Operating Stresses and Their Effects on Degradation of LSM-Based SOFC Cathodes

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Project objectives

LSM* cathodes in solid oxide fuel cells (SOFCs)

- Seeking correlations between microstructure and performance changes
- Testing under aggressive conditions
  - Show effects of non-ideal operating conditions
  - Replicate effects of much longer conventional conditions?

Microstructure	Performance
3-D reconstruction: ***3DR***	Area specific resistance vs. time: ***ASR(t)***
Phase fraction profiles	Durability testing under aggressive conditions
Three-phase boundaries: ***TPB density***	Electrochemical impedance spectroscopy: ***EIS***
Transmission electron microscopy & elemental mapping: ***TEM/EDXS***	

*) Lanthanum strontium manganite, $(La_{1-x}Sr_x)_yMnO_{3\pm\delta}$

Outline

- Effect of ***Mn excess*** (A-site deficiency) on performance
- ***EIS analysis***
- ***Conventional*** vs. ***aggressive*** testing
  - Microstructural evolution
  - Cell performance
- New activities
  - Testing under ***low p_{O2}***
  - ***Aging*** tests — baseline for effects of *T*, *t*
  - ***Reproducibility***
  - Effects of ***current load cycling***
  - Effects of ***ambient conditions***
    - Humidity
    - Barometric pressure
    - Inlet air temperature

Cell specifications; testing procedures

This study:

- Durability and aging tests
- **Conventional** or **aggressive** conditions
- LSV sweeps and EIS runs ⇒ ***current cycling*** every 24 h

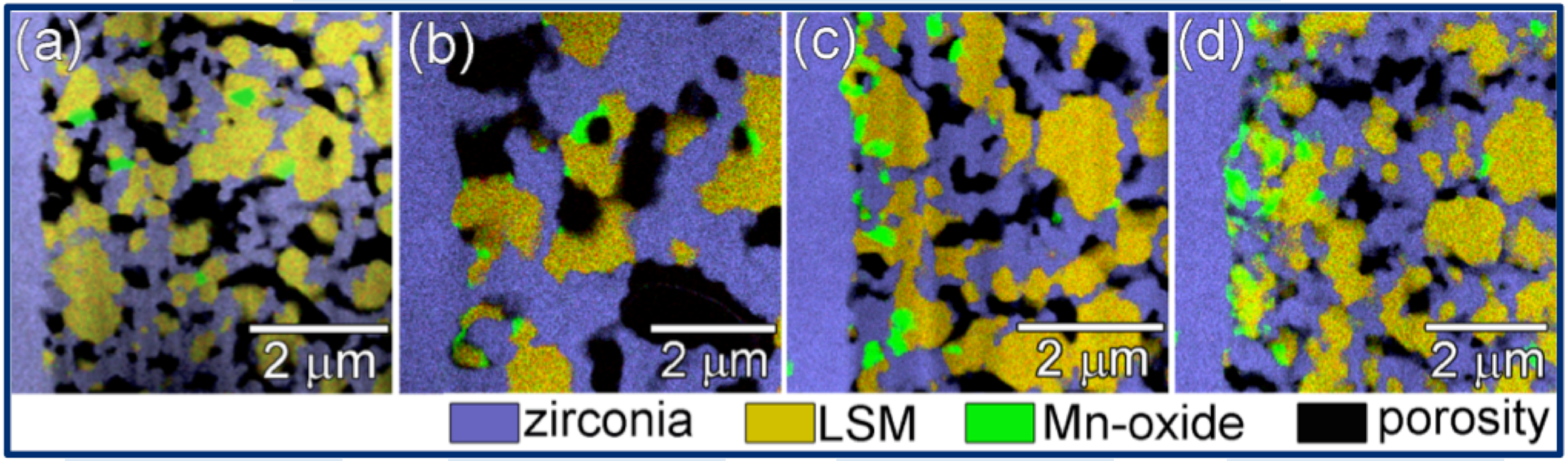
Button cells:

- 8YSZ electrolyte • Ni/8YSZ anode
- Cathodes: LSM / 8YSZ
  - $(La_{\boldsymbol{0.85}}Sr_{0.15})_{\boldsymbol{0.90}}MnO_{3\pm\delta}$ (LSM 85-90) — ***11%*** Mn excess
  - $(La_{\boldsymbol{0.80}}Sr_{0.20})_{\boldsymbol{0.95}}MnO_{3\pm\delta}$ (LSM 80-95) — ***5%*** Mn excess
  - $(La_{\boldsymbol{0.80}}Sr_{0.20})_{\boldsymbol{0.98}}MnO_{3\pm\delta}$ (LSM 80-98) — ***2%*** Mn excess

temperature [°C]	current density [mA cm^{-2}]	cathode p_{O_2}
900	380	0.2
	OCV (aging)	
1000	760	
	OCV (aging)	
900	380	0.1
	OCV (aging)	
1000	760	
	OCV (aging)	

Prior work, conventional conditions: TEM/EDXS

cells tested at **800 ºC; 11% Mn excess** cathodes



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]

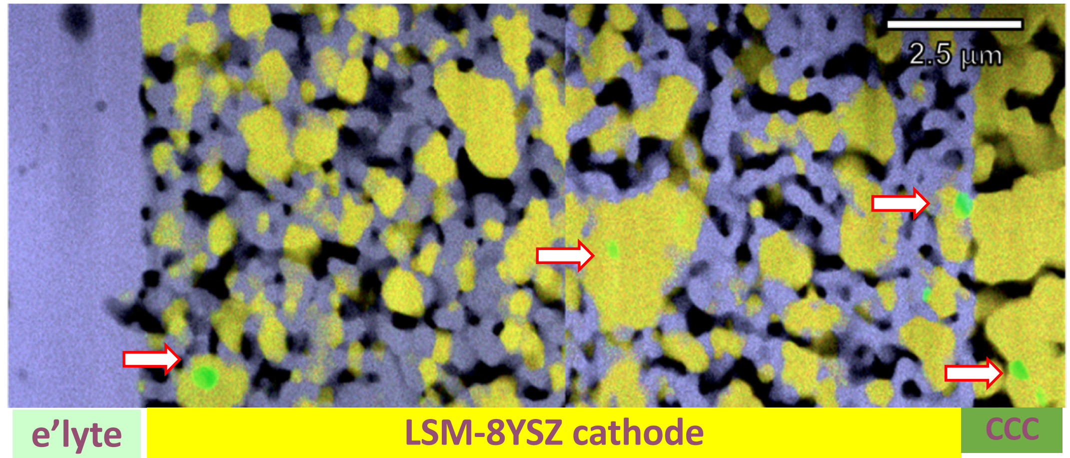
*) Left side of each image

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).

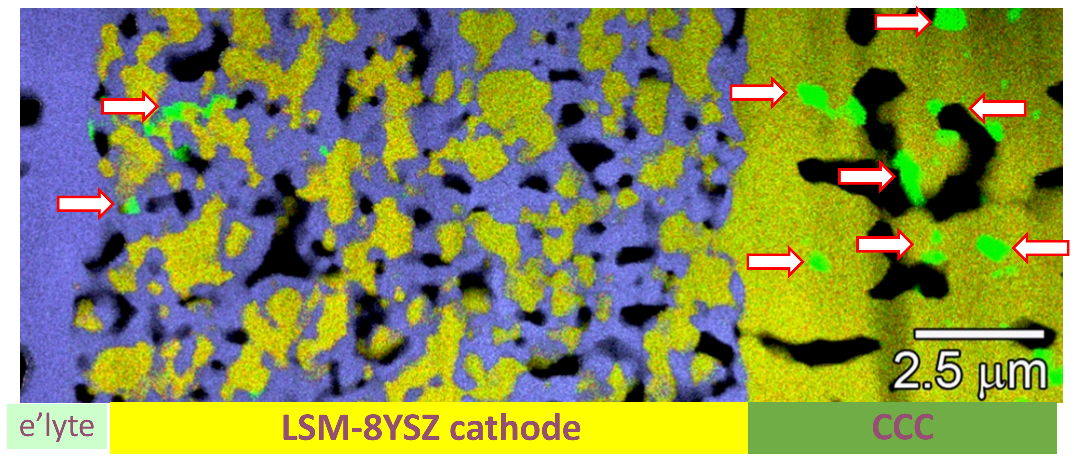
11% Mn excess: TEM w/EDXS, 0–500 h testing in air

- ***As received*** (0 h)
  - MnO_x seen sparingly across entire cathode

YSZ | LSM | pore | MnO_x



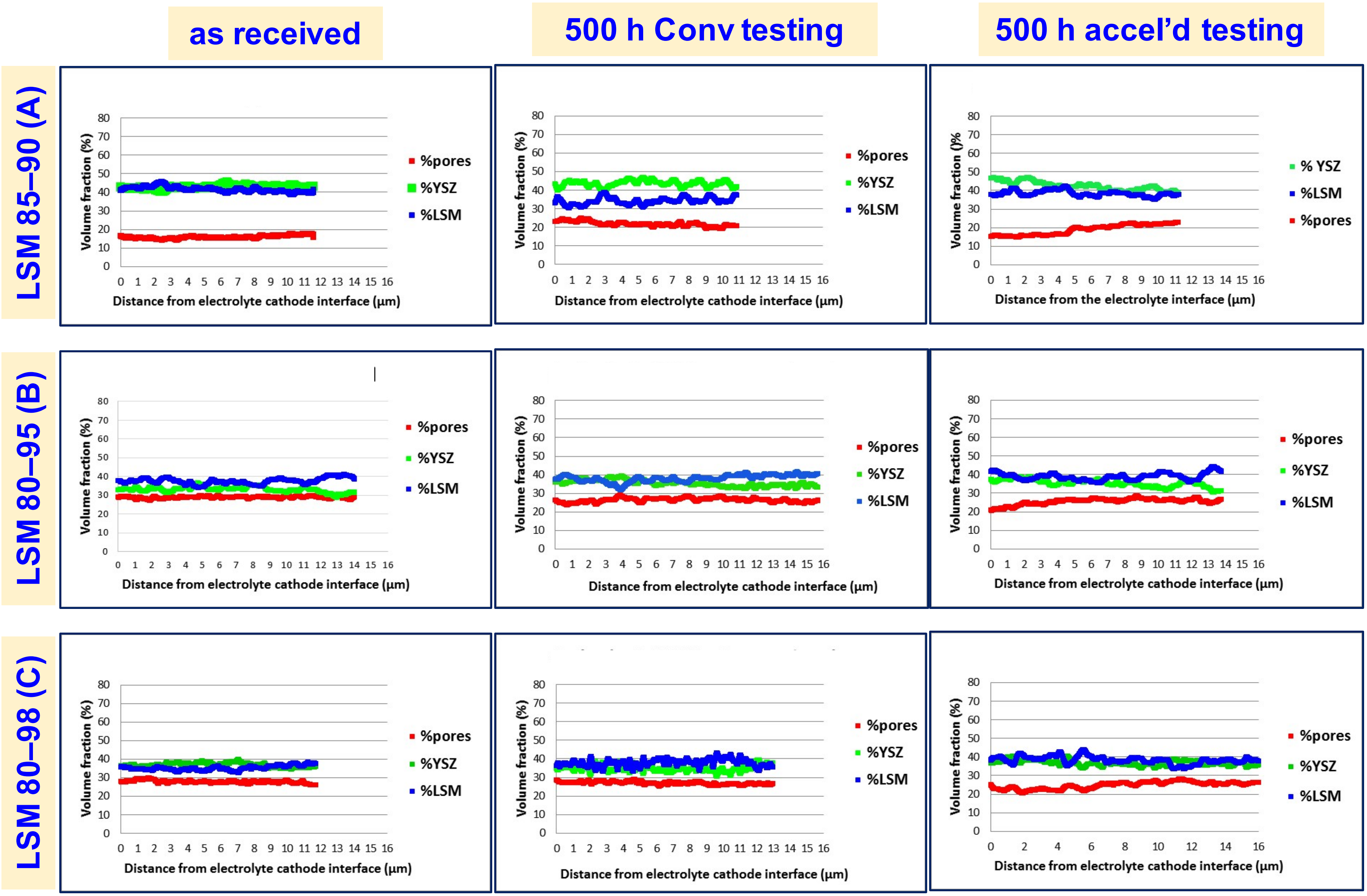
- ***493 h aggressive test***
  - MnO_x near cathode / electrolyte interface
  - MnO_x coarsened in CCC (cathode current collector)



For 11% excess Mn, 500 h aggressive testing reproduced some of the microstructural changes of 8–16 kh of conventional testing.

5% and 2% Mn excess: little or no MnO_x

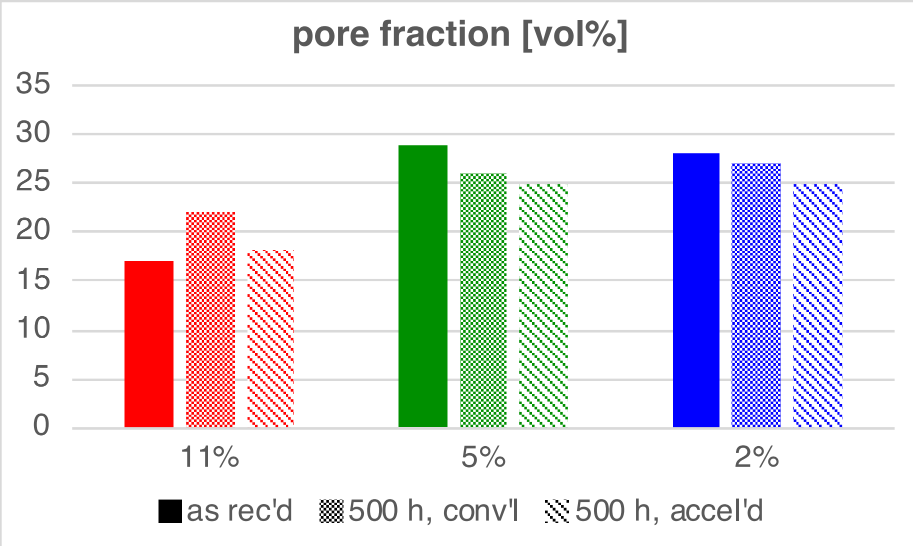
Phase profiles across cathodes from 3DR

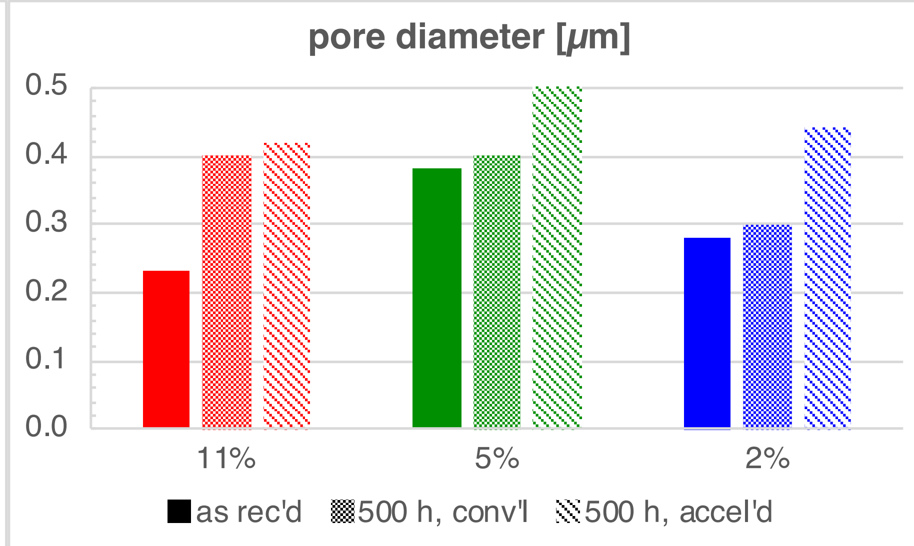


As-received and 500-h conv'l testing:
uniform phase profiles

Porosity gradients,
lowest at e'lyte interface

Microstructural parameters from 3DR





11% Mn excess:

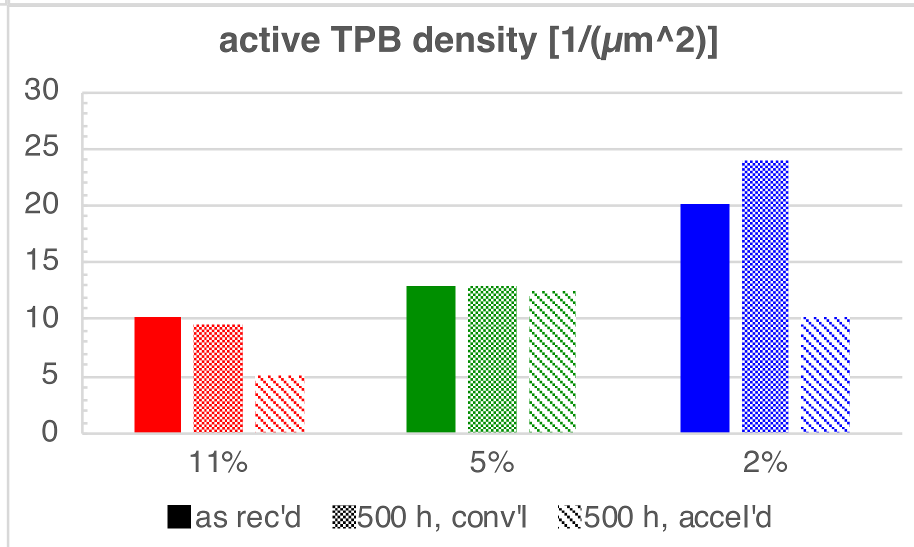
- Pore coarsening; lowest TPB density

5% Mn excess:

- Some pore coarsening; stable TPB density

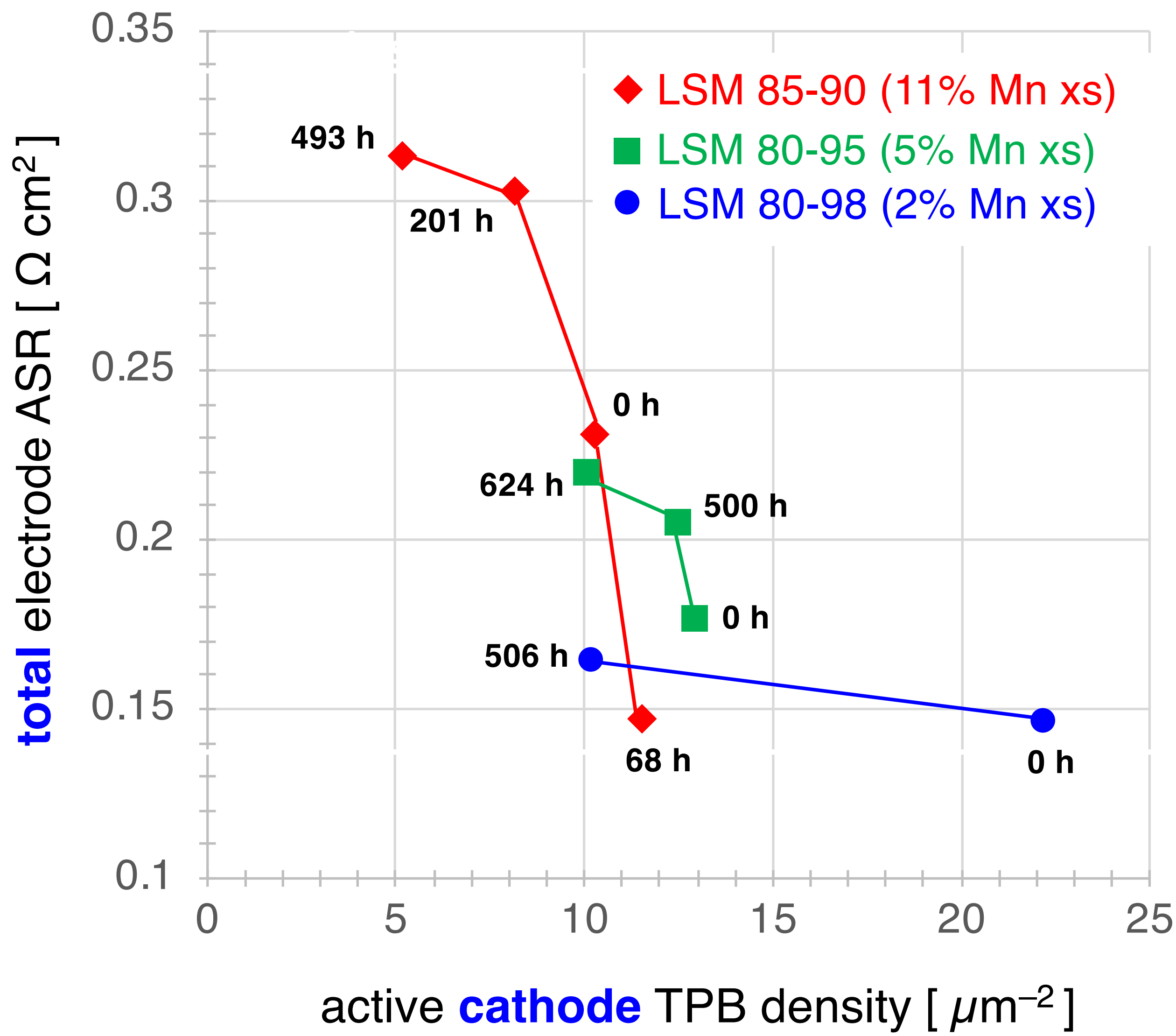
2% Mn excess:

- Pore coarsening; drop in TPB density



ASR and TPB density: role of Mn excess (aggr. testing, air)

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



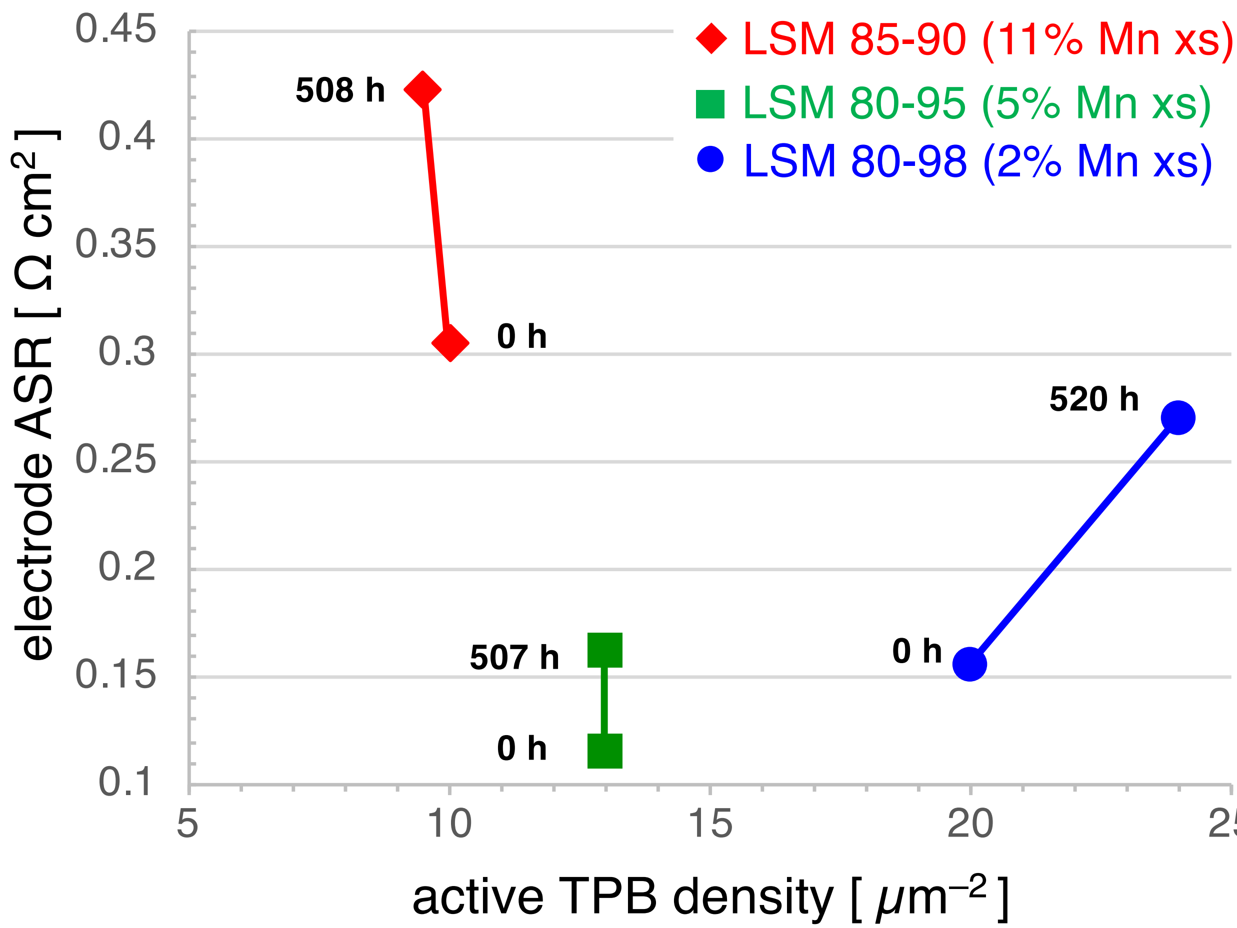
Summary: microstructural evolution and performance

- ***LSM 85–90 (11% Mn excess),*** 500 h of aggressive* testing in air:
  - ***Reproduced microstructure changes*** of 8 kh, conventional operation
    - ***Loss of porosity*** at cathode–electrolyte interface
    - ***MnO_x accumulation*** near cathode–electrolyte interface
  - Highest loss of active TPB density
  - Highest rise in electrode ASR
- ***Do these findings extrapolate to conventional test conditions?***

*) 1,000 vs. 900 °C; 760 vs. 380 mA cm^{-2}

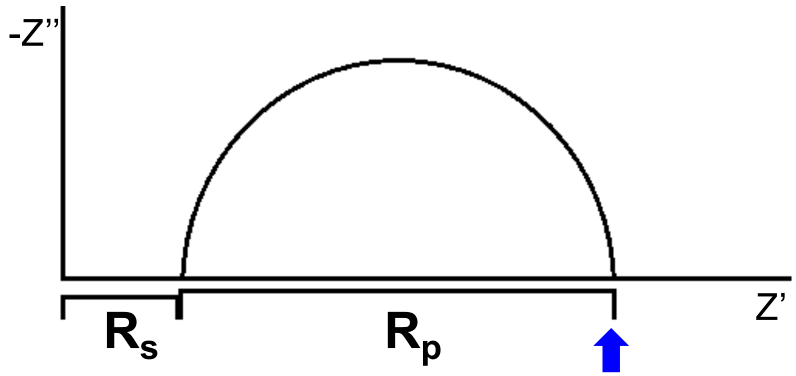
ASR and TPB density: role of Mn excess (conv'l testing)

- All compositions: ***ASR*** ↑ ***as t*** ↑, but microstructure change was slight
- 11% Mn xs: expected trend
- 5% Mn xs, ***ASR*** ↑ ***as t*** ↑ at ***const.*** TPB density
- 2% Mn xs: ***inverse*** of expected trend



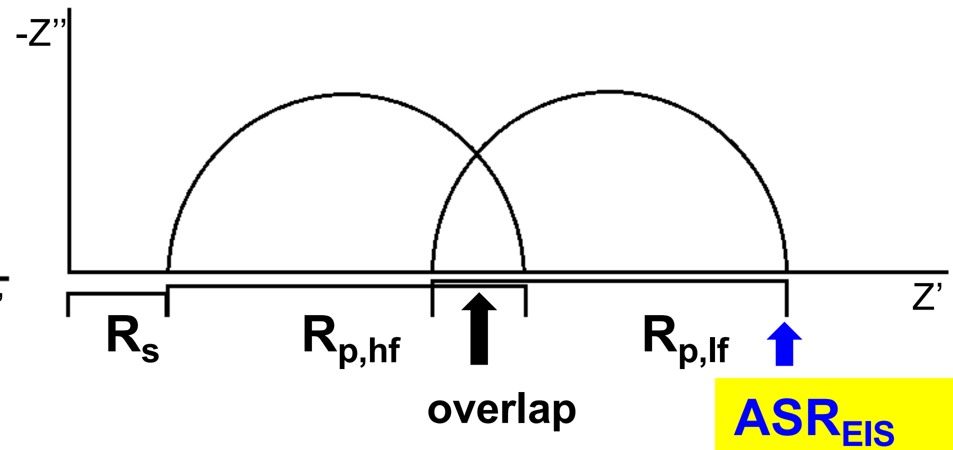
Electrochemical impedance spectroscopy

Fitting an arc with a single semicircle



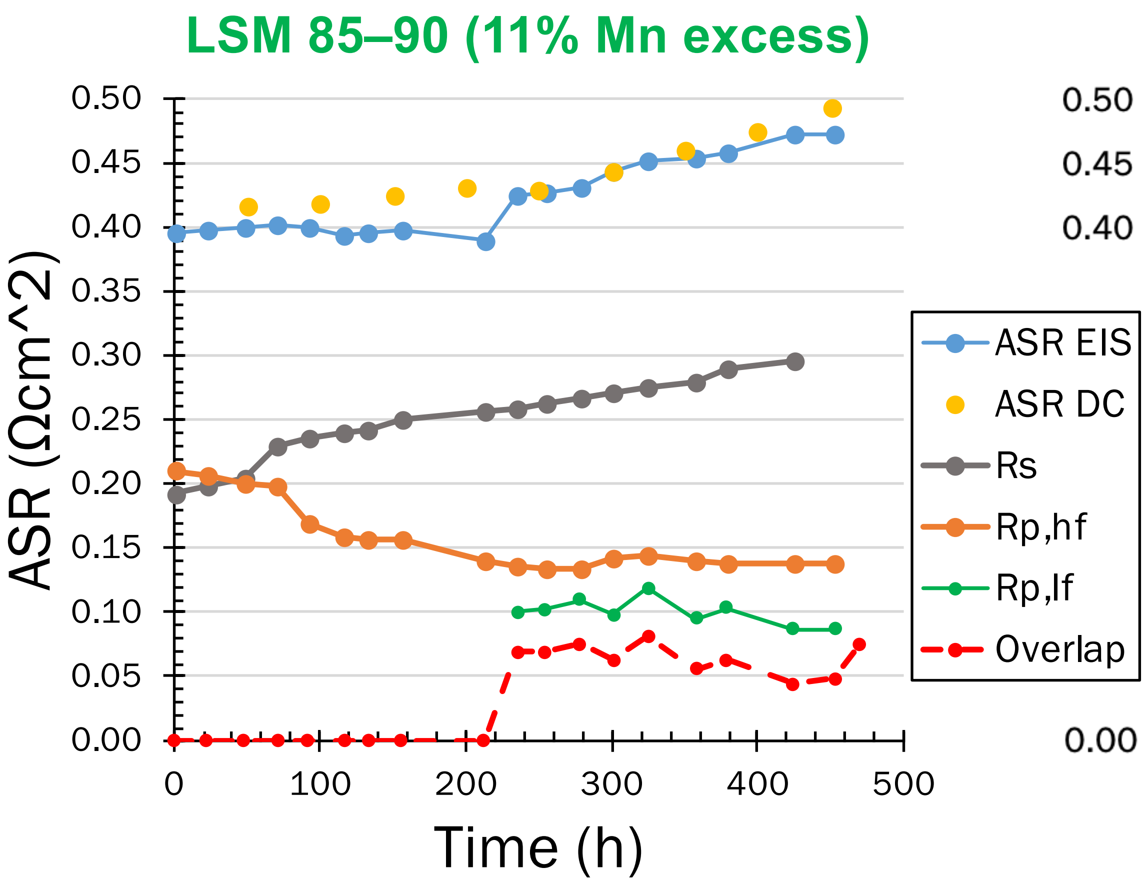
ASR_{EIS}
$= R_s + R_p$

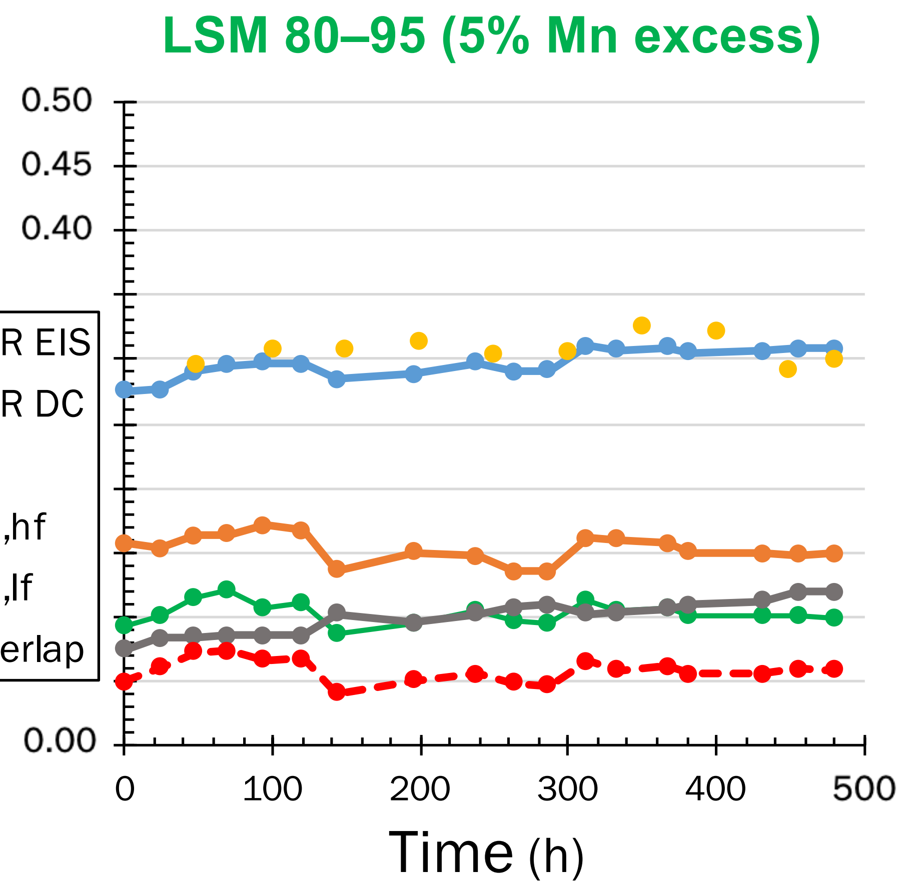
Fitting multiple arcs with overlapping semicircles



ASR_{EIS}
$= R_s + R_{p,hf} + R_{p,lf}$
– overlap

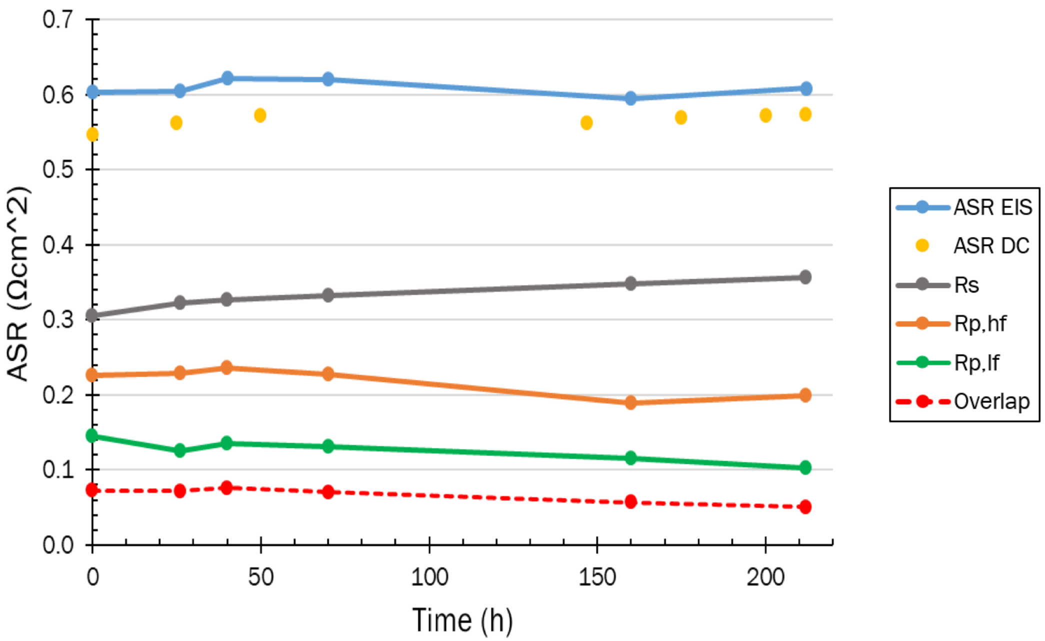
Effect of Mn excess: air, aggressive testing

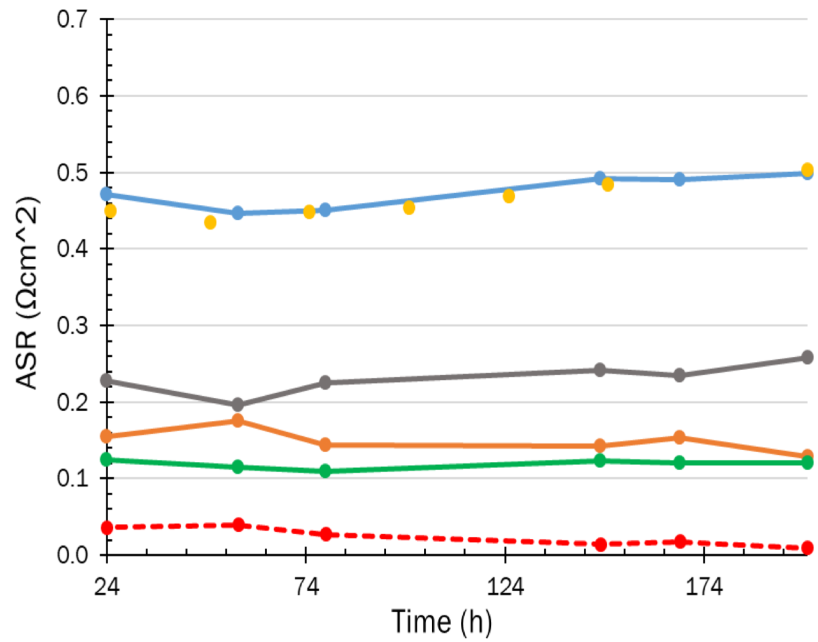




- ASR EIS is the sum of the gray, orange, and green, minus red curves.
- ***ASR EIS* gave good agreement with ASR DC** from durability testing:
  - (±0.03 Ω cm^2 for 5% Mn xs)
  - (±0.02 Ω cm^2 for 11% Mn xs)
- Rise in ASR DC with time comes ***from series resistance R_S,*** not from R_p

Reproducibility: LSM 85–90 (11% Mn xs), aggressive, air





- ***ASR EIS*** **gave good agreement with ASR DC** (~ –0.04 Ω cm^2).

- ***ASR EIS*** **gave excellent agreement with ASR DC** (± 0.01 Ω cm^2).

~20% difference in total ASR (0.1 Ω cm^2) between identical cells

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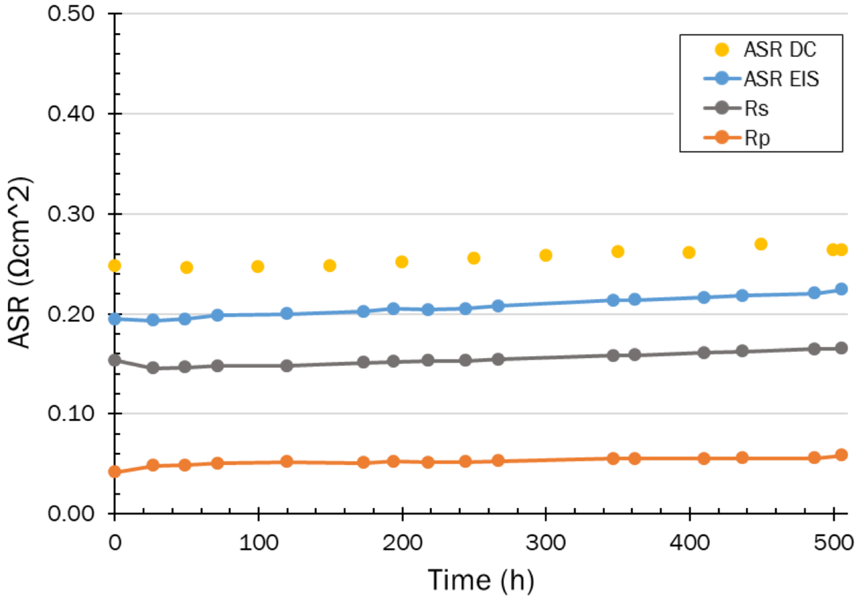
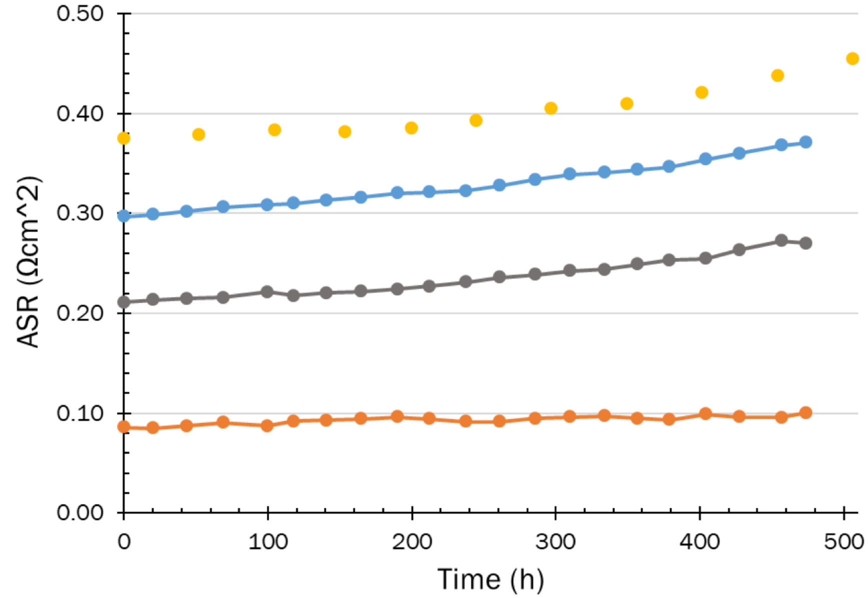
Aggressive vs. conventional: LSM 80–98 (2% Mn xs)

1,000 °C, 760 mA cm^{-2}, air



900 °C, 380 mA cm^{-2}, air

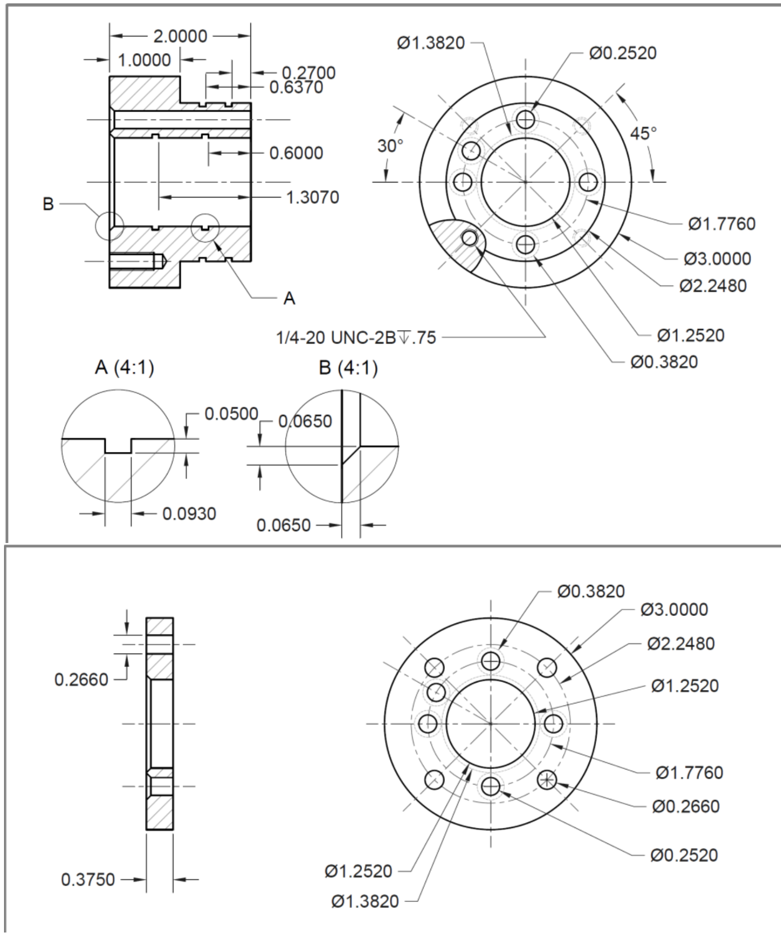


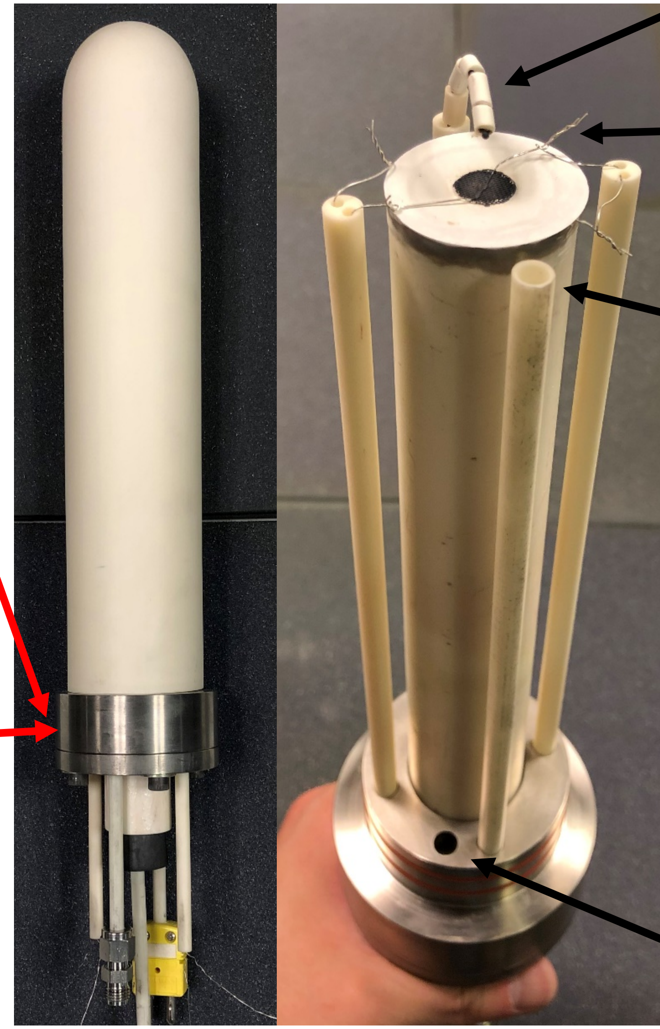
- ***All ASR components rose ~50%*** at 900 °C vs. 1,000 °C.
- All ASR components ***rose with t***, but more strongly at 900 °C
- High frequency: inductive component ⇒ lower ASR EIS vs. ASR DC
- EIS and DC ASR still agree within 0.06 Ωcm^2.

Conclusions: ASR, microstructure, and EIS analysis

- ***Microstructure and ASR***
  - ***Electrode ASR*** and ***active TPB density:*** mostly inverse relationship
  - … but does not separate the ***anode and cathode losses***, …
  - … nor the ***contribution of YSZ*** to the electrode ASR — part of R_s?
  - 11% Mn excess LSM cathodes:
    - largest microstructure changes
    - strongest ASR rise (500 h aggressive testing in air)
- Cautions about ASR comparisons between 900 and 1,000 °C
  - ASR degraded at 900 °C, despite stable cathode microstructures
  - Rise in R_s — not R_p — accounts for rise in ASR
  - Cathode (low-frequency) R_p was not the major source of ASR — consistent with the higher testing temperature

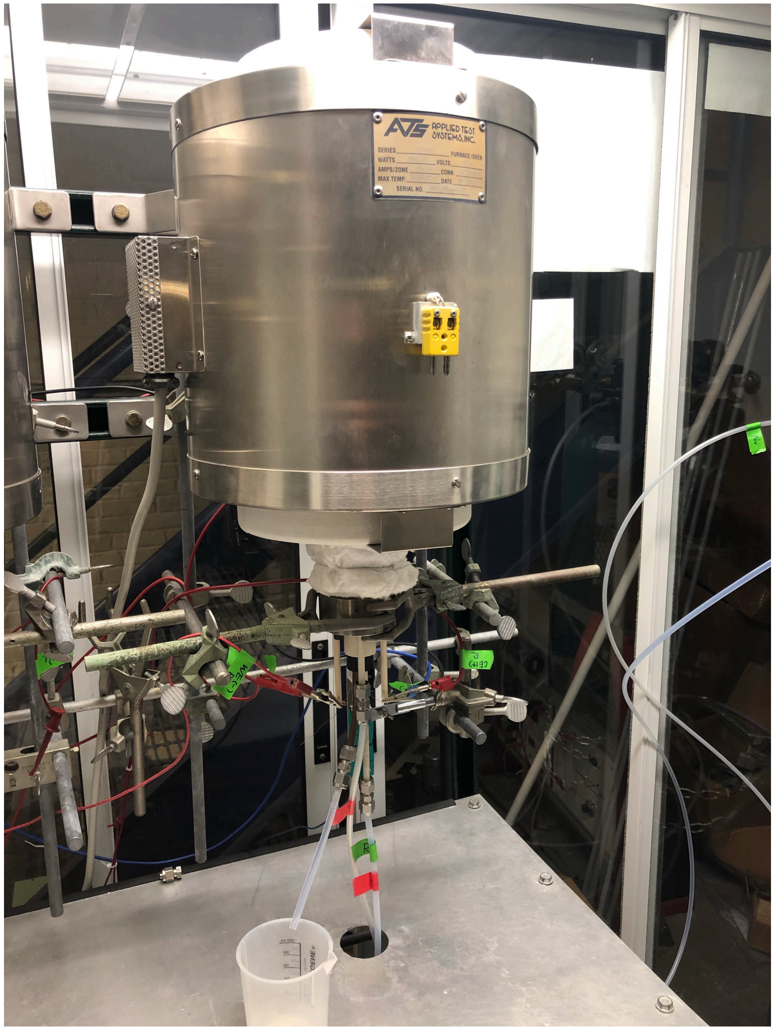
Test fixture for controlled cathode atmosphere

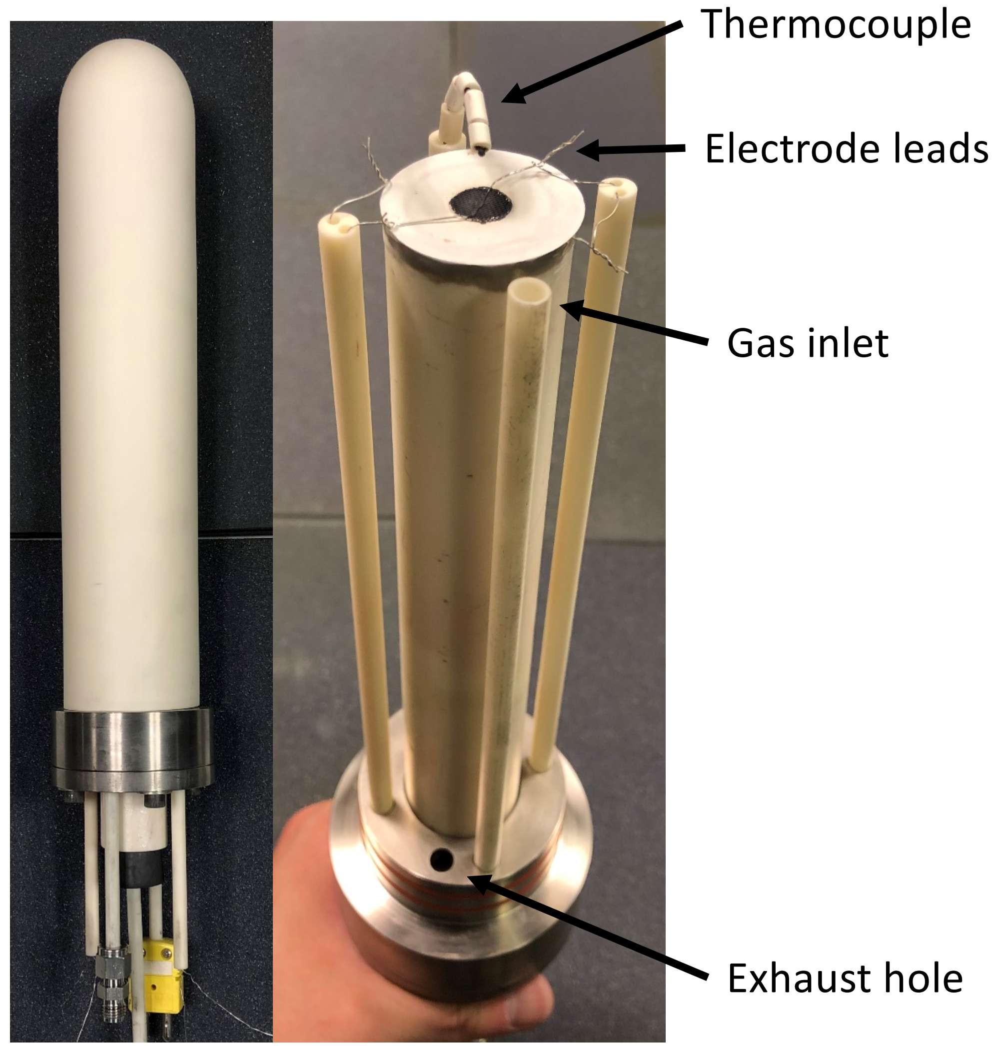




- Pt thermocouple to avoid Cr poisoning
- Testing in progress

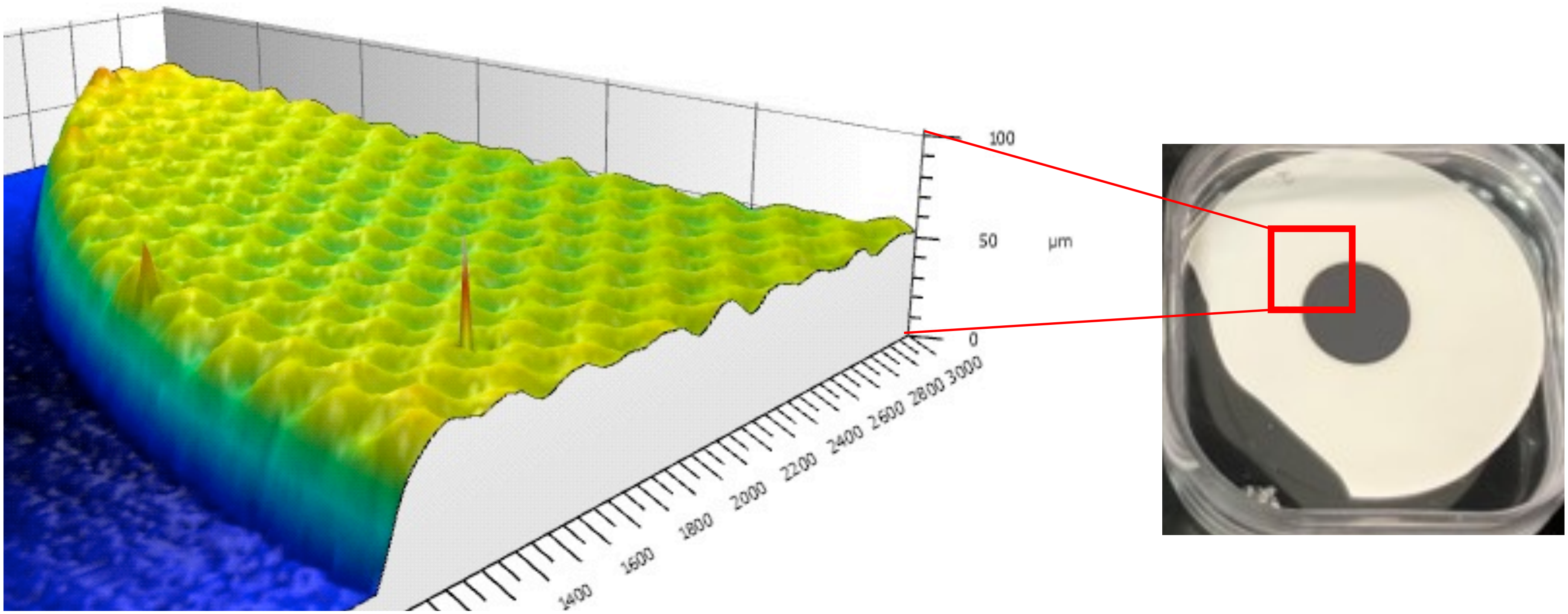
Test fixture for controlled cathode atmosphere





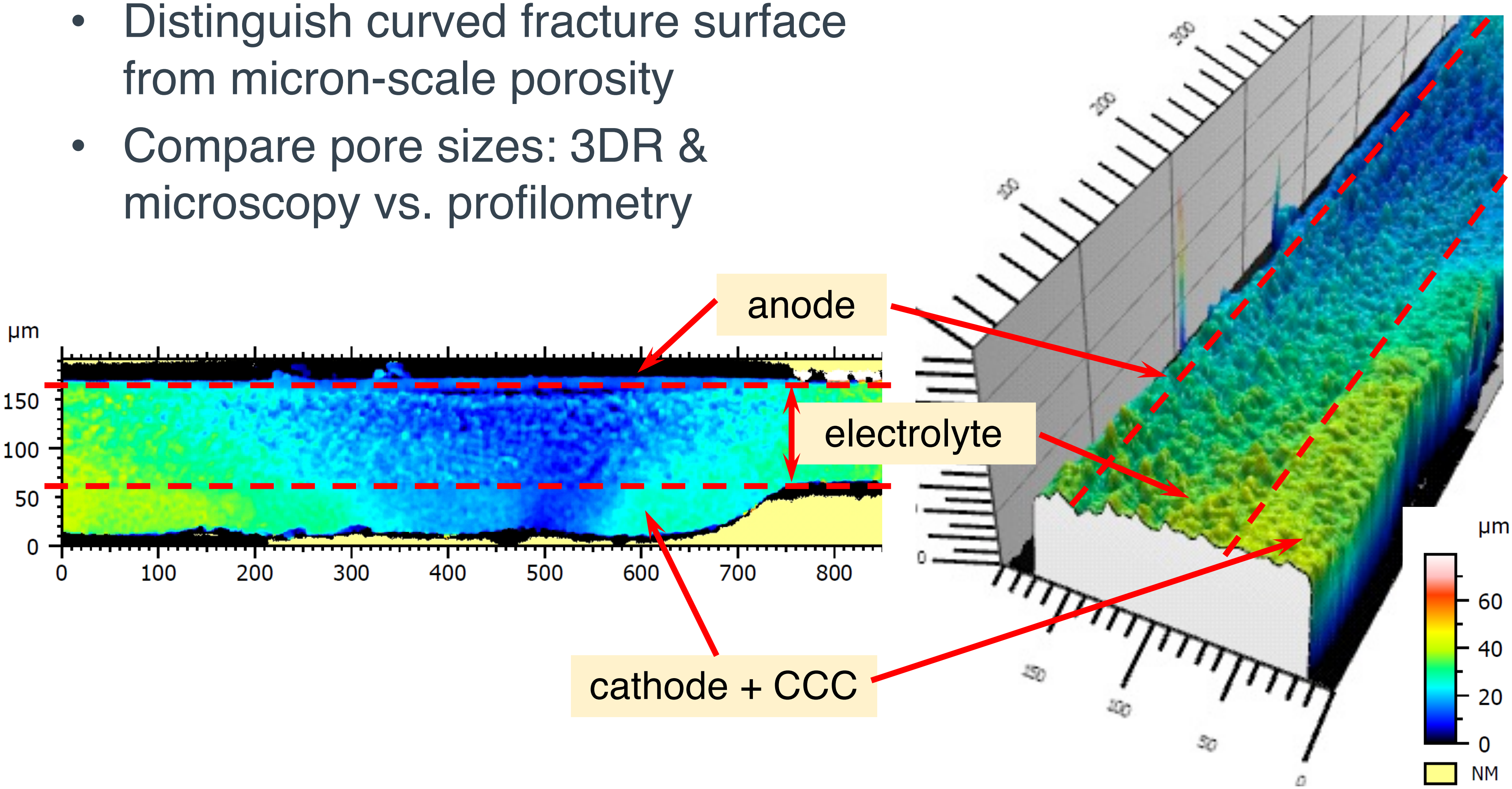
Optical profilometry of SOFCs

- Nanovea ST400
  - Quantitative topographical information
  - Scan much larger areas than electron microscopy — mm^2 vs. μm^2
  - Optical Pen 1: lateral accuracy = 1.1 μm
  - Optical Pen 3: lateral accuracy = 2.6 μm



Optical profilometry: cross section (fracture surface)

- Distinguish curved fracture surface from micron-scale porosity
- Compare pore sizes: 3DR & microscopy vs. profilometry



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