Study of the Durability of Doped Lanthanum Manganite Cathode Materials under "Real World" Air Exposure Atmospheres

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Outline

- Accomplishments
- Background
- Experimental
  - Role of Humidity and CO2
  - Contribution of IC- AE interface
  - Phase stability study using in-situ XRD
- Results and Discussion
- Future work
- Acknowledgements

Accomplishments

- Electrochemical testing of LSM/YSZ/LSM symmetric cell in humidified air and CO2/air has been conducted for up to100 h and post-test analytical study (XRD, SEM-EDS, XPS, FTIR) has been performed.
  - ✓ SrO/Sr(OH)2 has not been detected in the cells tested in dry air regardless of testing conditions.
  - ✓ SrO/Sr(OH)2 has been detected in the cells in presence of humidity in air.
  - ✓ Nucleation and growth of SrO increases with cathodic bias, increase in humidity content, temperature, and test duration.
  - ✓ LSM degradation mechanism in humidified air has been developed and proposed.
  - ✓ Formation of (Sr/La) carbonates have been identifies when the cell is tested in Air-10%CO2

- Ohmic contribution of AISI 441 interconnect on the performance of anode supported single cell (Ni-YSZ/YSZ/LSM-YSZ) has been measured and quantified.
- In-situ XRD investigation has been conducted to identify structural change of YSZ and compound formation/phase evolution due to interaction with manganese, LSM, and LSCF.
- XRD approach has been developed to detect tetragonal form of YSZ.
  - ✓ Manganese dissolution into YSZ destabilizes the cubic symmetry to tetragonal symmetry.
  - ✓ No reaction compound has been detected due to interaction of 20% LSM/LSCF with YSZ/GDC at 1400°C in air for <24h.

Impact and Technical Significance

- **Observations and mechanistic understanding of chemical and morphological changes, derived from long term experiments, have helped SECA industry teams in optimizing air electrode.**
- **Studies provide insight into long term interfacial porosity formation and delamination (AE/Elec.)**
- **Studies provide insight into destabilization of YSZ**
- **Accelerated tests in steam and CO2 containing atmospheres show air electrode decomposition.**

Project Objectives

Mechanistic understanding of lanthanum manganite and lanthanum cobaltite cathode degradation in 'real world' air exposure during SOFC operation

Long Term Bulk, Interfacial and Surface Stability

Dopants, Electric polarization, Gas phase contaminants (H_2O, CO_2, Cr-vapor species, stoichiometry)

Compound formation (Solid-solid/solid-gas reactions)
dopants exolution and oxides segregation at surface

- ✓ oxides and compounds at interface
- ✓ crystal symmetry
- ✓ microstructure
- ✓ Micro-cracking and/or delamination

Tools: EIS, DC conductivity, XRD, SEM, X-ray absorption spectroscopy, XPS, SIMS, TEM, HTXRD

Bulk, Interfaces, Surface Stability

Electrode – Electrolyte / Electrode - IC

Couple/ Symmetric / Full cell/ configurations

Air side contaminants:
Water, CO_2, Oxide vapors
Other contaminants

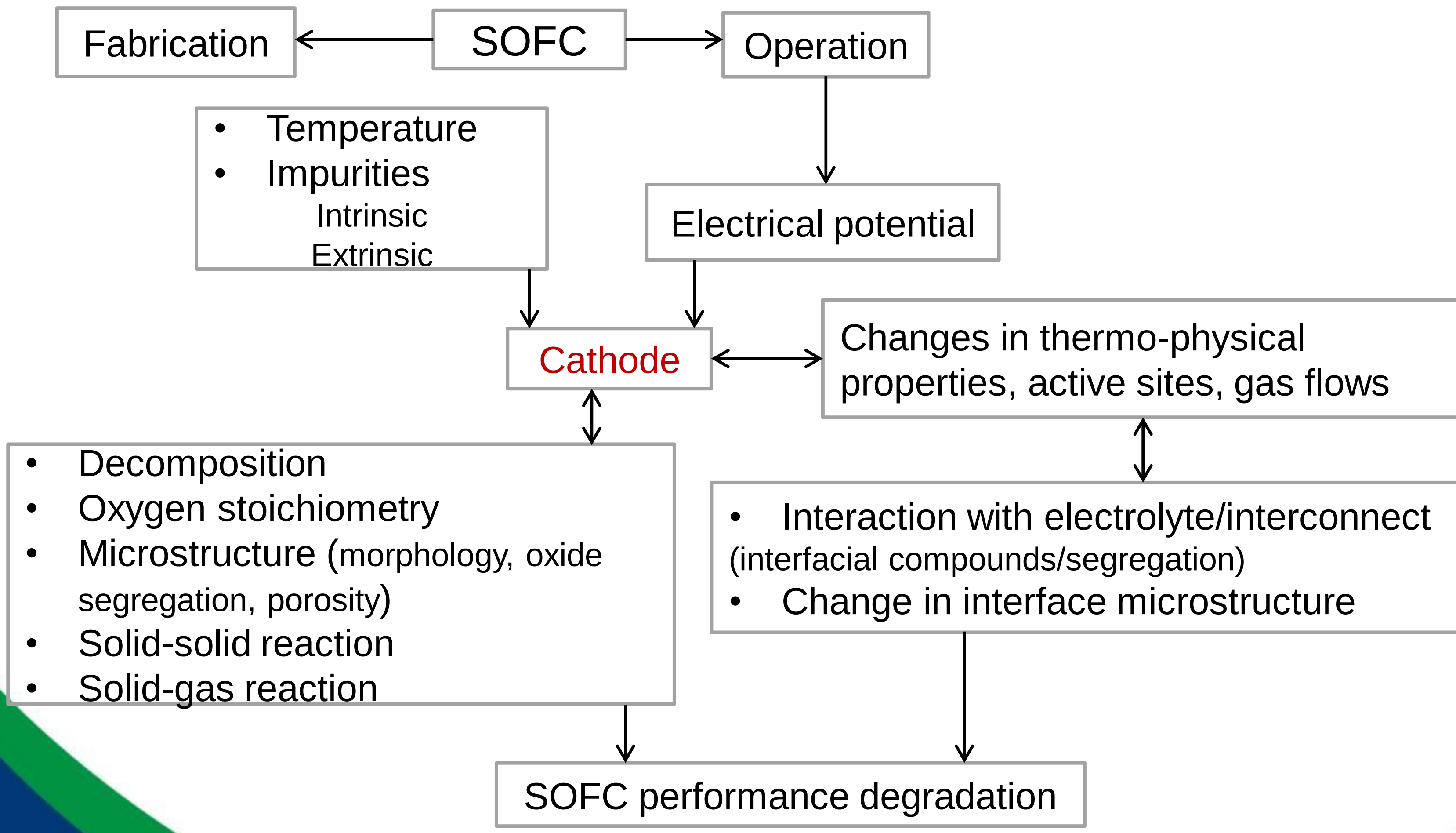
In-situ, Ex-situ Bench top tests

Background

- Cathode electrode maintain intimate contact with electrolyte and interconnect and exposed to air which contains H_2O, CO_2, H_2S/SO_2 etc.
- Bulk and interfacial stability of cathode due to solid-solid and solid-gas interactions significantly contributes to performance losses and degradation in SOFC stacks. Two key factors:
  - Polarization losses at cathode/electrolyte interface
  - Ohmic and contact losses at cathode/ interconnect interface, especially with metallic interconnect
- Poor contact (reduced contact area) between ceramic cells and metallic interconnects (even with use of contact paste) results in higher Ohmic loss. Contributing factors for poor contact include:
  - Operating characteristics (temperature distribution, thermal expansion mismatch)
  - Interfacial compound formation and morphology change
- Solid-solid and solid-gas interactions lead to undesirable compound formation at the cathode / electrolyte and cathode / interconnect interface, as well as well as at the surface.

Background

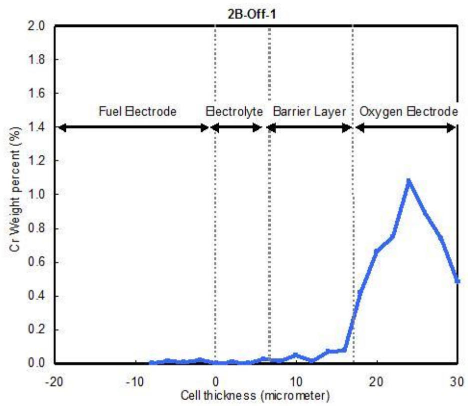
Cathode contributions: SOFC performance degradation



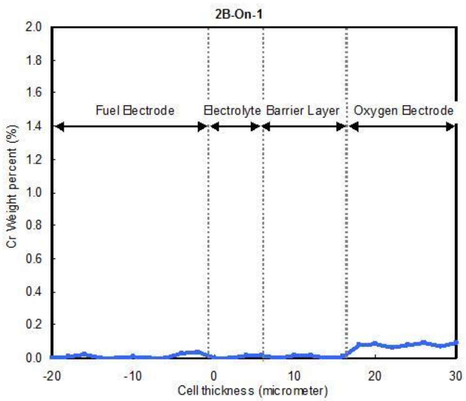
Examples of Elemental Migration

Stack Cathode Side

Cr Profile

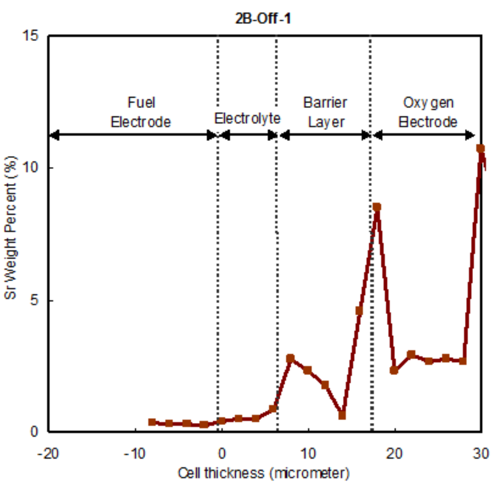


Region under channel

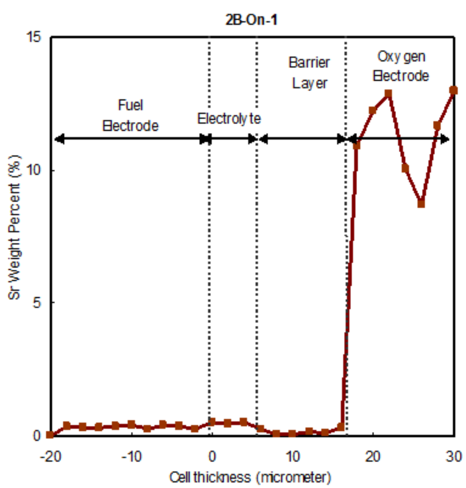


Region under rib

Sr Profile

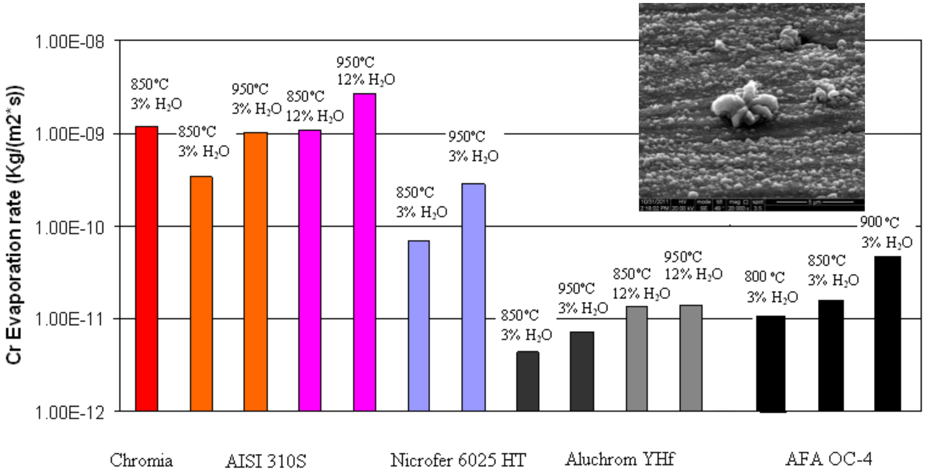


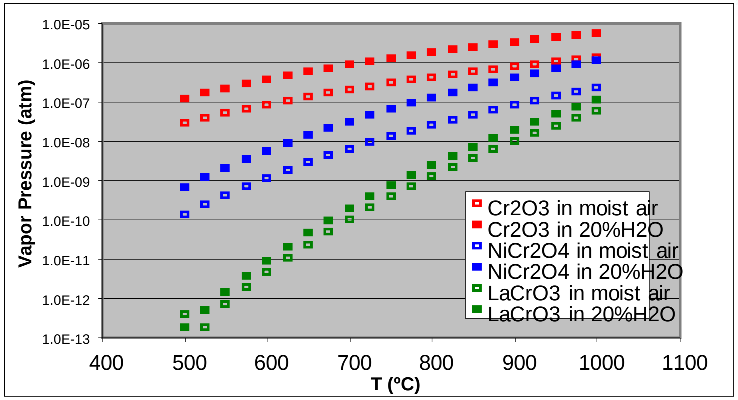
Region under channel

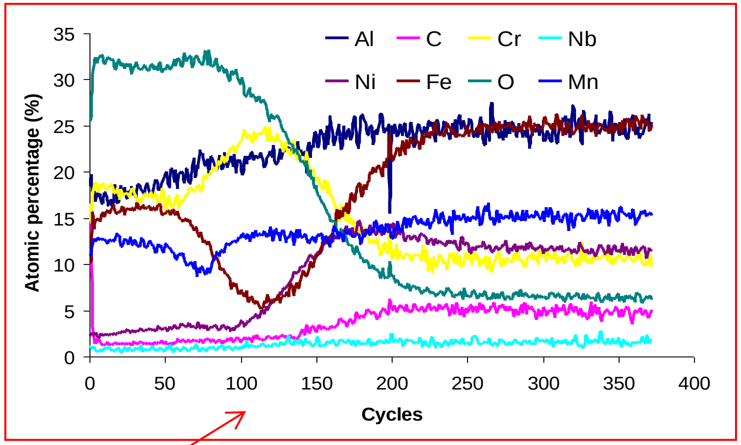


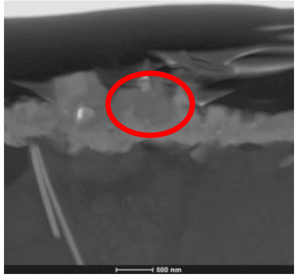
Region under rib

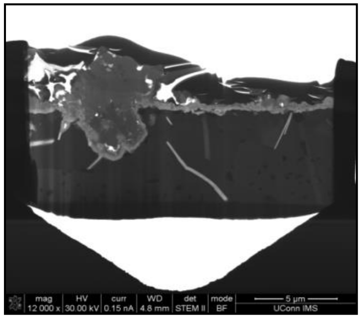
Background: Gas phase contamination and interaction

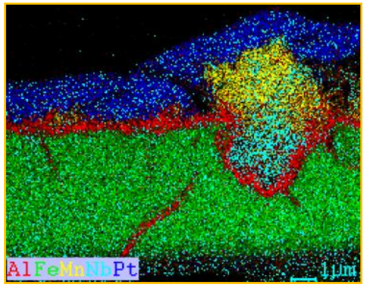






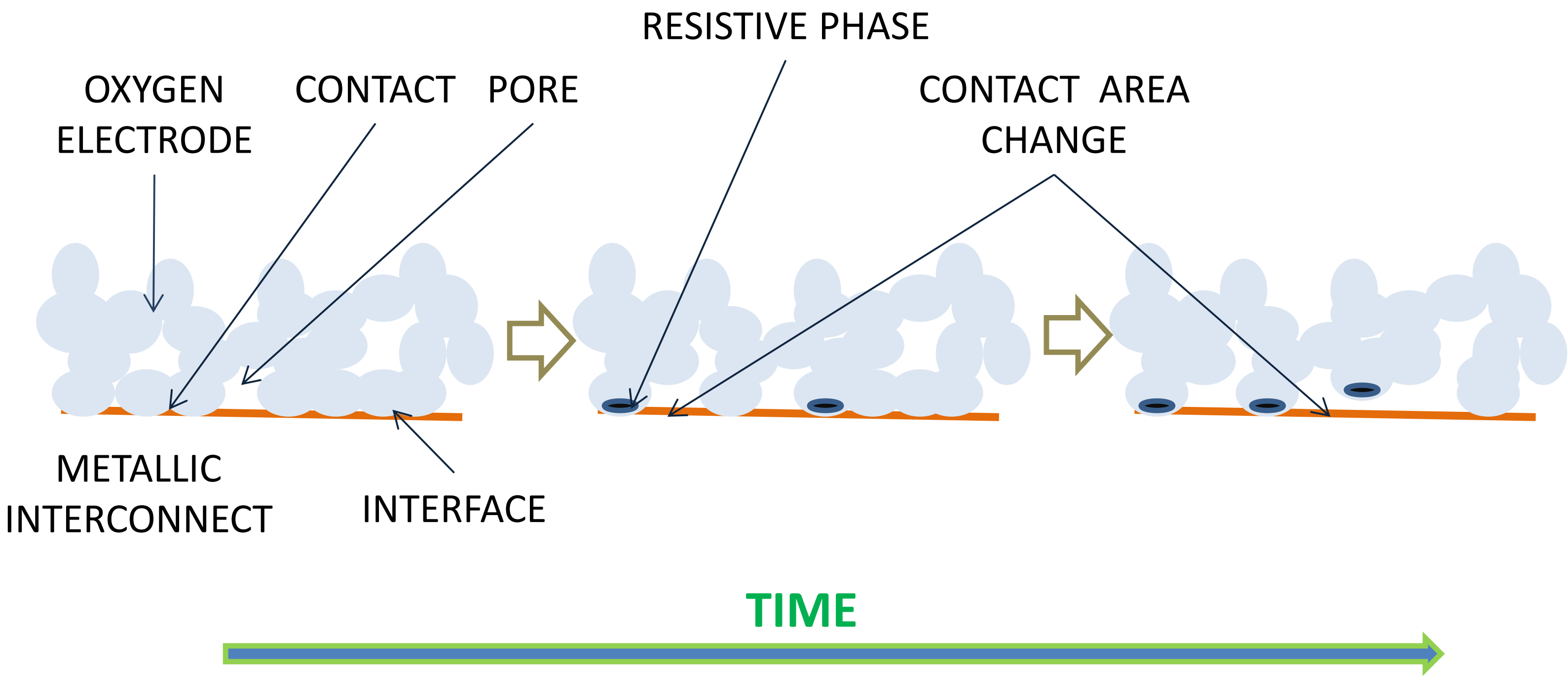






850°C for 1 min in Wet Air (3%H2O) (1200 grit polished)

Background: CE/MI Interface Evolution



Role of H_2O/Air and CO_2/Air on LSM Cathode Degradation

Experiments Conducted

Interfacial, Surface and Bulk Interactions

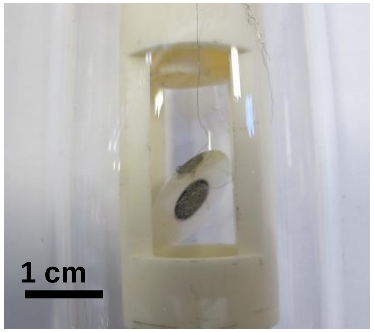
Analytical study for as fabricated cells (HTXRD, HRSEM, EDS)

Electrochemical testing

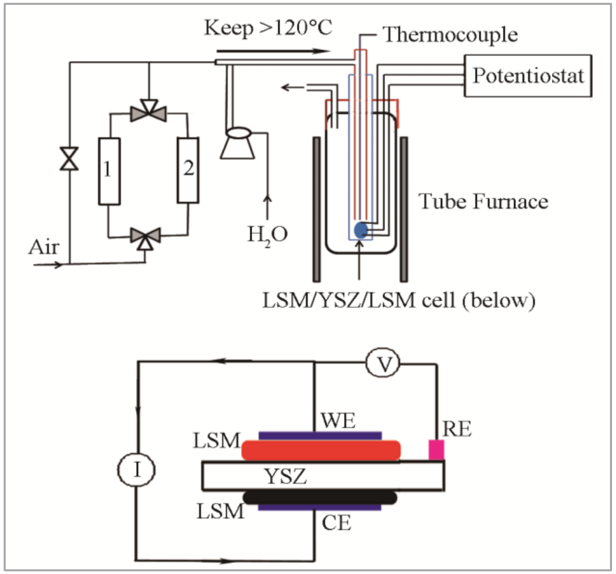
Input parameters
- Temperature (750 - 850°C)
- Atmosphere (air containing 0 - 50% H_2O, up to10% CO_2)
- Time (up to 100 h)
- Electrical bias (0-0.5V)

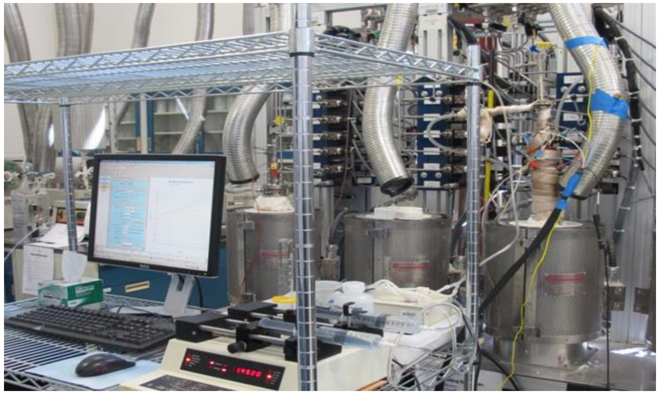
Post-test analysis: Bulk, interface, and surface XRD, SEM, XPS, and FTIR

Note: Dry air indicates the in-house compressed air flowing through molecular sieve column.



SOFC in an alumina test enclosure

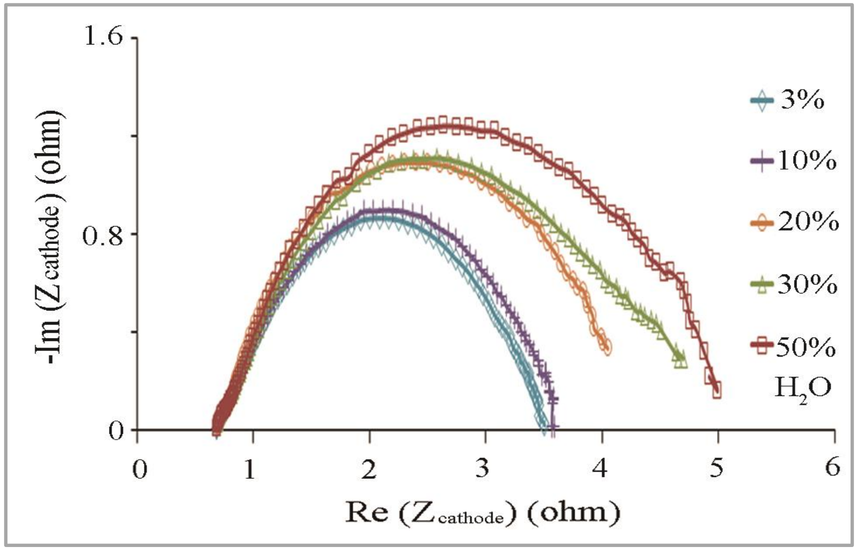




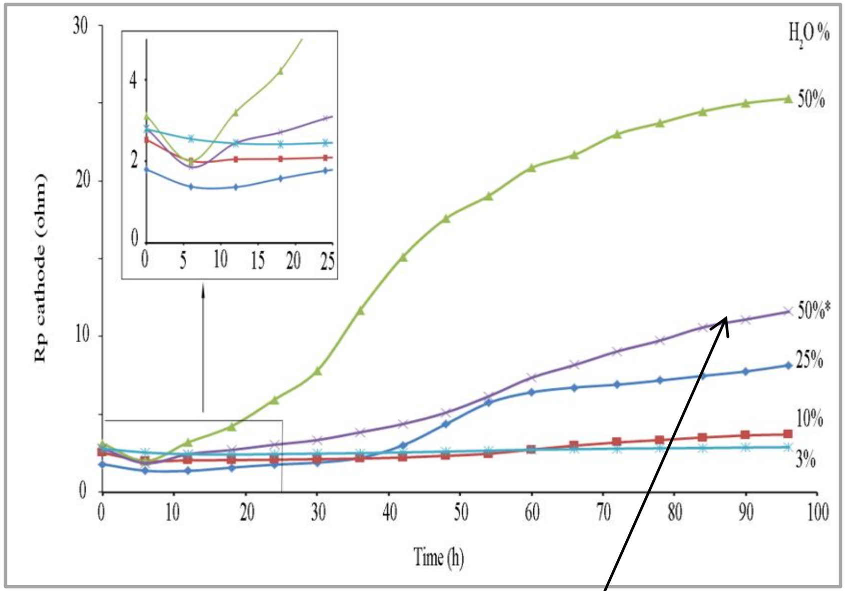
Integrated SOFC test system

Electrical Performance in Humidified Air

800°C, 0.5 V



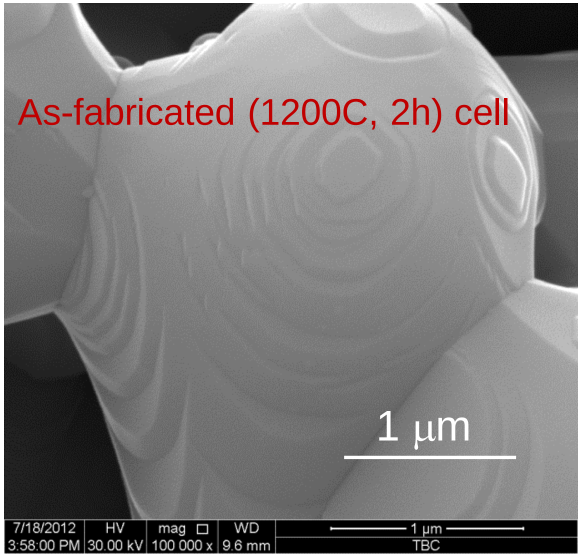
850°C, 0.5 V Non-Ohmic resistance

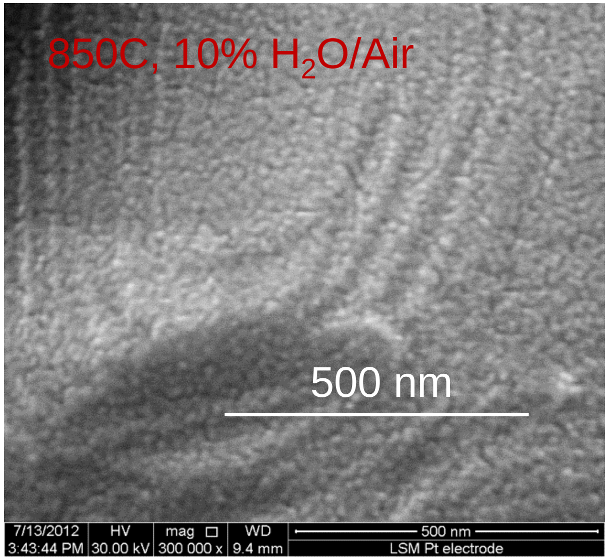


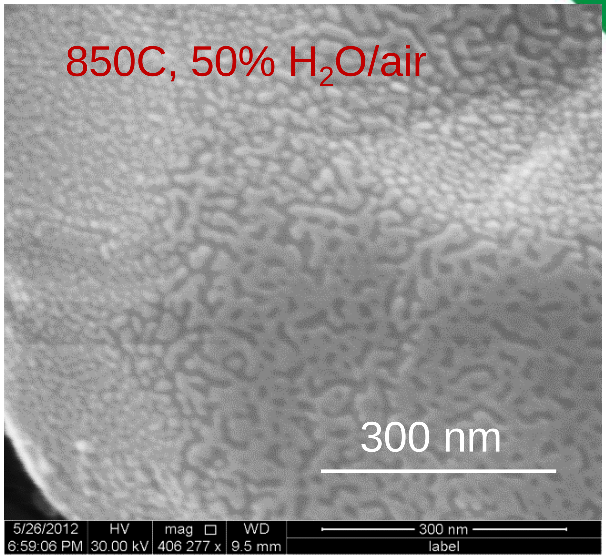
Oxygen added to maintain PO_2 = 0.21 atm

- ✓ Ohmic and non-ohmic resistance increases with increase in H_2O content
- ✓ The resistances decrease if the PO_2 is maintained at 0.21 atm in H_2O containing air

LSM Morphology: Without Applied Bias

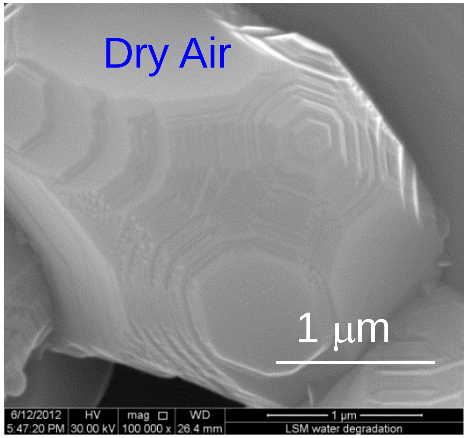


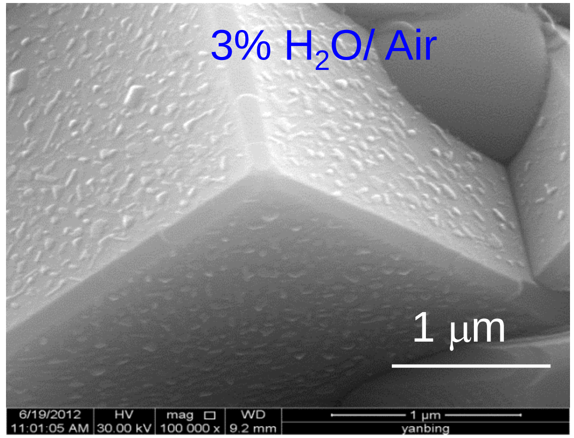


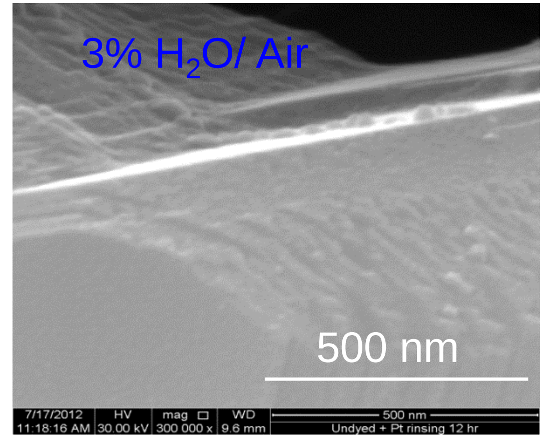


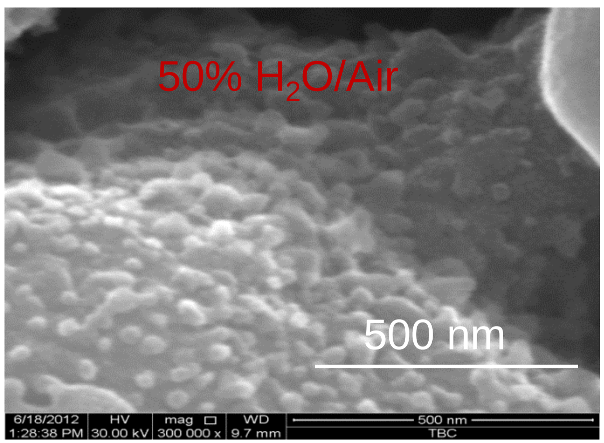
- Oxide segregation at the cathode surface in humidified air
- Extent of oxide segregation increases with H_2O content

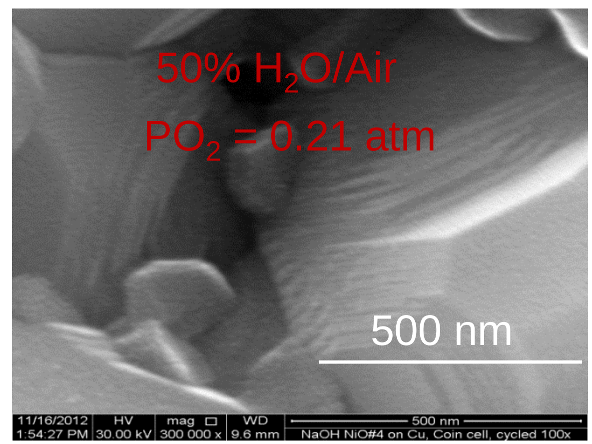
Morphology of LSM Cathode:0.5 V Bias, 850C, 100 h





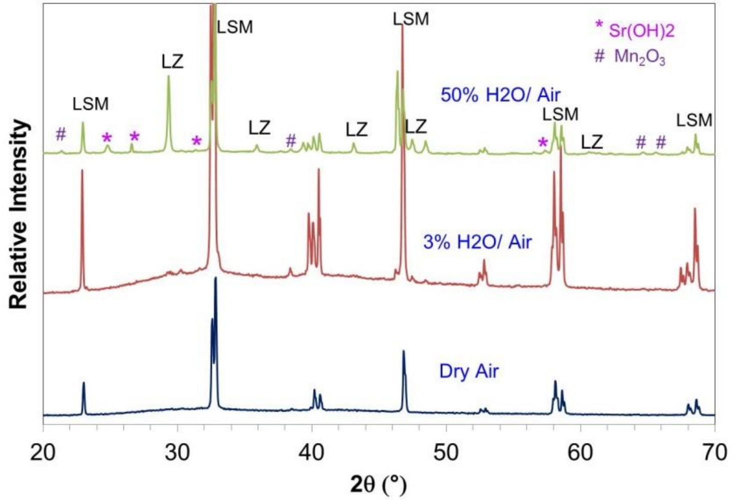






- No oxide segregation in dry air
- Oxide segregation increases with H_2O content
- Oxide segregation also decreases if PO_2 is maintained at 0.21 atm

Post-test Characterization - XRD



- SrO and Mn_2O_3 segregates on the LSM surface
- $Sr(OH)_2$ forms during cooling since it is favorable in lower temperature
- $La_2Zr_2O_7$ (LZ) forms at the LSM-YSZ interface
- Unidentified peaks are of Pt (from Pt-paste)
- H_2O content favors oxide segregation as well as interfacial compound formation
- Formation of $La_2Zr_2O_7$ (ΔG = -146.2± 5.0 kJ/mol at 1200K) is favorable than $SrZrO_3$ (ΔG = -92.01 kJ/mol at 1200K)

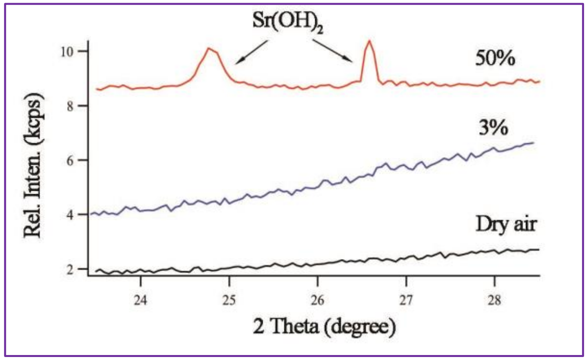
Free Energy Calculation for Hydroxide Formation on LSM

$SrO (s) + H_2O(g) = Sr(OH)_2 (s)$

T	Delta G
C	kJ
500	-23.7
600	-13.4
700	-4.1
800	4.5
900	12.6
1000	20.1

$La_2O_3 (S) + 3H_2O(g) = 2La(OH)_3 (s)$

T	Delta G
C	kJ
500	37.2
600	75.9
700	113.0
800	148.5
900	182.3
1000	214.5



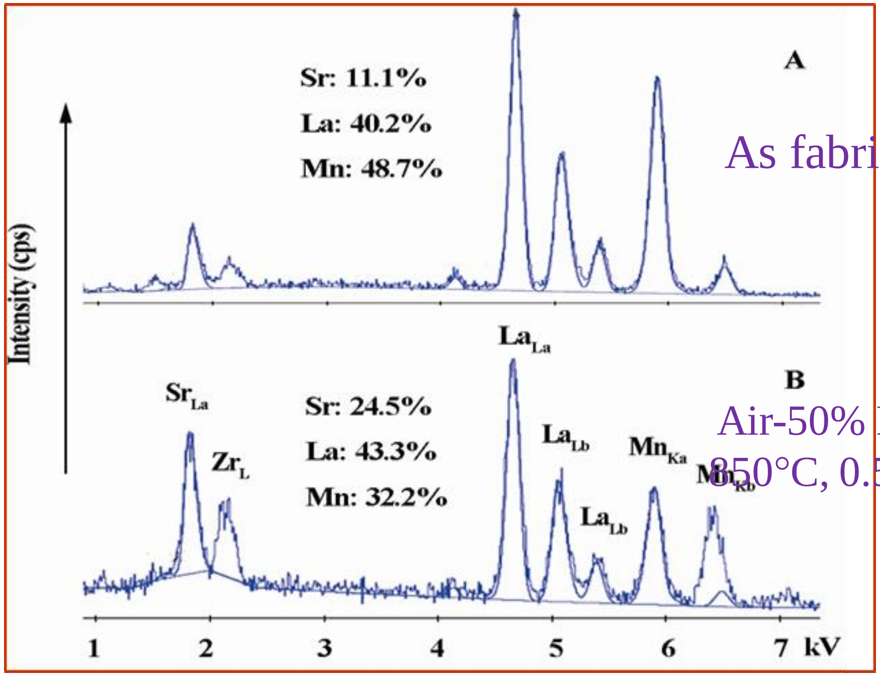
Elemental Analysis: LSM Cathode Surfaces

0.5 V, 850°C, 100 h

XPS

	Sr/La	Sr/(Mn+La)
	Molar ratio	Molar ratio
As-fabricated	0.23±0.01	0.13±0.01
Air-10% H_2O	0.34±0.02	0.21±0.01
Air-20% H_2O	0.58±0.04	0.24±0.01
Air-50% H_2O	1.89±0.09	0.76±0.04

SEM-EDAX



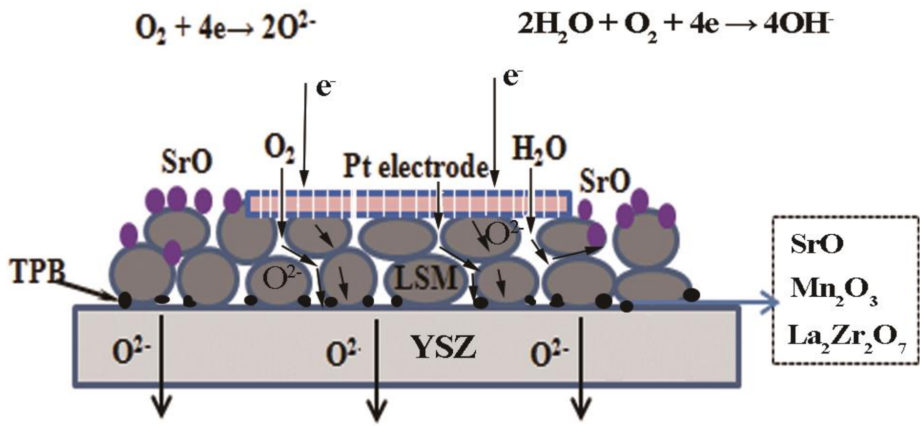
As fabricated

Air-50% H_2O, 850°C, 0.5 V, 100 h

- Sr- enriched LSM surface
- Sr-enrichment increases with increase in H_2O content

R. P. Vasquez , J. Electron Spectrosc. Relat. Phemon. 1991, 56, 217.

LSM Degradation: Hypothesis



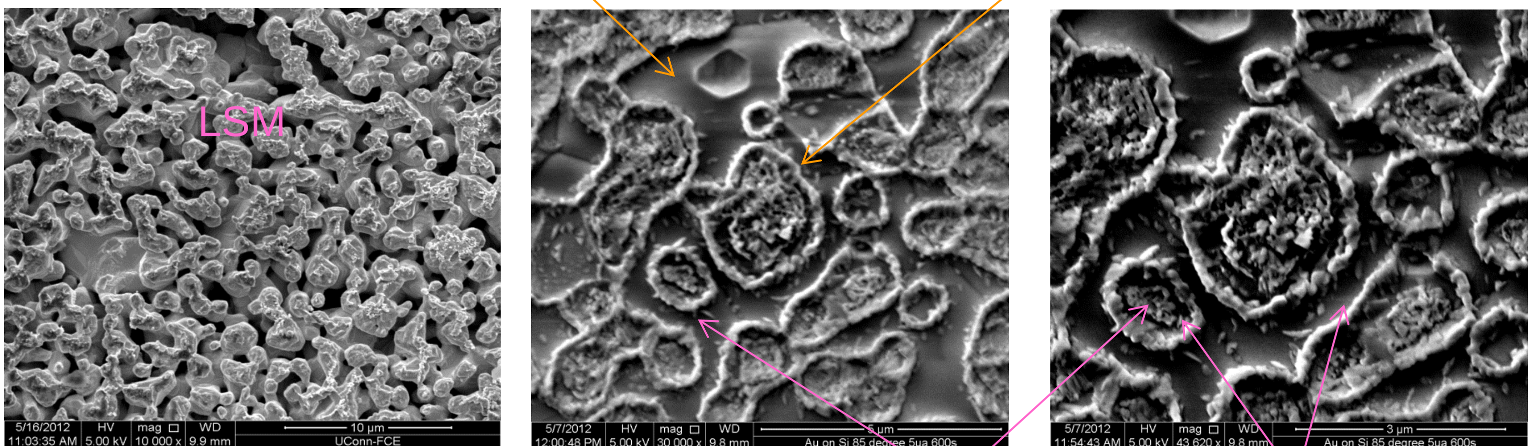
Dry air with bias :	$V_{La}''' + SrO + 3Mn_{Mn}^{\cdot} + e' \leftrightarrow Sr_{La}' + 0.5O_2 + 3Mn_{Mn}^{x}$
Wet air with no bias :	$Sr_{La}' + 2OH^- \rightarrow SrO + H_2O + V_{La}'''$
	$H_2O + Sr_{La}' + 2O_O \rightarrow SrO + V_{La}''' + 2OH_O^{\cdot}$
Wet air with bias :	$H_2O + Sr_{La}' + 2O_O \rightarrow SrO + V_{La}''' + 2OH_O^{\cdot}$
	$Sr_{La}' + 0.5O_2 + 2e' \rightarrow SrO + V_{La}'''$

J. Nowotny *et al.* J Phys Chem C, 114 (2010) 18215-18221.

LSM-YSZ Interface

Exposed electrolyte

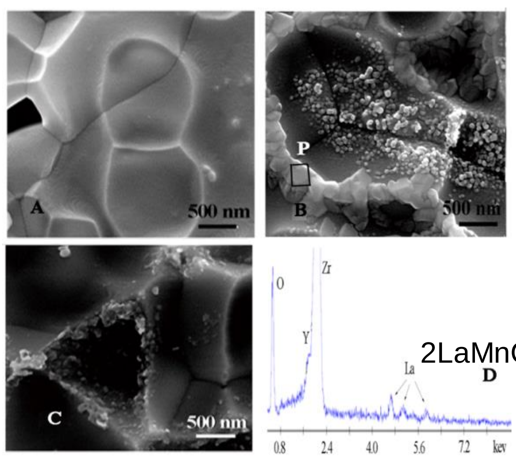
AE-Elec. Contact



800C, 100 h, 50% H_2O

AE Periphery

$La_2Zr_2O_7$

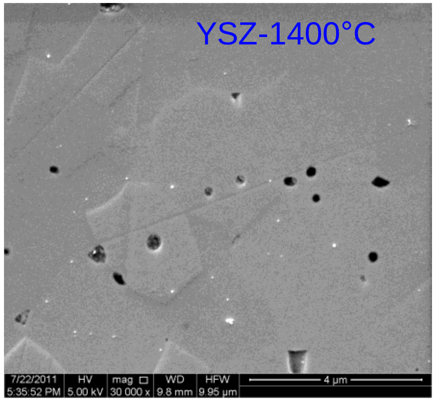


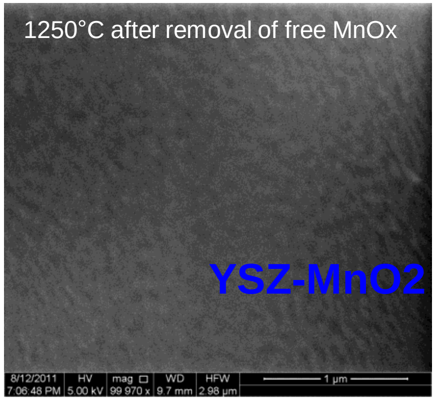
Electrolyte- Air electrode interface showing the air electrode contact area and formation of $La_2Zr_2O_7$ at the periphery

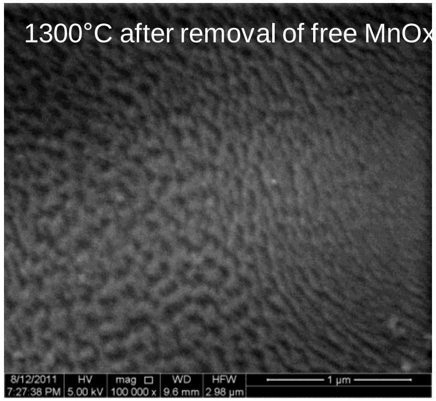
Formation of $La_2Zr_2O_7$ (ΔG = -146.2± 5.0 kJ/mol at 1200K) is favorable than $SrZrO_3$ (ΔG = -92.01 kJ/mol at 1200K)

$$2LaMnO_3(s) + 2ZrO_2\,(s) \rightarrow La_2Zr_2O_7(s) + Mn_2O_3\,(s)$$

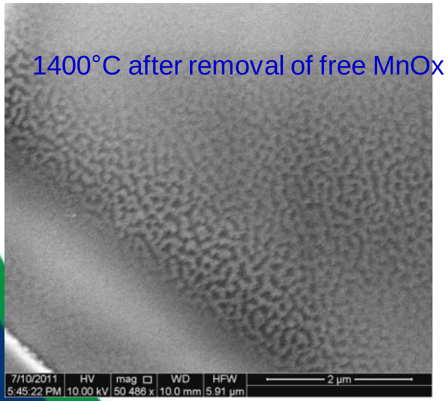
Microstructure Evolution - SEM

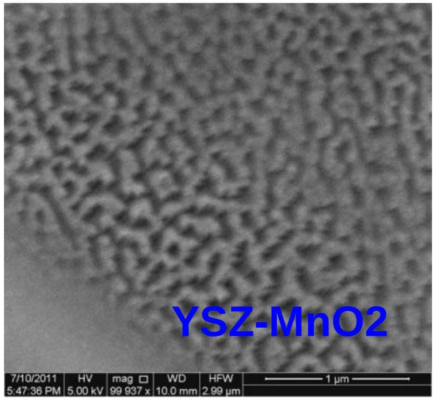


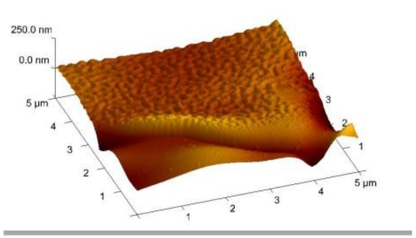


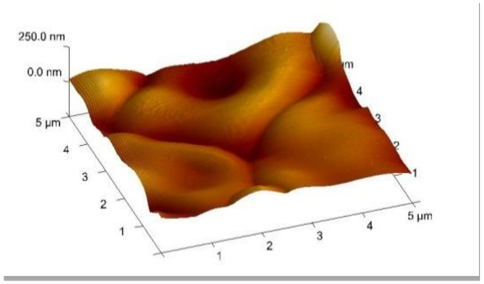


- Undulated surface
- Extent of undulation increases with increasing temperature
- EDS analysis shows the presence of ~ 10 at% Mn in YSZ







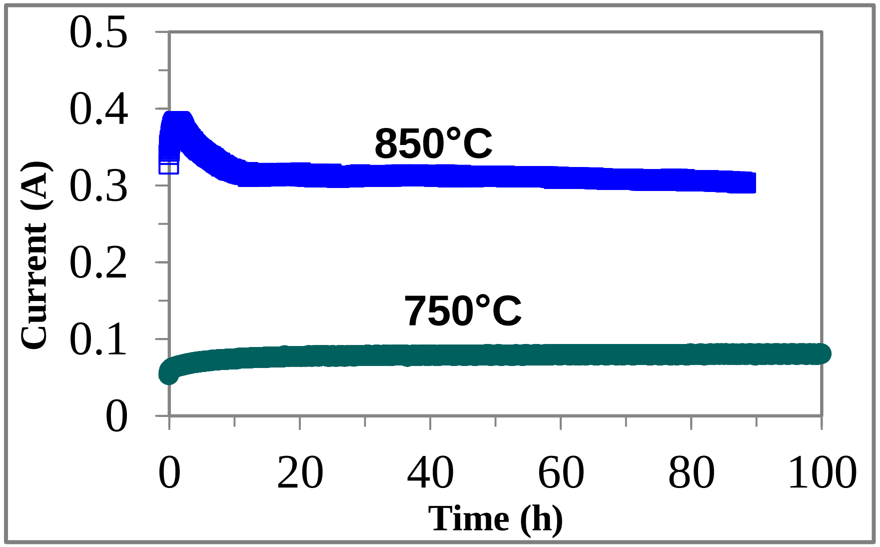


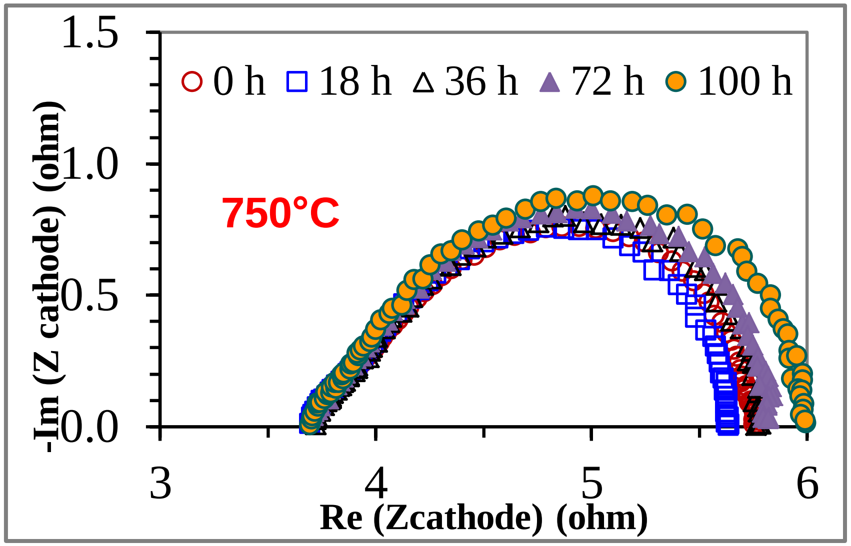
Dissolution of Mn in the YSZ lattice leads to structural destabilization leading to interface separation and increase in ASR.

Manoj K. Mahapatra, Prabhakar Singh and Scott T. Misture, "Manganese induced modifications in yttria stabilized zirconia" *Applied Physics Letters* 101, 131606, 2012.

SOFC Stability in CO_2/air

- Ambient **air** contains 78.09% nitrogen, 20.95% oxygen, 0.93% argon, 0.039% **carbon dioxide**, and small amounts of other gases.
- Higher carbon dioxide contents are used for accelerated degradation.

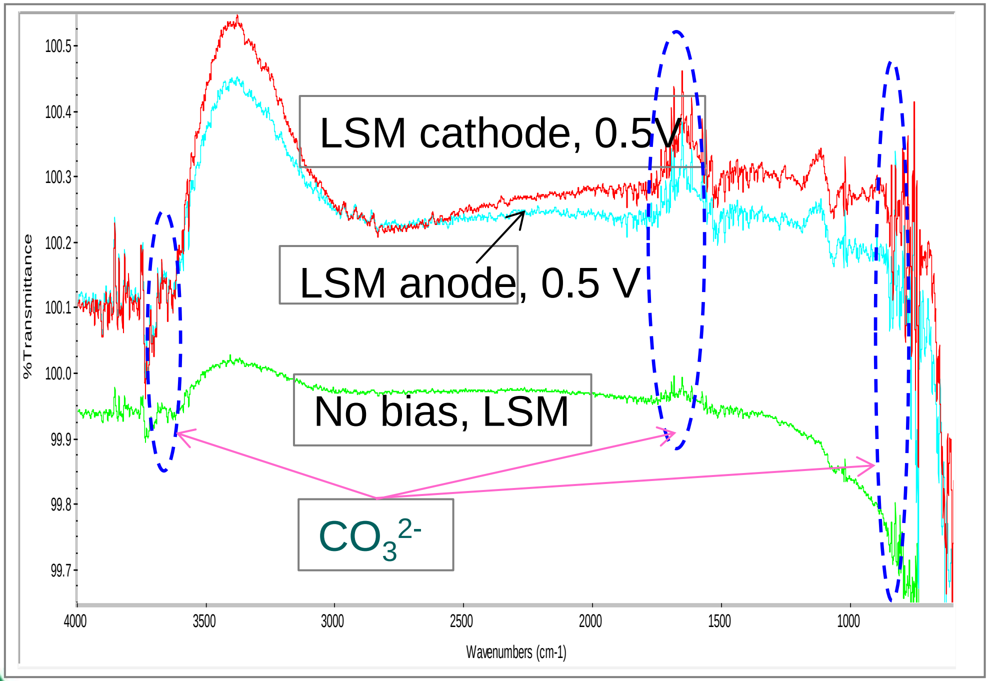




- Role of CO2 may vary with temperature.
- Polarization resistances increases with cell operating time.

10% CO_2/air, 0.5 V, 100 h

FT-ATR Spectra of LSM Exposed to 10% CO_2/Air at 750 °C



Free Energy for Carbonate Formation

$SrO(s) + CO_2(g) = SrCO_3(s)$	
T	Delta G
C	kJ
25	-189.2
100	-176.3
200	-159.2
300	-142.4
400	-125.7
500	-109.1
600	-92.6
700	-76.3
800	-60.2
900	-44.3
1000	-29.7

$2Mn_2O_3(s) + 4CO_2(g) = 4MnCO_3(s) + O_2(g)$	
T	Delta G
C	kJ
25	99.7
100	133.2
200	177.3
300	220.7
400	263.4
500	305.5
600	346.9
700	387.7
800	427.9
900	467.5
1000	506.6

- Sr- rich carbonates have formed at LSM surface (Free energy of $La_2(CO_3)_3$ formation is not found.
- More carbonates formed on working LSM electrodes than the LSM without a bias.

C. K. Huang and P. F. Kerr, The American Mineralogist, 1960, 45, 311-324.

Investigation of AE/IC Contacts

Experimental Approaches

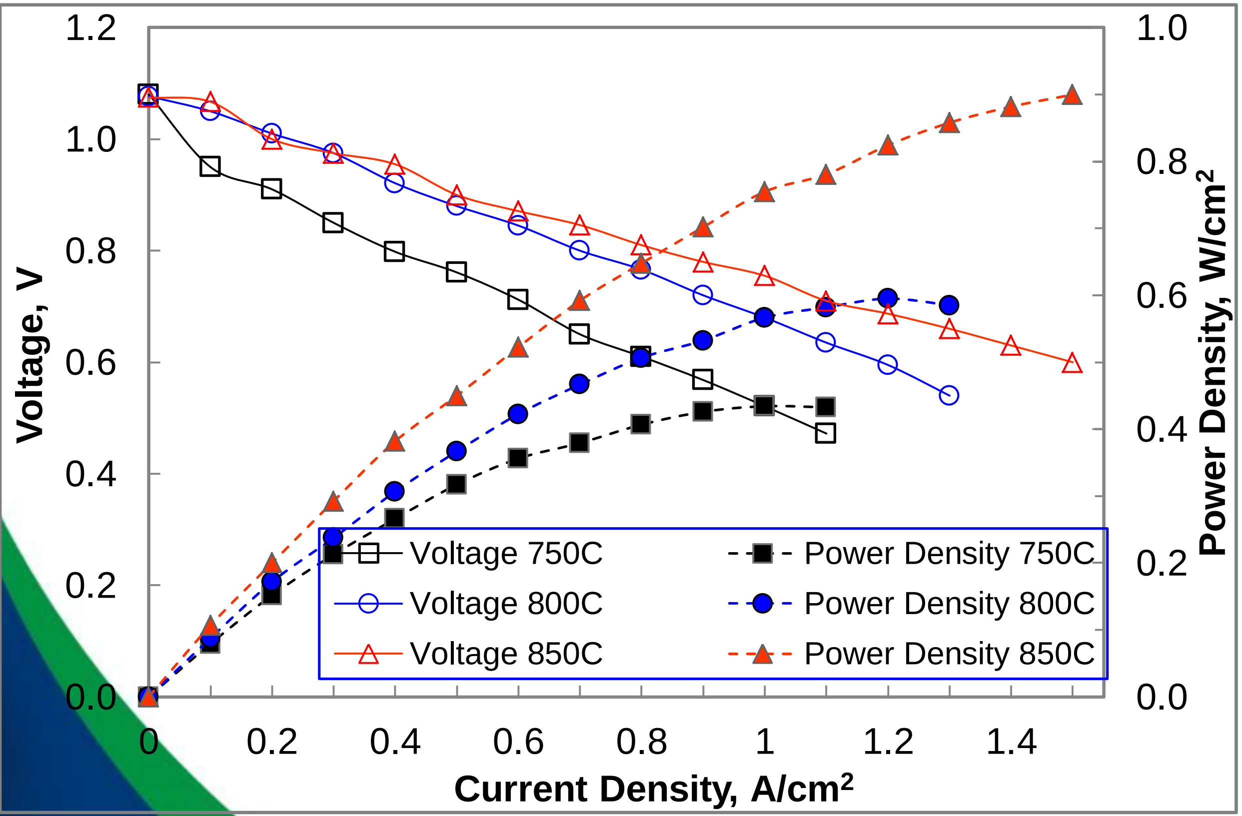
- Experiments with single cells and single cells combined with metallic interconnects to determine contribution of CE/MI contact resistances to performance losses
  - Techniques: I/V measurements, AC impedance
- Experiments with cells and symmetrical samples to investigate and correlate contact resistance changes and microstructural and chemical/phase composition evolution
  - Techniques: AC impedance, van der Pauw, 4 point DC, SEM, EDAX and others

Single Cell Testing

- Button cells (anode supported): YSZ electrolyte, Ni/YSZ anode, LSM/YSZ cathode
- Ag current collectors and pastes
- Test conditions:
  - Fuel: Hydrogen-3% H_2O, Oxidant: Air
  - Temperature: 750^{o}C, 800^{o}C, 850^{o}C
- I-V curves after cell conditioning

Single Cell Performance

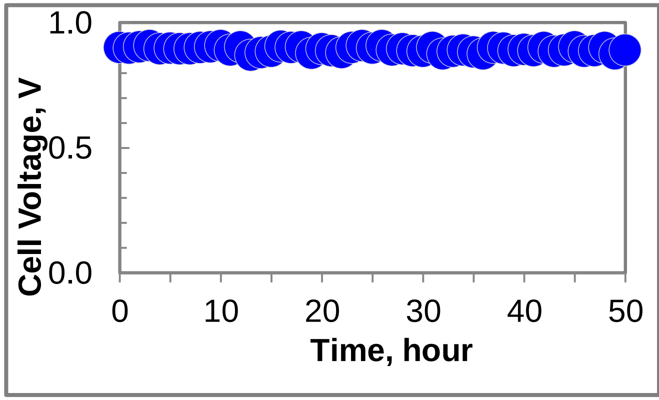
Fuel: H_2 – 3% H_2O
Oxidant: Air



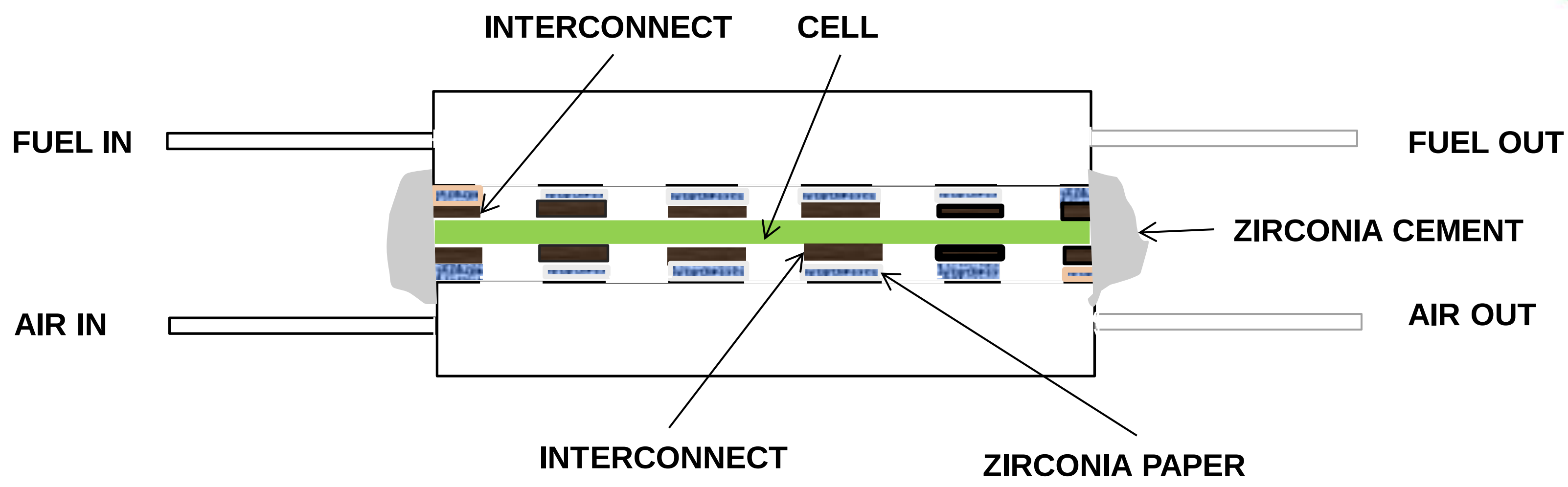
ASR (750ºC): 0.47 ohm-cm²
ASR (800ºC): 0.41 ohm-cm²
ASR (850ºC): 0.31 0hm-cm²

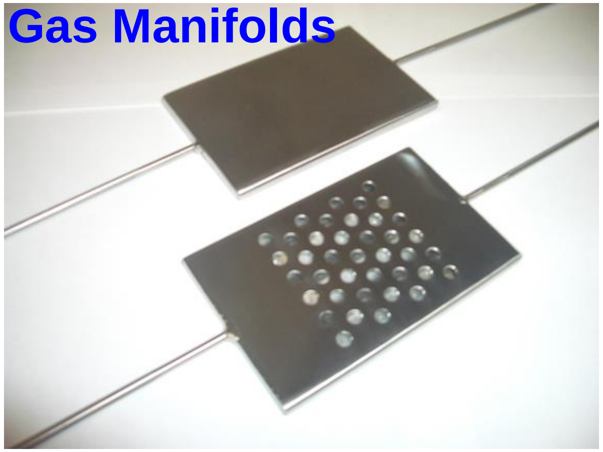
Endurance Cell Testing

800ºC, 0.425A/cm²



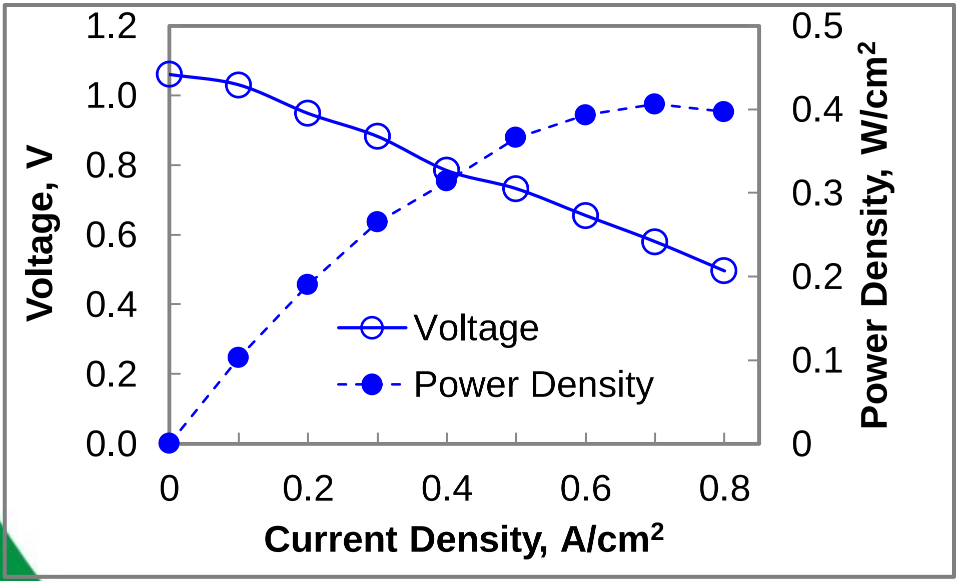
Single Cell Stack Setup



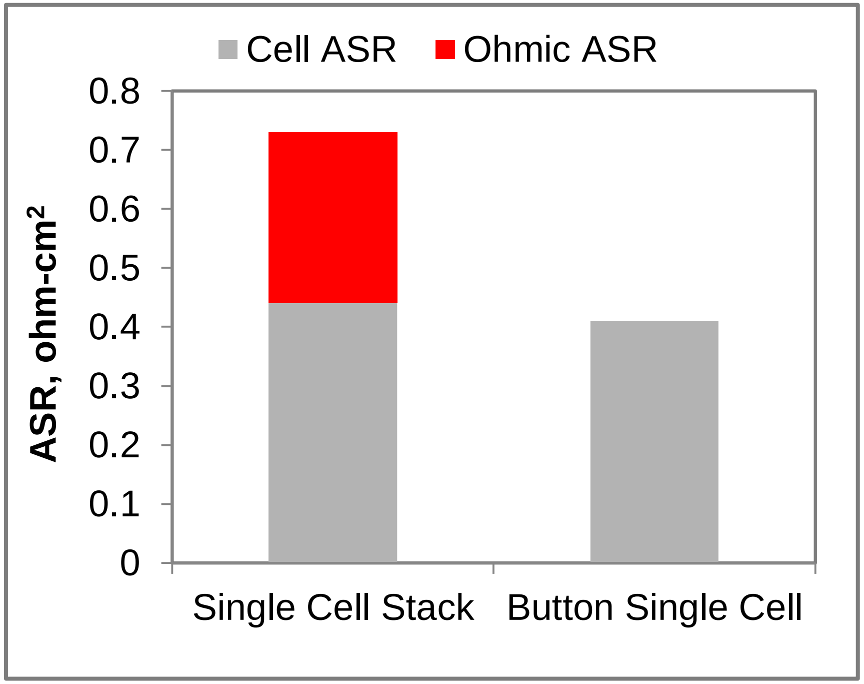


Performance of Single Cell Stack

Temperature: 800ºC
Fuel: Hydrogen-3%H_2O
Oxidant: Air



Ohmic Contribution in Single Cell Stack



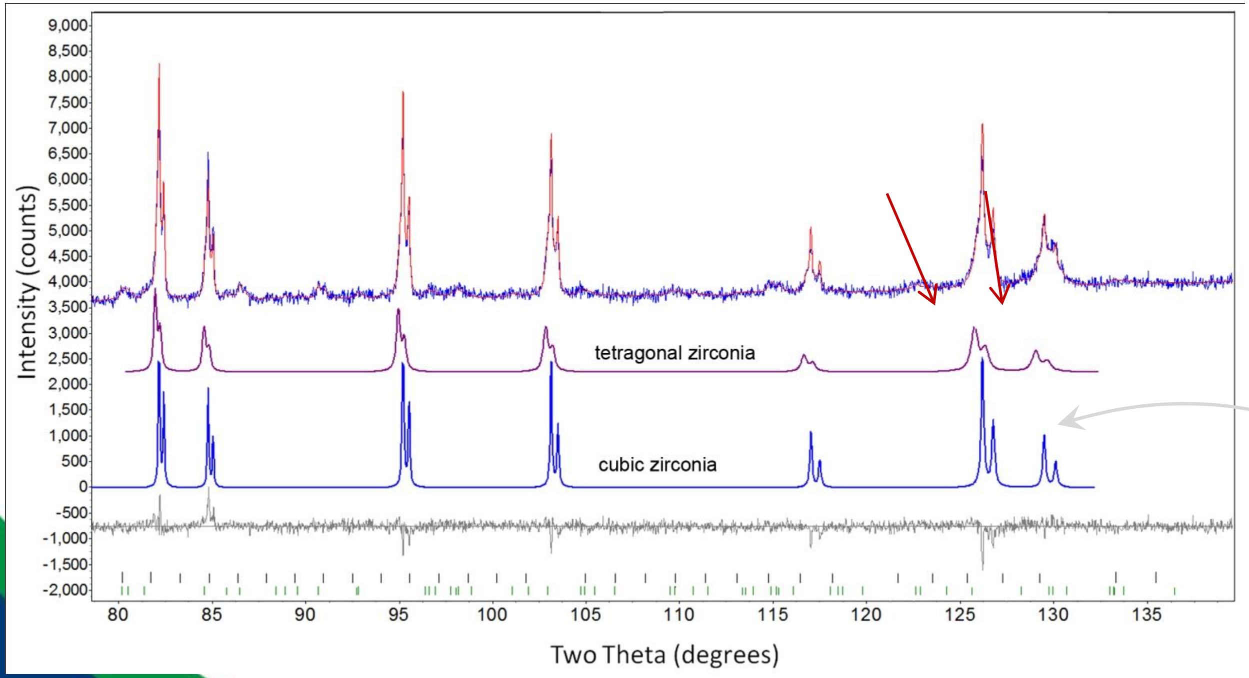
Ohmic contribution of interconnect in stack performance is significant

Bulk and Interfacial Stability: In-situ XRD Studies

XRD Approach to Detect Tetragonal form of YSZ

Mechanics of XRD: De-stabilization of the YSZ is invisible except under carefully optimized conditions

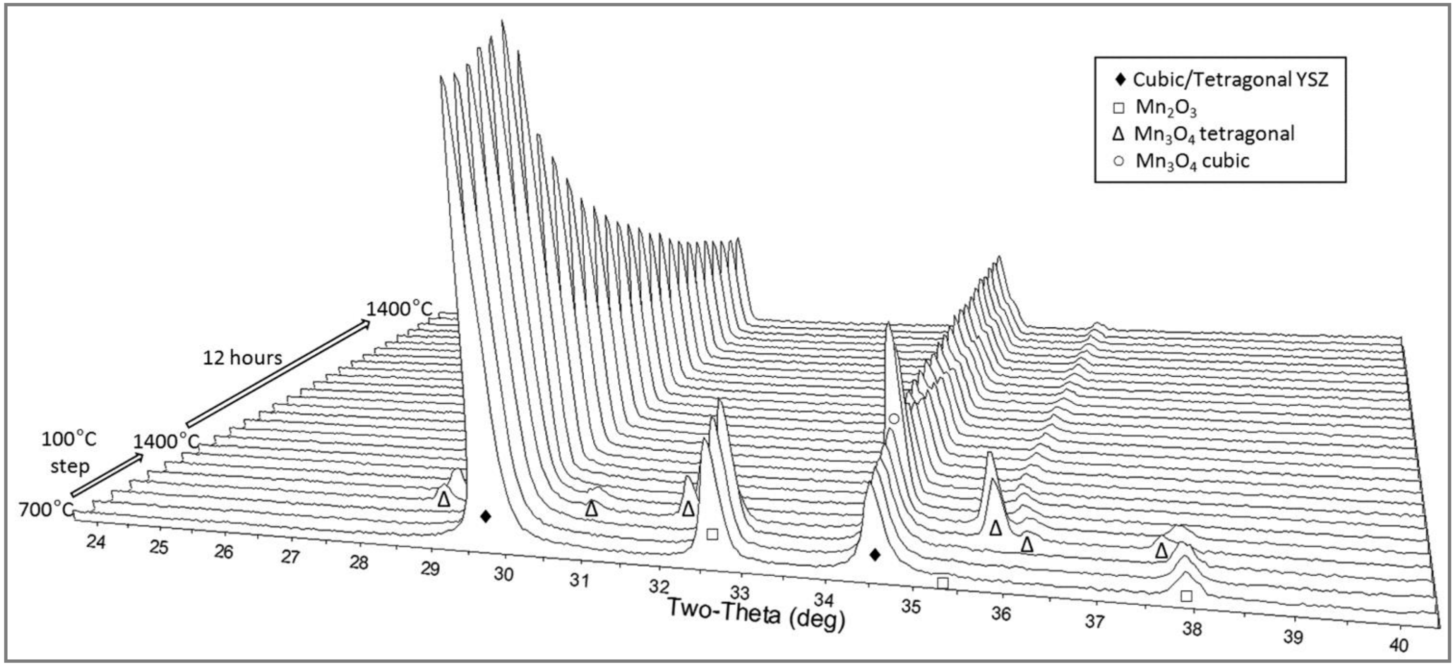
- Optimized XRD approach: Grazing incidence at 2, 4, and 6 degrees vs. coupled measurements – coupled measurements provide better peak shapes and more reliable quantification.
- Optimized fitting approach: Full-pattern Rietveld with very high 2θ data, fixed cubic YSZ initial lattice parameter, introduce T-ZrO_2, and then freely refine all variables



Peak width analysis shows small TYSZ crystallite size, suggests core-shell, diffusion-controlled reaction

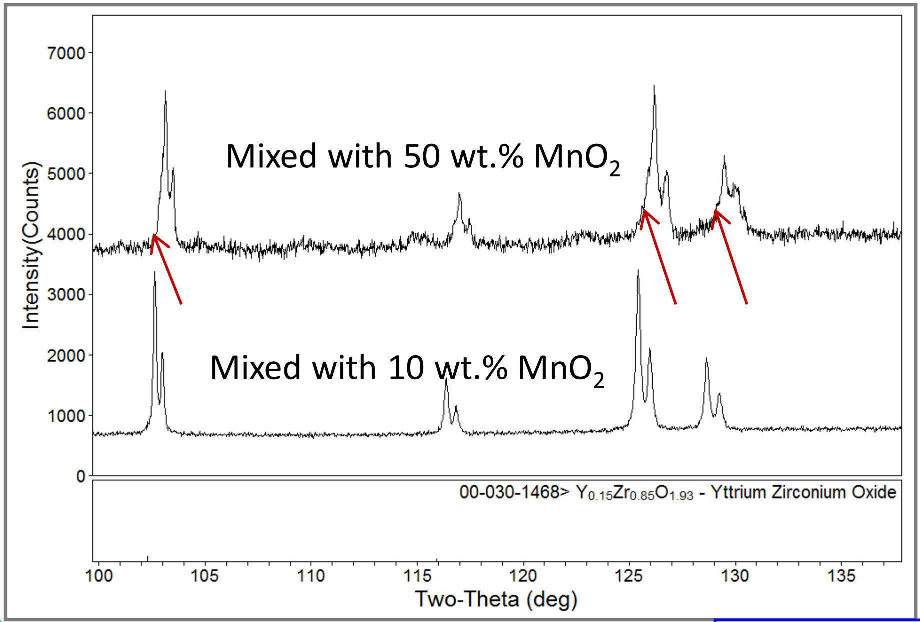
Mn Interaction with YSZ

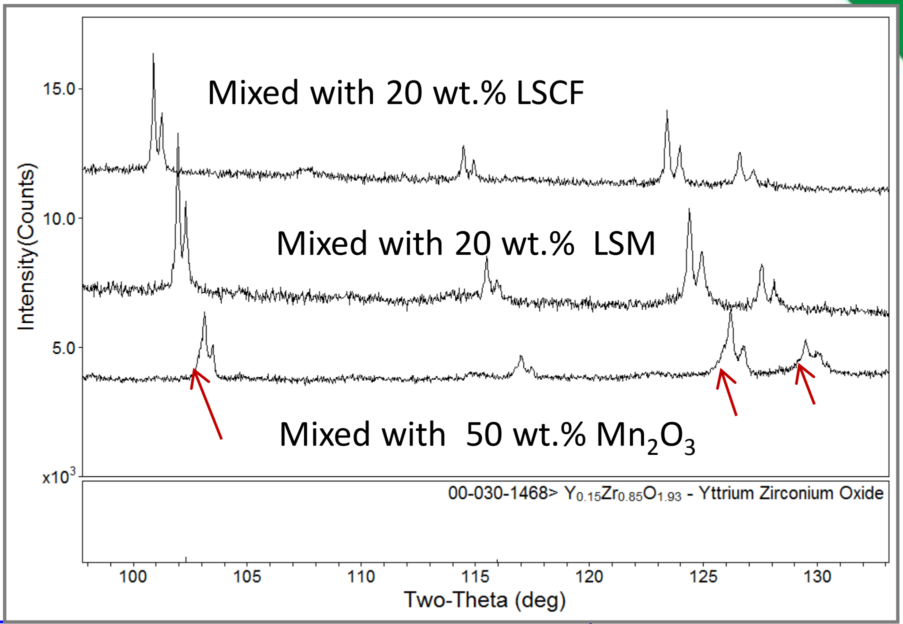
Can be observed using in-situ XRD with 1400°C hold, 12 hours, with MnO_2 admixed at 50 wt.%.



Mn Interaction with YSZ

Data are offset in x and y for clarity



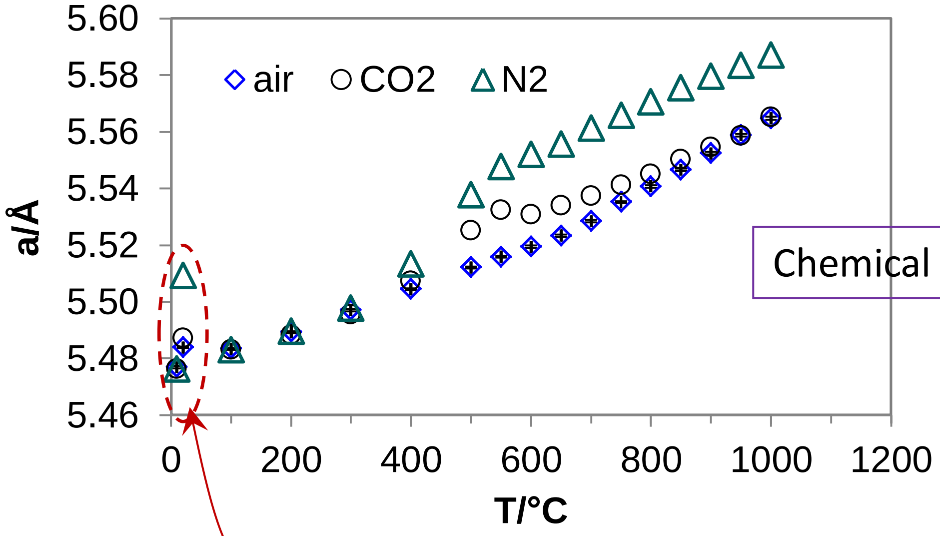


Low-angle shoulders are from tetragonal ZrO_2

- Lower MnO_2 concentrations make detection more difficult, as this is a diffusion-controlled reaction
- The reaction was NOT observed under <20wt.% added LSM and LSCF with YSZ
- No reaction of LSM with GDC noted in 12h at 1400°C (data not shown)

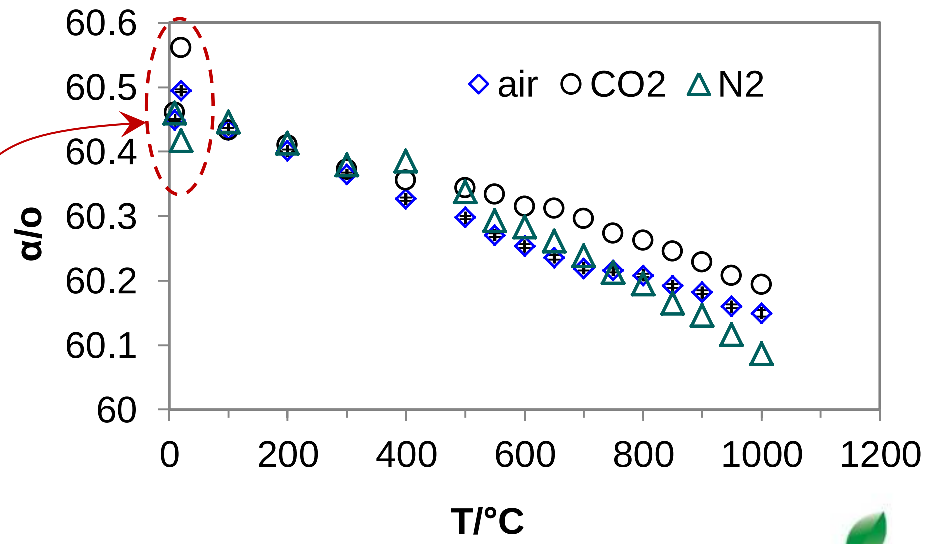
CTE for LSM in Different Atmospheres

Track unit cell size/volume with high accuracy *and* cell distortion (alpha angle for trigonal LSM)



Chemical expansion noted under reduced pO_2, as expected

RT values before and after cooling differ because of oxygen nonstoichiometry equilibration (chemical expansion)



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Summary

- LSM/YSZ/LSM symmetric cells have been tested in humidified air and CO2/air for up to 100hrs.
  - ✓ SrO/Sr(OH)2 has not been detected in the cells tested in dry air regardless of testing conditions.
  - ✓ SrO/Sr(OH)2 has been detected in the cells in presence of humidity in air.
  - ✓ Formation of (Sr/La) carbonates have been detected when the cell is tested in Air-10%CO2
- LSM degradation mechanism in humidified air has been developed.
- Ohmic contribution of AISI 441 interconnect on the performance of anode supported single cell (Ni-YSZ/YSZ/LSM-YSZ) has been measured and quantified.
- In-situ XRD investigation has been conducted to identify structural change of YSZ and compound formation/phase evolution due to interaction with manganese, LSM, and LSCF.
- XRD approach has been developed to detect tetragonal form of YSZ.
  - ✓ Manganese dissolution into YSZ destabilizes the cubic symmetry to tetragonal symmetry.
  - ✓ No reaction compound has been detected due to interaction of 20% LSM/LSCF with YSZ/GDC at 1400°C in air for <24h.

Future Work

- Post-test analytical study of cells operated in Air-10%CO_2 and development of degradation mechanisms
- AFM analysis of the post-test cathodes
- Electrochemical testing in Air/3% CO_2, Air-CO_2-H_2O atmospheres
- Evaluation of the role of air contaminants on the ohmic contribution from metallic interconnect in a single cell stack test approach
- Post test analytical study to find the source of ohmic contribution and related mechanisms
- In situ XRD study to precisely detect the phase evolution and structural changes of various cathodes and electrolytes resulting from solid-solid and solid-gas interaction
- Development of mechanistic understanding of cathode performance degradation Development of mitigation approaches for cathode degradation

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Thank You

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