface (3DR)

as received

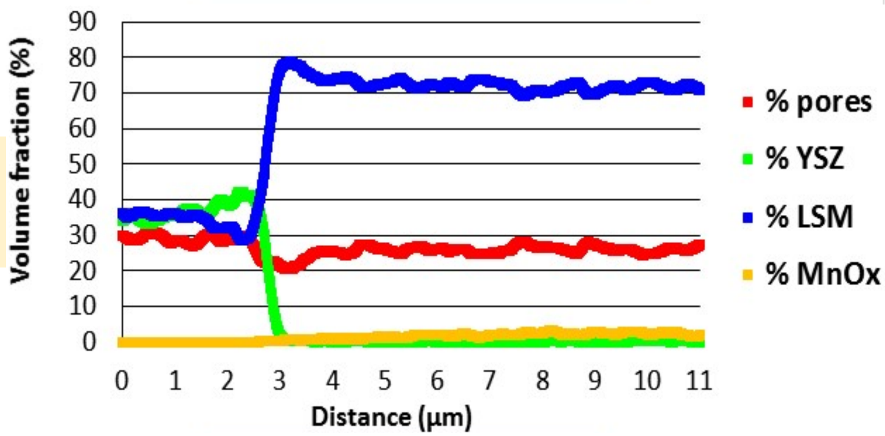
500 h accel'd testing

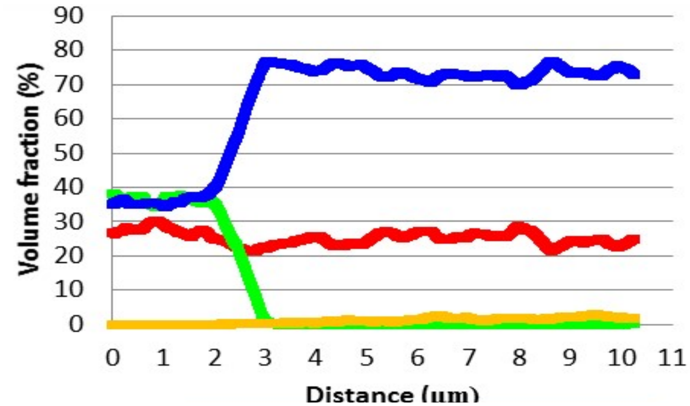
LSM 85-90 (A)
11% Mn xs



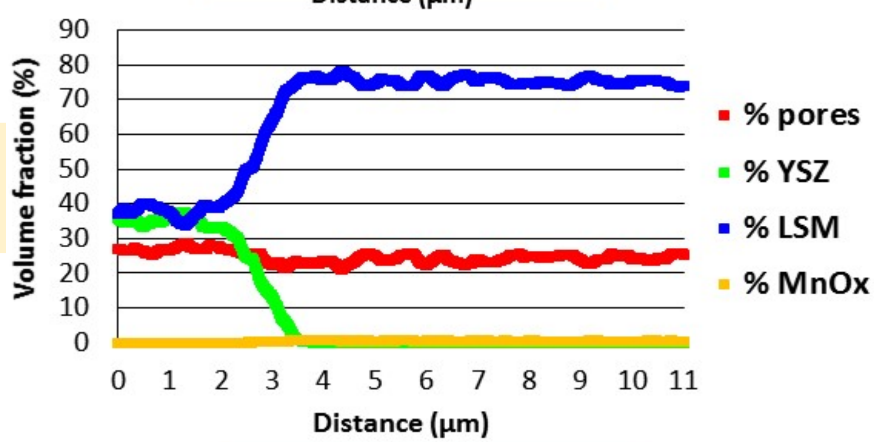


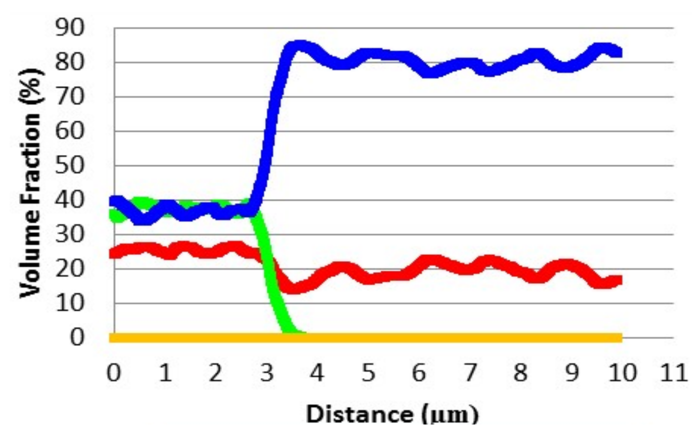
LSM 80-95 (B)
5% Mn xs



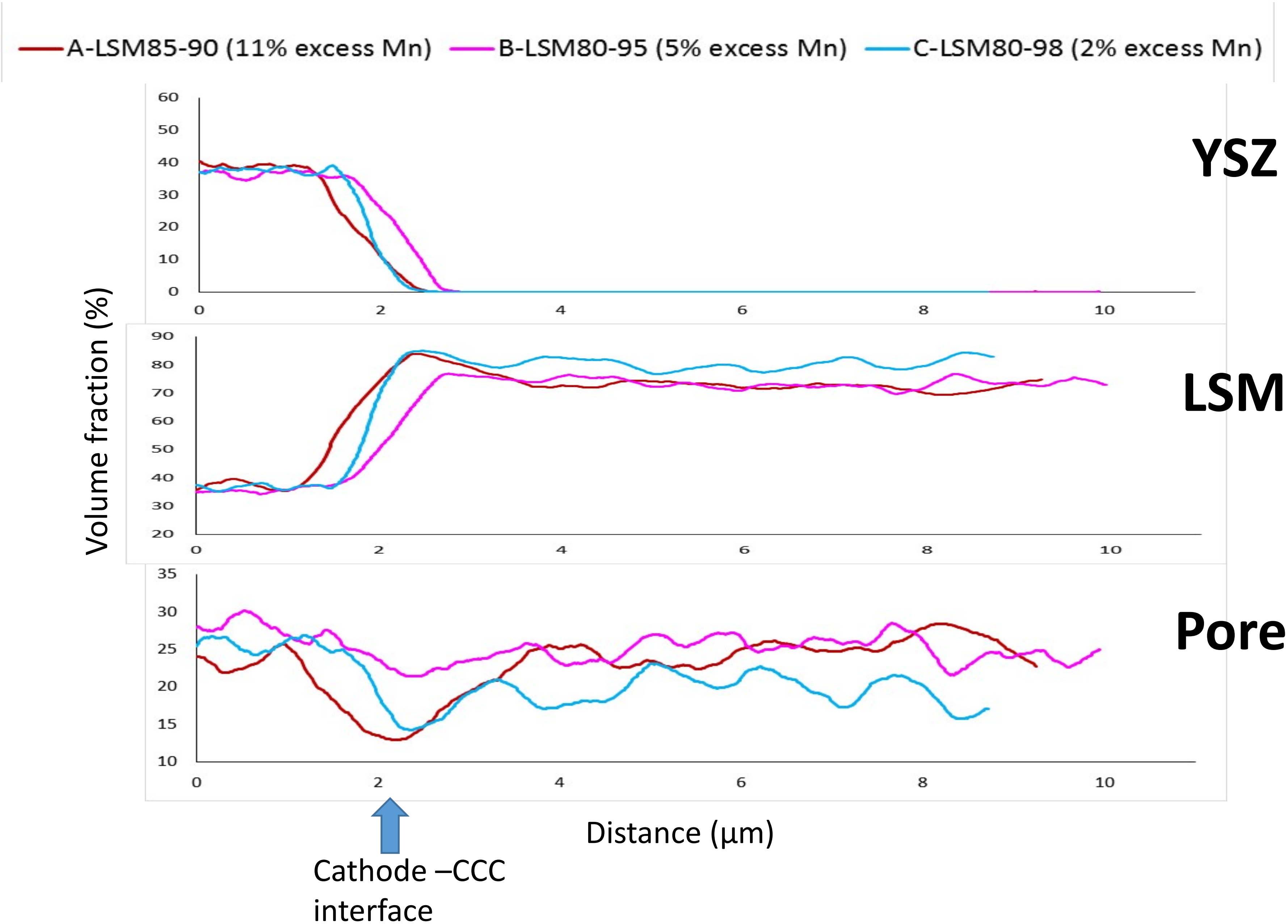


LSM 80-98 (C)
2% Mn xs





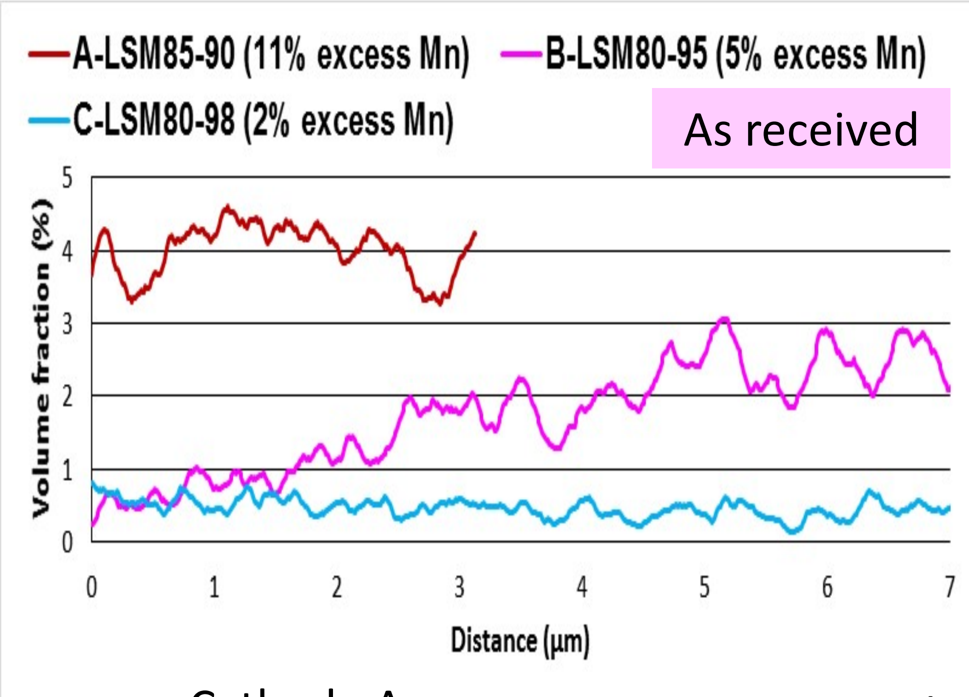
A – B – C comparison: cathode-CCC interface (500 h accel'd testing)

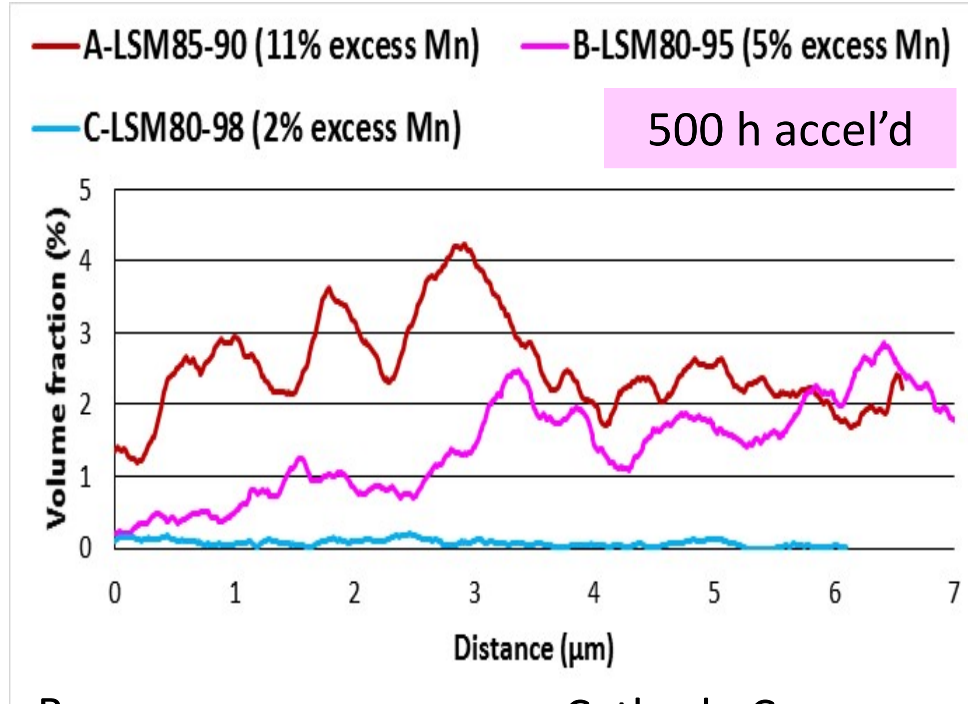


In LSM 85-90 (A) and LSM 80-98 (C), at cathode-CCC interface:

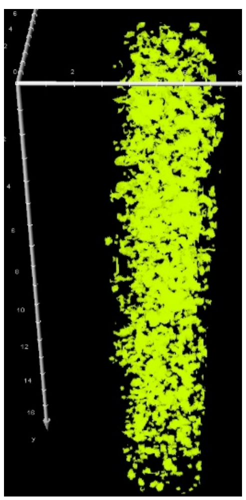
- ***Densification*** (bottom plot)

Effect of excess Mn: MnO_x in CCC before and after 500 h accel'd testing

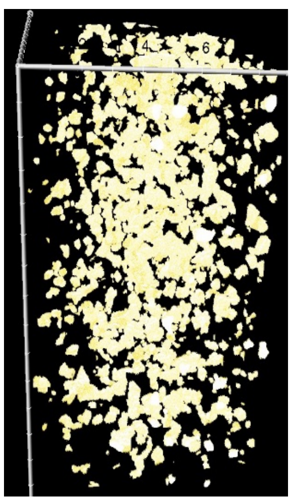




Cathode A

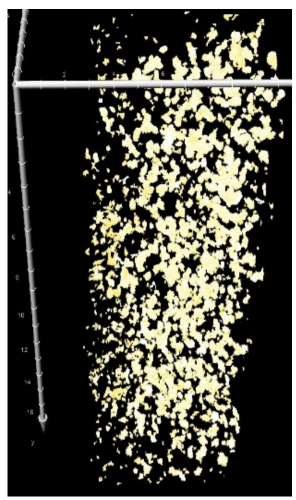


As received
Mn=4%

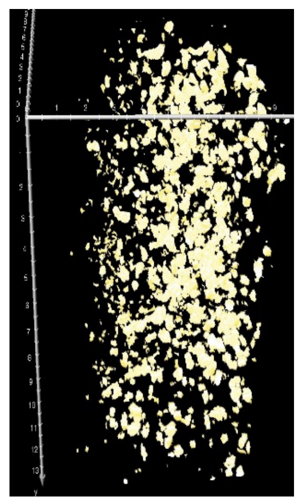


500 hrs Accel
Mn=2.5%

Cathode B

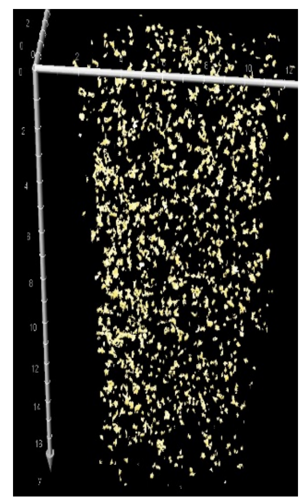


As received
Mn=2%

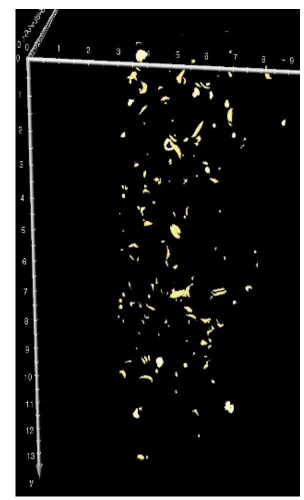


500 hrs Accel
Mn=1.5%

Cathode C



As received
Mn=0.5%



500 hrs Accel
Mn≤0.1%

A – B – C comparison: porosity and TPB density

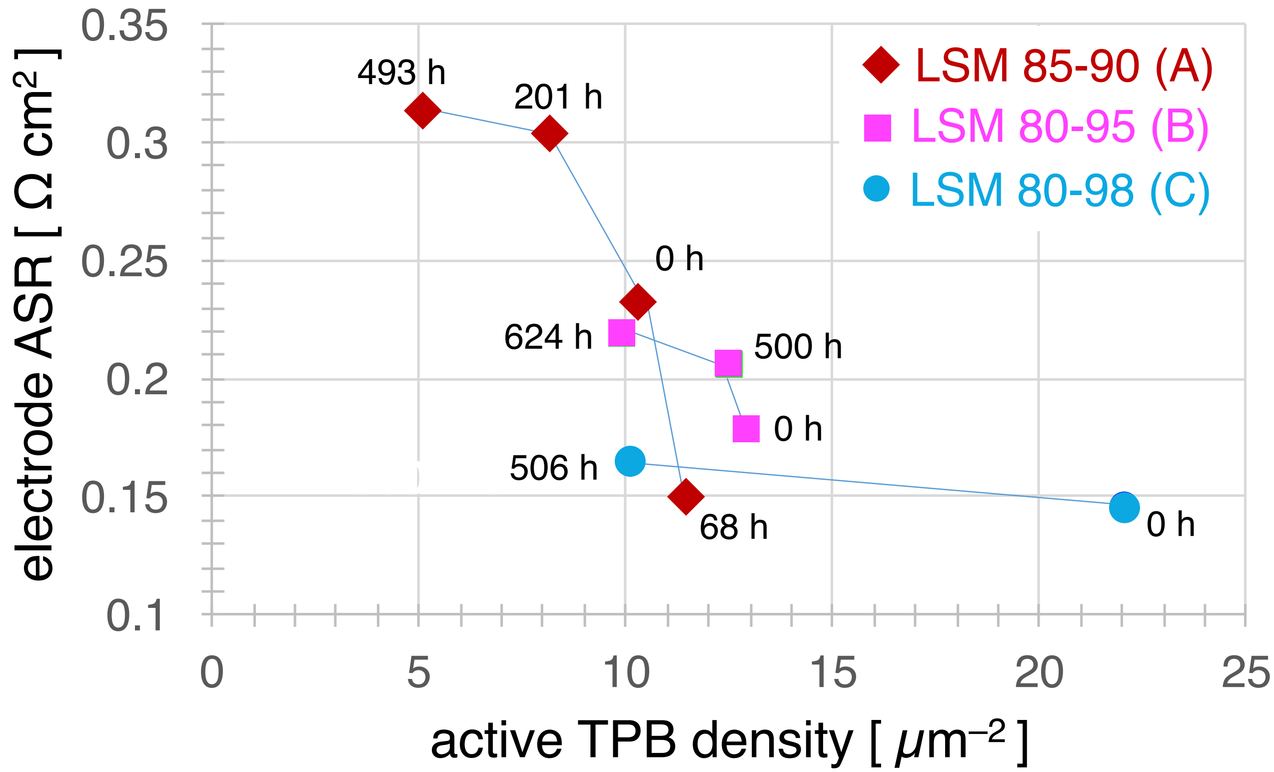
	LSM 85-90 (A); 11% Mn xs		LSM 80-95 (B); 5% Mn xs			LSM 80-98 (C); 2% Mn xs	
	as rec'd	493h accel	as rec'd	500h accel	624h accel	as rec'd	500h accel
sample volume, μm^3	4350	4525	6300	5096	4550	4100	5012
porosity, volume %	**17**	**18**	**29**	**25**	**25**	**28**	**25**
pore diameter, µm	**0.23**	**0.42**	**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)

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 cm^2], 0 h: ± 0.08 (A); ± 0.03 (B)
active TPB density [μm^{-2}], 0 h: ± 3.0 (C)

Summary & Conclusions

- During accelerated testing up to 624 h:
  - ***LSM 85-90*** (A) cathode:
    - Pore coarsening
    - Densification at cathode/CCC interface
    - MnO_x segregation at electrolyte-cathode interface
  - ***LSM 80-95*** (B) cathode:
    - Stablest microstructure
  - ***LSM 80-98*** (C) cathode:
    - ***Lowest initial TPB density,*** but decreased markedly w/time
    - ***Lowest ASR***, highest power
- Microstructure–performance trend over time:
  - ***TPB density*** ↓
  - ***ASR*** ↑
- These trends are ***less pronounced as Mn excess decreases***

Ongoing & Future Work

- Cathode D: composition selected; powder ordered
- Cathode A on same electrolyte as B and C (and (soon) D)
- Continue to explore relationship between TPB and ASR
  - vs. LSM composition
  - Accelerated vs. conventional testing
- Exploring other effects — see poster (Gu et al.)
  - Diurnal (24-h) periodicity
  - LSV / EIS checks — a source of degradation?

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