Theory, Investigation, and Stability of Cathode Electrocatalytic Activity

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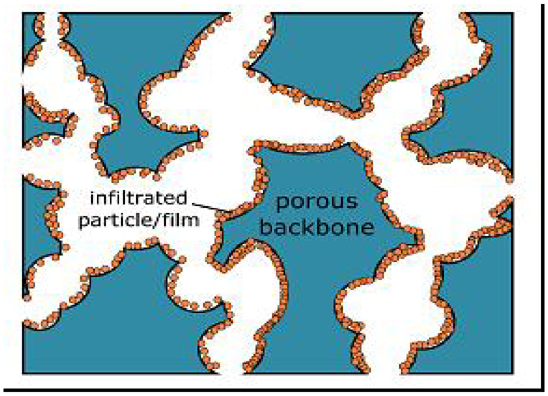
Outline

- **Introduction**
- **Project Objectives**
- **Results and Discussions**
  - Optimization of the infiltration process
  - Performance of catalyst-infiltrated LSCF
  - Continuum modelling and simulation
  - Microanalyses of surfaces and interfaces
- **Accomplishments to Date**
- **Future Work**

Target: A Catalyst-Infiltrated Cathode

- **Surface**
  High catalytic activity

- **Backbone**
  Fast transport of ionic and electronic species



A porous MIEC backbone with a thin-film coating of catalytically active materials for oxygen reduction

Project Objectives

- To fabricate and test catalyst-infiltrated LSCF cathodes for better performance and stability
- To characterize structure, composition, and morphology of surface and interfaces
- To develop models for data interpretation and for gaining insights into rational design of better electrode materials or microstructures
- To validate theories & models w/experiments
- To fabricate and test improvements in commercial cells

Part 1

Optimization of
the Infiltration Process

Precursors for **LSM Sol** Preparation

- For most of lanthanide and transition metal, metal alkoxide is not stable or is very expansive due to their high reactivity

- Acetate and nitrate are relatively cheap and stable

$$(La_{0.8}Sr_{0.2})MnO_{3-\delta}$$

$La(CH_3COO)_3 \cdot xH_2O$
$La(NO_3)_3 \bullet 6H_2O$

$Sr(CH_3COO)_2$
$Sr(NO_3)_2$

$Mn(CH_3COO)_2 \bullet 4H_2O$
$Mn(NO_3)_3 \cdot xH_2O$

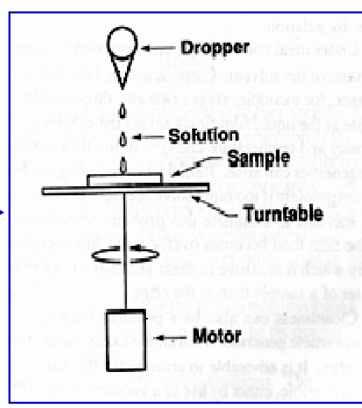
Solvents for LSM Sol Preparation

- Water is a strong solvent for most kinds of metal nitrate and acetate precursors due to its high polarity
- Water-based sol has poor wettability due to high surface tension
- Water-based sol has hard-to-control gelation rate (easy film cracking)

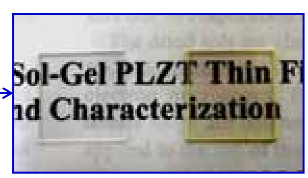
	Surface Tension (mN/m, at RT)
Ethanol	**22.3**
i-Propanol	**21.7**
Acetone	**23.7**
2-methoxyethanol	**30.8**
Acetic acid	**27.6**
Ethylene glycol	**47.3**
Water	**72.0**

Spin Coating of LSM Sol on dense substrates

- **For fundamental study of surface & interface of thin films**
- **Thickness can be controlled by rotation RPM, independent of the amount of sol dropped**



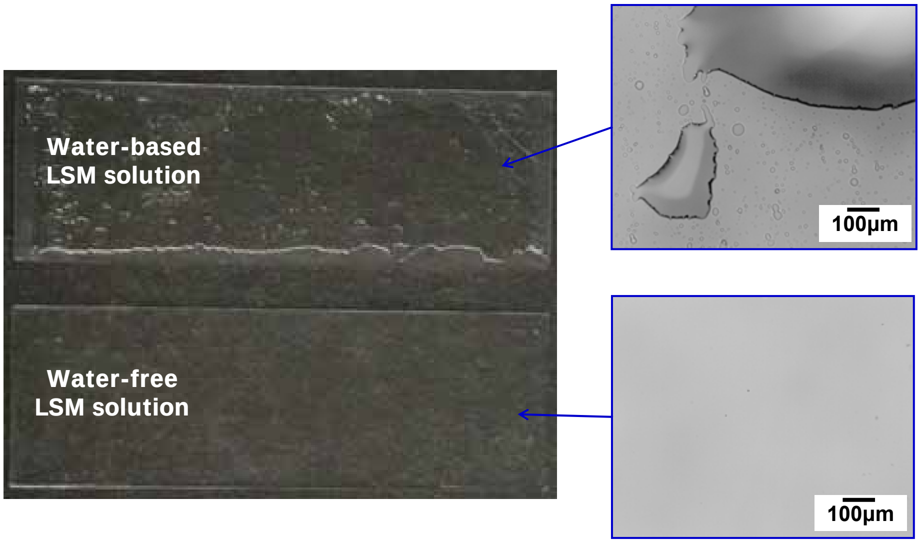
$$t = \frac{(C)^{\alpha}(\mu)^{\beta}}{(RPM)^{\gamma}}$$



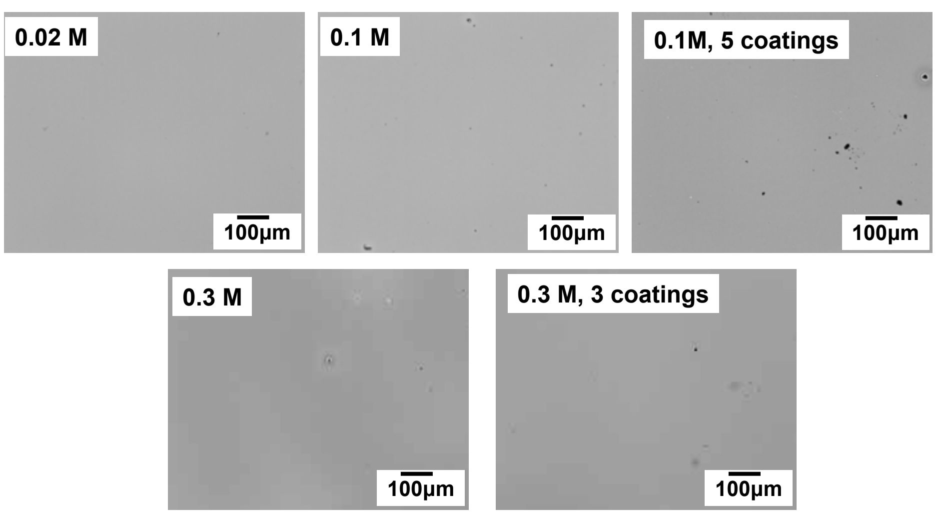
Thin Film

Theory, Investigation, and Stability of Cathodes

Wetting Characteristics of LSM Sol on LSCF

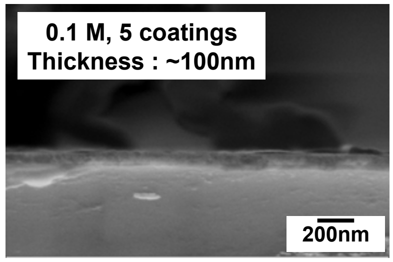


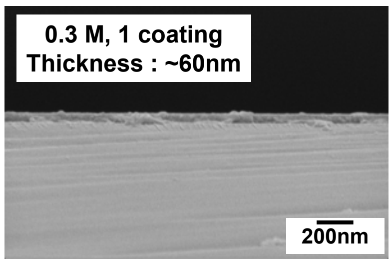
LSM Spin-coated on Silicon Wafer

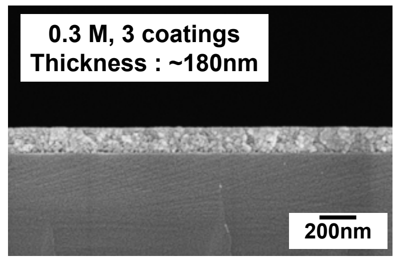


No cracks were observed

Thickness Measurement by SEM





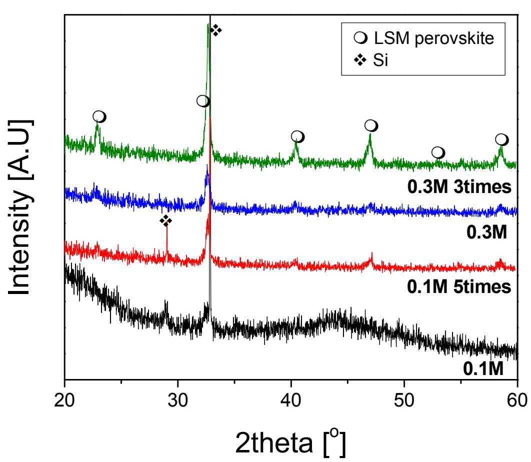


XRD Phase Analysis of LSM Films (on Si wafer)

Coating Condition (3000RPM)	Thickness
0.02M	<5nm
0.1M	~20nm
0.1M x 5 times	~100 nm*
0.3M	~60nm*
0.3M x 3 times	~180nm*

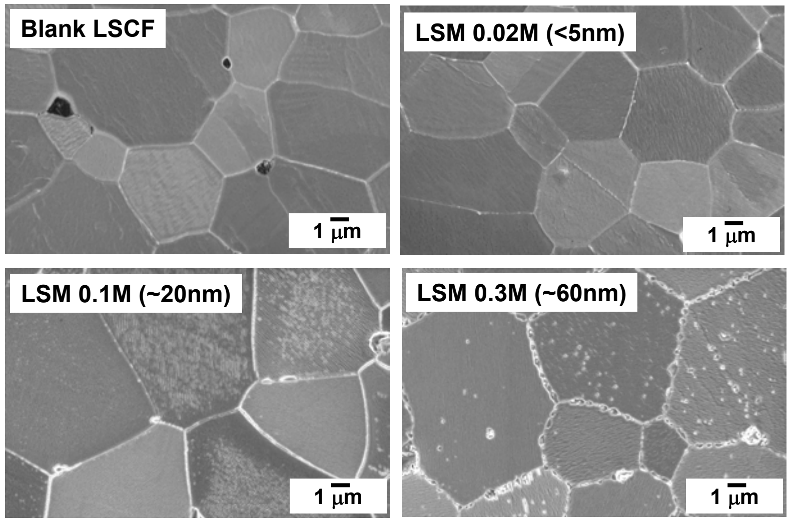
*measured from SEM microstructures

$$t = \frac{(C)^{\alpha}(\mu)^{\beta}}{(RPM)^{\gamma}}$$

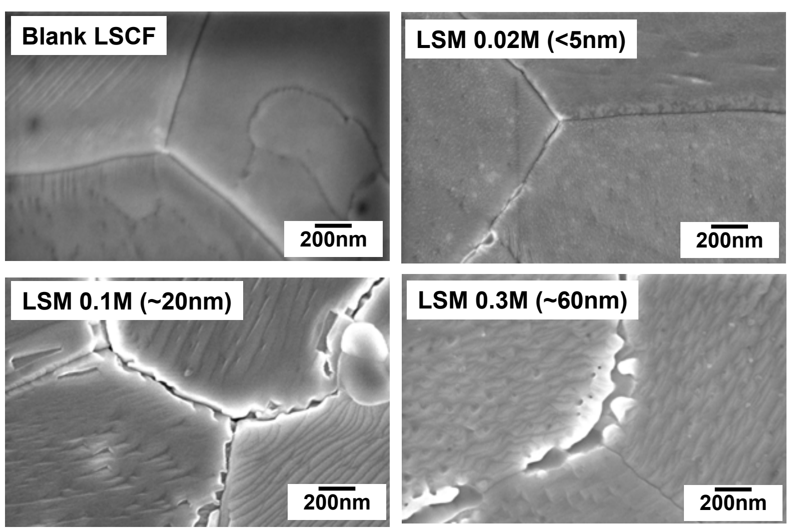


Annealed at 800°C for 1h

LSM film on dense LSCF (low magnification, x5k)

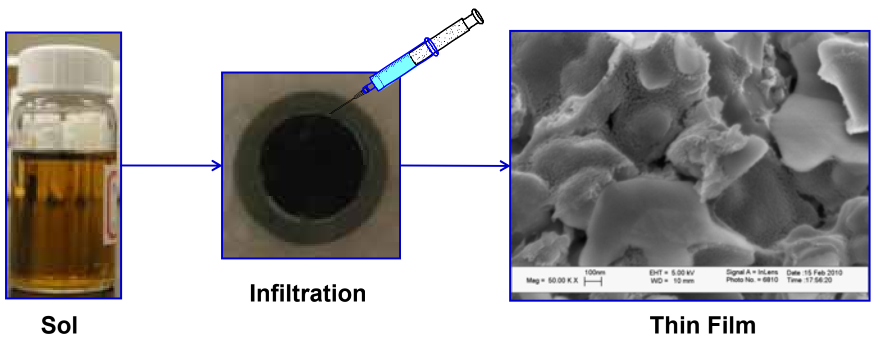


LSM film on dense LSCF (high magnification, x50k)

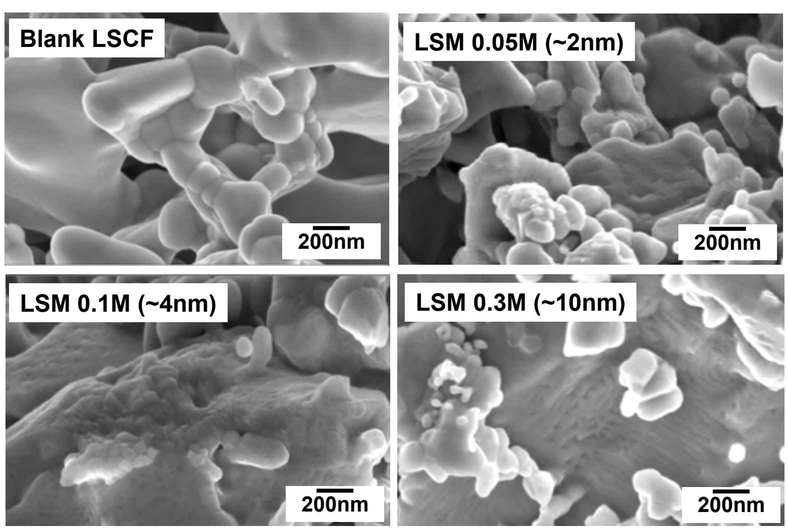


Infiltration of LSM into porous LSCF backbones

- For real application of a catalyst coating on porous cathodes
- Thickness can be controlled by concentration and amount of the sol



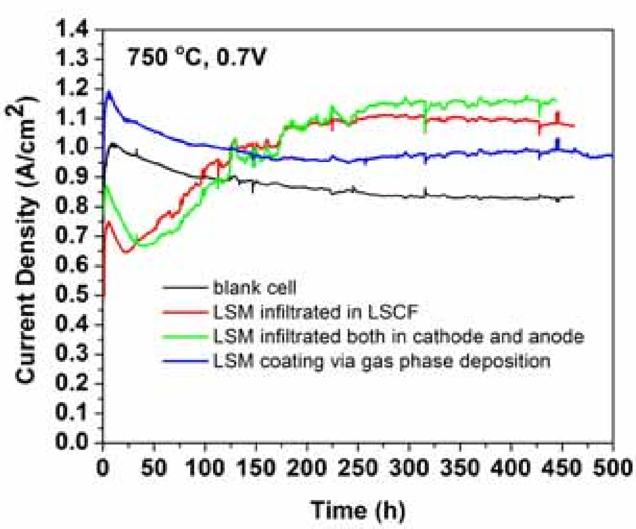
LSM-infiltrated LSCF (high magnification, x50k)



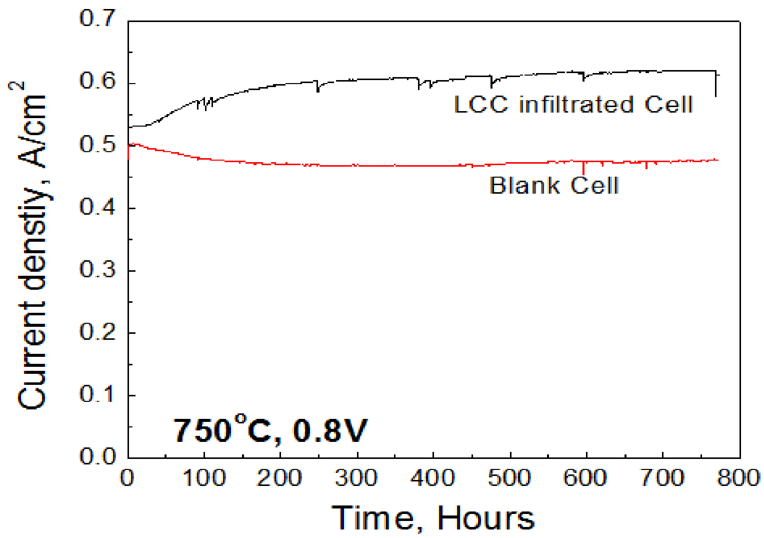
Part 2

Performance of Cells with Catalyst-Infiltrated LSCF Cathodes

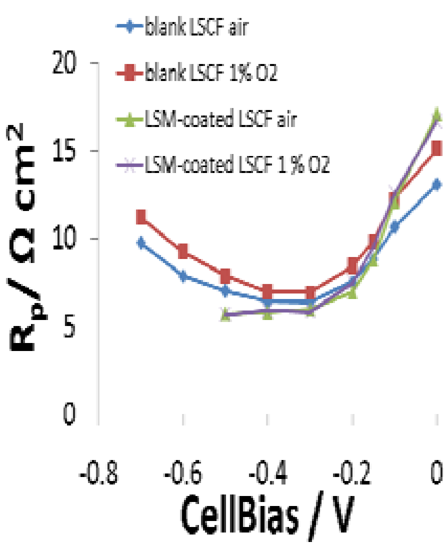
Stability of LSCF with and without LSM infiltration



Performance of LCC-Infiltrated LSCF



Dependence on DC Polarization



- Blank LSCF has lower R_p at OCV
- But the R_p for LSM-infiltrated LSCF diminishes quickly with the magnitude of cathodic polarization
- the R_p for LSM-coated LSCF is less sensitive to pO_2.

Part 3

Continuum modelling and simulation

Modeling Activities

- Simulation of
  - Mass transport/defect chemistry
  - Charge transport/sheet resistance
  - Interfacial/surface kinetics
- Conformal to material geometry
- Application to thin film test cells
  - Refine
  - Calibrate with experiments
  - Extend to porous structures

Recent Progress

- Designed test cells for more accurate electrochemical measurements;
- Analyzed data from LSM and LSCF thin films and LSM-coated LSCF cathodes using refined micro-kinetic models;
- Gained critical insights into the mechanisms for observed performance enhancement by an LSM coating on LSCF cathodes.

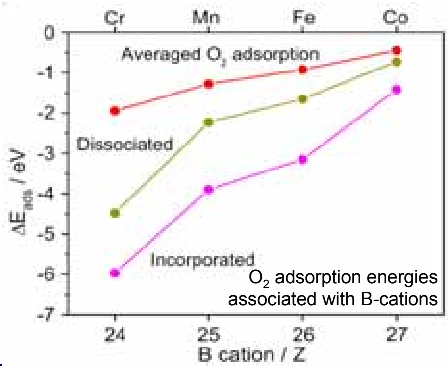
Hypotheses for LSM-Enhancement

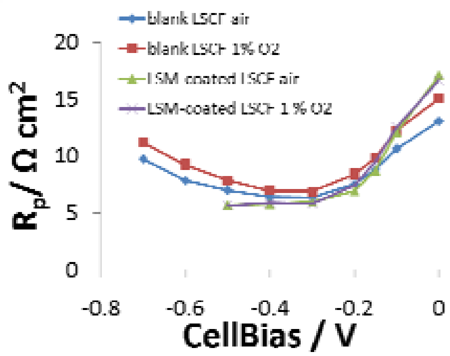
- LSM promotes O_2 adsorption through the more-active Mn-site on surface;
- LSM coating is more strongly activated under a cathodic polarization;
- Fast grain boundary diffusion and large vacancy concentration under polarization mitigate the limited ionic transport through LSM film;
- LSM coating stabilizes the surface of LSCF and prevents it from degrading.

Theory, Investigation, and Stability of Cathodes

1. Mn-Site Promotes O_2 Adsorption

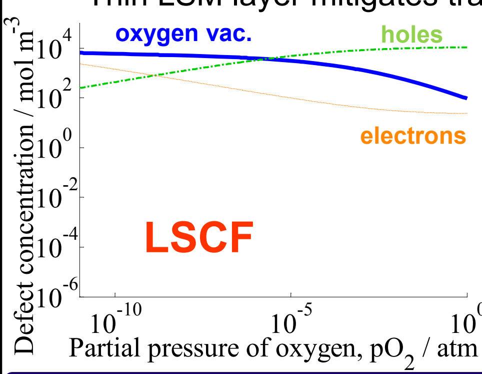
- Mn in LSM promotes stronger O_2 adsorption than either Fe or Co, as predicted by DFT simulations.
- Blank LSCF film polarization resistance is much more sensitive to pO2 than is that of LSM-coated films, reflecting some limitation by adsorption.

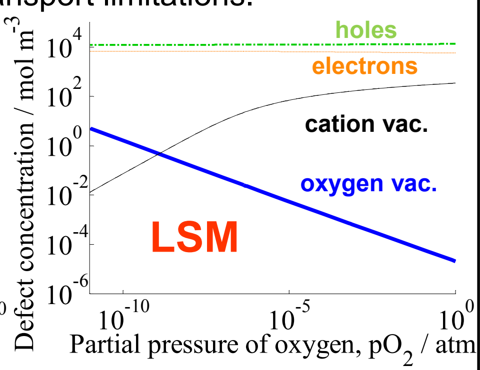




2. Surface ORR Activity is Linked to Bulk Defect Chemistry

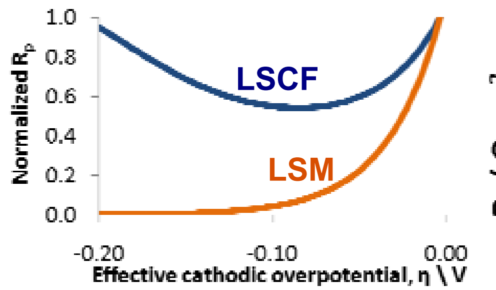
- c_v increased by a larger relative amount in LSM than in LSCF as pO_2 decreases or under cathodic polarization;
- An LSM surface's R_p decreases faster than blank LSCF due to strong relative vacancy infusion;
- Thin LSM layer mitigates transport limitations.



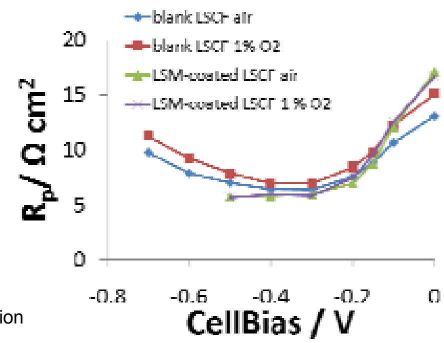


Activation Under Cathodic Polarization

- The trend toward stronger activation is qualitatively matched when the ORR is proportional to the bulk c_v, determined by the effective cathodic polarization.
- LSM-coated LSCF films have larger R_p at OCV, but R_p decreases faster than blank LSCF as η becomes more cathodic, ending up lower and indicating stronger activation.

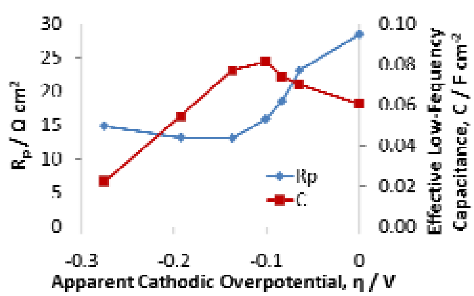


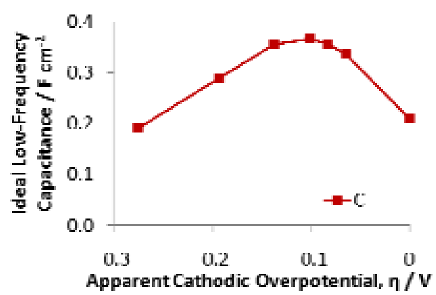
Assuming current proportional to ox. vac. concentration



R_p & C of LSCF Film under Polarization

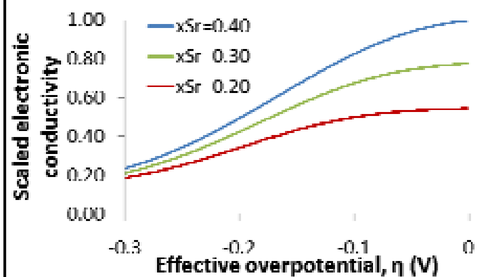
- R_P and effective low-frequency capacitance, C, of a LSCF film as a function of apparent cathodic polarization (C obtained by using a parallel RC circuit to fit the low-frequency part of spectrum, Rp is from the real-axis intercepts, not the fitted value of R).
- Ideal C as a function of cathodic polarization (Value simulated using 1D vacancy diffusion in film with blocking air surface boundary condition).

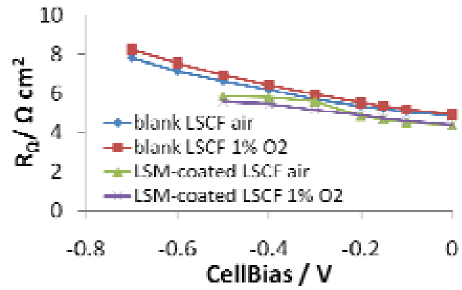




R_Ω & σ of LSCF Film under Polarization

- Decreasing film σ could be expected during polarization
- Sheet resistance may play some important role in the apparent R_p and capacitance
- R_Ω that increases faster for the blank LSCF cell may indicate that there is degradation in the LSCF taking place which the LSM layer blocks

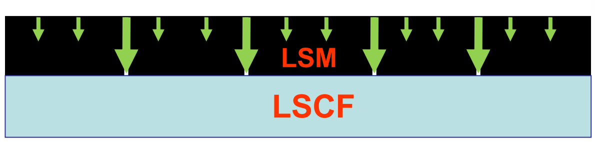




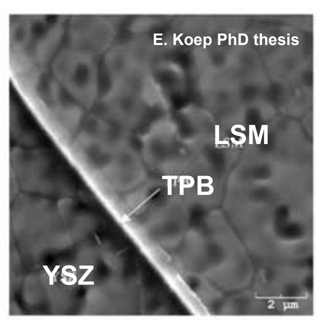
3. Large Bulk Pathways in LSM Films

- The GBs could act as a short-circuit pathway for vacancy transport from LSCF to LSM surface; $^{18}O_2$ oxygen tracer diffusivity can be ~1000 times larger along the GBs than expected for bulk diffusion, especially at lower temperatures (source: DeSouza & Kilner)

- The dramatically increased $\mathbf{c_v}$ in LSM under polarization and $\mathbf{\Delta c_v}$ across LSM/LSCF interface may enhance vacancy transport



Schematic of short-circuit diffusion pathways in an LSM thin film



SEM micrograph of grain boundaries in an LSM film deposited onto polycrystalline YSZ (Source: E. Koep PhD thesis)

4. LSM Coating Stabilizes LSCF Surface

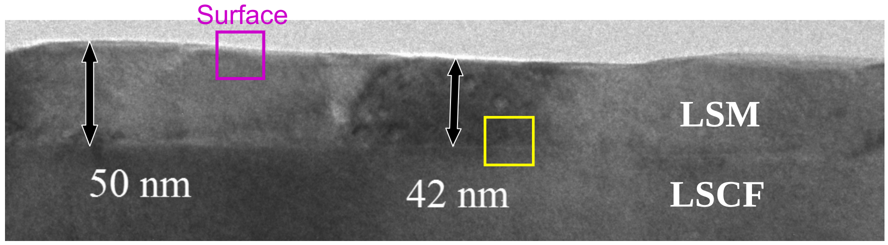
- LSM coating is largely stable on LSCF
  - no appreciable change in thickness
  - Mn confined within the LSM coating although small amounts of Co and Fe are present in LSM
- LSM inhibits surface Sr-enrichment, preventing surface properties from degradation
  - Microanalysis confirms that there was no Sr-enriched phases on the surface of LSM-coated LSCF.
  - Raman spectroscopy showed shift in main peak for blank LSCF film, reflecting possible surface Sr^{2+} enrichment; while no corresponding shift in LSM coated LSCF.

Part 4

Microanalysis of
Structure, Composition, & Morphology
of Surfaces and Interfaces

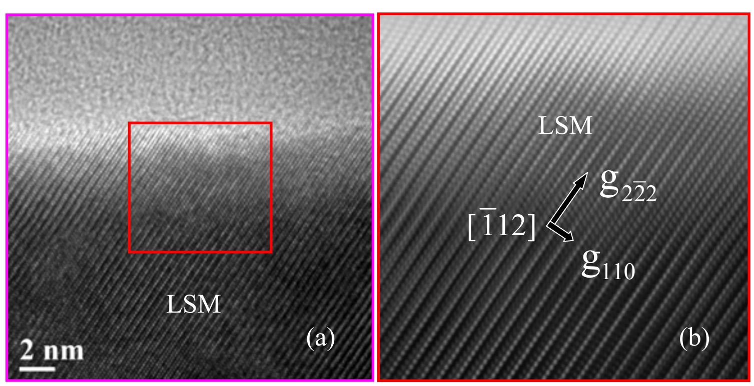
FC/BT Theory, Investigation, and Stability of Cathodes Georgia Institute of Technology

As-prepared LSM film on an LSCF Pellet



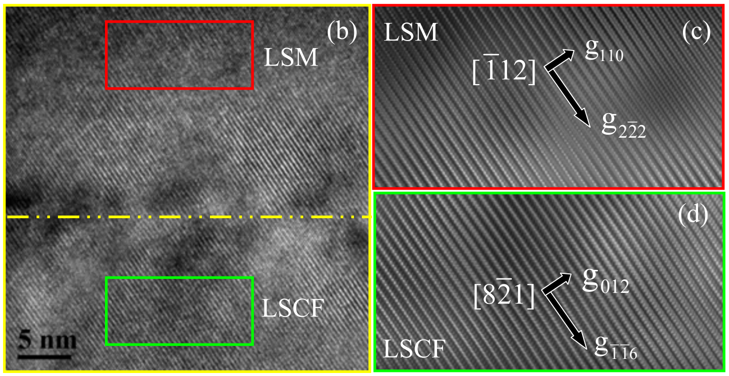
- An LSM film derived from a sol-gel process (as-prepared: annealed at 900ºC/1 h?)
- LSM film thickness: ~40 to 50 nm
- LSM film stoichiometry: $La_{0.8}Sr_{0.2}MnO_3$.

The Surface and Interior of the LSM Film



- Both the surface (left) and the interior (right) display perovskite structure.

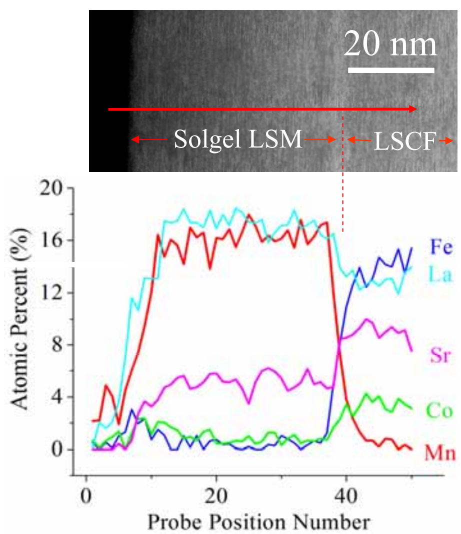
The LSM / LSCF Interface



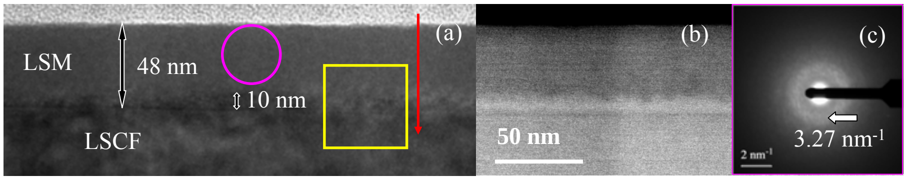
- Single crystalline throughout LSM thickness
- LSM epitaxial to the LSCF substrate
- Strain-field ~10 nm along interface, nonetheless

Profile across the LSM Layer

- **The random variations in the spectra represent the error or noise of the EDS measurements.**
- **Elemental distributions in each layer are as expected.**

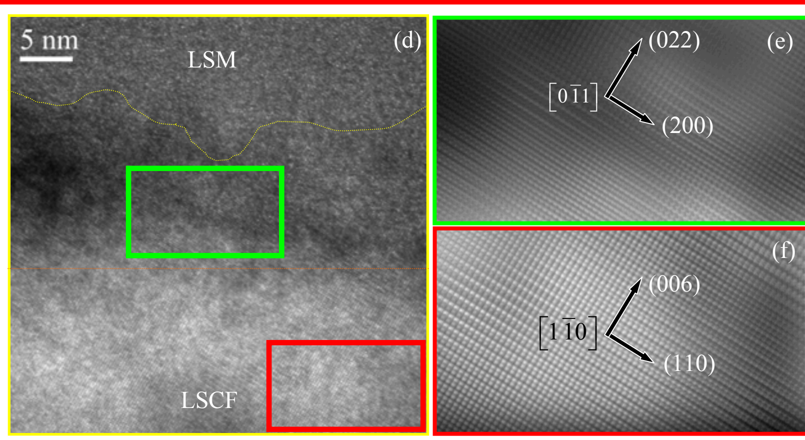


LSM film on LSCF after Annealing: 850°C/900h



- No noticeable change in LSM thickness or other visible characteristics.
- SAED indicates that the top ~80% (~40 nm) of the LSM film became amorphous after the annealing.
- The bottom ~20% (~10 nm) remained crystalline and appears to be coherent with the LSCF substrate.

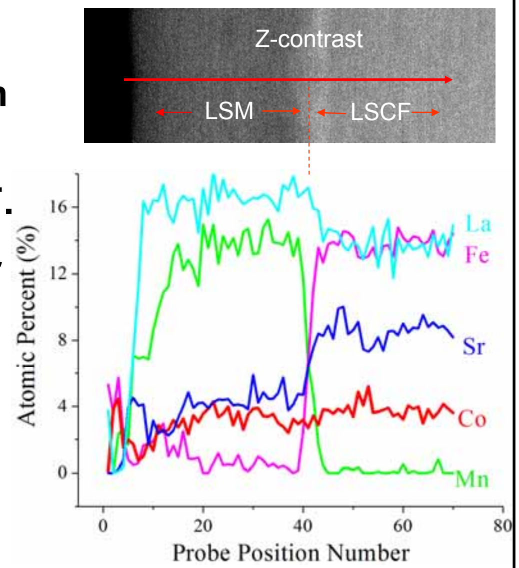
Lattice Image of LSM / LSCF Interface



- Near the interface, LSM epitaxial w.r.t. LSCF
- Both LSM and LSCF retained perovskite structures

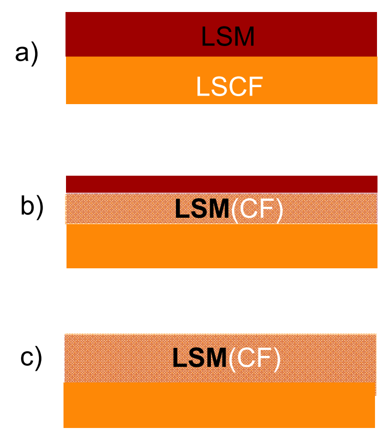
Profile across LSM Layer

- **Mn remains within LSM; no detectable Mn in LSCF.**
- **LSM is stable on LSCF.**
- **No Sr enrichment near LSM surface or LSM/LSCF interfaces.**
- **Co diffused into LSM layer, ~2- 4 at.%.**



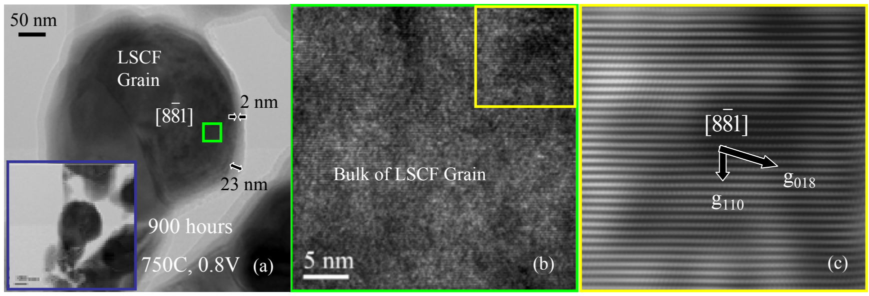
Effect of Inter-diffusion

- Interdiffusion during operation likely brings the properties of the two layers closer together
- Space-charge is also probably important
- The defect chemistry is likely a hybrid of the two materials
  - More oxygen vacancies than LSM, fewer than LSCF
    - Higher R_p at OCV than pure LSM layer
    - Stronger activation under polarization than blank LSCF
  - Stronger adsorption than LSCF due to presence of Mn



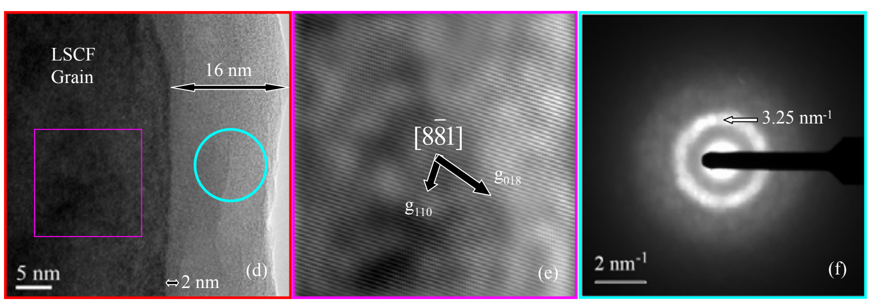
Schematic illustrating interdiffusion between the LSM layer and LSCF: a) as-deposited, b) during operation, c) after a long time.

An LSCF Grain in a porous LSM/LSCF



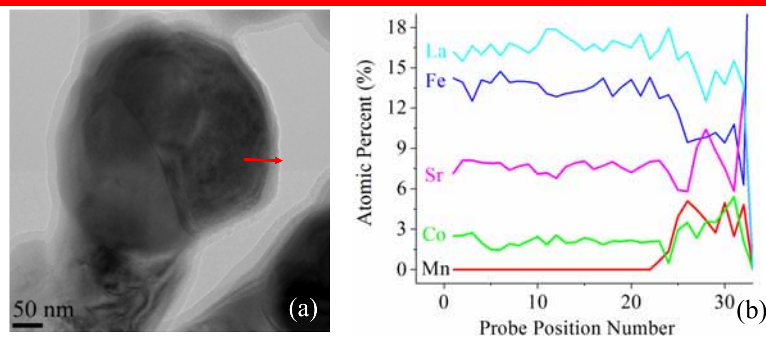
- An LSCF grain in a porous LSCF cathode infiltrated with LSM, operated at 750ºC for 900 h
- The LSCF grain size is ~0.3×0.3 μm
- The LSCF grain retains perovskite structure.
- The projected thickness of the surface layer: 2–23nm

The LSM/LSCF Interface



- LSM / LSCF interface well-defined
- While the LSCF grain is crystalline, the LSM coating is amorphous (it may facilitate ionic conduction).

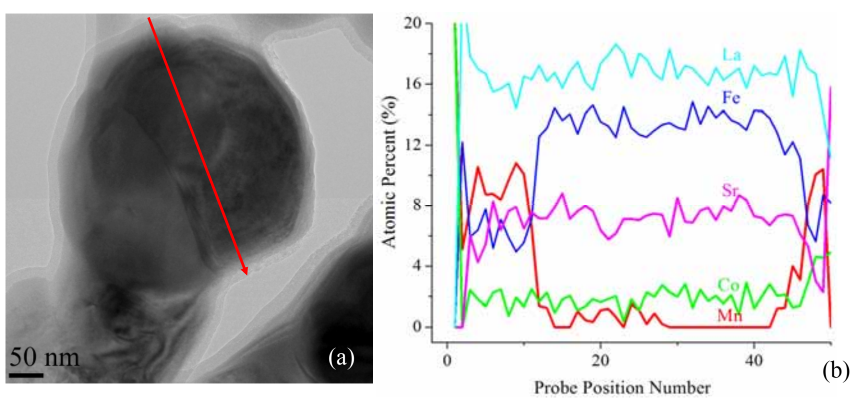
Profile across Exposed Surface Layer



- Sum of cation atomic percents normalized to 40%
- Surface layer is LSCFM (La, Sr, Co, Fe & Mn)
- **Mn retained in the surface layer**
- From LSCF to LSM
  - ➢ Slight increase of Co atomic percentage
  - ➢ Decrease of Fe atomic percentage

- In LSCFM
  - ➢ ~ 3 % Co & ~ 3 % Mn

Profile across the Entire Grain



- Similar to previous profile
- ~10 % Mn in the top layer, witch contains La, Sr, Mn, Co, and Fe
- The LSCF grain is completely coated with a thin layer of LSM
- LSM may diffuse along the grain boundaries of LSCF

Summary for Microanalyses

- LSM coatings are stable on LSCF: Mn is retained in the top layer and no appreciable thickness change after annealing;
- While LSCF remains crystalline, the top layer of LSM became amorphous and doped with some Co and Fe;
- Estimated LSM(CF) thickness: 2–23 nm;
- Mn presence in the surface reaches up to about 10 at.%; No Sr-enriched phases observed on the surface of LSM-coated LSCF.

Accomplishments to date

- Developed processes for fabrication of anode-supported and symmetrical cells with porous LSCF electrodes with controlled microstructures;
- Optimized infiltration and sputtering for preparation of thin films/coatings of cathode/catalyst materials;
- Demonstrated that the performance and stability of LSCF-based cathodes can be improved by infiltration of LSM, SDC, and LCC;
- Developed continuum models for design of test cells, prediction of performance, and determination of some key properties of cathode materials;

Accomplishments to date

- Characterized the local structure, composition, and morphology of surfaces and interfaces in LSM-infiltrated LSCF cathodes;
- Confirmed the absence of surface oxides (Sr/La) or Sr-enriched phases on LSM-infiltrated LSCF surface under operating conditions, which may be the origin of performance degradation;
- Gained critical insights into the mechanisms for observed performance enhancement by an LSM coating on LSCF cathodes: LSM promotes O_2 adsorption, activated more strongly by cathodic polarization, and stabilizes the surface of LSCF.

Future Work

- **To perfect the infiltration processes for control of thickness and coverage of catalyst coatings in larger cells;**
- **To understand the evolution of morphology, structure, and composition of surface & LSM/LSCF interfaces under different operating conditions;**
- **To correlate the microscopic features of catalysts coatings with cell performance & stability;**
- **Validate and perfect continuum models to gain insights for design of more efficient cathodes;**
- **Demonstrate the benefits of infiltration in commercial cells.**

Acknowledgement

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