Performance and Stability of Catalyst-Infiltrated LSCF Cathodes

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Outline

- **Introduction: Motivation**
- **Project Objective / Approach**
- **Results and Discussions**
  - Performance of catalyst-infiltrated LSCF
  - Microanalyses of surfaces & interfaces (LSMCo)
  - Continuum modelling and simulation
- **Accomplishments to Date**
- **Future Work**

Why Surface Modification of Cathode?

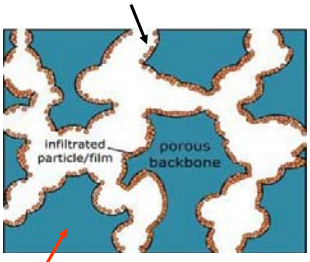
- Cathode makes the most contribution to energy loss.
- Why not using more active cathode materials?
  - **Issues** with chemical, physical, and thermal ***compatibility*** between new electrode materials and other components
- Why not using Scaffolds of electrolyte for infiltration?
  - **Issues** with ***poor electrical conductivity*** or current collection
  - Issue of long-term stability
- **Excellent flexibility** in catalysts that may be used.
  - Mixed conductors (continuous coating, e.g., LSM, PSM, etc…)
  - Discrete metallic or Discrete ionic particles (SDC, LCC, etc…)
- Surface modification of existing electrode is the most efficient and practical approach to better performance.
  - **LSCF** backbone for cathodes
  - **Ni-YSZ** backbone for anodes

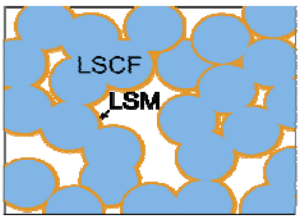
Target: A Catalyst-Infiltrated Cathode

A continuous dense film of catalyst coating

Surface:

High catalytic activity



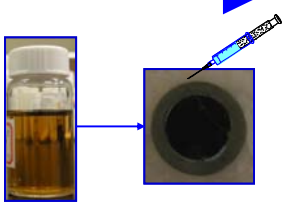


Activity improvement

Stability enhancement

Backbone (LSCF):

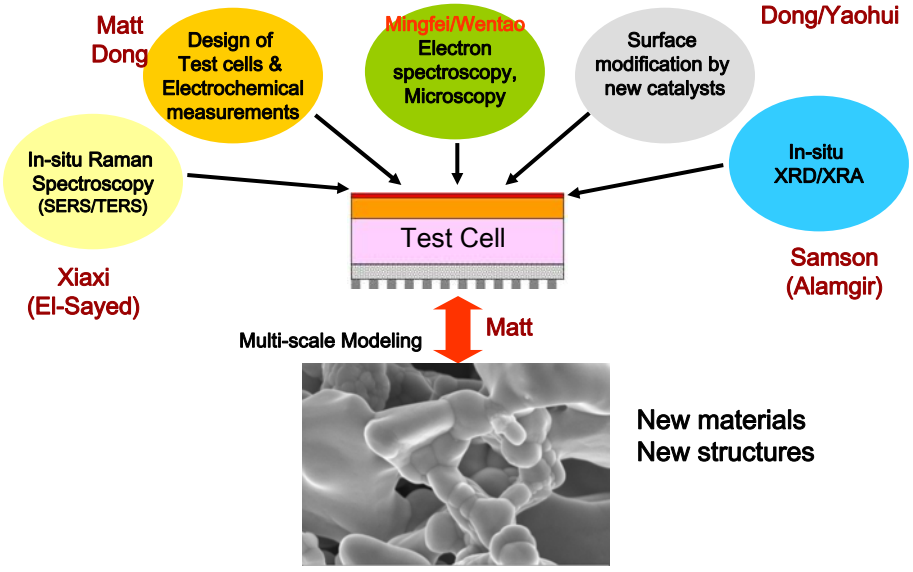
Fast ionic and electronic conductivity



Objectives

- To fabricate and test catalyst-infiltrated LSCF cathodes for better performance and stability;
- To correlate electrochemical performance with structure, composition, and morphology of the surface and interfaces;
- To develop theories/models for interpretation of electrode performance;
- To validate theories/models w/experiments in order to gain insights into rational design of better electrode materials or architectures;
- To demonstrate performance enhancement in commercial cells

Technical Approach



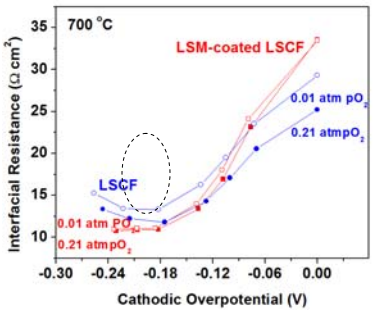
Part 1

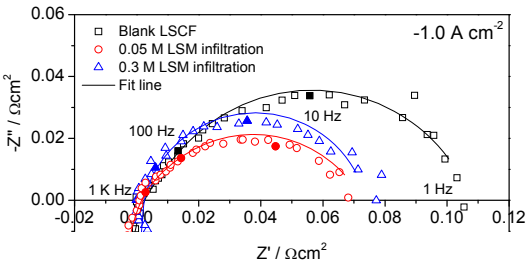
Performance of Cells with Catalysts-Infiltrated LSCF Cathodes

Dependence on DC Polarization

Thin-film cells by sputtering:
dense LSCF substrate

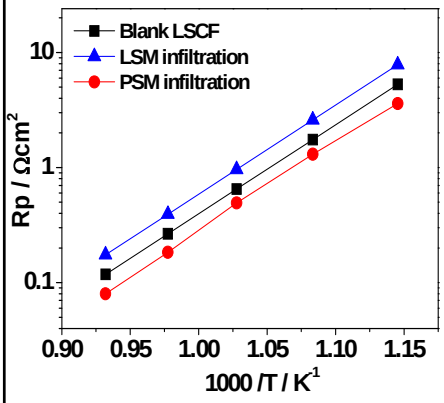
Symmetrical cells:
Porous LSCF backbone



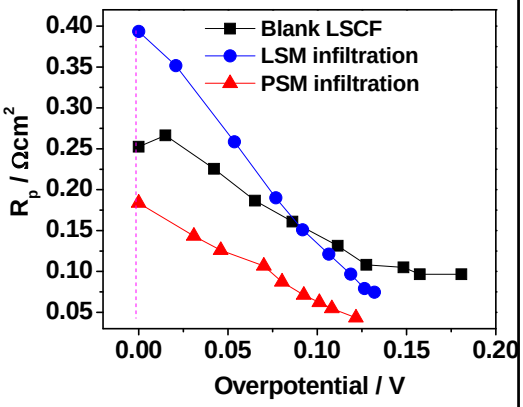


M. Lynch et al., Energy & Environmental Sci., 4, 2249-2258 (2011). DOI: 10.1039/c1ee01188j

$Pr_{1-x}Sr_xMnO_{3-\delta}$ vs $La_{1-x}Sr_xMnO_{3-\delta}$

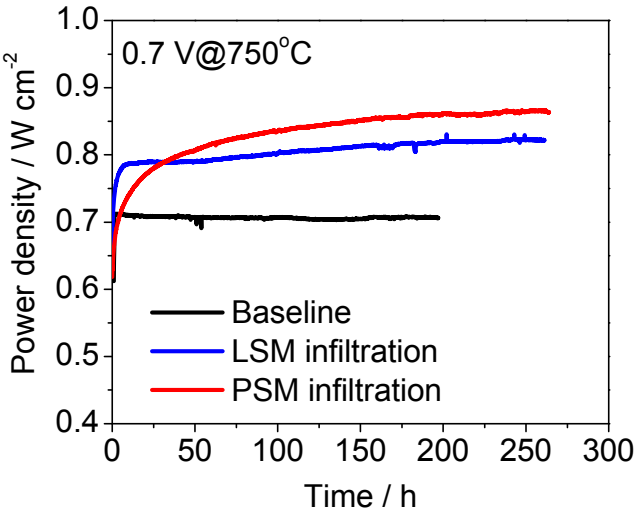


At OCV



Under Polarization

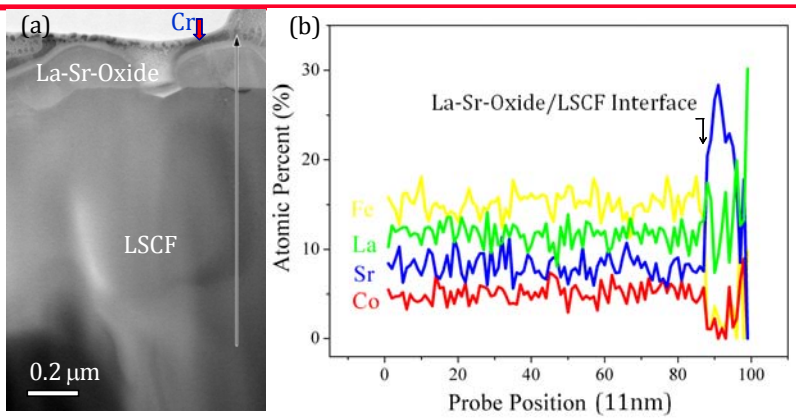
Performance of PSM and LSM infiltration



Part 2

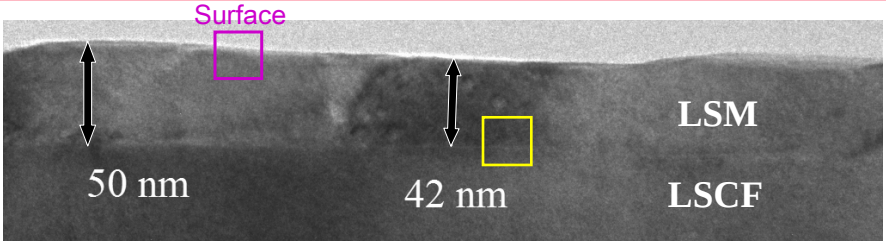
Microanalysis of Structure, Composition, & Morphology of Surfaces and Interfaces

LSCF Annealed at 850°C/900 h



- Only Sr and La were detected on the surface (bulk 6428).
- Oxides of Sr/La reduce surface catalytic activity for ORR.
- Growth of Sr/La oxide layer may cause degradation.

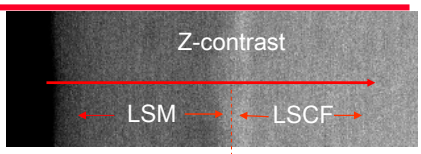
As-prepared LSM film on LSCF

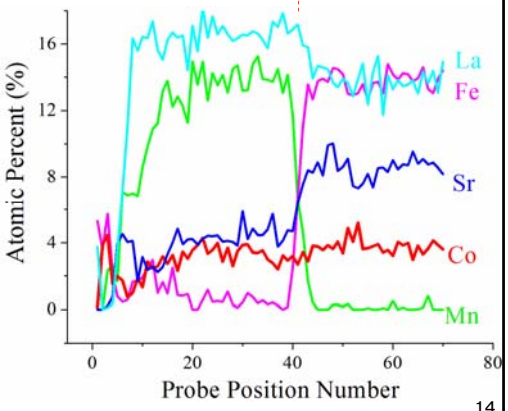


- An LSM film derived from a sol-gel process (as-prepared: annealed at 900ºC/1 h)
- LSM film thickness: ~40 to 50 nm
- LSM film stoichiometry: $La_{0.8}Sr_{0.2}MnO_{3.}$

LSM Film on LSCF Annealed at 850ºC/900 h

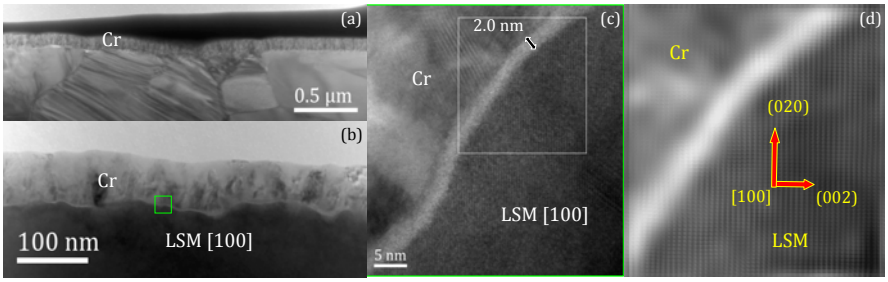
- **Mn remains within LSM; no detectable Mn in LSCF**
- **LSM is stable on LSCF**
- **No Sr enrichment near LSM surface or LSM/LSCF interfaces**
- **Co diffused into LSM layer, ~2- 4 at.%**





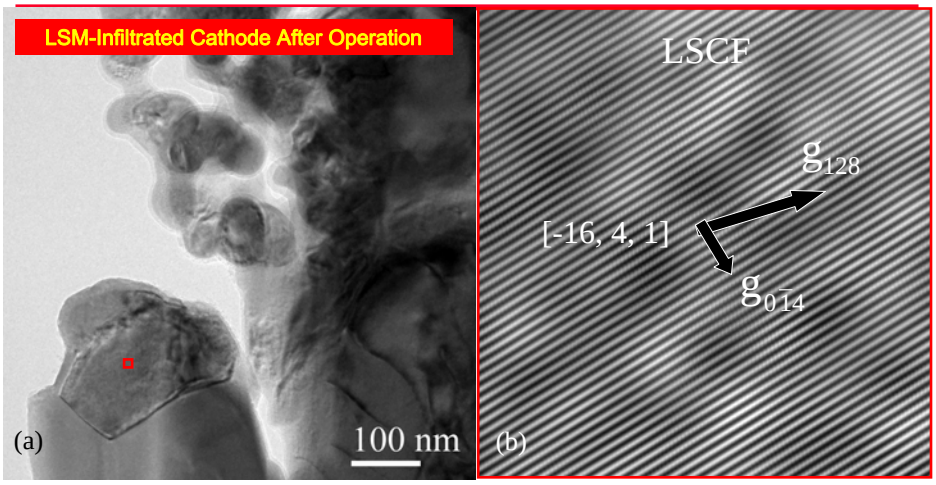
Samples are annealed at 850ºC for 900 h

LSM film on LSM annealed at 850°C/900 h



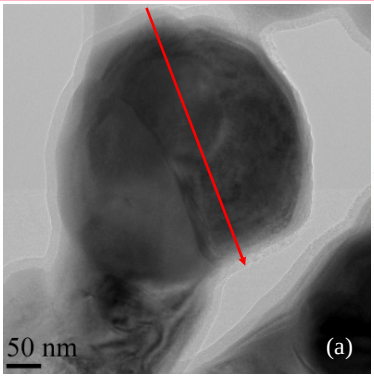
- **No La or Sr enrichment on the surface**
- **There is no LSM film observed possibly due to an epitaxial relationship with the substrate**

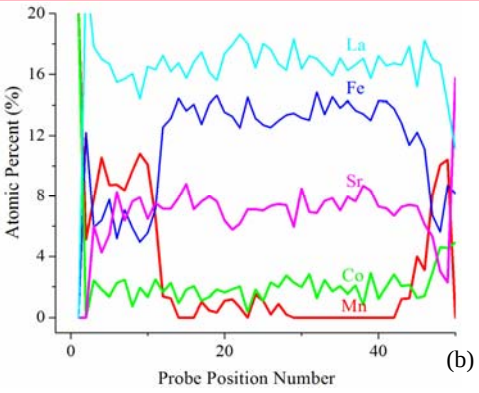
LSM-Infiltrated Cell After Operation



LSCF Grain Identified for GB analysis

Profile across a LSM coated LSCF Grain





- **Similar to previous profile**

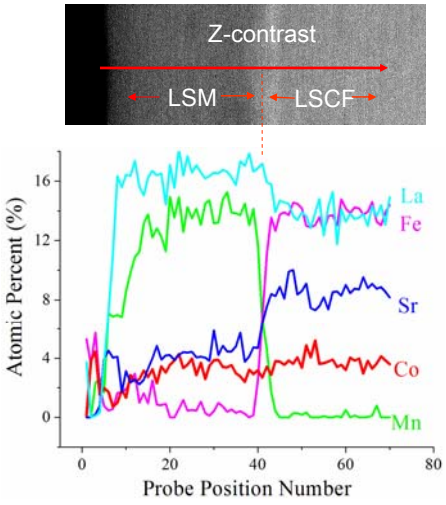
Samples are annealed at 850°C for 900 h

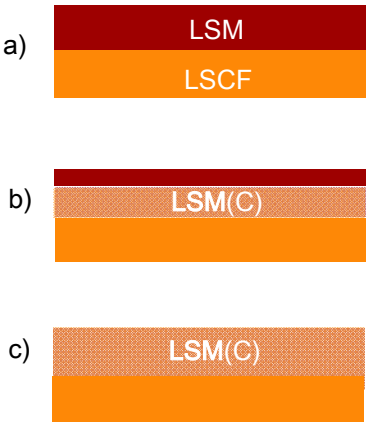
- **~10 % Mn in the top layer, which contains La, Sr, Mn, Co, and Fe**
- **The LSCF grain is completely coated with a thin layer of LSM**
- **LSM may diffuse along the grain boundaries of LSCF**

Summary of Microanalyses

- Observed Sr/La-enriched particles on LSCF surface. This may be the origin of poor performance or degradation during operation.
- Confirmed the absence of surface oxides (Sr/La) or Sr-enriched phases on LSM-infiltrated LSCF surface under operating conditions. This can be evidence of LSM suppression of (Sr/La) surface enrichment on LSCF.
- LSM coatings are stable on LSCF: Mn is retained in the top layer and no appreciable thickness change after annealing.
- Estimated LSM(C) thickness: 2–23 nm.

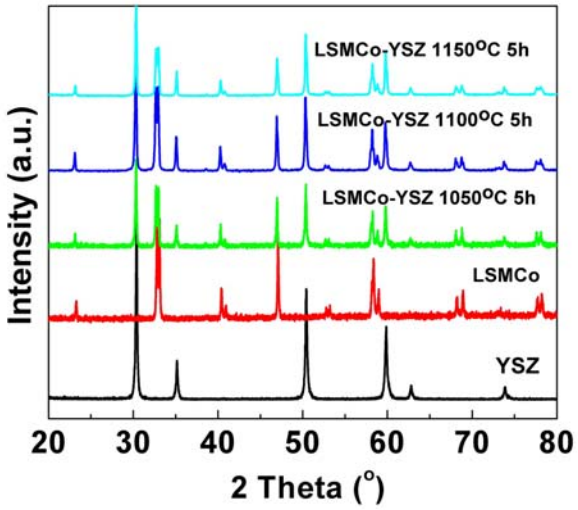
Effect of Inter-diffusion



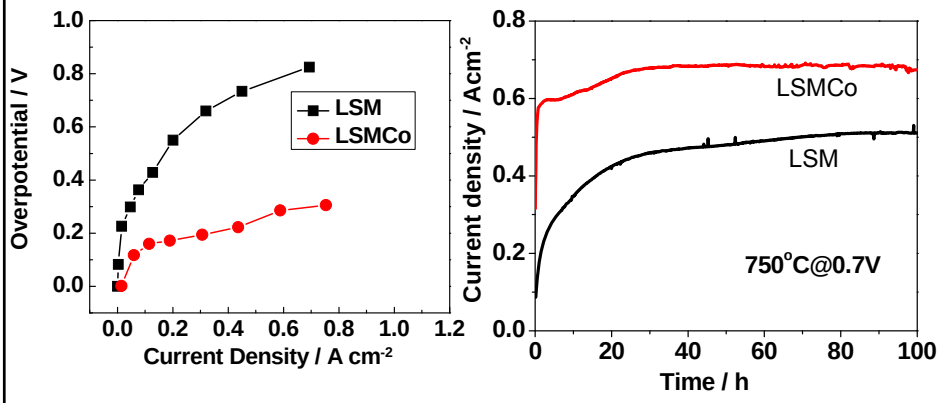


Schematic illustrating inter-diffusion between the LSM layer and LSCF: a) as-deposited, b) during operation, c) after a long time.

Chemical compatibility with YSZ



Performance of LSMCo as a single phase cathode



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 degrading
  - 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.
  - Microanalysis confirms that there was no Sr-enriched phases on the surface of LSM-coated LSCF.
- Diffusion of Co into LSM results in LSM(C), which has properties intermediate between LSM and LSCF – better incorporation than LSM, better adsorption than LSCF

Part 3

Modelling and Simulation: Quantifying the effects of Microstructure

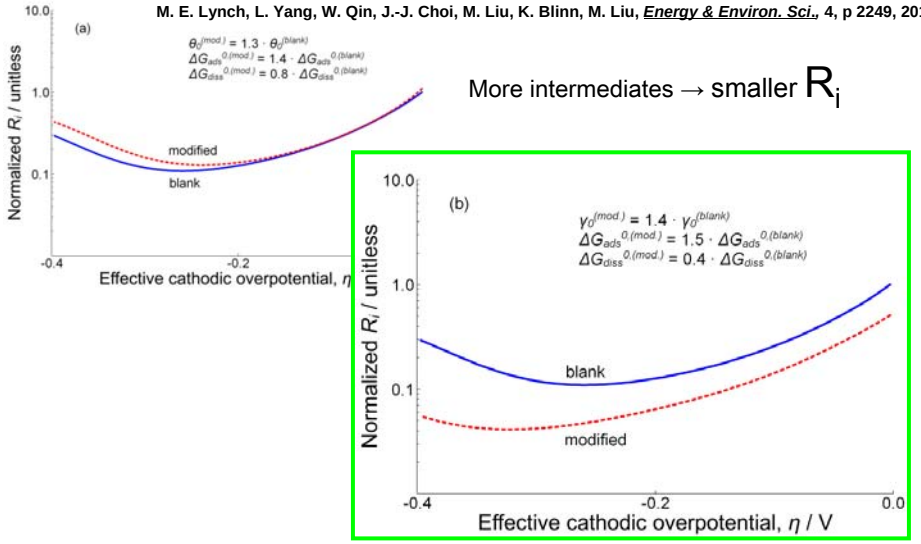
M. Lynch et al., Energy & Environmental Sci., 4, 2249-2258 (2011). DOI: 10.1039/c1ee01188j

Mechanism for LSM-Enhancement

- LSM coating is more strongly activated under a cathodic polarization;
- LSM promotes O_2 adsorption through the more-active Mn-site on surface;
- Fast grain boundary diffusion, short diffusion distance, and large vacancy concentration under polarization mitigate the limited ionic transport through LSM film;
- Long-term time-dependent activation
  - LSM coating stabilizes the surface of LSCF and prevents it from degrading and intermixing enhances the properties through formation of LSM(C)

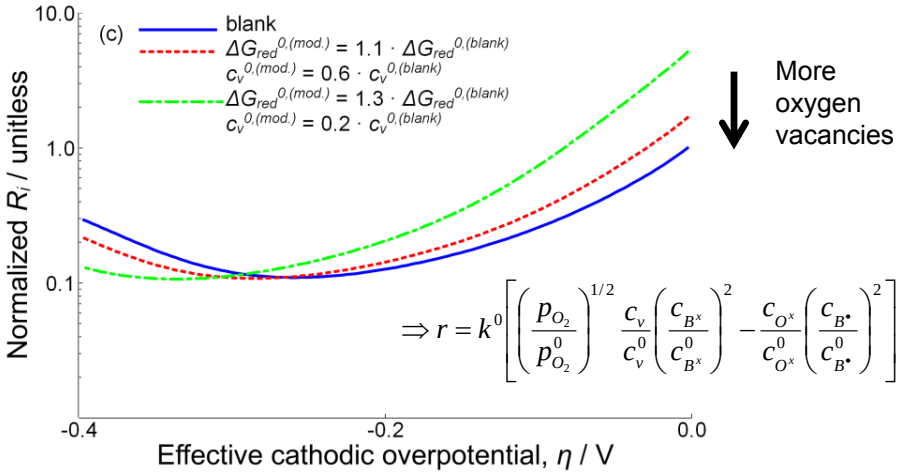
Effect of Surface Intermediates

M. E. Lynch, L. Yang, W. Qin, J.-J. Choi, M. Liu, K. Blinn, M. Liu, ***Energy & Environ. Sci.,*** 4, p 2249, 2011.



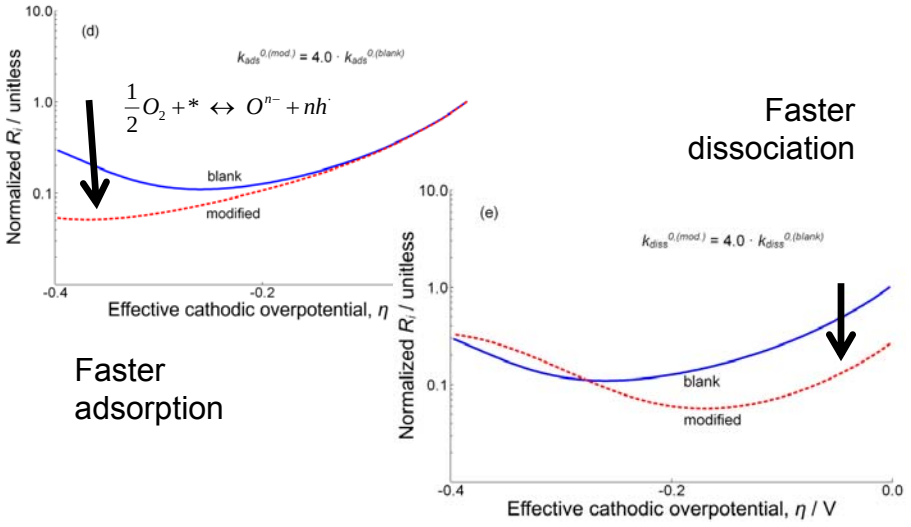
More intermediates → smaller R_i

Effect of Surface Point Defects



M. E. Lynch, L. Yang, W. Qin, J.-J. Choi, M. Liu, K. Blinn, M. Liu, ***Energy & Environ. Sci.,*** 4, p 2249, 2011.

Effect of Reaction Barrier Heights



M. E. Lynch, L. Yang, W. Qin, J.-J. Choi, M. Liu, K. Blinn, M. Liu, ***Energy & Environ. Sci.***, 4, p 2249, 2011.

Motivation/Objective

- Porous electrode microstructure has important impact on performance of electrochemical devices
- Local deviations in electric potential, point defect concentration, etc. caused by microstructure/geometry impact performance at surface and interfaces
- Quantitative tools needed to help understand and design electrodes with respect to local microstructure

Objectives:

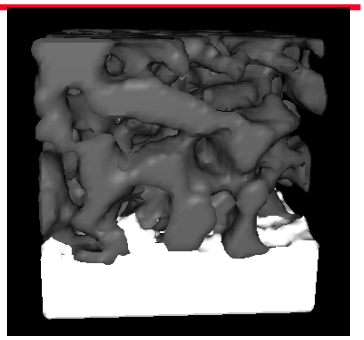
  - To use 3D microstructural reconstructions as the domain for electrochemical simulations – capture effect of local details
  - To maintain inherent physically interdependent nature of the problem – coupled interfaces, bulk, and gas-phase interactions at interfaces

Technical Approach

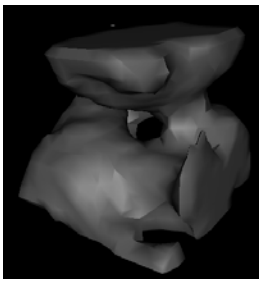
3D microstructure reconstruction using new imaging techniques

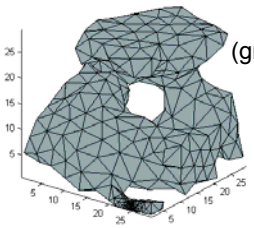
- Porous LSM on dense YSZ
- Samples sent to HeteroFoaM EFRC collaborators (Wilson Chiu's group, U. Conn) for x-ray tomography

3D FE meshing of volumetric phase data



Digital representation of porous LSM (gray) on YSZ (white). Side length 2 μm.

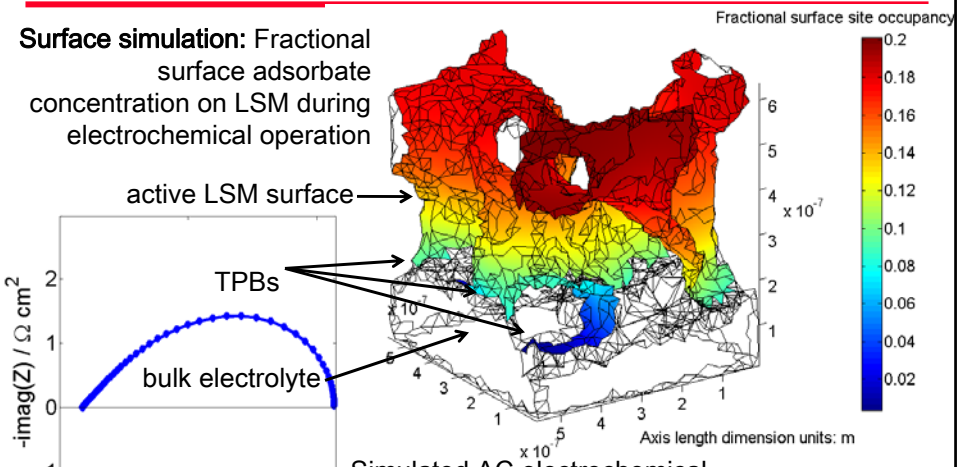




Application of electrochemical constitutive equations to the meshed microstructure by FEM

Preliminary Results

Surface simulation: Fractional surface adsorbate concentration on LSM during electrochemical operation



Simulated AC electrochemical impedance of the surface processes on the microstructure

Accomplishments to date

- Demonstrated that surface modification of existing electrode is an efficient and practical approach to better performance.
- 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 and $Pr_{1-x}Sr_xMnO_{3-\delta}$;
- Developed models for design of test cells, prediction of performance, and determination of some key properties of cathode materials;

Future Work

- **To perfect the infiltration processes for control of thickness and coverage of catalyst coatings in larger commercial cells;**
- **To validate and perfect continuum models in order to gain insights for design of more efficient cathodes;**
- **To demonstrate the benefits of infiltration in commercial cells.**

Acknowledgement

Discussions with
Briggs White, Joseph Stoffa, & Wayne Surdoval

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Thanks to Prof. Wilson Chiu's group (U. Conn.) for x-ray tomography data and Shawn Reeves, Dorothy Coffey, & Karren More at SHaRE, ORNL, for support to TEM Analysis