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

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Kickoff meeting for DE-FE0031189

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CASE SCHOOL OF ENGINEERING

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Outline

- Background
- Technical approach
- Project objective(s)
- Project structure
- Project schedule
- Project budget
- Project Management Plan, including Risk Management

Background

- Goal: ***reduce long-term performance loss*** in SOFCs
  - Metric: area specific resistance (ASR)
  - Lifetime: ≥ 5 years (40 kh)
  - Target: total average ASR rise <1% / kh
- Focus of this work: ***cathode optimization***

Background

- Causes of long-term performance loss in SOFCs?
  - Microstructural evolution
  - Loss of catalytic activity in electrodes
  - Mechanical degradation
  - Others …
  - Effects are probably ***coupled***
- Focus of this work: Cathode optimization
  - ***Composition — microstructure — performance*** relationships

Background

- What drives microstructural change in SOFC cathodes?
  - ***Temperature*** • ***Current density*** ← **prior work**
  - ***Cathode atmosphere*** ← **this project**
- Plausible microstructure / performance links
  - ***Coarsening*** of microstructure (pores, YSZ, LSM) ← **SEM, 3DR**
  - Loss of three-phase boundary ***(TPB)*** density ← **3DR**
  - ***Interdiffusion*** ⇒ changes in conductivity, ← **TEM + EDXS**

    catalytic activity, mechanical strength …

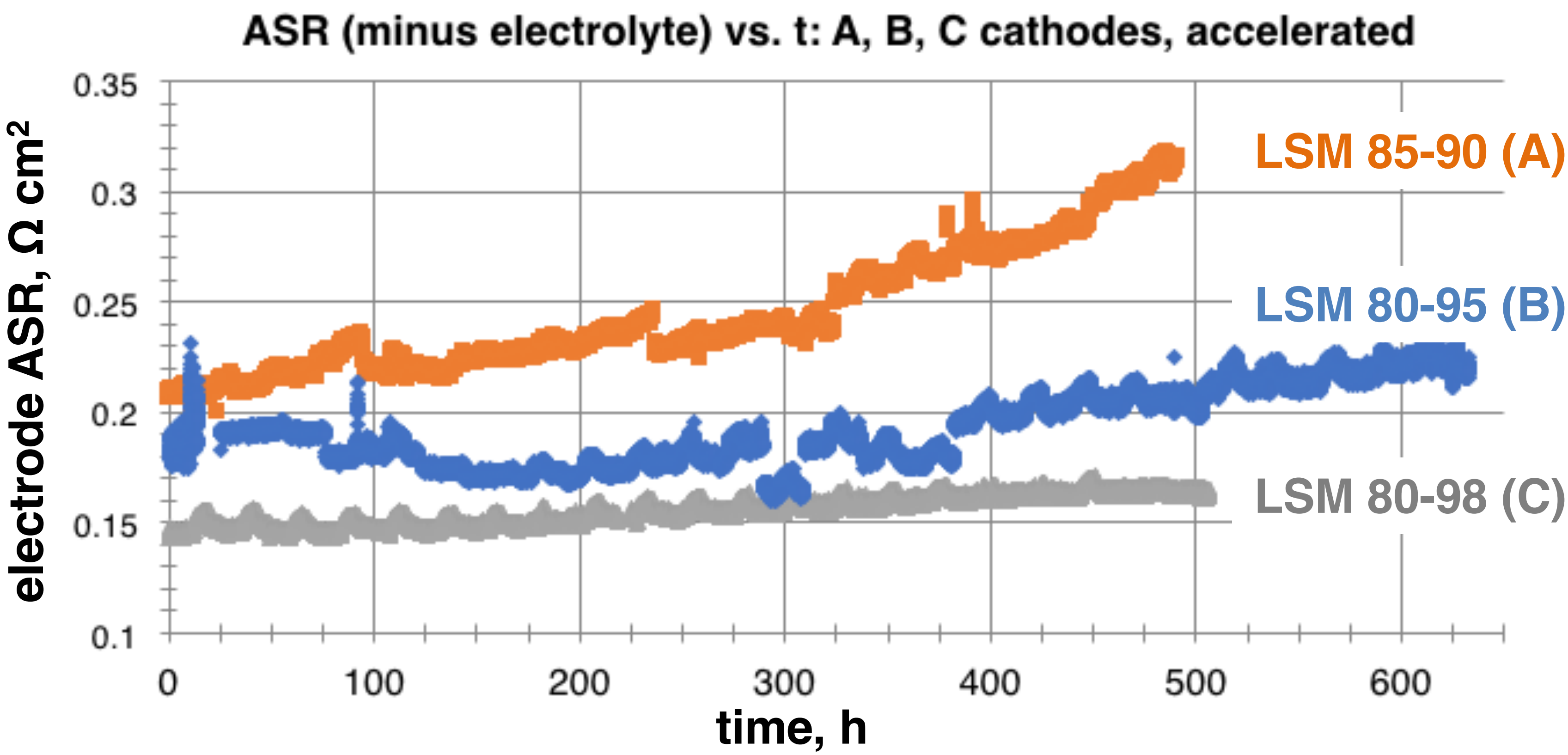
SEM: scanning electron microscopy 3DR: three-dimensional reconstruction

TEM: transmission electron microscopy EDXS: energy-dispersive x-ray spectroscopy

Background

- What drives microstructural change in SOFC cathodes?
  - ***Temperature***
  - ***Current density*** ← **prior work**
  - ***Cathode atmosphere*** ← **this project**
- Test conditions in prior work:
  - ***Accelerated:*** 1000 °C, 760 mA cm^{-2}; ambient air at cathode
  - ***Conventional:*** 900 °C, 380 mA cm^{-2} ; ambient air at cathode
- In LSM cathodes: role of Mn excess? ← **prior work & this project**
  - A: $(La_{\mathbf{0.85}}Sr_{0.15})_{\mathbf{0.90}}MnO_{3\pm\delta}$ (LSM 85-90) — ***11%*** Mn excess
  - B: $(La_{\mathbf{0.80}}Sr_{0.20})_{\mathbf{0.95}}MnO_{3\pm\delta}$ (LSM 80-95) — ***5%*** Mn excess
  - C: $(La_{\mathbf{0.80}}Sr_{0.20})_{\mathbf{0.98}}MnO_{3\pm\delta}$ (LSM 80-98) — ***2%*** Mn excess

Prior work: Electrode ASR vs. t — accelerated testing



LSM 85-90 (A):

- ***Highest ASR*** overall
- ***Highest rise in ASR*** over time

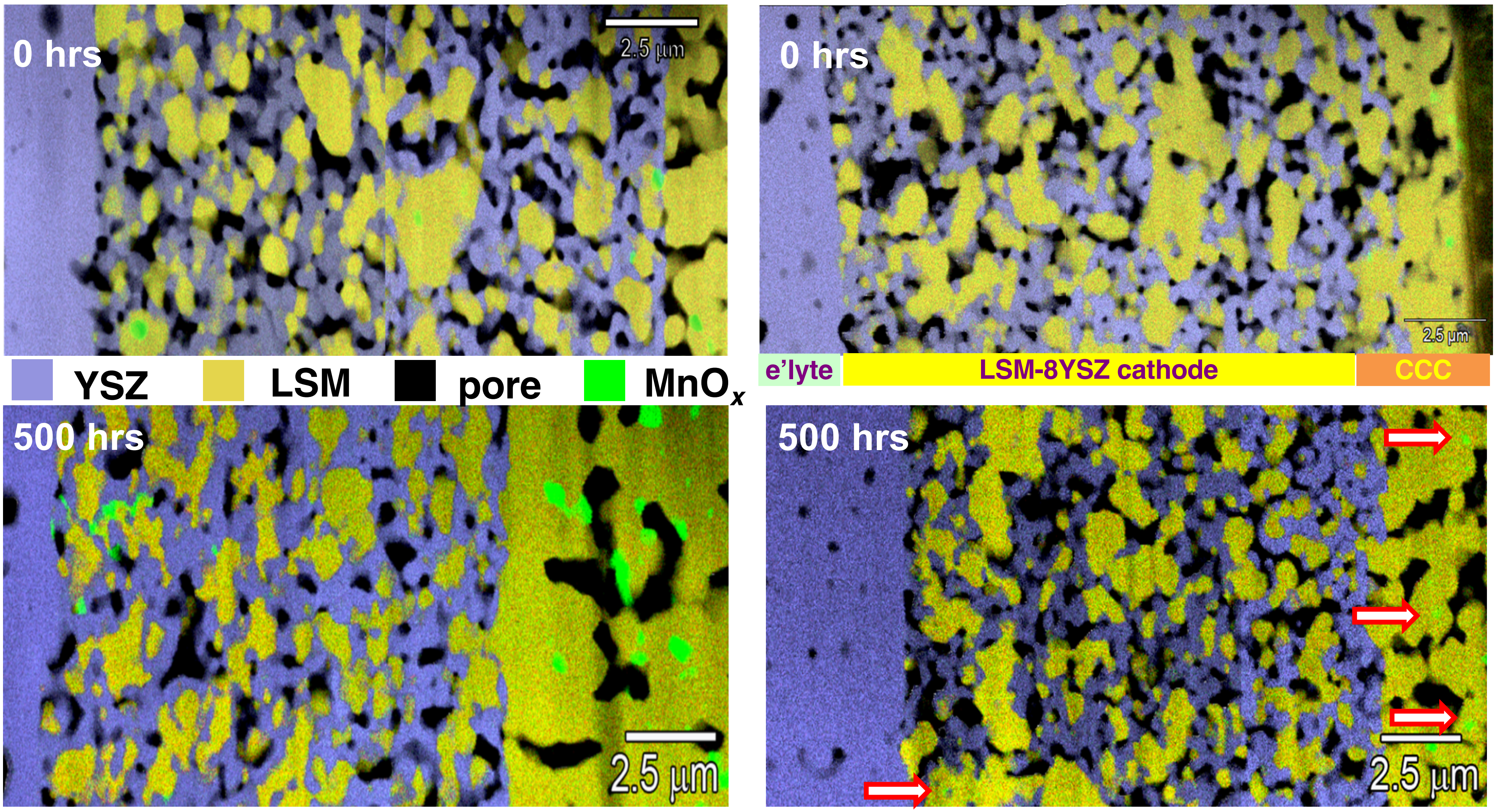
ASR ↓ as Mn excess ↓
(A → B → C)

LSM 80-98 (C):

- ***Lowest ASR*** overall
- ***Highest power*** in 500 h

Prior work: Mn excess and MnO_x formation (TEM + EDXS)

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



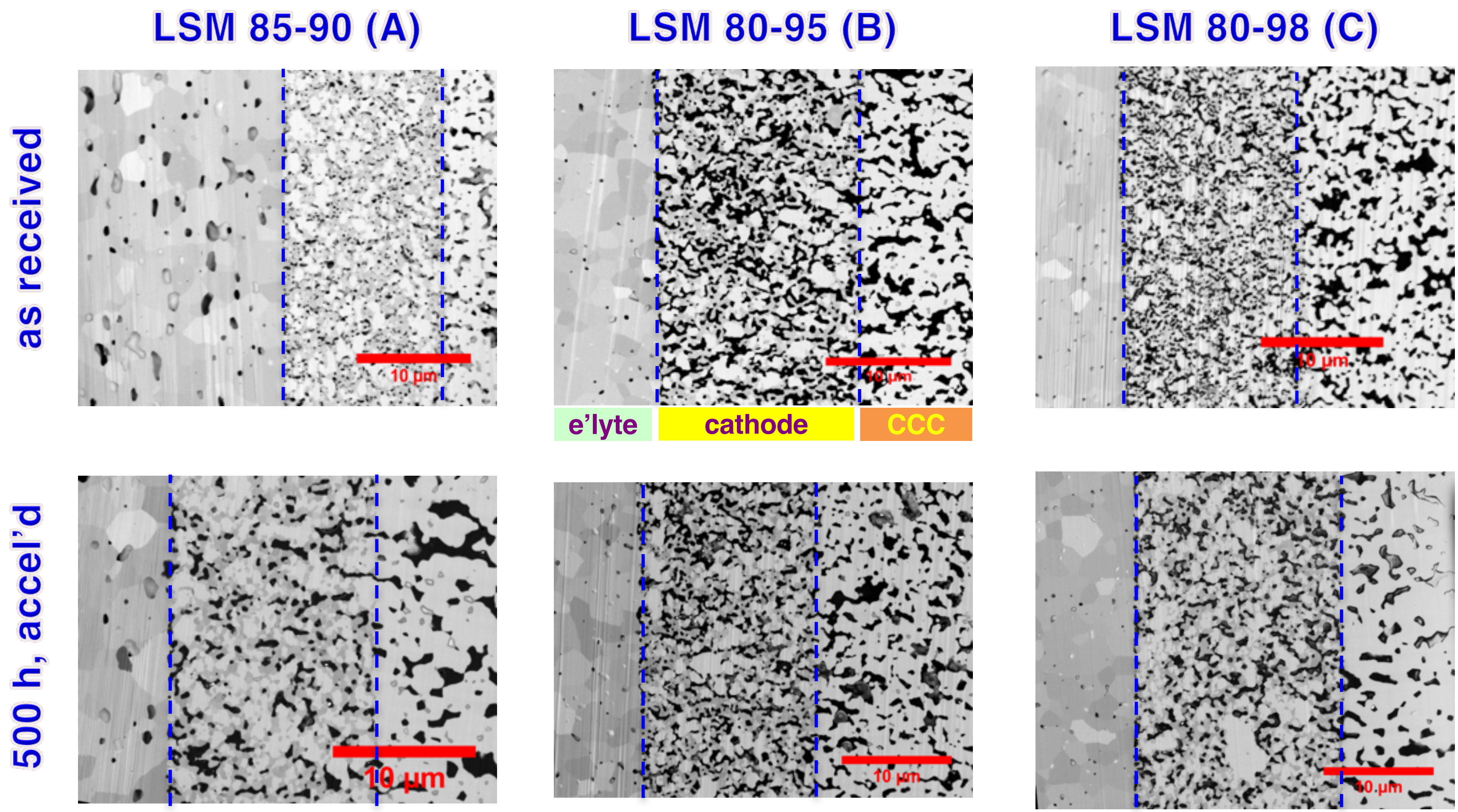
- More, larger MnO_x
- Accumulation of MnO_x at electrolyte interface

- Sparse MnO_x (arrows)

LSM 80-98 (C) (not shown): ***no*** MnO_x

Wang et al., *Met. Mater. Trans E* **1** [3] 263-271 (2014).

Prior work: Microstructure after 500 h accel'd testing

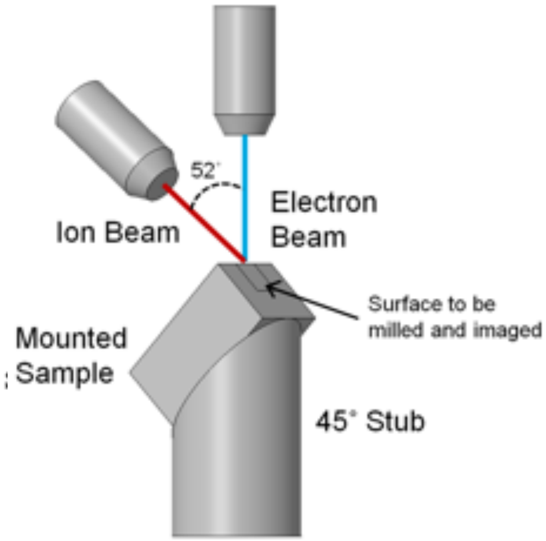


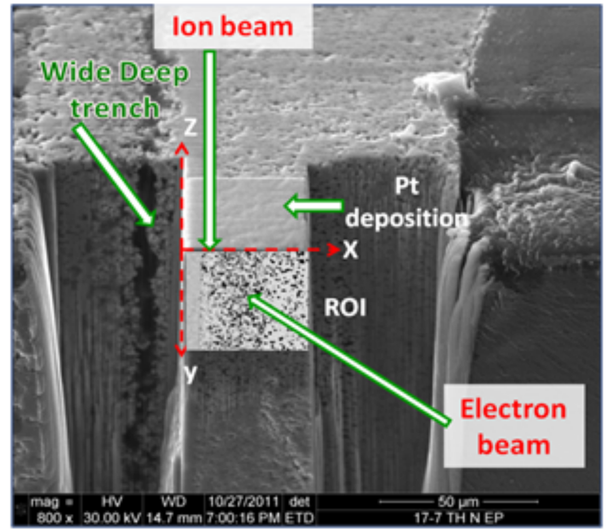
- Coarsening of pores & LSM
- Densification of CCC

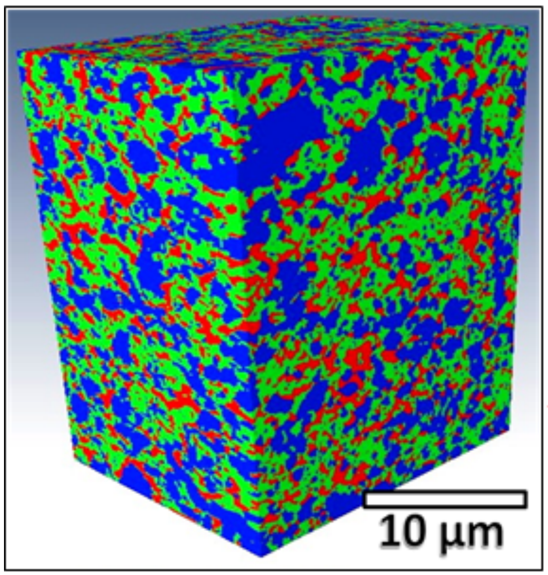
- Highest overall microstructural stability

- Coarsening of pores & LSM
- Densification of CCC

Procedure: Focused Ion Beam Slice & View for 3DR







each slice
150 nm thick

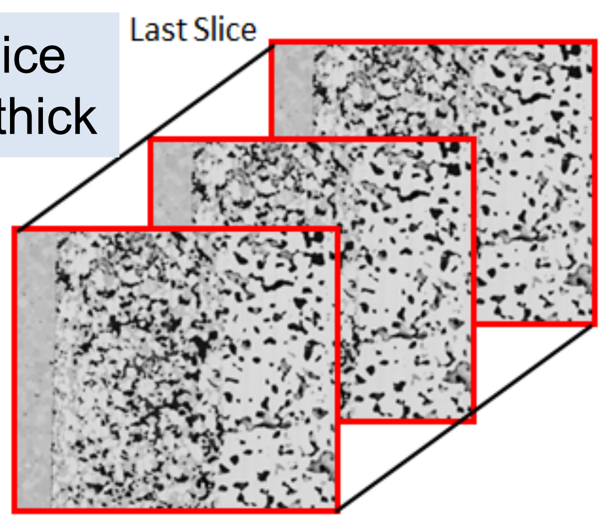


Image resolution:
4096*3536 pixels
Imaging mode:
backscattered
(Immersion detector)

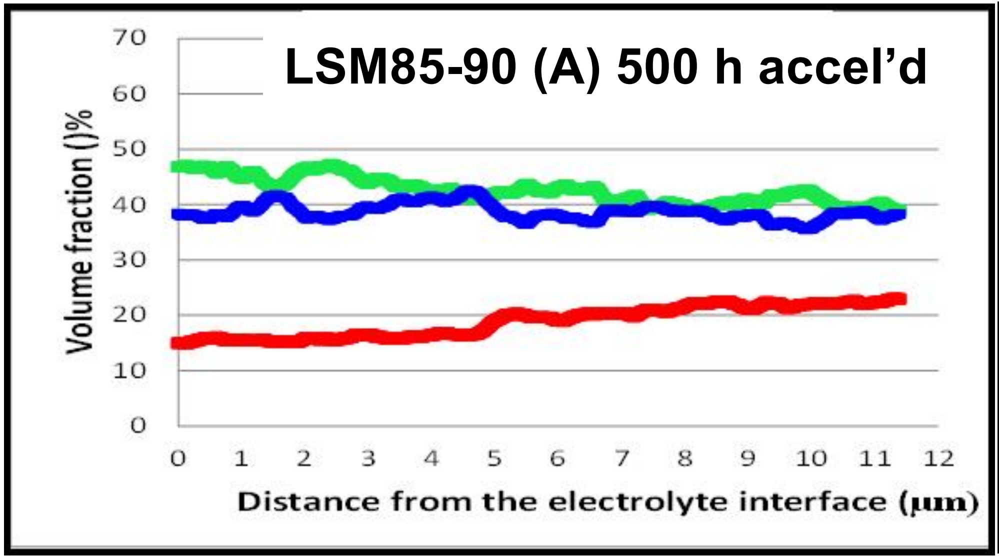
Prior work: 3-D reconstruction

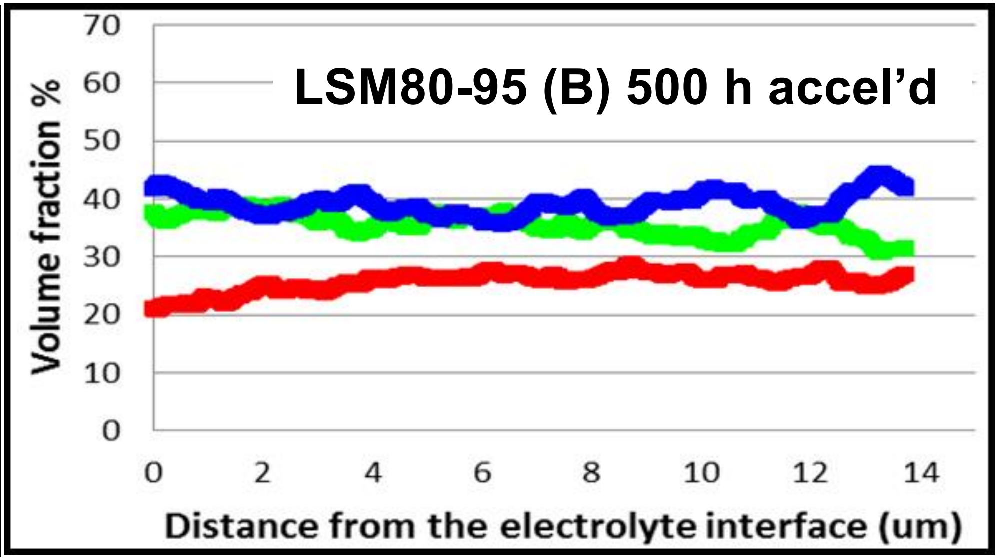
	LSM 85-90 (A); 11% Mn xs		LSM 80-95 (B); 5% Mn xs			LSM 80-98 (C); 2% Mn xs	
	as rec'd	493h accel	as rec'd	500h accel	624h accel	as rec'd	500h accel
sample volume, μm^3	4350	4525	6300	5096	4550	4100	5012
porosity, volume %	**17**	**18**	**29**	**25**	**25**	**28**	**25**
pore diameter, µm	**0.23**	**0.42**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

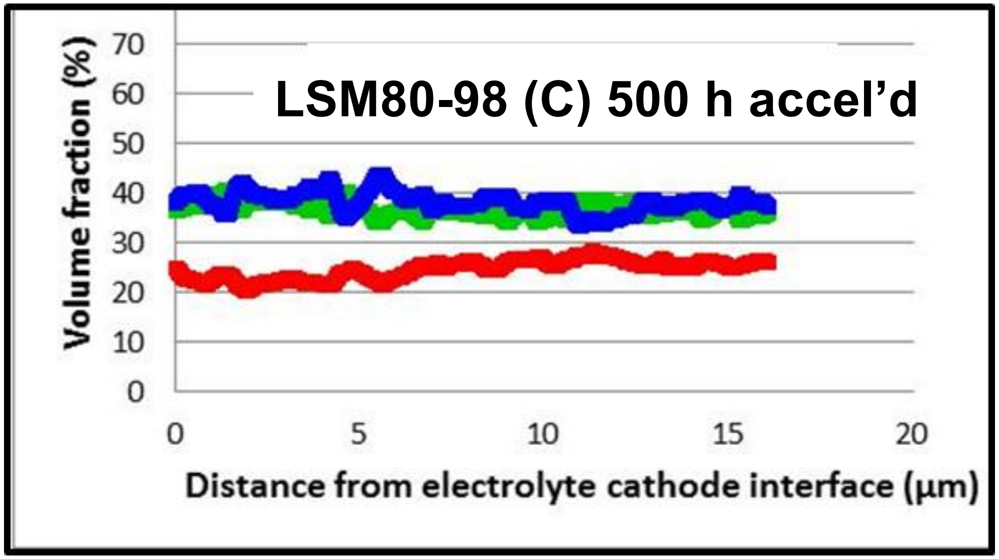
Vs. LSM 85-90 (A) and 80-98 (C), ***LSM 80-95*** (B) shows:

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

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



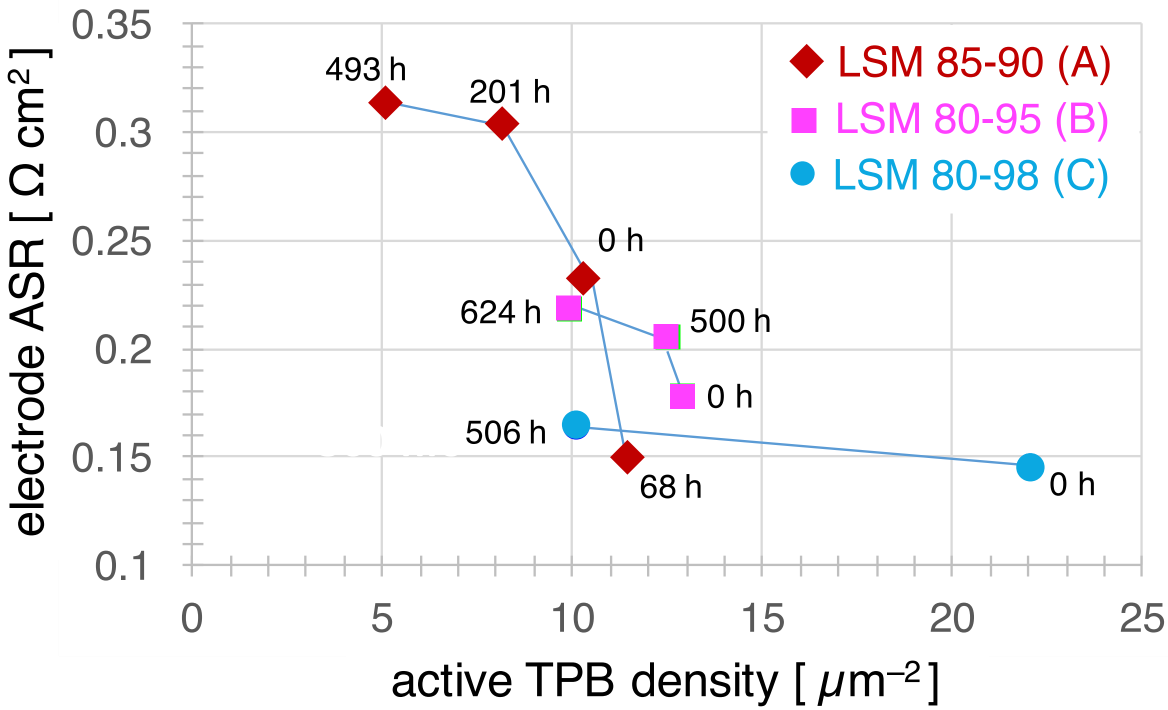




All three cathodes developed slight ***porosity gradients*** after 500 h of accelerated testing, with ***lowest porosity at cathode-electrolyte interface***

Emerging relationships: Mn excess, ASR, 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)

Technical approach: overview of new project

TESTING

- ***Operational parameters:*** aggressive vs. conventional
  - ***Cathode p_{O2}***
  - Current density (incl. intermittent cycling)
  - Temperature
  - ***Aging***
- ***LSM composition***
  - Mn excess

CHARACTERIZATION

- ***Performance***
  - $OCV(t)$, $V(t)$, $ASR(t)$
  - EIS
  - LSV
- ***Microstructual evolution***
  - TEM / EDS
  - 3-D reconstruction

OUTCOMES

- ***Mechanistic understanding***
- ***Optimized cathodes*** for various operating scenarios

Technical approach: button cells

- 8YSZ electrolyte from tape (Electro-Science Laboratories)
  - 32 mm in diameter • 100 μm thick (fired)
- Screen-printed electrodes, 9.5 mm dia.
  - NiO-8YSZ anode — same in all cells
  - LSM-8YSZ cathodes
    - Select ≥ two of compositions A, B, C, & D

Technical approach: cell testing

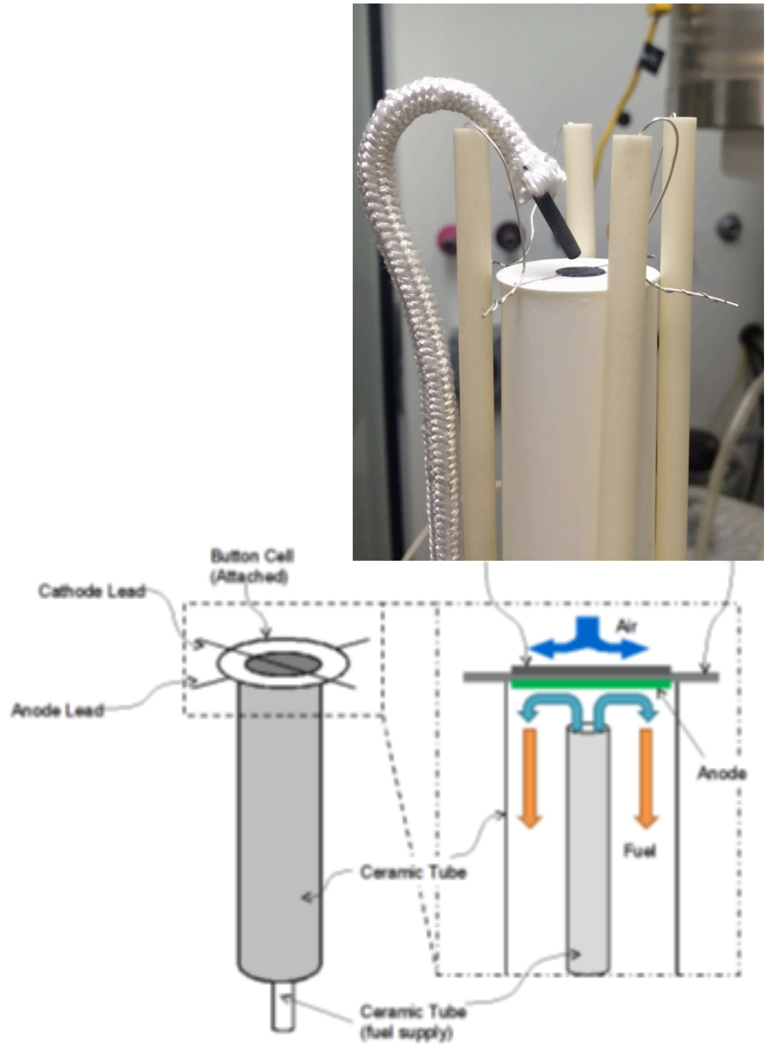
	temperature [°C]	current density [mA cm^{-2}]	oxygen partial pressure, p_{O2}
conventional	900	380	0.2
aggressive	1000	760	0.1

<table>
<tr><th></th><th>temperature [°C]</th><th>current density [mA cm^{-2}]</th><th>cathode p_{O2}</th></tr>
<tr><td rowspan="2">prior work</td><td>900</td><td>380</td><td rowspan="2">0.2</td></tr>
<tr><td>1000</td><td>760</td></tr>
<tr><td rowspan="4">current work</td><td rowspan="2">900</td><td>380</td><td rowspan="4">0.1</td></tr>
<tr><td>OCV (control)</td></tr>
<tr><td rowspan="2">1000</td><td>760</td></tr>
<tr><td>OCV (control)</td></tr>
</table>

- ***Aging tests:*** effects of operating temperature at OCV
- ***Durability testing:*** effects of operating conditions

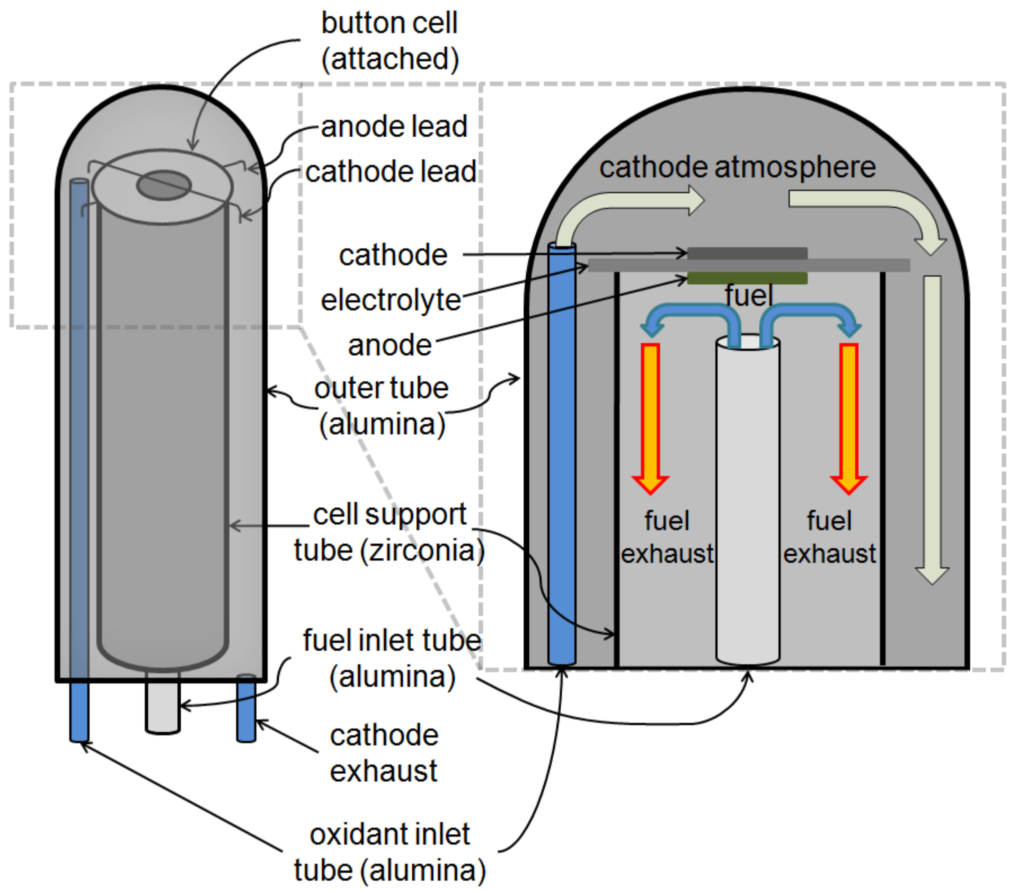
Technical approach: low-p_{O_2} cathode atmosphere

- Past work: ambient air (p_{O_2} = 0.2) for cathode atmosphere

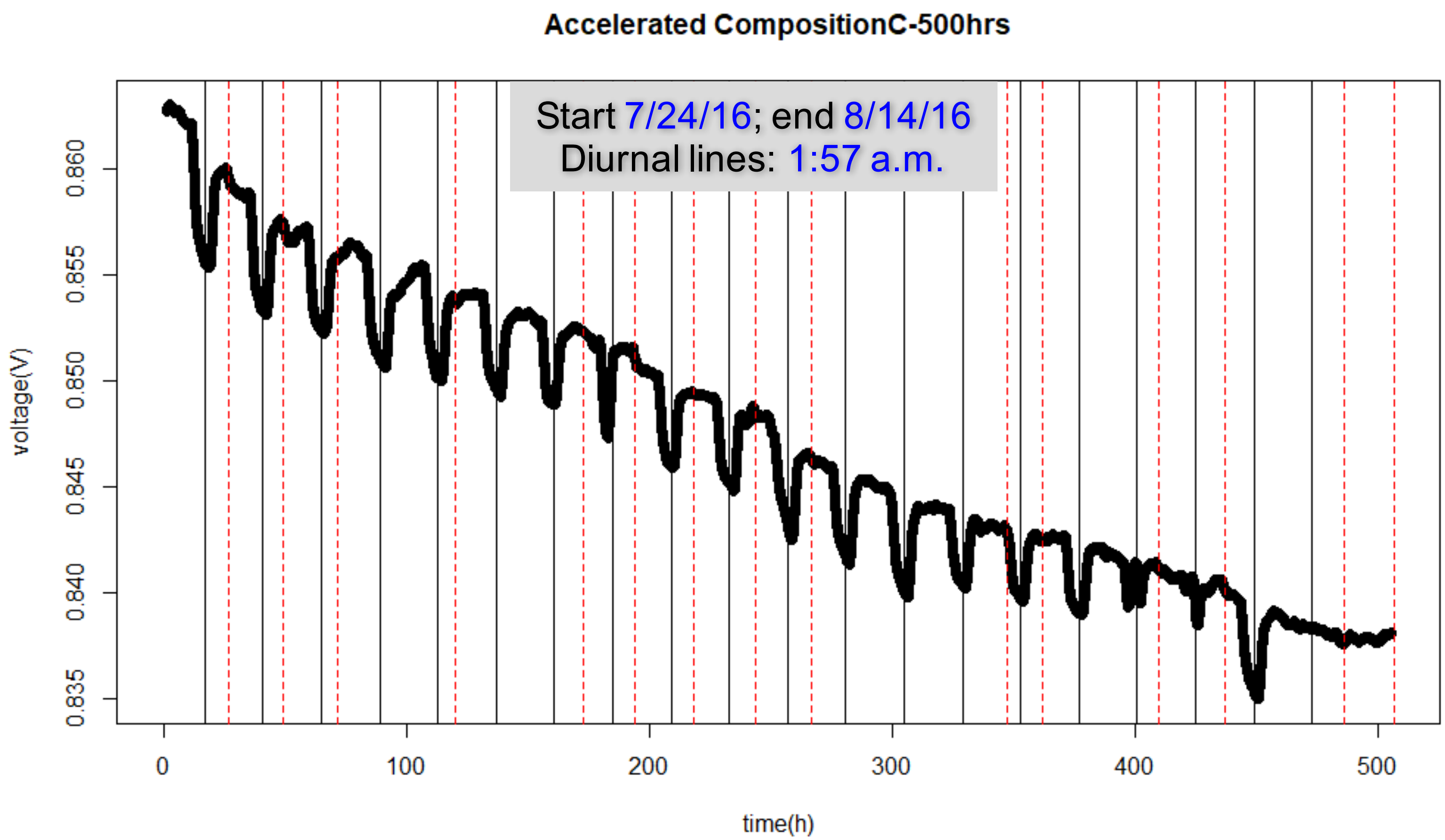


Technical approach: low-p_{O_2} cathode atmosphere

- Past work: ambient air (p_{O2} = 0.2) for cathode atmosphere
- This work: ***tube-in-tube test fixture***
  - Proven design
  - Controlled p_{O2}
  - ***Aggressive condition (p_{O_2} = 0.1)***



Technical approach: intermittent cycling



- Example of observed voltage fluctuations
  - ***24-h cycle*** (17 of 20 d)
  - ***Current cycling*** (10 of 15 LSV sweeps)

Project objectives

- Overall objectives:
    - Understand effect of operational parameters on performance in SOFCs with LSM / YSZ cathodes
    - Relate performance changes to microstructural changes (and Mn excess)

Project objectives

- Specific objectives:
  - Test cells under ***reduced p_{O_2}, ≥ 500 h***
    - Aging
    - Durability
    - Diagnostic (all cells)
    - Current load cycling (all cells)
  - Use ≥ 2 LSM compositions from prior work
  - Conduct detailed ***microstructural characterization***
    - TEM
    - EDXS
    - 3DR (FIB/SEM)
  - Relate cell performance to operating conditions and microstructural changes — ***design rules***

Project structure: Personnel

- Project Director: Mark R. De Guire, Ph.D.
- Principal Investigators:
  - Mark R. De Guire, Ph.D.

    Associate Professor, Department of Materials Science and Engineering, CWRU
  - Arthur H. Heuer, Ph.D.

    Distinguished University Professor and Kyocera Professor of Materials Emeritus, Department of Materials Science and Engineering, CWRU
- Other personnel: Amir Avishai, Ph.D. Swagelok Center for Surface Analysis of Materials, CWRU
- Graduate Assistant: TBD CWRU

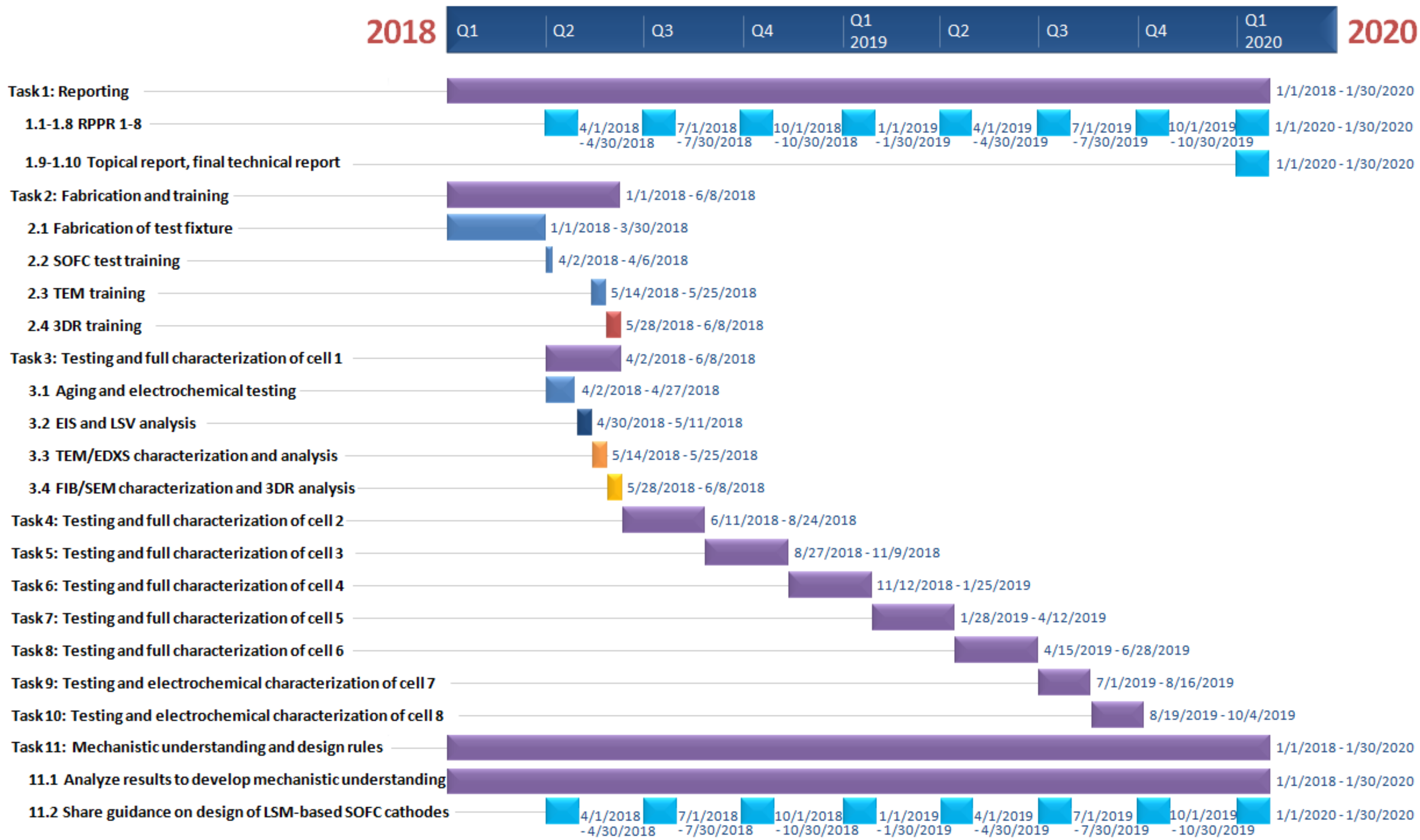
Project structure

Project management & planning (T1)	De Guire
Fabricate controlled-p_{O2} test fixtures (T2)	Graduate Assistant; ESFC*
Training cell testing & analysis (T2)	Graduate Assistant, SCSAM† staff
Test eight cells (T3–T10)	Graduate Assistant
Characterize tested cells (T3–T10)	
<u>Electrochemical</u>: ASR, LSV, EIS analysis	Graduate Assistant
<u>Microstructural</u>:	
TEM/EDS	SCSAM† staff
3DR Slice & View	SCSAM † staff
3DR segmentation	Graduate Assistant
Mechanistic understanding & design rules (T11)	De Guire, Heuer, Graduate Assistant

*) Engineering Services Fabrication Center, CWRU

†) Swagelok Center for Surface Analysis of Materials, CWRU

*Project schedule**



*) PMP to be revised to reflect actual start/end dates of 10/01/2017 – 09/30/2019

Project budget — by budget period*

	budget period 1 10/01/17–09/30/18			budget period 2 10/01/18–09/30/17			total	
	gov't funding	cost share	**total**	gov't funding	cost share	**total**	gov't funding	cost share
CWRU	$151,270	$37,260	**$188,530**	$148,730	$38,240	**$186,970**	**$300,000**	**$75,500**
CS %:		**19.8%**			**20.4%**			**20.1%**

*) To be confirmed by CWRU financial support staff

Project budget — by task*

DOE, + CWRU cost share

	Task1	Task2	Task3	Task4	Task5	Tasks6	Task7	Task8	Task9	Task10	Task11	Total
a. Personnel	22,736	8,477	9,625	9,625	9,625	9,625	9,625	9,625	7,616	7,616	19,425	123,620
b. Fringe Benefits	5,960	993	993	993	993	993	993	993	993	993	4,967	19,866
c. Travel	4,500	-	-	-	-	-	-	-	-	-	4,500	9,000
d. Equipment	-	-	-	-	-	-	-	-	-	-	-	-
e. Supplies	-	3,091	1,545	1,545	1,545	1,545	1,545	1,545	1,545	1,545	-	15,454
f. Contractual	-	-	-	-	-	-	-	-	-	-	-	-
g. Construction	-	-	-	-	-	-	-	-	-	-	-	-
h. Other Direct Costs	3,421	10,955	9,925	9,925	9,925	9,925	9,925	9,925	7,530	7,530	3,421	92,409
Total Direct Costs	36,617	23,516	22,089	22,089	22,089	22,089	22,089	22,089	17,685	17,685	32,313	260,349
Indirect Costs	19,917	10,414	8,737	8,737	8,737	8,737	8,737	8,737	7,532	7,532	17,335	115,151
Total Costs	56,534	33,930	30,826	30,826	30,826	30,826	30,826	30,826	25,216	25,216	49,648	375,500

*) To be confirmed by CWRU financial support staff

Project Management Plan: Risk management

Risk: Delay in starting a test
Category: Schedule
Impact: Moderate
Mitigation & response:

- Budget for replacement hardware
- Two test stands are available; schedule presumes one

Risk: Disruption of test in progress
Category: Schedule; Resource
Impact: Moderate
Mitigation & response:

- Thorough training
- Adherence to standard test protocols
- Design fixture to eliminate water buildup in exhaust line
- Have additional backup cells

Project Management Plan: Risk management

Risk: Intermittent unavailability of SCSAM facilities
Category: Schedule
Impact: Low
Mitigation & response:

- Test schedule is independent of microstructural characterization schedule
- Test schedule includes breaks in SCSAM usage

Risk: Delay in fabricating test fixtures
Category: Schedule
Impact: High
Mitigation & response:

- Close consultation with original designers
- Thoroughly test first fixture before building second

Project Management Plan: Risk management

Risk: Unexpected outcomes of low-p_{O_2} testing
Category: Technical/Scope
Impact: Moderate
Mitigation & response:
- Check that fixture delivers intended atmosphere
- In consultation with FPO, modify work scope to include other variations in test conditions, e.g. longer time, higher current density (e.g. 1,000 mA cm^{-2}),

Risk: High variability between tests
Category: Technical/Scope
Impact: Moderate
Mitigation & response:
- Thorough training
- Adherence to standard test protocols
- Accept that other uncontrolled variables may be in play

Project Management Plan: Risk management

Risk: Exceed allotted SCSAM budget
Category: Budgetary
Impact: Low
Mitigation & response:

- Conserve usage hours: analyze smaller 3D volumes, conduct fewer point-and-shoot analyses

Risk: Unavailability of personnel
Category: External influences; Schedule
Impact: Moderate
Mitigation & response:

- Design project schedule with academic schedule in mind (exams, breaks)
- Conduct training sessions on actual test specimens

- **Environmental, safety, and health risks** — None foreseen

Summary

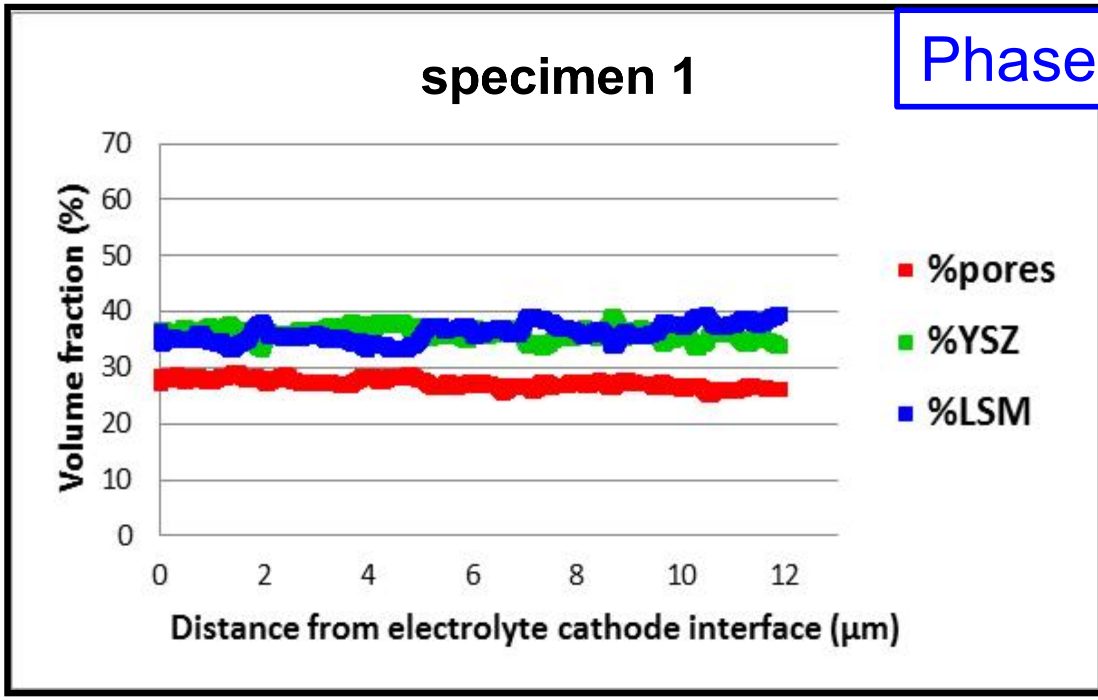
- Significance
  - Practical LSM compositions
  - Realistic initial LSM/YSZ microstructures
  - Standard anodes and electrolytes
  - “Aggressive” conditions have practical precedents
    - Temperature gradients
    - Hot spots
    - Disruptions in air supply
- ***Mechanistic understanding and design rules:*** Anchor observed composition – microstructure – performance relationships in sound materials science and electrochemistry principles

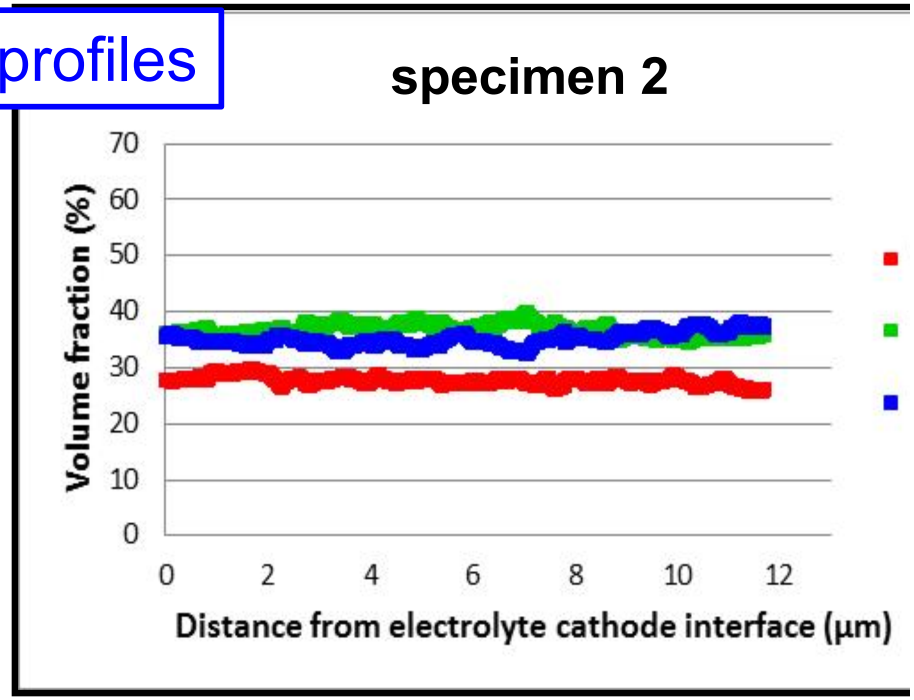
Discussion

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}

standard deviations
avg. microstructural params.:
TPB: