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

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WORK PERFORMED UNDER AGREEMENT DE-FE - 0009682

15th Annual SECA Workshop
July 22-23, 2014, Pittsburgh, PA

Technical Contributors

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Outline

- Accomplishments
- Background
- Experimental
  - Role of Humidity and CO_2 on LSM and LSCF cathodes
    - Electrochemical performance
    - Post-test analytical study
- Results and Discussion
- Future Work
- Acknowledgements

Ambient Air Constituents

Gas	Concentration
Oxygen	20.9 v%
Nitrogen	78 v%
Water	<1 to 3 v%
Carbon dioxide	350 ppm
Sulfur dioxide	<1 ppm
Noble gases	<1 v%
Particulate matter (PM)	<50 μg/m^3

Air in fuel cell stack and system may also contain component derived impurities such as Cr (from metals and alloys) and Si, B, and alkali (from glass and insulation).

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

- In “real world” environment, cathode remains in intimate contact with electrolyte and interconnect at 750-900˚C to air which contains H_2O, CO_2, H_2S/SO_2 etc. The nominal intrinsic impurities in air contain ~3% H_2O, ~400 ppm CO_2 and 0.05-0.15 ppm SO_2
- Bulk and interfacial stability of cathode due to solid-solid and solid-gas interactions significantly contributes to the performance losses and degradation in planar 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) resulting in higher Ohmic loss.

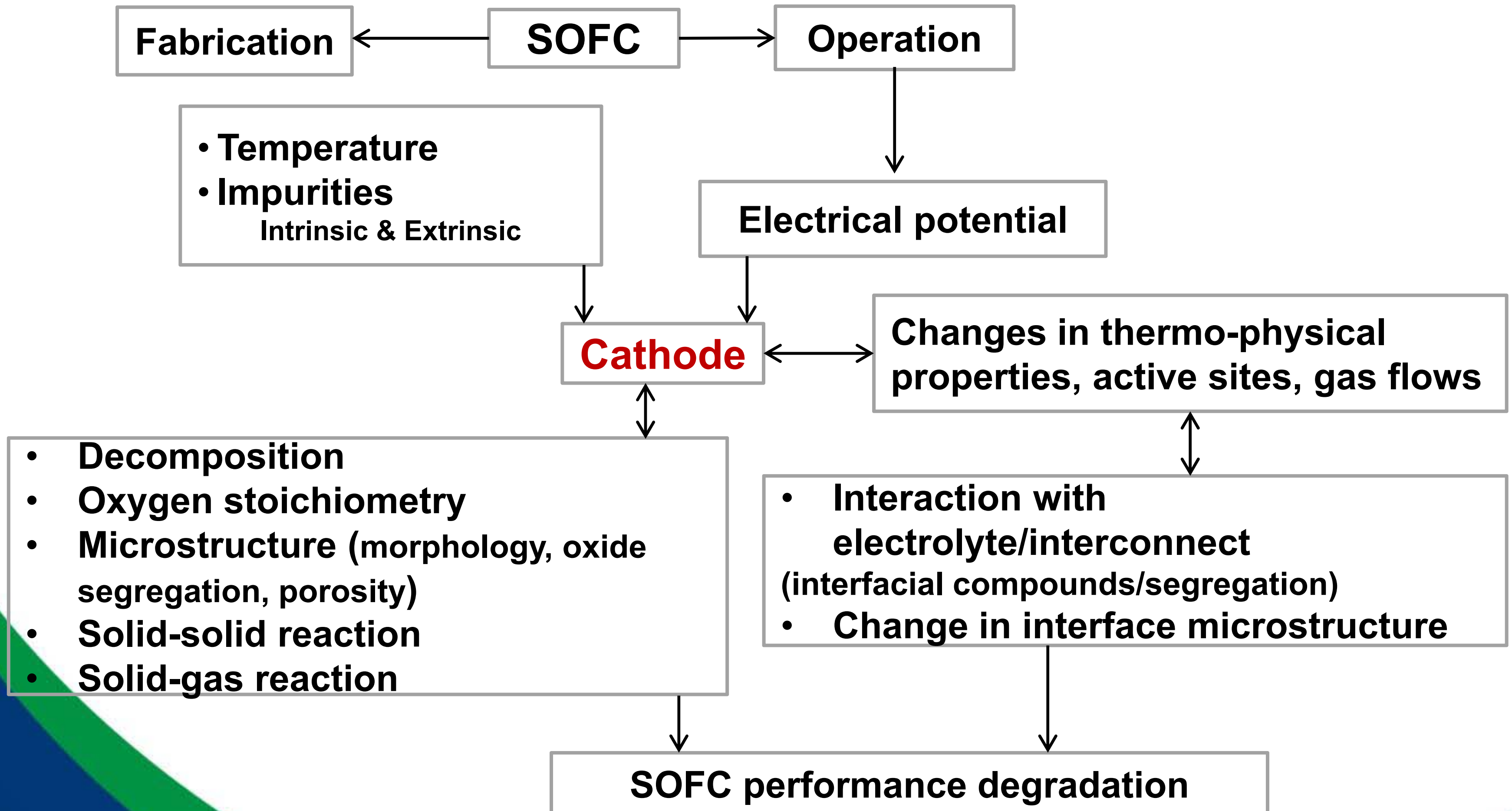
Contributing factors for poor contact:

- ✓ Thermodynamic driving force
- ✓ Operating characteristics (temperature distribution, thermal expansion mismatch, impurities in inlet air)
- ✓ Formation of interfacial compound and morphology change

- Solid-solid and solid-gas chemical interactions and elemental migration across bulk/interface also increases ohmic resistance due to insulating compounds formation and oxide segregation at the interface cathode/electrolyte and cathode/interconnect interface, and bulk cathode as well as well as at the surface.

Background

Cathode contributions: SOFC performance degradation



Accomplishments

- ❑ Electrochemical testing of LSM/YSZ/LSM symmetric cells in humidified air and CO_2/ air has been conducted and post-test analytical study (XRD, SEM-EDS, XPS, FTIR) have been performed.
- ❑ Electrochemical testing of LSCF/GDC/LSCF symmetric cells in CO_2/air has been conducted and post-test analytical study (XRD, SEM-EDS) has been performed.
- ❑ A1500-hour test of the LSM/YSZ/LSM symmetric cell has been performed in 3% H_2O and 0.5% CO_2 containing air. The findings include:
  - ✓ $SrO/Sr(OH)_2$ contribute to the cathode electrochemical degradation in humidified air.
  - ✓ Formation of (Sr/La) carbonates lead to the cathode degradation in CO_2/air.
  - ✓ LSM cathode degradation is more in humidified air than that in CO_2/air. Cathodic pre-activation in dry air minimizes the degradation. The effect of ≤0.5% CO_2 in air on LSM degradation is not measurable.
- ❑ Mechanisms for LSM cathode degradation in humidified air and CO_2/air have been developed and documented.

Technical Findings

- **Presence of H2O and CO2:**
- SrO segregates on LSM electrode surface in humidified air.
- Compound formation and segregation increase with water content and electric bias.
- Exposure of LSCF to Air-CO2 (10%) shows degradation. Further structural analysis is in progress.
- Carbonate (Sr/La) reaction products are not expected to form in ambient air (~400ppmCO2).
- Solid-solid and solid-gas interaction also increases ohmic resistance due to insulating compound formation and oxide segregation .
- LSM cathode performance during exposure to Air-CO_2 (10%) shows initial degradation.
- LSM cathode pre-activated in air reduces degradation during subsequent exposure to 10% CO_2-air
- Effect of CO_2 on the LSM stability is less pronounced than that of H_2O.
- Simultaneous exposure of LSM to 3%H_2O and 0.5% CO_2 in atmospheric air shows degradation. Further analysis is in progress.
- CE/MI interface ohmic resistance – a major contributor to stack performance losses
- Stack performance and ohmic resistance – not affected by 0.1% CO_2 and saturated H_2O in air in short term tests
- Coarsening of cathode microstructure, especially cathode surface, in long-term exposure at 800^{o}C (indicating potential of CE/MI interface contact evolution during long-term operation)

LSM-YSZ Interactions

- Addition of Ni and (Ni + Ca) to LSM eliminates YSZ phase transformation / degradation in air
- H_2O presence minimizes YSZ phase transformation
- Ni additions cause ~10% $La_2Zr_2O_7$ formation. (Ni+Ca) additions cause ~5% $La_2Zr_2O_7$ formation vs. ~3% for base LSM

Computational study:

- The surface cation chemistry in (La,*A*)MnO_3 (*A* = Ca, Sr and Ba) has been studied using first-principles thermodynamics.
- Surface remains significantly enriched with dopants under all realistic conditions.
- Over a wide range of T-pO_2 conditions the cation surface segregation is favored.
- With increasing dopant size the tendency for cation surface segregation increases.

Temperature : 750-850C
Time : 100 hrs. to >1000hrs.
Bias : 0 &0.5 V
H2O level : 0 -10%; CO2 level : 0 - 10%
H2O+CO2 : above combination.
Air electrode: LSM, LSCF
Electrolyte : YSZ, GDC

Impact and Technical Significance

- Observations and mechanistic understanding of chemical and morphological changes, derived from long term experiments, provide pathway for optimizing SOFC air electrode.
- Long term tests in CO_2 containing air atmospheres show LSM air electrode to remain chemically and structurally stable. Presence of H2O (RT saturated), however, show LSM to be susceptible to morphological changes.
- Studies provide insight into destabilization of YSZ
- The guideline for the selection of dopants obtained from DFT calculation is helpful in selecting suitable dopant and minimize strontium segregation issue.

Publications, Outreach

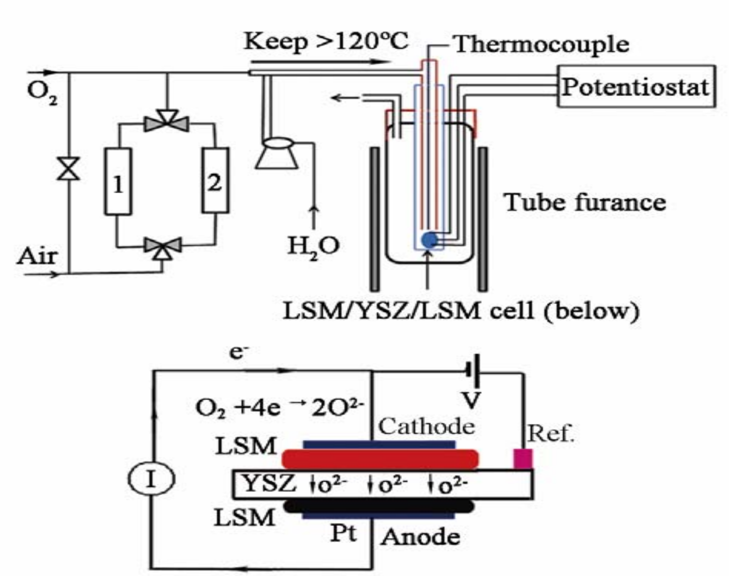
Publications/Presentations:

1. Boxun Hu, Michael Keane, Manoj K. Mahapatra, Prabhakar Singh" Stability of strontium-doped lanthanum manganite cathode in humidified air" Journal of Power Sources 248, 196-204, 2014
2. Boxun Hu, Manoj Kumar Mahapatra, Michael Keane, Heng Zhang, and Prabhakar Singh "Effect of CO_2 on the Stability of Strontium Doped Lanthanum Manganite Cathode" Journal of Power Sources 268, 404-413, 2014
3. Vinit Sharma, M.K. Mahapatra, P. Singh,& R. Ramprasad: Cationic surface segregation in doped LaMnO3, submitted to surface Science 2014
4. Manoj K. Mahapatra, Prabhakar Singh, Kyle McDevitt and Scott T. Misture, "Interfacial reactions of Mn-containing cathodes on YSZ electrolytes," Materials Research Society Spring Meeting 2014

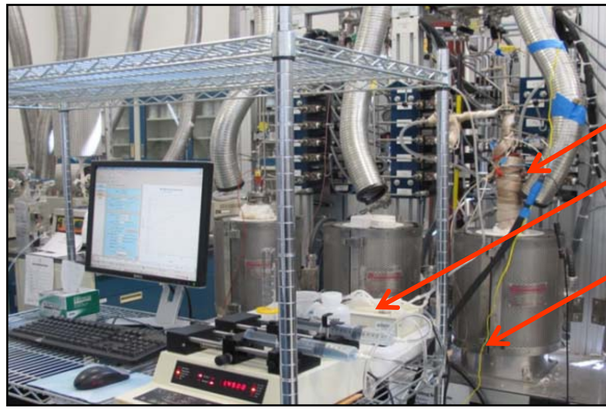
Outreach:

1. Industries : LG Fuel cells, FCE
2. STEM: K-12 , Undergraduate internship (2)
3. State Organization: CT DEEP
4. National Laboratory: PNNL
5. Training: 3 Post-doctoral Fellows, 3 Graduate students

Experimental



Schematic of the stability tests

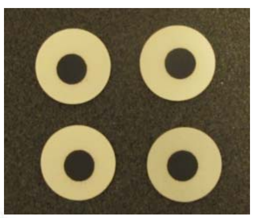


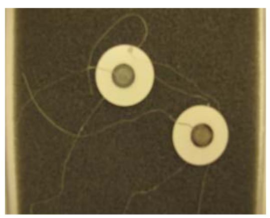
1. Reactor

2. Water Syringe pump

3. VMP2 Multichannel potentiostat

Facilities for the stability tests





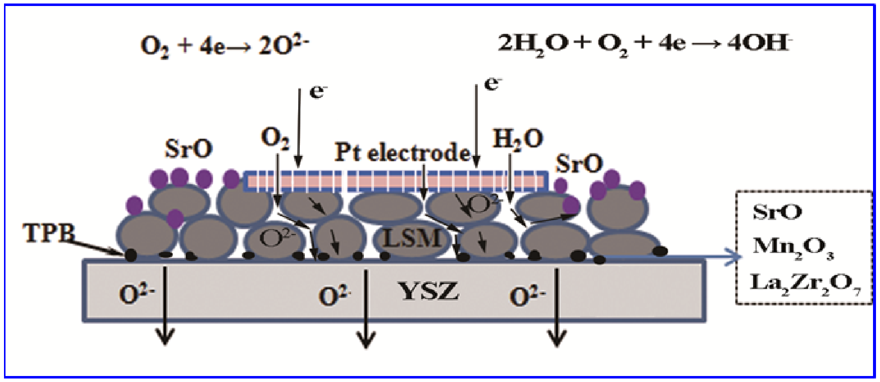
2.5 cm

LSM/YSZ/LSM cells

Screen printing

Temperature : 750-850C
Time : 100 hrs. to >1000hrs.
Bias : 0 &0.5 V
H2O level : 0 -10%
CO2 level : 0 -10%
H2O+CO2 : above comb.
Air electrode: LSM, LSCF
Electrolyte : YSZ, GDC

LSM Degradation Mechanism in Humidified Air



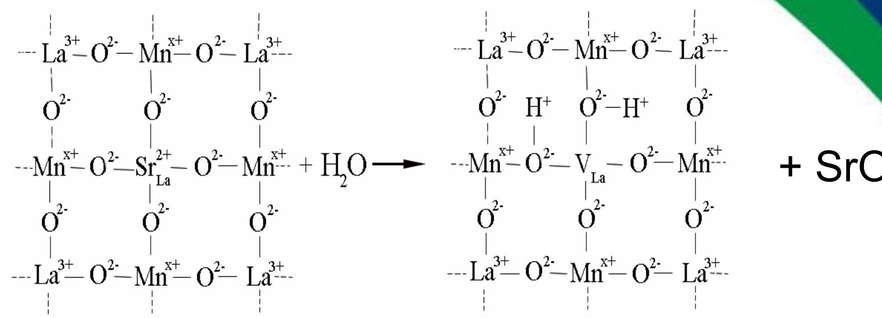


Illustration of the degradation of the LSM electrode in humidified air

A: SrO incorporation in the LSM lattice during activation:

$$V_{La}''' + SrO + 3Mn_{Mn}^{\bullet} + e' \leftrightarrow Sr_{La}' + 0.5O_2 + 3Mn_{Mn}^{x} \quad (1)$$

B: SrO segregation from the LSM lattice:

$$H_2O + Sr_{La}' + 2O_O \rightarrow SrO + V_{La}''' + 2OH_o^{\bullet} \quad (2)$$

without bias

$$1.5H_2O + 0.75O_2 + 3e' \rightarrow 3OH_o^{\bullet} + V_{La}''' + V_{Mn}'''$$

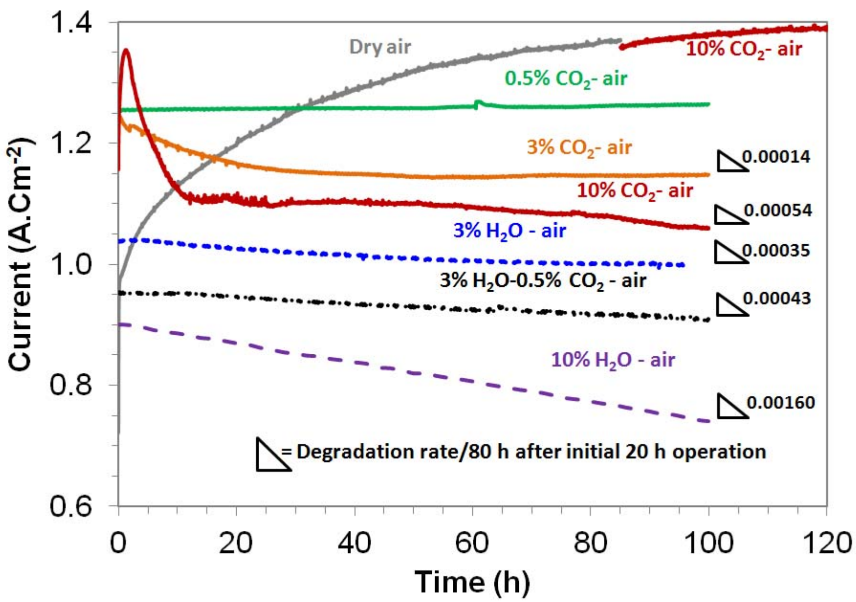
$$1.5Sr_{La}' + 3OH_o^{\bullet} + V_{Mn}''' \rightarrow 1.5SrO + 1.5H_2O + 0.5V_{La}'''$$

$$Sr_{La}' + 0.5O_2 + 2e' \rightarrow SrO + V_{La}''' \quad (3)$$

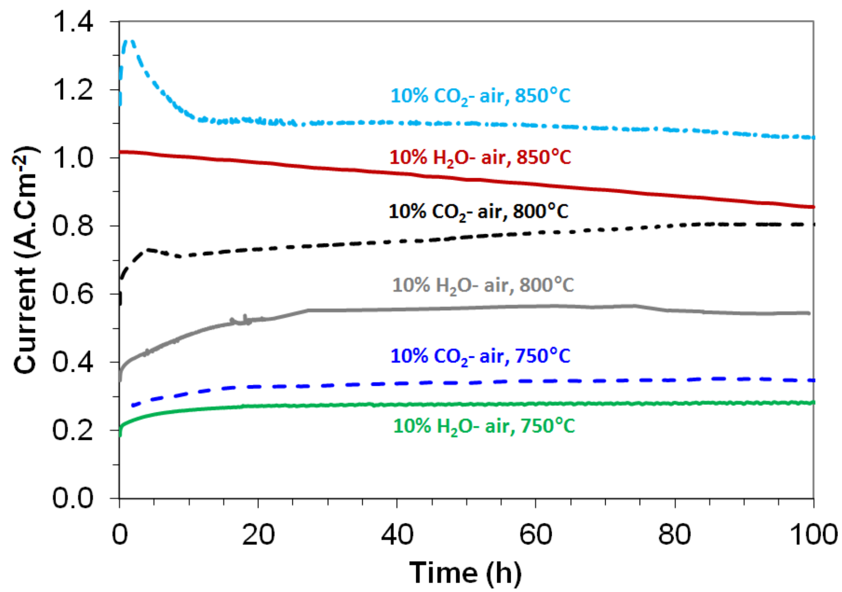
with bias

B. Hu, M. Keane, M. K. Mahapatra, P. Singh, Stability of strontium-doped lanthanum manganite cathode in humidified air, J. Power Sources, 248, (2014) 196-204.

Electrical Performance of LSM/YSZ/LSM cells



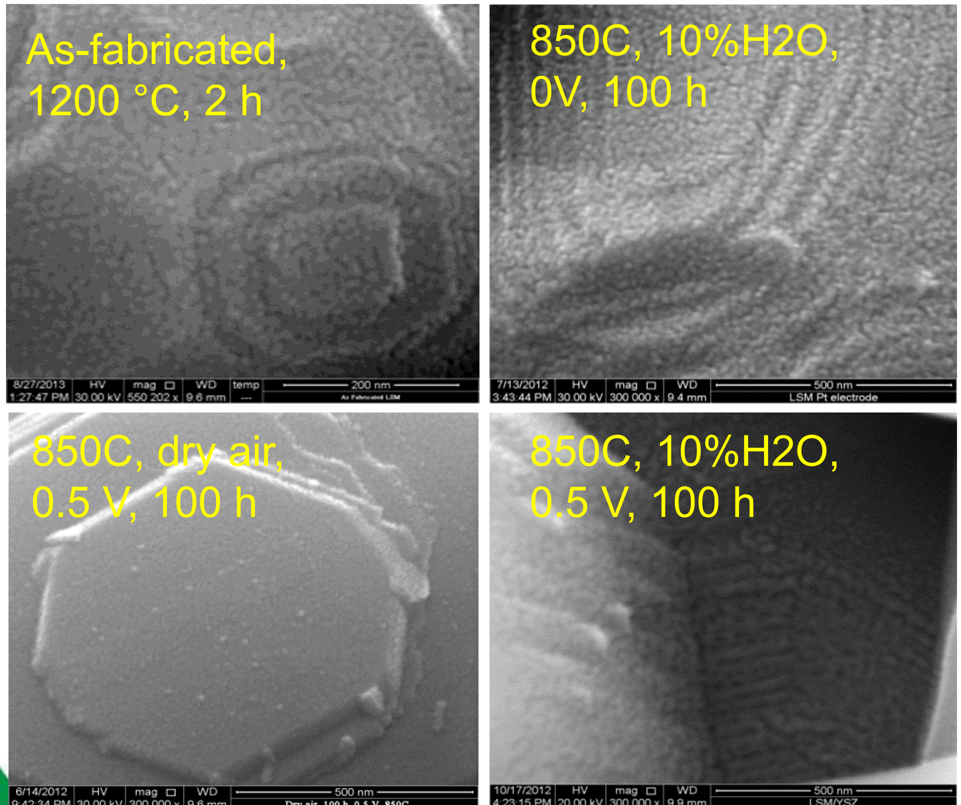
I-t plots of the LSM/YSZ/LSM cells at 850°C at different atmospheres



I-t plots of the LSM/YSZ/LSM cells at different temperatures

- H2O in air is more detrimental on the cell performance than CO2 in air.
- CO2 ≤0.5% in air has no/negligible effect.
- Cell performance degradation is not discernable for 10% CO2 in air for the cell preactivated in air.

LSM Cathode Morphology in Humidified Air

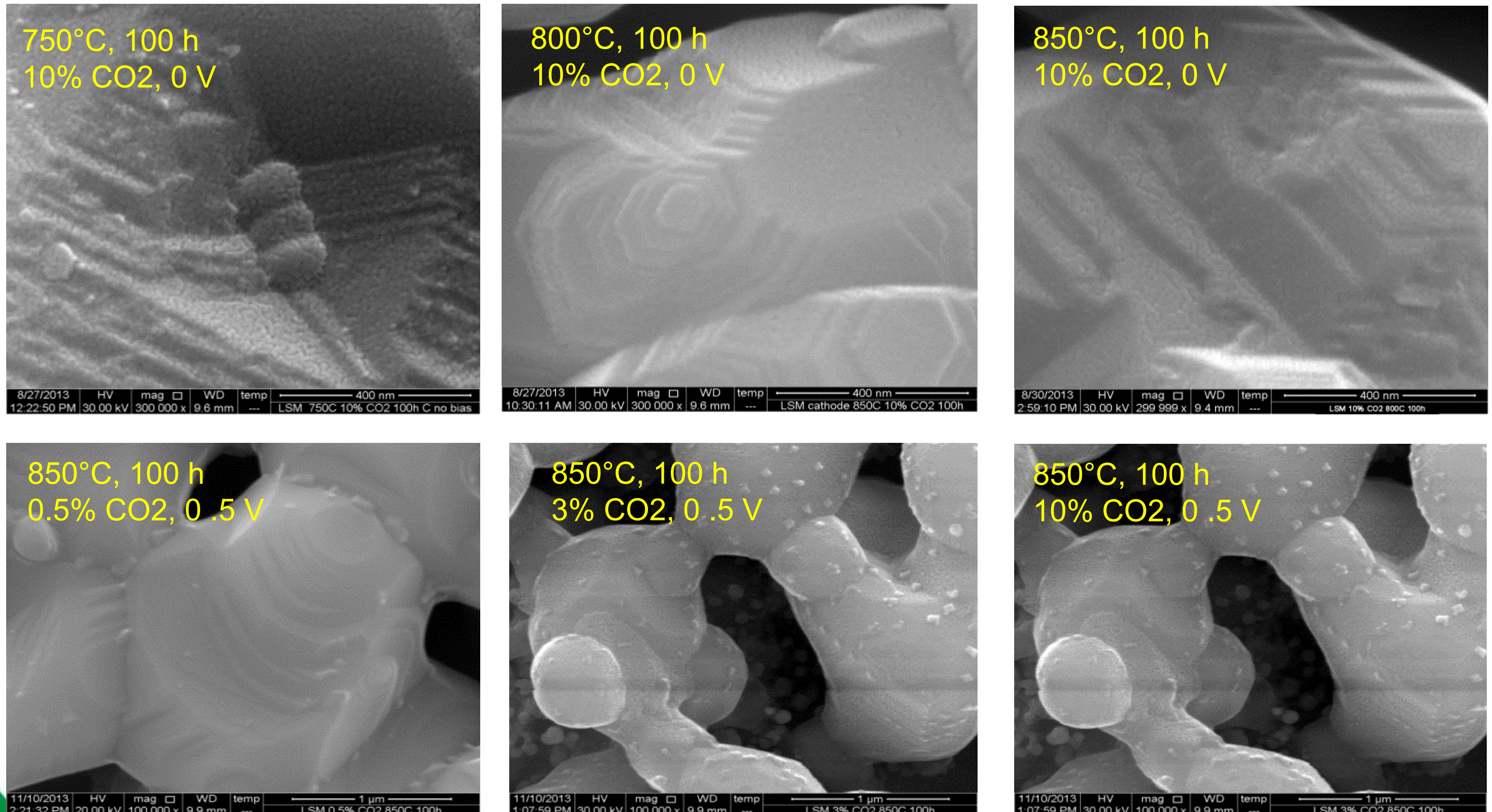


XPS analysis results of the LSM cathodes

Sample	Water%	Sr/La Molar ratio	Sr/(Mn+La) Molar ratio
Pre-test LSM	0	**0.23±0.01**	0.13±0.01
Post-test LSM	10	0.34±0.02	0.21±0.01
Post-test LSM	20	0.58±0.04	0.24±0.01
Post-test LSM	50	1.89±0.09	0.76±0.04

Morphology of LSM cathode at 850°C for 100 h without bias and with 0.5 V bias

LSM Cathode Morphology in CO_2- Air

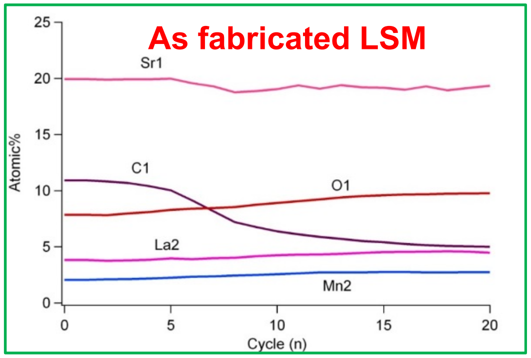


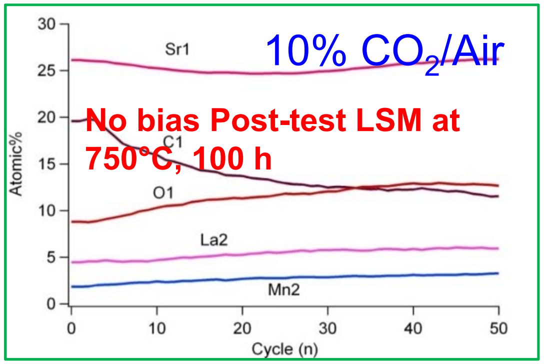
SEM images of the post-test LSM cathode in 10% CO_2/Air for 100h.

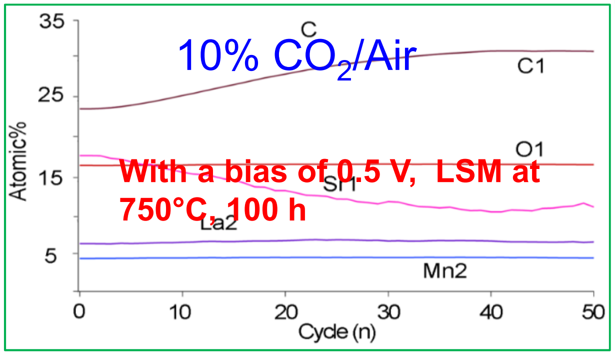
- segregation at the cathode surface for as-fabricated sample
- segregation ($SrCO_3$) decreases with increase in temperature in 10% CO_2/air

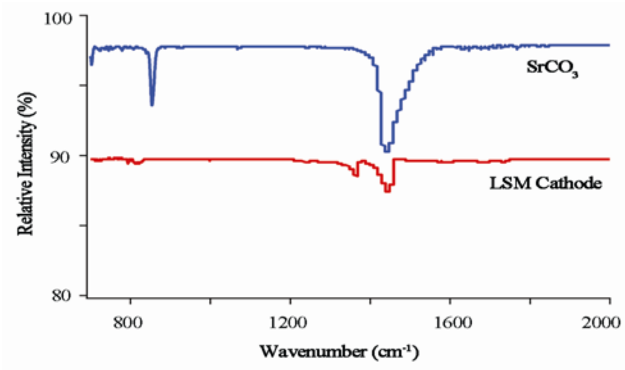
Spectroscopic study of LSM cathode

Auger depth profiling









LSM Surface rich in Sr and carbon (about 30-40 nm), indicating the existence of $SrCO_3$

FT-IR patterns of the post-test LSM cathode in 10% CO2-air with 0.5 V for 100 h (750C)

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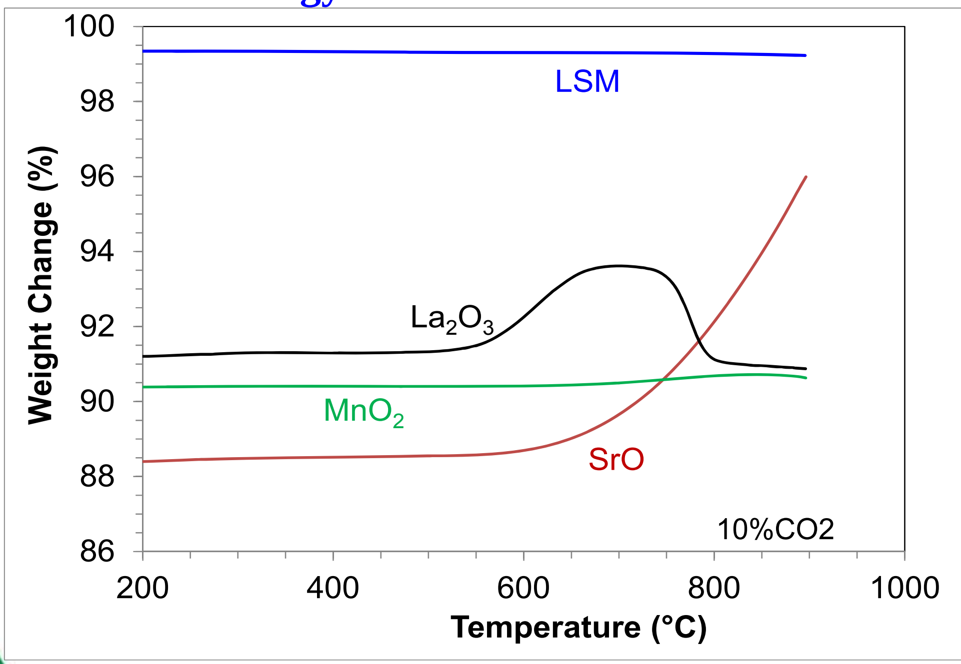
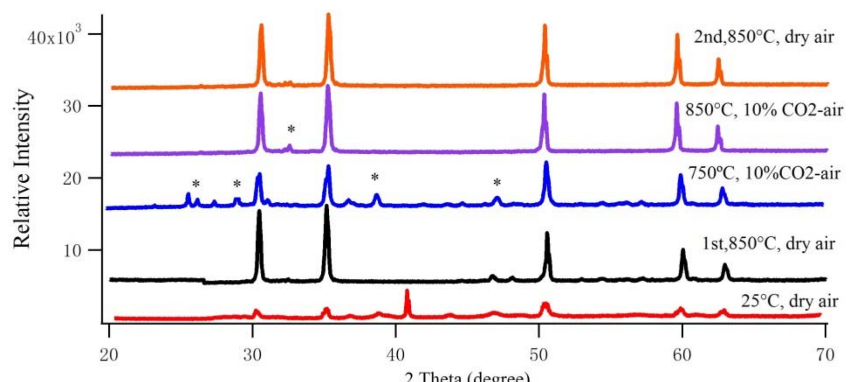
Thermochemical Analysis

Gibbs free energy of the carbonate formation



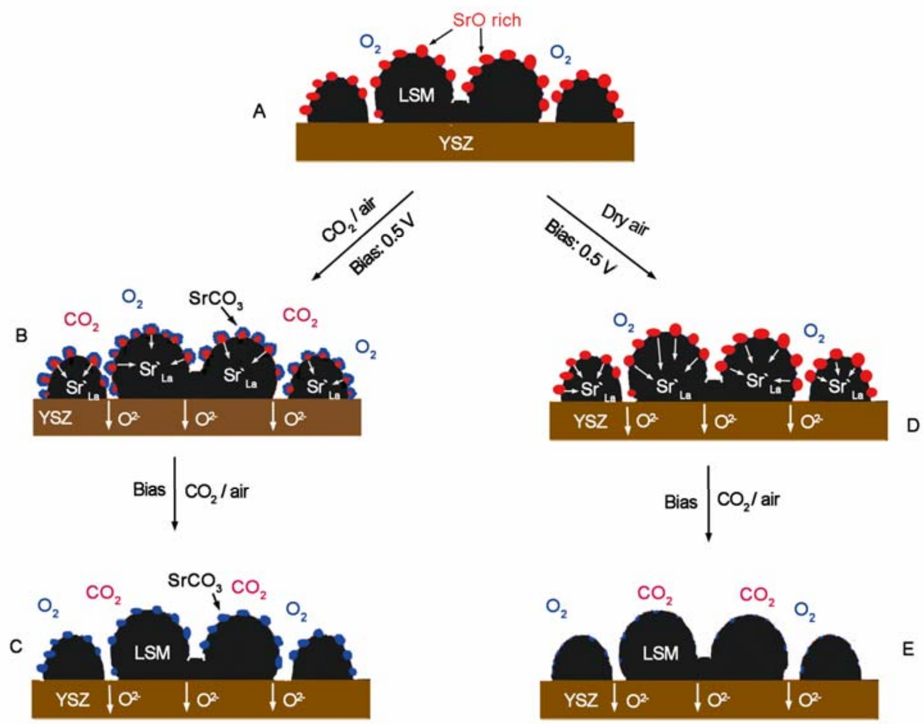
Temp (K)	CO_2 content	298	1000	1100	1200
ΔG_{SrCO_3}	100%	-189.2	-71.9	-55.9	-40.1
ΔG_{SrCO_3}	10% in air	-183.5	-52.8	-34.9	-17.1
ΔG_{SrCO_3}	400 ppm in air	-163.0	16.2	41.0	65.6
$\Delta G_{La_2O_2CO_3}$	100%	-147.3	-31.6	-15.9	-0.5
$\Delta G_{La_2O_2CO_3}$	10% in air	-141.6	-12.5	5.1	22.5
$\Delta G_{La_2O_2CO_3}$	400 ppm in air	-121.1	56.5	81.0	105.2



$$SrO(s) + CO_2(g) \leftrightarrow SrCO_3$$

$$La_2O_3(s) + CO_2(g) \leftrightarrow La_2O_2CO_3$$

LSM degradation in CO_2



Observation I: The electrical performance of LSM cathode initially increases in CO_2-air : It is known that the LSM surface is SrO enriched. The change in cathode performance during initial testing in CO_2-air can be explained similarly as LSM activation mechanism in dry air. With cathodic bias (0.5 V), SrO incorporates into the LSM lattice and oxygen vacancies form at the LSM .

Observation II: The electrical performance of LSM decreases after initial activation and remains unchanged for the remaining test period**.** SrO at the surface reacts with CO_2 to form $SrCO_3$ simultaneously with the CO_2 adsorption. $SrCO_3$ at the surface may block oxygen adsorption sites and subsequent desorption, decreasing the cathode performance. Once the SrO at the surface is incorporated completely into the LSM lattice during activation stage, no more $SrCO_3$ may form at the surface to block sites for oxygen reduction reaction. As a result, the performance does not degrade further with time.

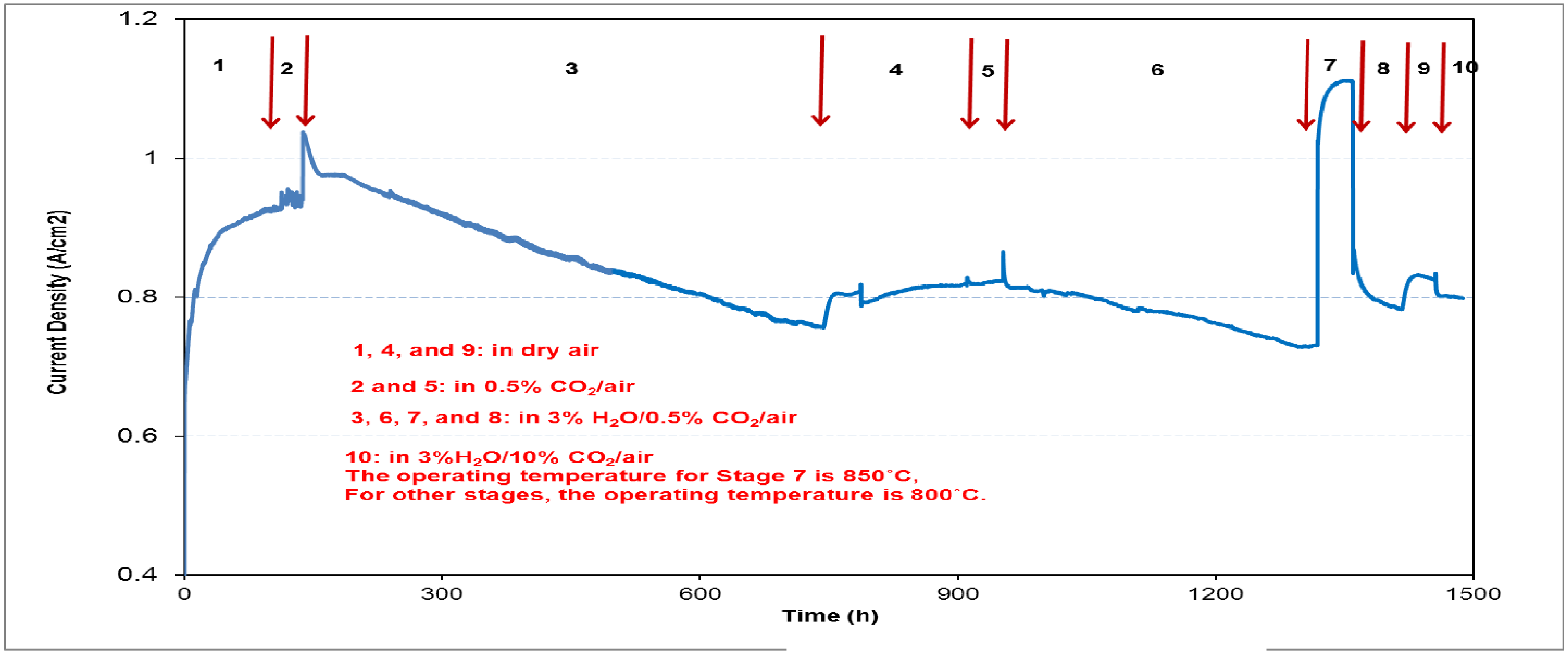
Observation III: The electrical performance of LSM does not decrease in CO_2-air for the samples pre-activated in air. After the activation of LSM in air, the $SrCO_3$ content will not increase due to absence of SrO at the LSM surface. As a result, the electrical performance does not decrease.

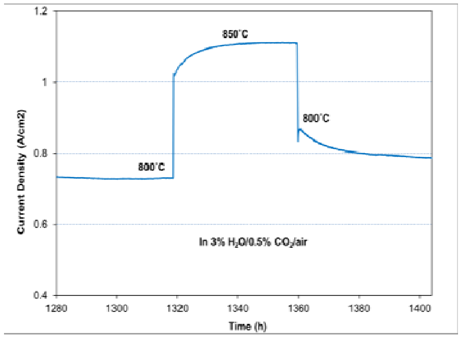
$$V'''_{La,LSM} + SrO + 3Mn^{\cdot}_{Mn,LSM} + e' \leftrightarrow Sr'_{La,LSM} + O^{x}_{o,YSZ} + 3Mn^{x}_{Mn,LSM}$$

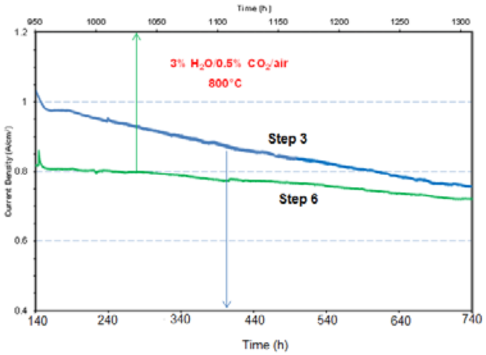
$$O^{x}_{O,LSM} + 2Mn^{x}_{Mn,LSM} + V^{\bullet\bullet}_{O,YSZ} + 2e' \leftrightarrow V^{\bullet\bullet}_{O,LSM} + 2Mn'_{Mn,LSM} + O^{x}_{O,YSZ}$$

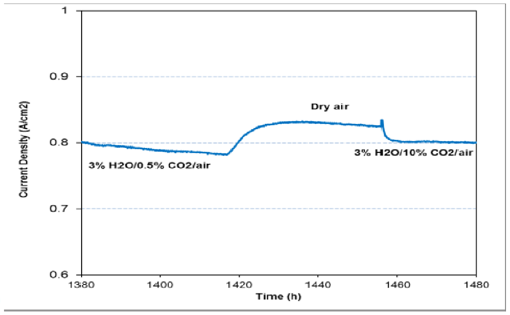
Boxun Hu, Manoj Kumar Mahapatra, Michael Keane, Heng Zhang, and Prabhakar Singh "Effect of CO_2 on the Stability of Strontium Doped Lanthanum Manganite Cathode" Journal of Power Sources 268, 404-413, 2014

Long Term Electrochemical Performance









Zoom-in I-t curves of the LSM/YSZ/LSM symmetrical cell testing in 3% H2O-0.5% CO2-air with 0.5 V bias

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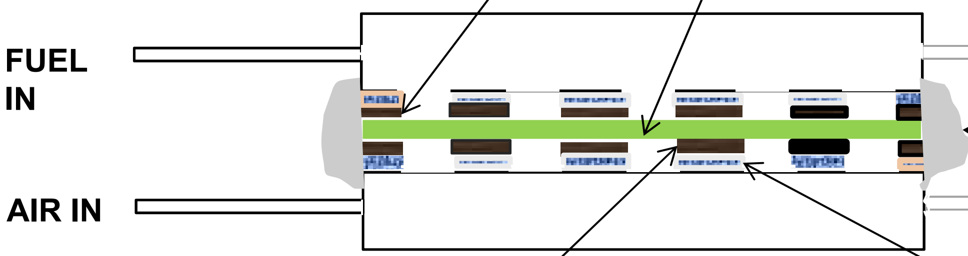
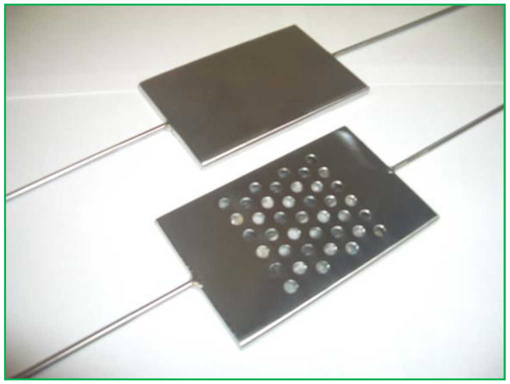
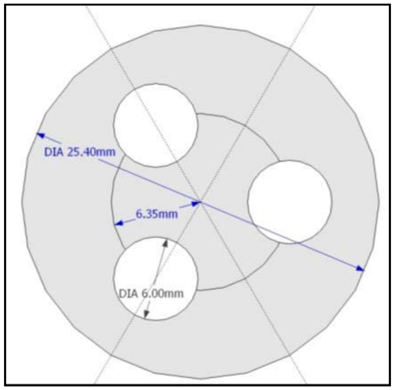
Single Cell (Ni-YSZ/YSZ/LSM) Stack Setup

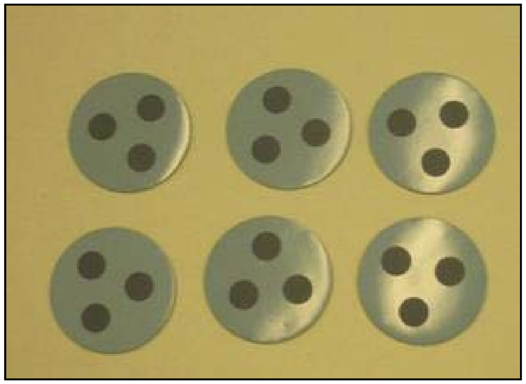




Gas Manifolds

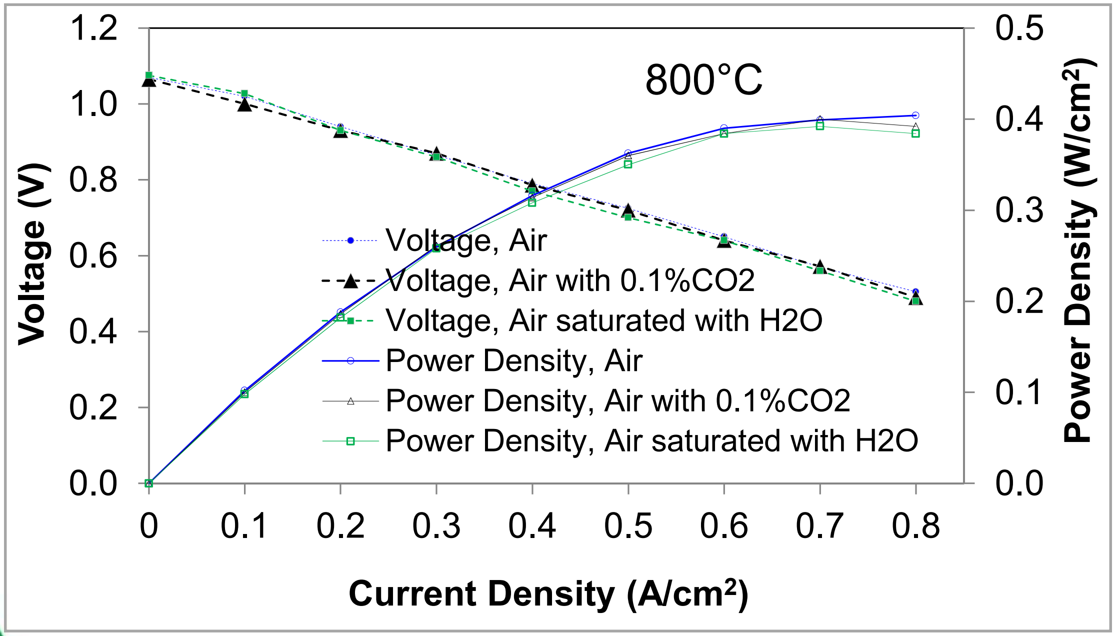


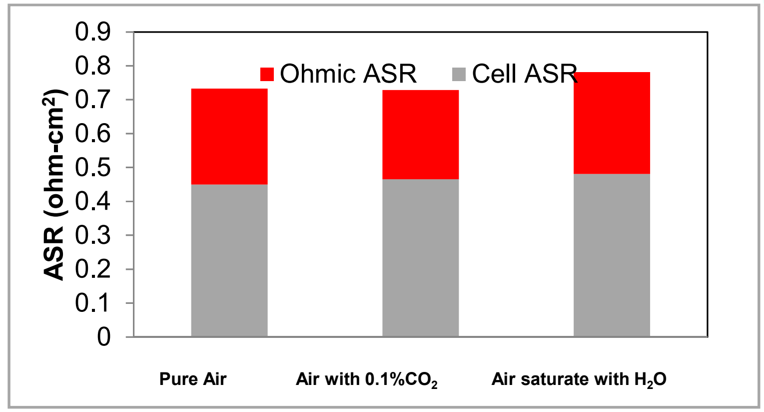
Button Cell Design



Photograph of Fabricated Cells

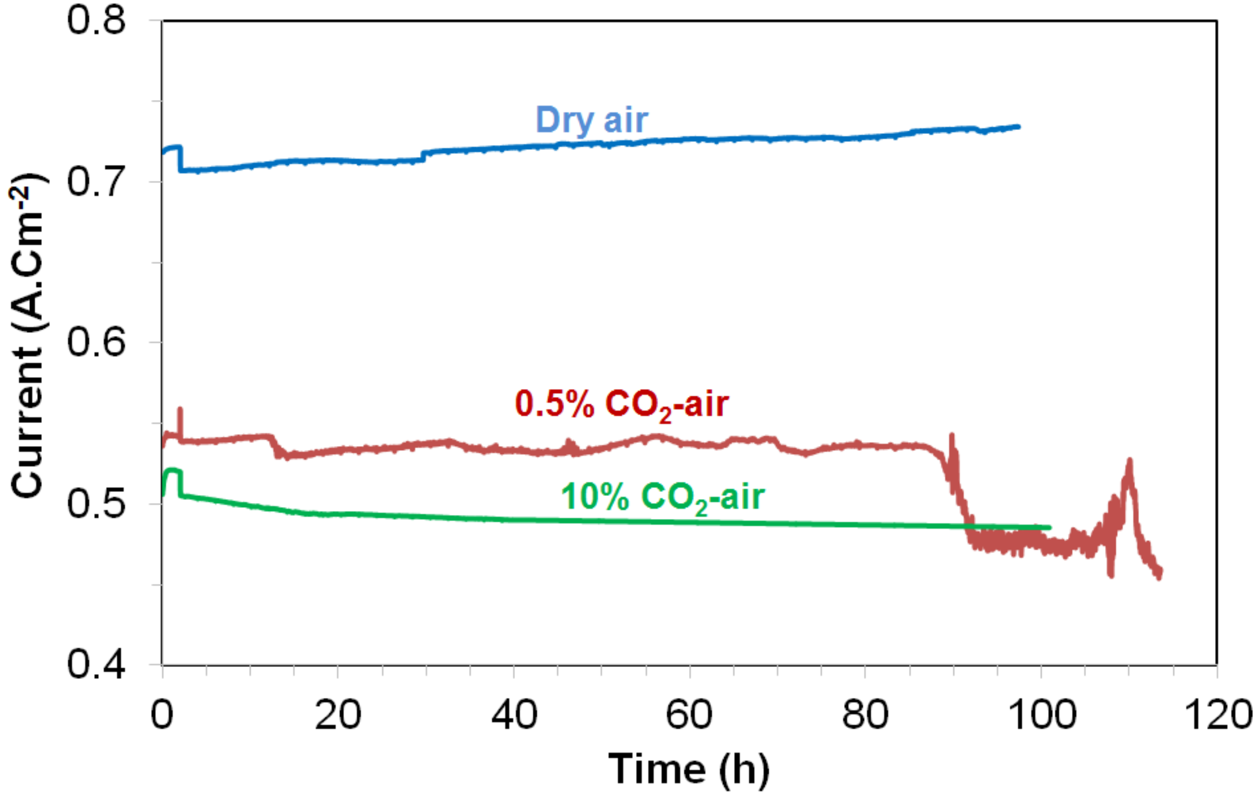
Performance of Single Cell Stack in different atmosphere





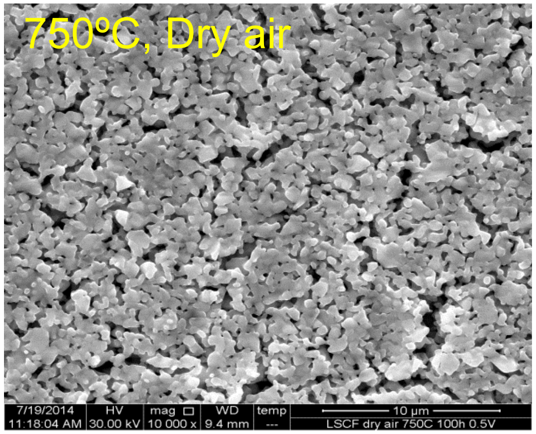
Performance as well as ASR is comparable in air, 0.1% CO_2/air, and air with H_2O (~3%)

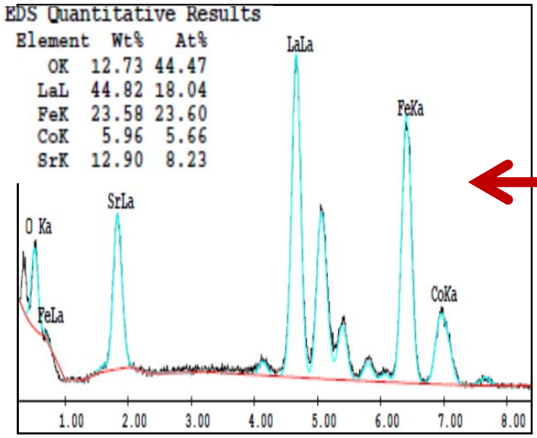
LSCF: CO_2-air

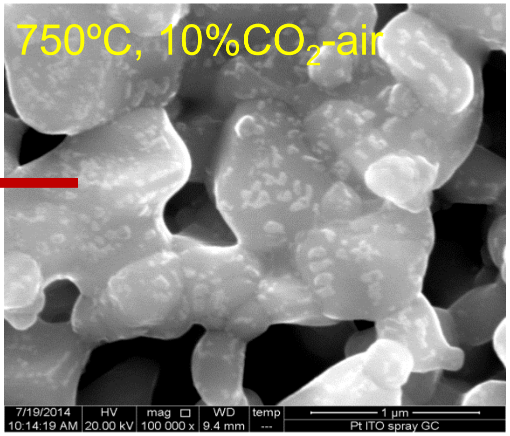


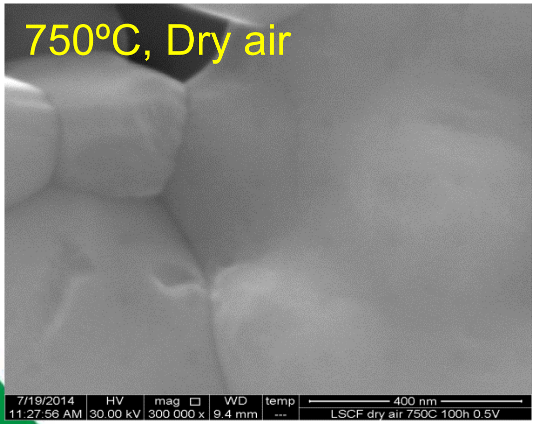
I-t plots of the LSCF/GDC/LSCF cells at 750°C with 0.5 V bias

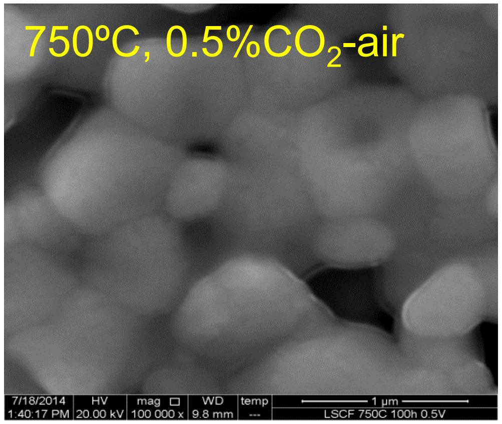
LSCF Cathode Morphology in Air- CO_2

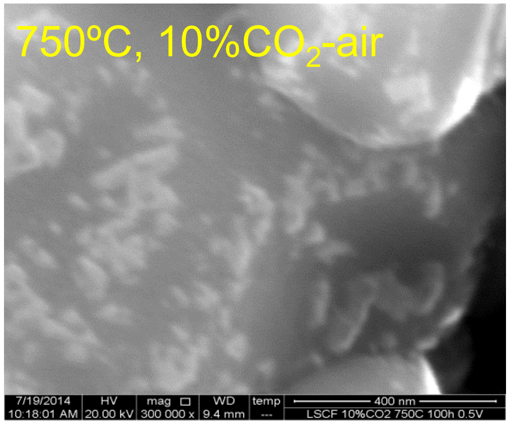






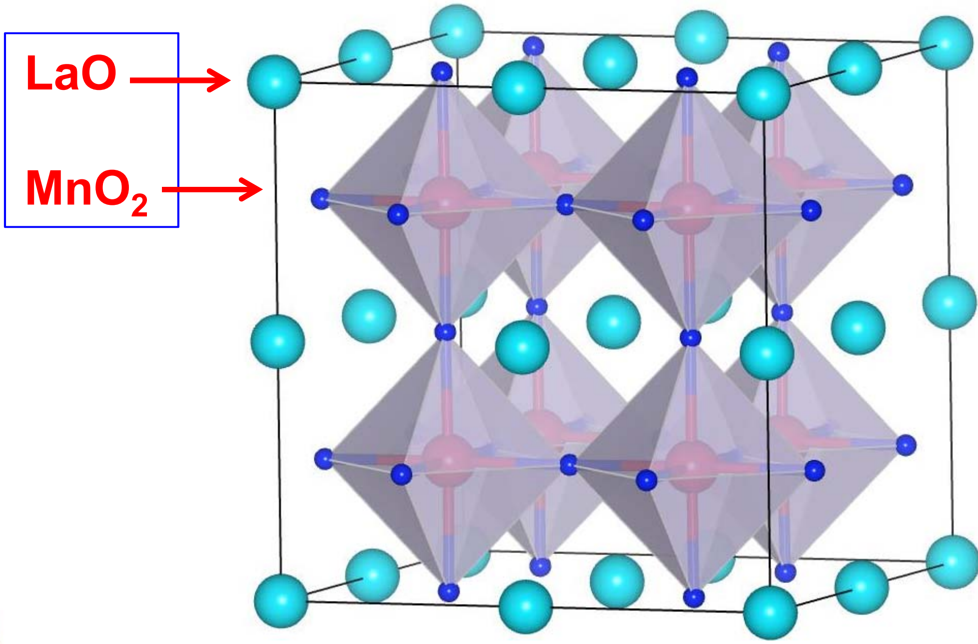






- Three LSCF/GDC/LSCF cells have been tested at 750ºC with 0.5 V bias for 100 hours.
- Extent of segregation (Sr /La Carbonate) increases with CO_2 contents in air

Computational Details



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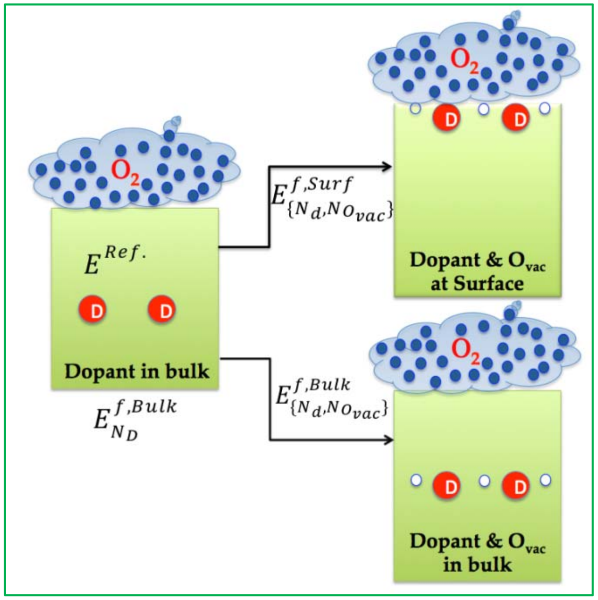
- Density Functional Theory (DFT) as implemented in Vienna *ab initio* Simulation Package (VASP) is used.
- Exchange-Correlation: Perdew-Burke-Ernzerhof (PBE).

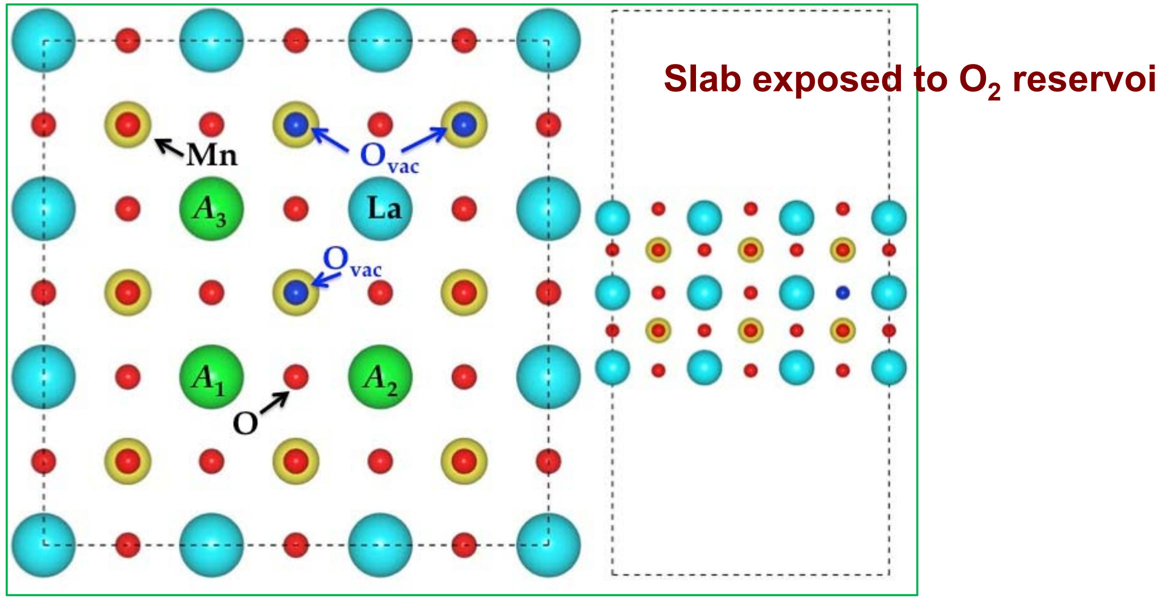
- For undoped LMO- MnO_2 terminated surfaces are energetically favored.
- In the presence of dopants LaO-terminated surfaces are favored.
- LaO-terminated (001) surfaces are considered.
- In (3x2) surface unit cell two La atoms are substituted by Sr.

Surface chemistry of (La,*A*)MnO_3

We investigated the surface cation chemistry in (La,*A*)MnO_3 where *A*=Ca, Sr or Ba when exposed to pure oxygen using first-principles thermodynamics.



Schematic representation of the surface segregation (La,*A*)O terminated slab.

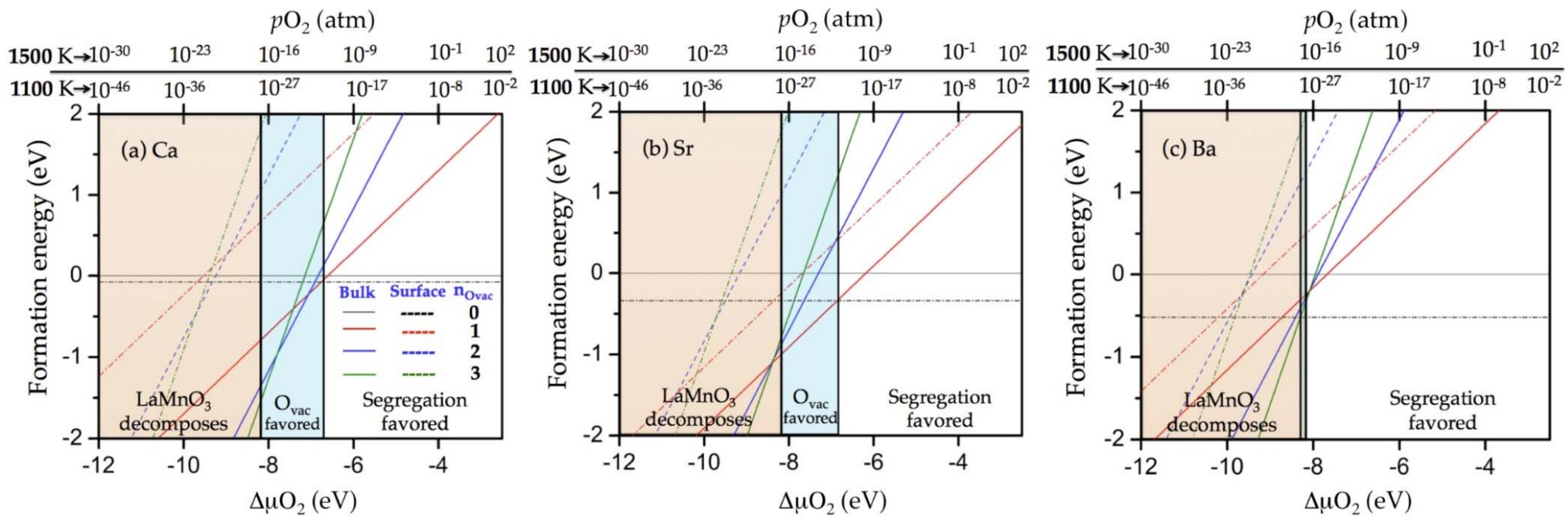


Top-view and side-view of the (La,*A*)O terminated (001) surface model.

Formation energy

$$E^{f,Surf/Bulk}_{\{n_D,n_{O_{vac}}\}} = \left(E^{Surf/Bulk}_{\{n_D,n_{O_{vac}}\}} - E^{Bulk}_{\{n_D,n_{O_{vac}}=0\}}\right) + \frac{n_{O_{vac}}}{2}\mu O_2$$

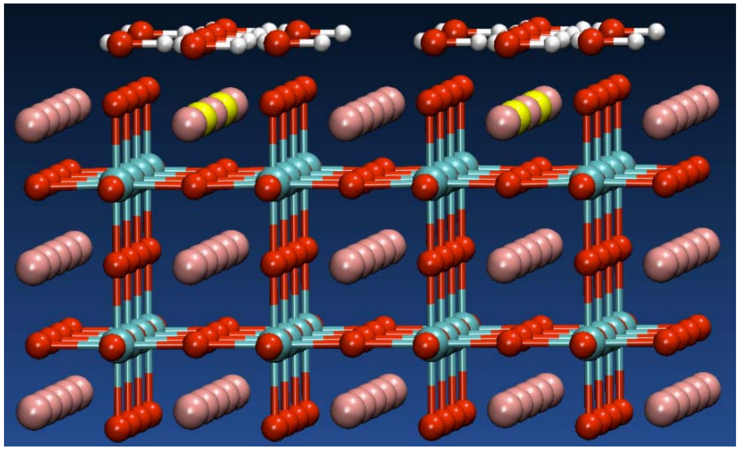
Cationic surface segregation under O_2 environment



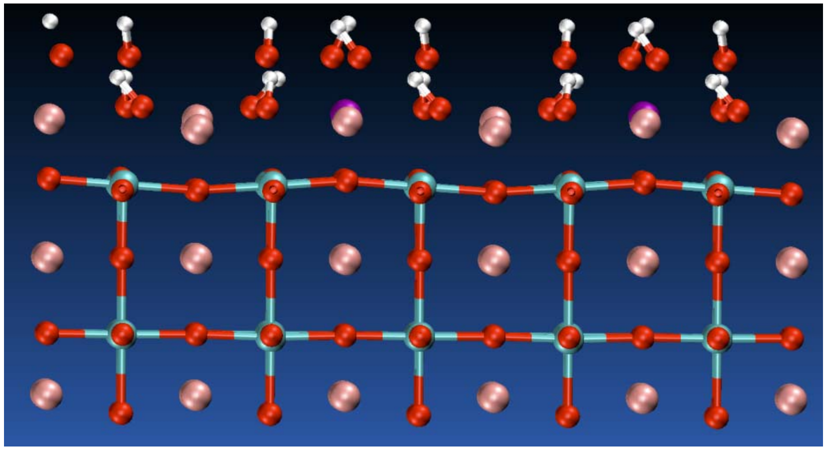
- **Surface remains significantly enriched with dopants under all realistic conditions.**
- **Over a wide range of *T-pO*$_2$ conditions the cation surface segregation is favored.**
- **Under low *O*$_2$ pressures and/or high *T* the segregation behavior is suppressed.**
- **With increasing dopant size the tendency for cation surface segregation increases.**

Vinit Sharma, M.K. Mahapatra, P. Singh,& R. Ramprasad: Cationic surface segregation in doped LaMnO3, submitted to surface Science 2014

Model details



Initial



Final

- The water molecule dissociates into two adjacent hydroxyl groups.
- The two hydroxyl groups are tilted toward each other, suggesting the formation of a hydrogen bond.

Work in progress

Effect of water on cation surface segregation.

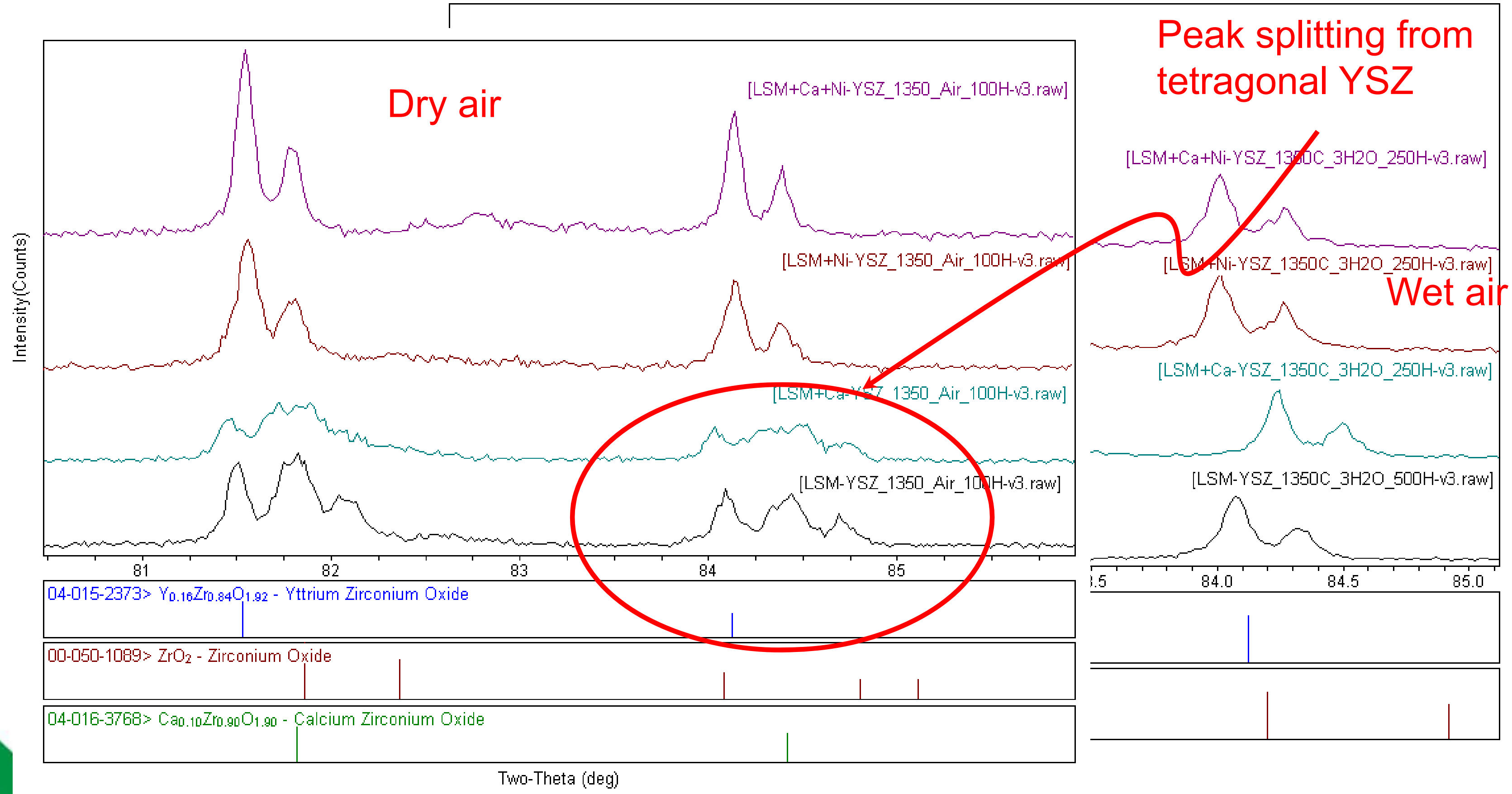
How Oxygen vacancies affect the cation surface segregation in presence of water.

Summary

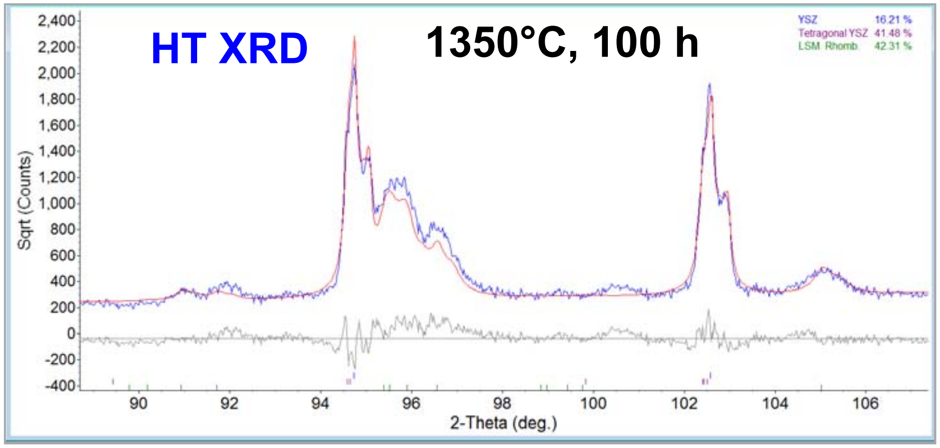
- **The surface cation chemistry in (La,*A*)MnO_3 (*A* = Ca, Sr and Ba) has been studied using first-principles thermodynamics.**
- **Surface remains significantly enriched with dopants under all realistic conditions.**
- **Over a wide range of T-pO_2 conditions the cation surface segregation is favored.**
- **Under low O_2 pressures and/or high *T* the segregation behavior is suppressed.**
- **With increasing dopant size the tendency for cation surface segregation increases.**
- **Dissociative absorption of water on (La,*A*)O-terminated surface in energetically more favored.**

Impact of 3% H_2O: Accelerated condition of 1350°C

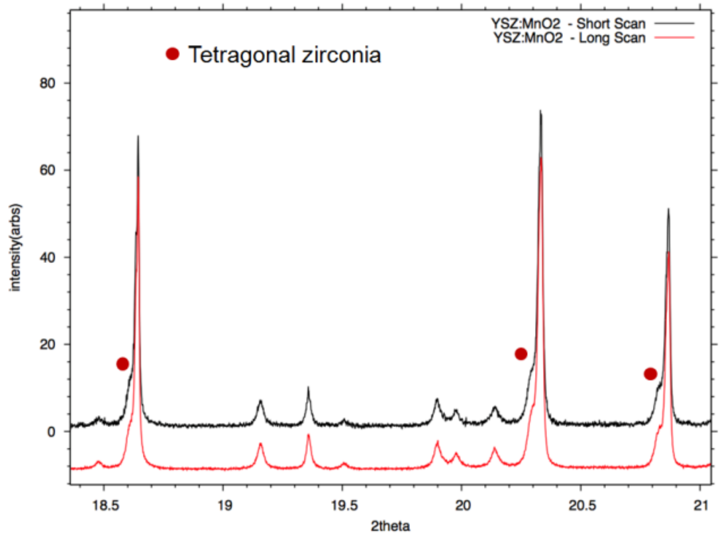
- Water inhibits the degradation to tetragonal YSZ
- Ni and Ni + Ca inhibit degradation



Stability of LSM and YSZ



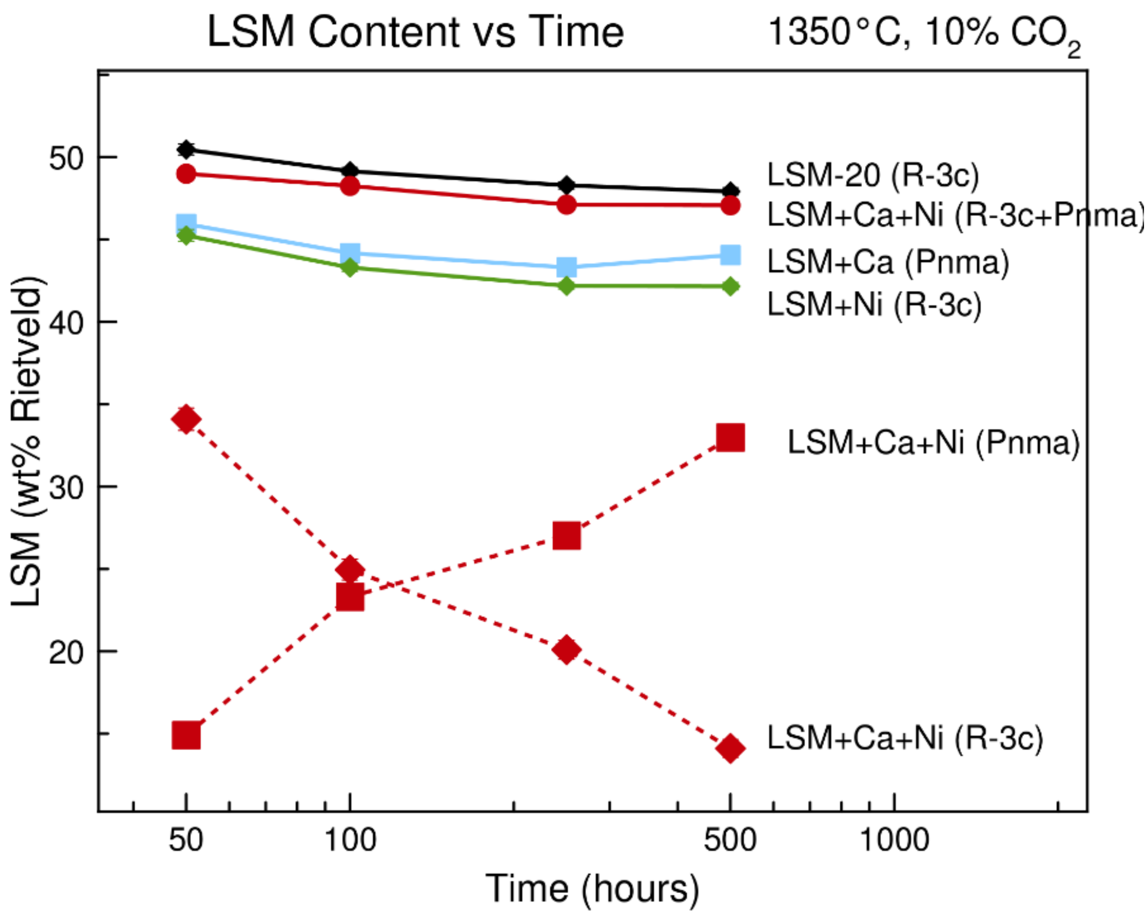
Optimized fitting of the pattern



Synchrotron data from BM-11 at APS for the MnO-YSZ sample reacted at 1400°C for 12 hours

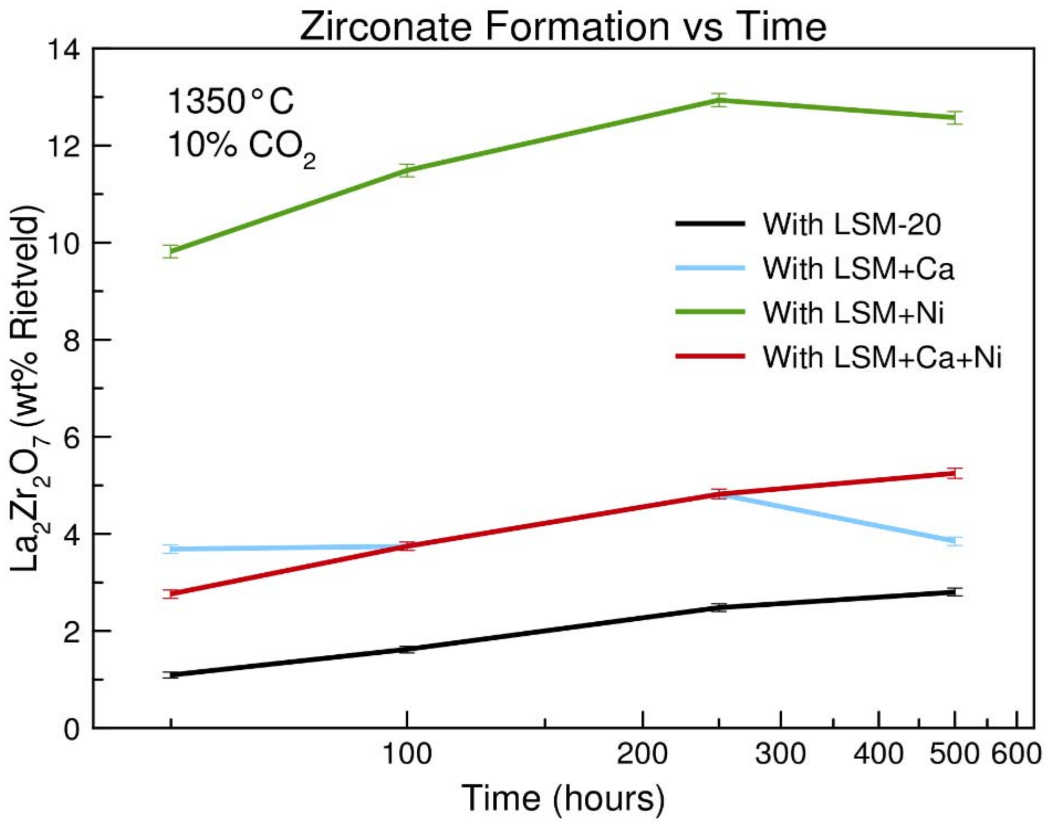
Cubic YSZ transforms partially to tetragonal polymorph due to LSM/YSZ and YSZ/MnO_2 interaction

Rhombohedral to orthorhombic transformation



1350°C, 10% CO_2 in air: Ca-modified LSM transforms quickly to orthorhombic. (Ca+Ni) stabilized LSM transform partially to the orthorhombic form over 500+ hours. Probably related to Mn oxidation state changes.

Ni substitution increases $La_2Zr_2O_7$ formation for 10% CO_2 in air



$La_2Zr_2O_7$ was not detected in other samples, regardless of atmosphere or temperature (1350 and 850°C)

Summary and Conclusions

- Ambient CO2 level is considered benign for the Sr /La carbonate formation
- Surface segregation of SrO/ SrCO3 have been observed on LSM during exposures to H2O and CO2. Compound formation and segregation increase with water content and electric bias.
- Effect of CO_2 on the LSM stability is less pronounced than that of H_2O.
- Addition of Ni and (Ni + Ca) to LSM eliminates YSZ phase transformation / degradation in air, however, cause $La_2Zr_2O_7$ formation.
- With increasing dopant size the tendency for cation surface segregation increases.

Work in Progress

- ✓ Electrochemical testing of LSM and LSCF in Air-CO2-H2O atmospheres
- ✓ In situ XRD study to precisely detect the phase evolution and structural changes of LSM and YSZ resulting from solid-solid and solid-gas interaction in CO2 and H2O containing air at 850C as well as 1350C for longer duration (>500 h).
- ✓ Development of mechanistic understanding of cathode performance degradation
- ✓ DFT modeling to identify suitable dopants to mitigate surface segregation

Acknowledgments

- Work performed under US DOE Office of Fossil Energy contract DE FE – 0009682
- Drs. Joe Stoffa, Rin Burke, Briggs White and Shailesh Vora for guidance and technical discussion
- Dr. Jeff Stevenson for technical discussion
- Mr. Rich Goettler for technical discussion

Thank you

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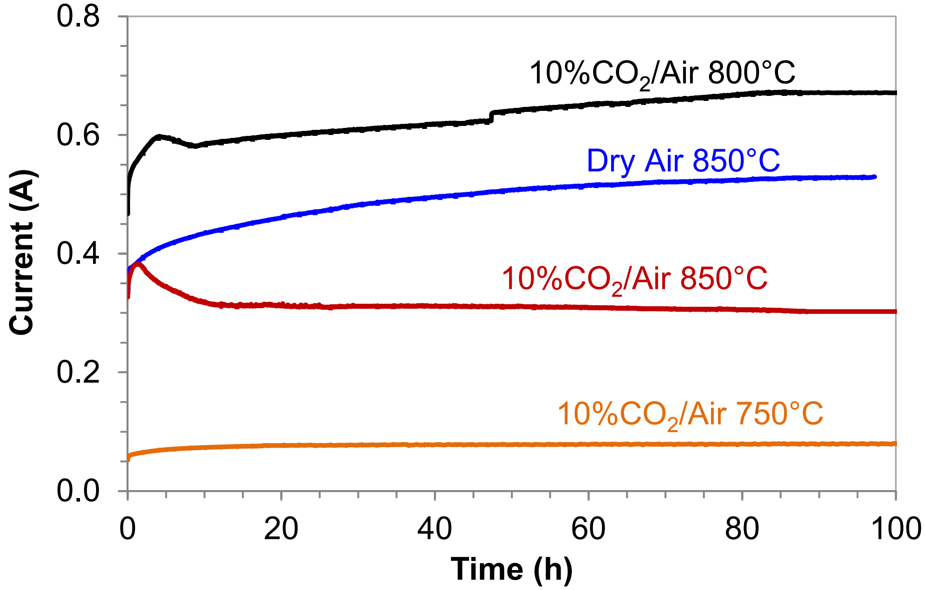
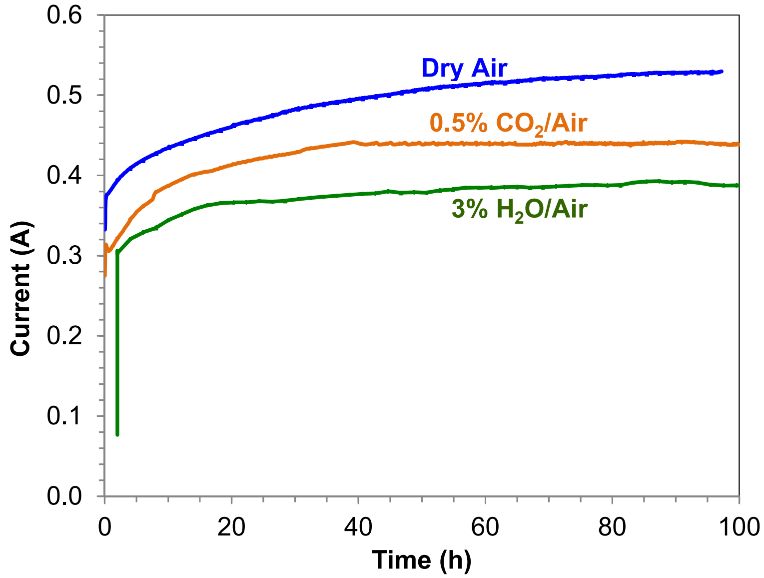
Electrical Performance

Test conditions: **10% CO_2/air, 0.5 V, 100 h**





The performance remains almost stable after initial activation