Enhancing Cathode Performance & Stability through Infiltration

Project Number: FC26-08NT0006557
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Presented to
The 13th Annual SECA Workshop
Pittsburgh, July 24-25, 2012

DOE-NETL SECA-CTP

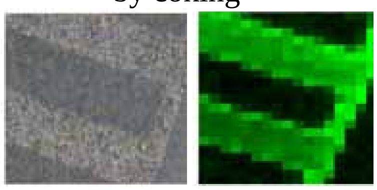
Outline

- **Motivation**
- **Project Objective/Approach**
- **Results and Discussions**
  - Enhancing Performance of Commercial Cells
  - *Ex Situ* Electron Microscopy/Spectroscopy
  - *In Situ* **Synchrotron Enabled X-Ray Analysis**
  - Surface Enhanced **Raman Spectroscopy**
  - Modelling and simulation
- **Accomplishments to Date**
- **Acknowledgement**

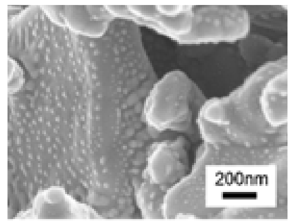
Role of Surface Species/Phases

- **Surface** may dramatically enhance or hinder electrode performance.

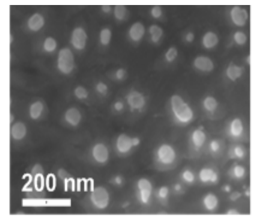
Anode deactivation by coking



Cathode performance enhancement by infiltration



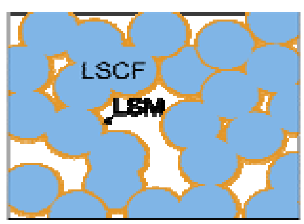
Coking tolerance by BaO/Ni interfaces



- Liu et al., *Materials Today*, 2011, **14**, 534.
- Lynch, EES, **4**, 2249-2258 (2011); Lou et al., *S. S. Ionics*, 2009, **180**, 1285.
- Yang et al., *Nature Comms*, 2011, **2**, 357; Liu, *Nano Energy*, 2012, **1**, 448.

Target: A Catalyst-Infiltrated Cathode

A continuous dense film of catalyst coating

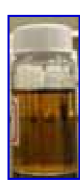


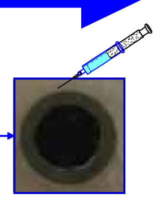
Surface:

High catalytic activity

Backbone (LSCF):

Fast ionic and electronic conductivity



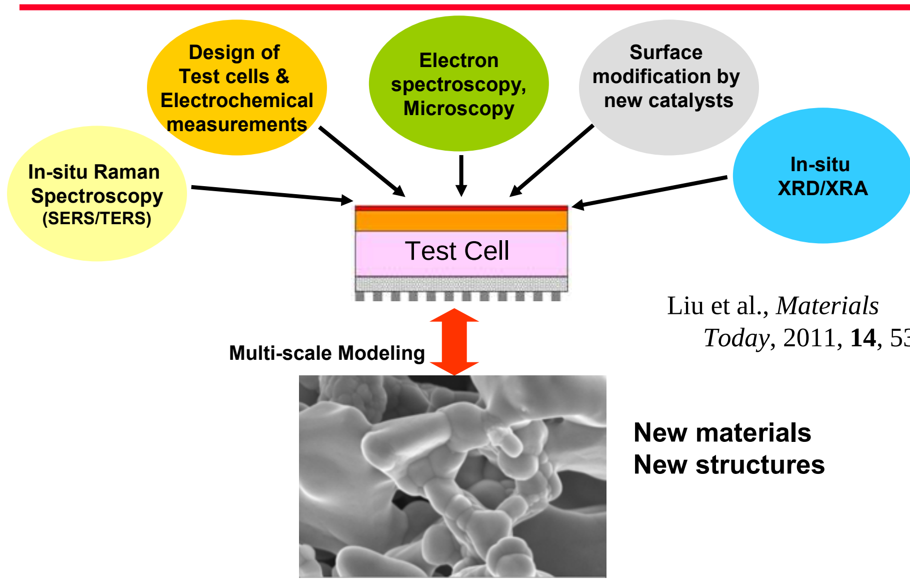


Activity improvement

Stability enhancement

J Choi et al., JACerS, 2011,**94**, 3340-3345.

Technical Approach



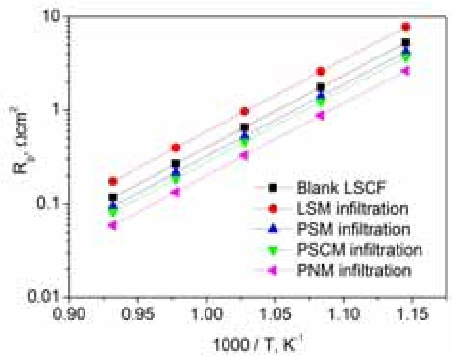
Liu et al., *Materials Today*, 2011, **14**, 534.

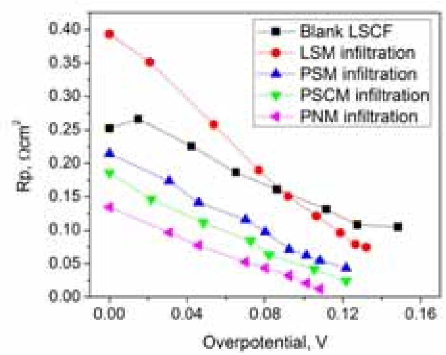
New materials
New structures

Part 1

Enhancing Performance of Commercial Cells through infiltration of Mn-Containing Catalysts

Symmetrical Cells with Catalyst-Infiltrated LSCF

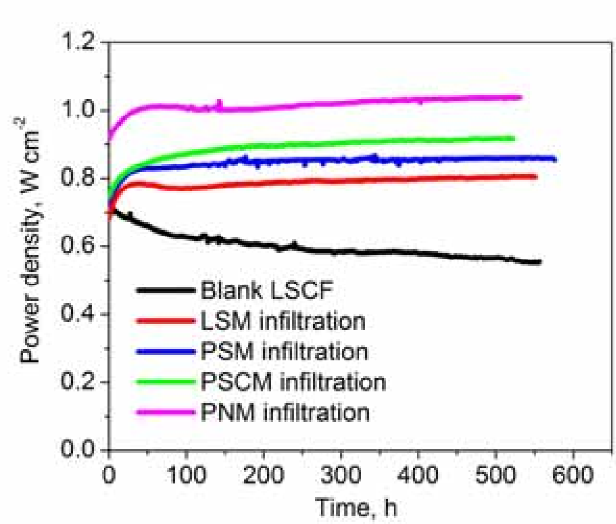




At OCV

Under Polarization

Button Cells with Catalyst-Infiltrated LSCF



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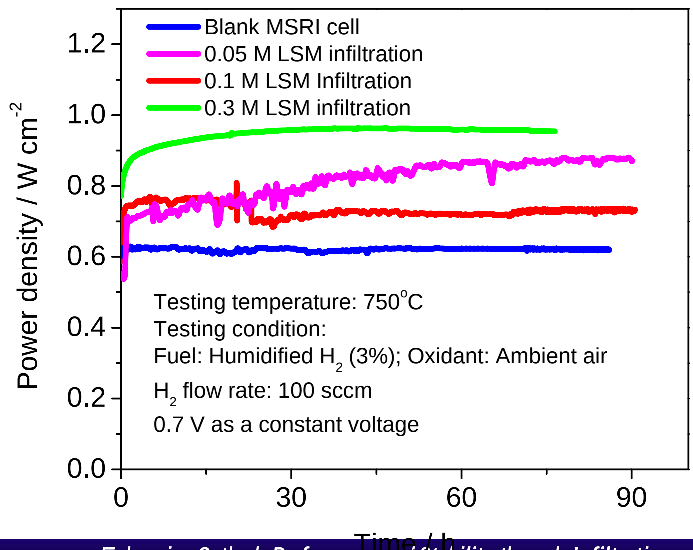
FC26-08NT0006557

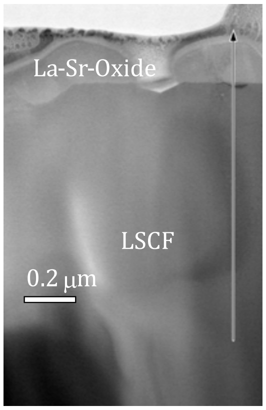
LSM-Infiltrated MSRI Cells

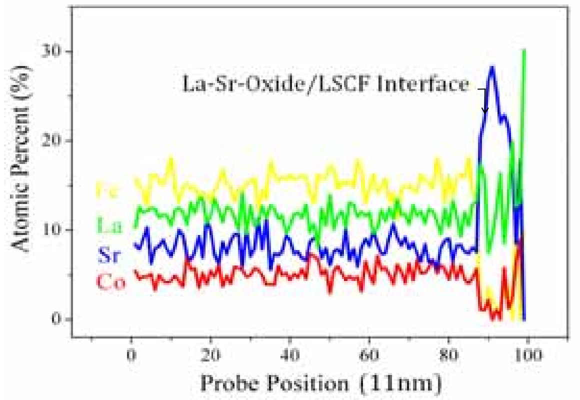


Part 2

Ex Situ Analysis: Electron Microscopy and Spectroscopy

LSCF Annealed at 850^oC/900 h





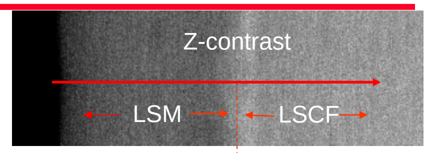
- Excess Sr & La were detected on the surface (bulk 6428).
- Oxides of Sr/La reduce surface catalytic activity for ORR.
- Growth of Sr/La oxide layer may cause degradation.

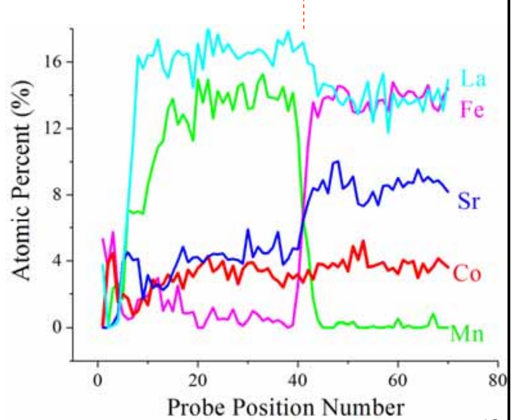
LSM Film on LSCF (Annealed at 850^oC/900 h)

- **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 to 4 at.%**

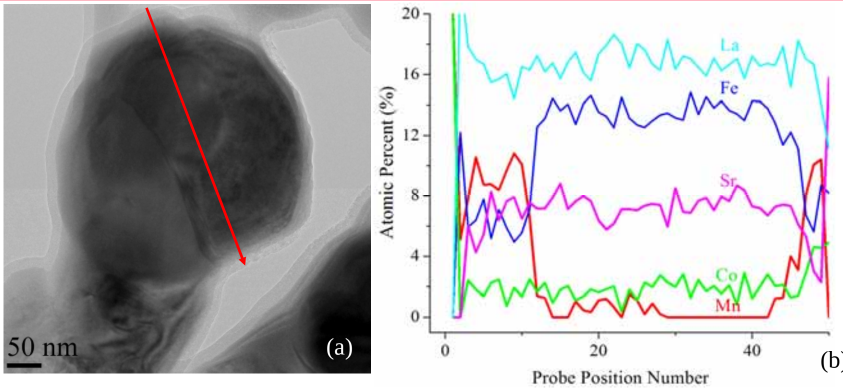
Samples are annealed at 850^oC for 900 h

Lynch, EES, 4, 2249-2258 (2011).





Profile across a LSM coated LSCF Grain



Samples are annealed at 850°C for 900 h

- **Similar to previous profile**
- **~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**

Implications of Microanalyses

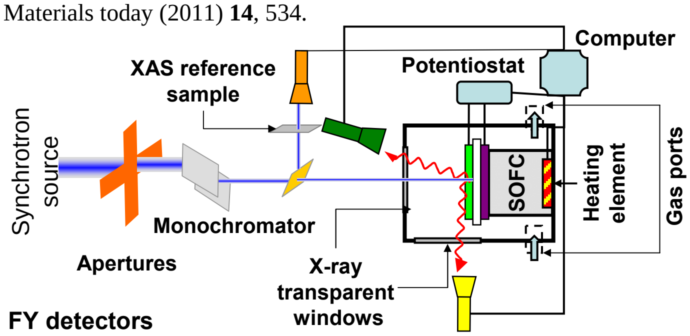
- Observed Sr/La-enriched particles on LSCF surface. This may be the origin of poor performance or degradation during operation.
- Confirmed the absence of surface Sr oxides or Sr-enriched phases on LSM-infiltrated LSCF surface under operating conditions, an indication that LSM suppresses Sr enrichment on LSCF surface.
- LSM coatings are stable on LSCF: Mn is retained in the top layer and no appreciable thickness change after annealing.

Part 3

In Situ Synchrotron-Based X-Ray Analysis

Synchrotron-Enabled XRD, XAS, & XPS

Liu et al., Materials today (2011) **14**, 534.

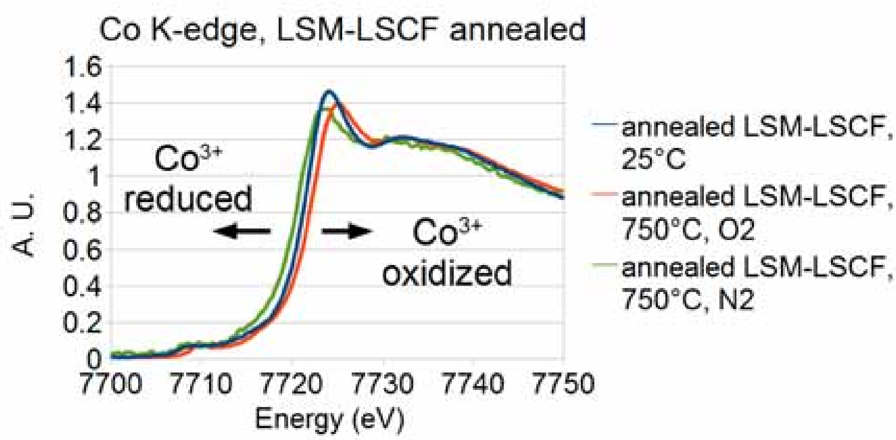


- Provides unique ability to study *bulk and surface structures* simultaneously via fluorescent X-ray absorption spectroscopy (XAS), Auger electron yield, and X-ray diffraction (XRD)
- Probe *near-surface* of electrode and identify surface composition, structure and chemical environment of specified element under *in situ* conditions: temperature, atmosphere, and bias
- Examine *interface reactions* between electrode and electrolyte under *in situ* conditions: temperature, atmosphere and bias

Critical questions to be answered

- **How do specific elements/dopants in electrodes *change chemically* and *structurally* under operating conditions?**
- **How does the electrode *surface* differ from the *bulk* chemically and structurally under operating conditions?**
- **How are these phenomena related to the observed electrode kinetics, catalytic properties, and performance?**

Redox behavior of Co in LSCF

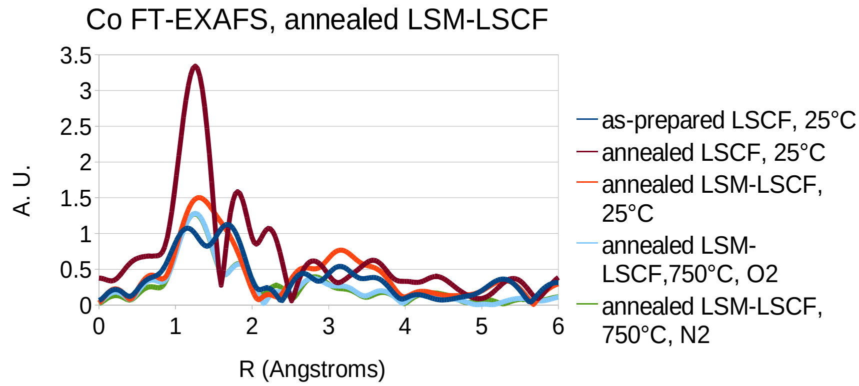


- **The edge shifts represent reversible changes in oxidation state.**
- **Directly observed *in situ* Co ions in response to pO2 at 750°C.**

Lai, Liu, Alamgir, et al., under review

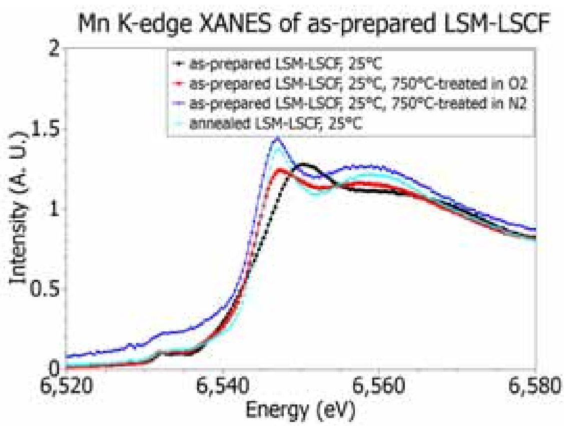
Local Structure of Co in LSCF

- Local structure of Co bonds relaxing due to thermal annealing based peak splitting and growth in FT-EXAFS (dark blue vs. brown)
- Local structure of Co unaffected by oxidizing/reducing (light blue and green) although Co oxidation state changes immediately



Lai, Liu, Alamgir, et al., under review

Partial Reduction of Mn upon Annealing

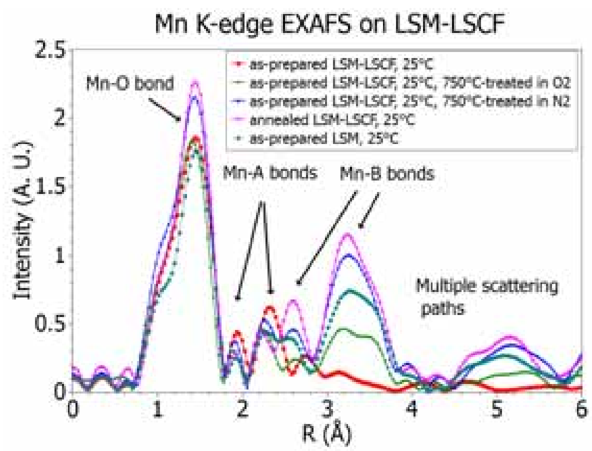


Regardless of atmosphere, the Mn edge shifts to lower energy with annealing at 750C, indicating reduction in the oxidation state.

The Mn K-edge XANES of as-prepared LSM-LSCF measured under ambient conditions and after thermal treatments of 750°C under oxygen and nitrogen.

Lai, Liu, Alamgir, et al., under review

Ordering of Mn During Annealing

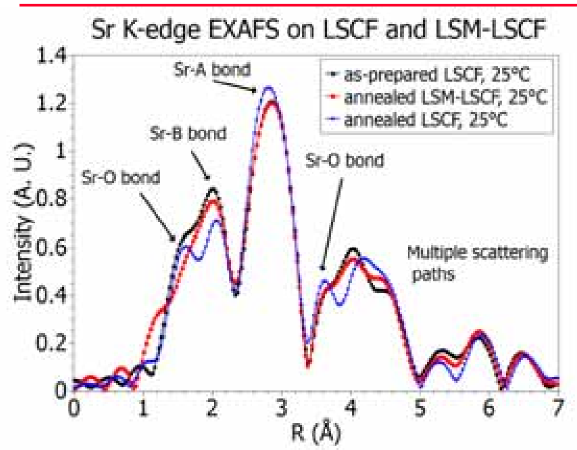


The Mn K-edge FT EXAFS of as-prepared LSM-LSCF measured under ambient conditions and after thermal treatments of 750°C under oxygen and nitrogen.

The peak growth and new features indicate ordering of the Mn local structure during annealing.

Lai, Liu, Alamgir, et al., under review

Changes in local structures of Sr



Peak splitting and peak shifting (at 2.8 Å) represent slight structural deformation, implying Sr segragation.

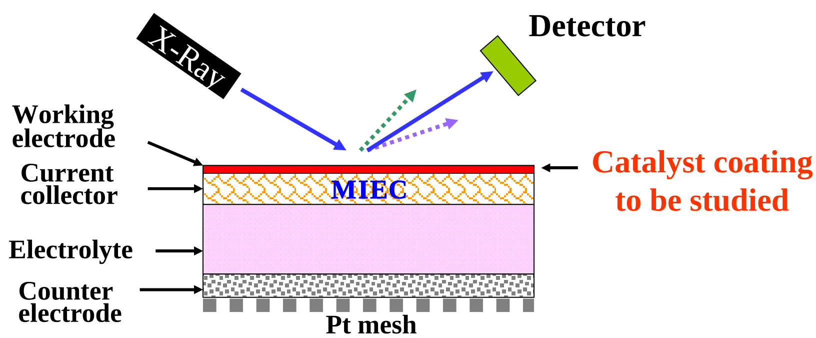
The Sr K-edge Fourier-transformed (FT) EXAFS of as-prepared LSCF, annealed LSCF, and annealed LSM-infiltrated LSCF at ambient temperature and pressure.

Lai, Liu, Alamgir, et al., under review

Effect of Change in pO_2 at 750°C

- The oxidation states of Mn and Co are both affected in the as-prepared LSM-infiltrated LSCF but in the annealed version of the cathode (i.e., LSM-Co, only the oxidation state of the Co was affected by the oxygen partial pressure stimulus at operating temperature.
- When Co cation has diffused into the LSM thin film, it is preferable for Co to be reduced or oxidized, instead of Mn, in response to change in pO2.
- It appears that Co is structurally more stable in the LSM structure than in the LSCF structure, which enables long-term durability of LSM-infiltrated LSCF compared to the gradual degradation of the blank LSCF cathode.
- There is difference in Fe-O, Co-O, and Sr-O coordination shells in annealed LSCF and LSM-infiltrated LSCF, especially for Sr-O near surface, implying Sr enrichment or segregation.

Glancing Angle Geometry for X-ray Analysis

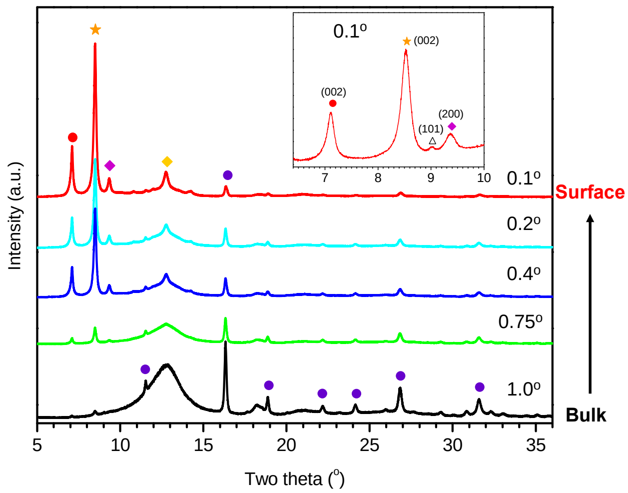


The information depth of XRA (to be bulk- or surface-sensitive) can also be tuned to varying degrees by using a combination of transmission spectroscopy and glancing angle geometries.

Control of the information depth is especially important for catalyst-coated cathodes because of the nature of their thin film.

Glancing-Angle XRD

"Surface" is structurally quite different from that of "bulk"

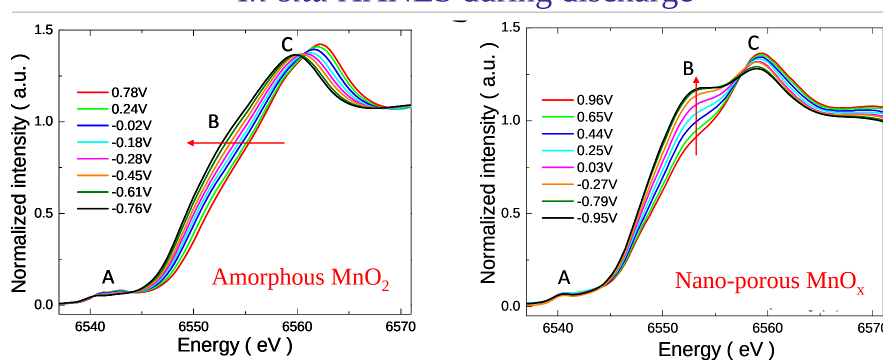


A gradient in oxidation state of cation along the thickness direction.

Nano Lett., 2012, 12 (7) 3483; **dx.doi.org/10.1021/nl300984y**

Effect of Electrical Polarization

In-situ XANES during discharge



(a) In-situ XANES spectra showed an entire edge shift towards lower energy in a continuous manner, suggesting that the charge storage is mostly associated with the Mn^{3+}/Mn^{4+} redox reactions as conventionally believed. (b) The behavior of the nano-porous MnOx is different.

Nano Lett., 2012, 12 (7) 3483; **dx.doi.org/10.1021/nl300984y**

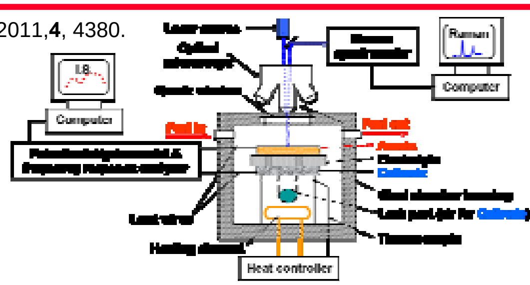
Part 4

Raman Spectroscopy

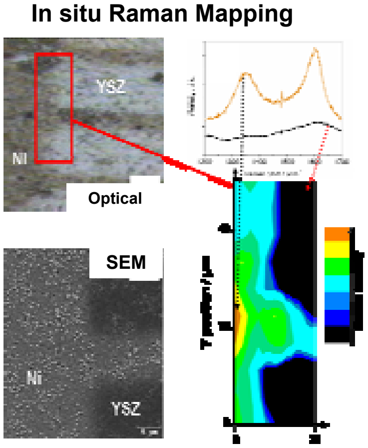
Surface Enhanced Raman Spectroscopy

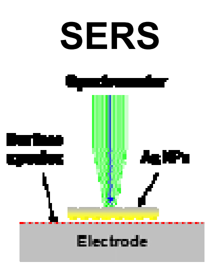
In Situ Raman Spectroscopy

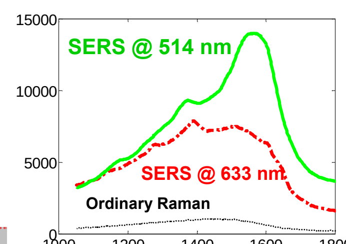
Cheng et al., Energy & Env. Sci., 2011,**4**, 4380.



In situ Raman Mapping







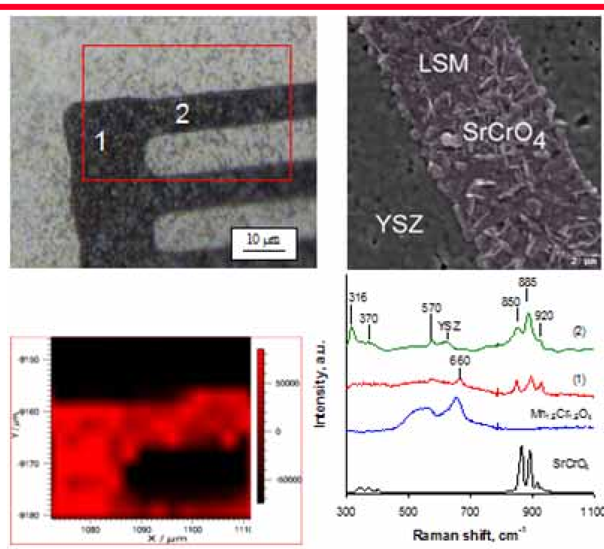
Blinn et al., Energy & Env. Sci., 2012,**5**, 7913

Li et al., PCCP, 14, 5919, 2012

Potential Applications

- Many species of interest are Raman-active:
  - Many fuel cell electrolyte/electrode materials
  - Carbon, sulfur, Cr, and other contaminants
  - Water, CO2, etc..
- Potential Applications:
  - Surface stoichiometry of electrodes
  - Surface phase evolution during operation
    - SrO segregation on LSCF surface
    - LSM surface chemistry relevant to activation
  - Interpret the catalytic properties and degradation mechanism

Cr Poisoning of LSM cathodes



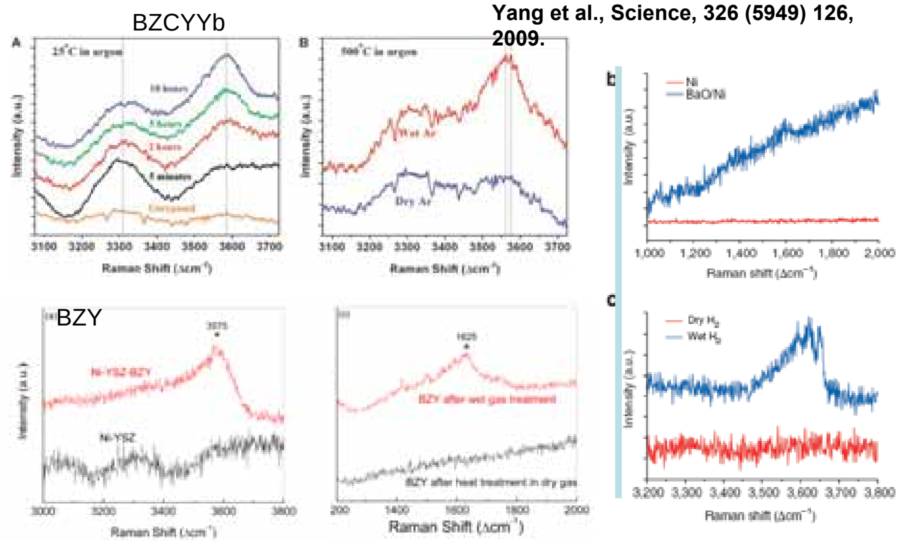
Raman mapping of $SrCrO_4$ on patterned LSM cathode exposed to Cr-containing vapor at 625ºC for 24 hrs.

Abernathy et al., J. Phy. Chem. C, 112 (34), 13299-13303, 2008

Enhancing Cathode Performance and Stability through Infiltration
FC26-08NT0006557

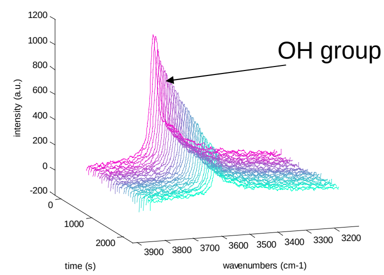
OH stretching ($3300 cm^{-1}$) and water bending ($1600 cm^{-1}$)

Yang et al., Science, 326 (5949) 126, 2009.



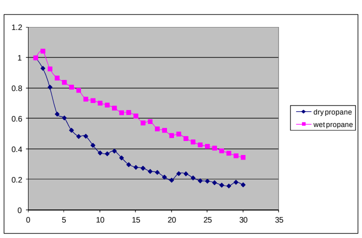
Liu et al., Nano Energy, 1, 448-455, 2012.

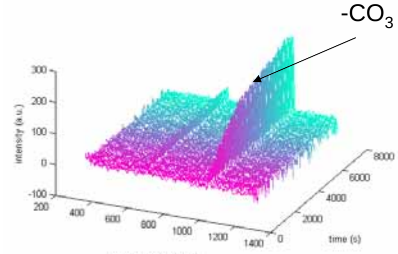
In situ Raman study of BaO exposed to C_3H_8



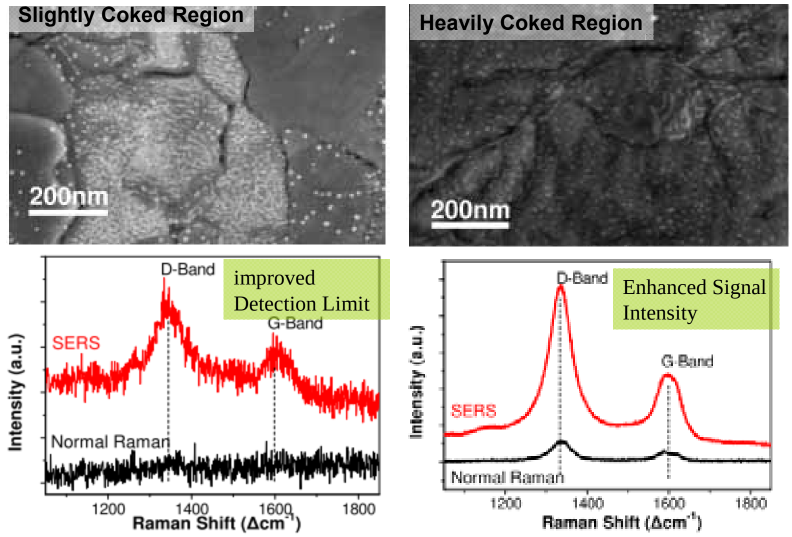
Peak normalized by the –OH at t=0

The elimination of –OH group with wet propane is slower than with dry propane



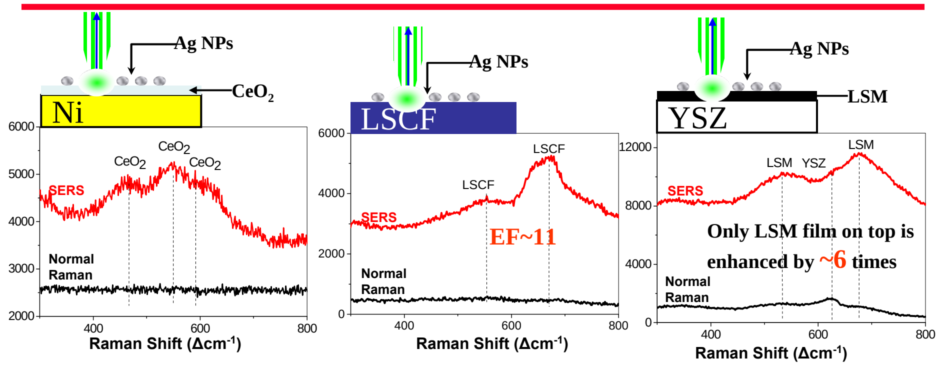


SERS Enhanced Sensitivity to Coking



Blinn et al., Energy & Env. Sci., 2012, **5**, 7913, DOI:10.1039/c2ee21499g

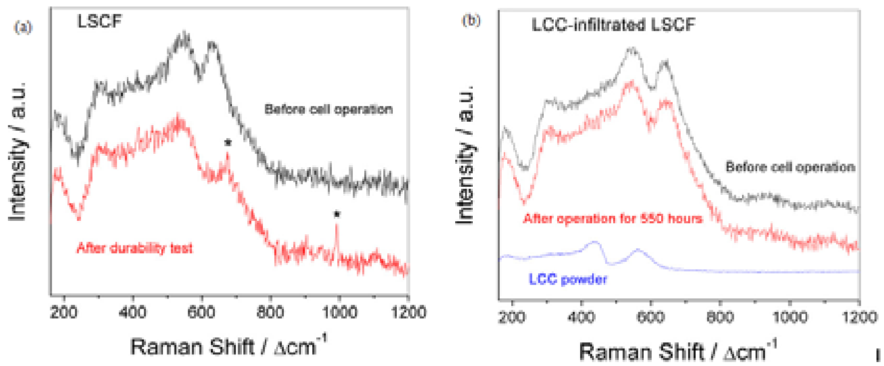
Sensitivity & Surface Specificity



- **SERS allowed detection of**
  - ***Electro-deposited CeO_2 on Ni*** **otherwise not observable by normal Raman or SEM**
  - **Phases of weak Raman response** (e.g., E_g modes of **rhombohedral** LSCF)
  - **Surface signal mixed with bulk signal** (E_g bands **of 100 nm LSM on YSZ)**
- **Considerable signal boost and surface specificity**

Li et al., Phy. Chem. Chem. Phy., 14, 5919, 2012.

SERS for Catalyst-Coated LSCF Cathodes



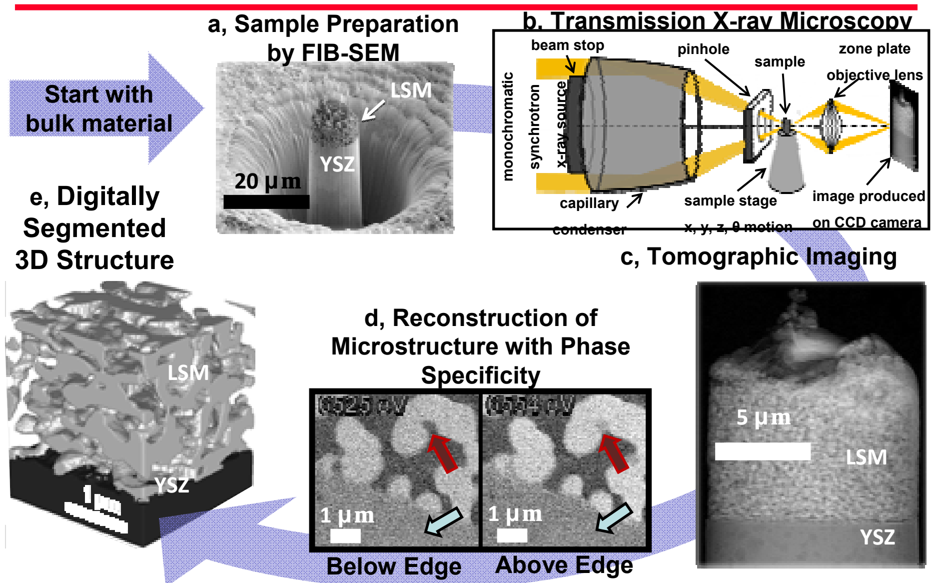
- The peaks at 1000 cm-1 and 675 cm-1 might represent A1g mode of Co_3O_4 phase (Ref . J Phys. C Solid State Phys. 21(1988) L199.)
- A small sloped shoulder centered at 435 cm-1 in the spectra for the LCC-infiltrated sample corresponding to a broad peak in the spectrum collected from LCC powder.

Part 5

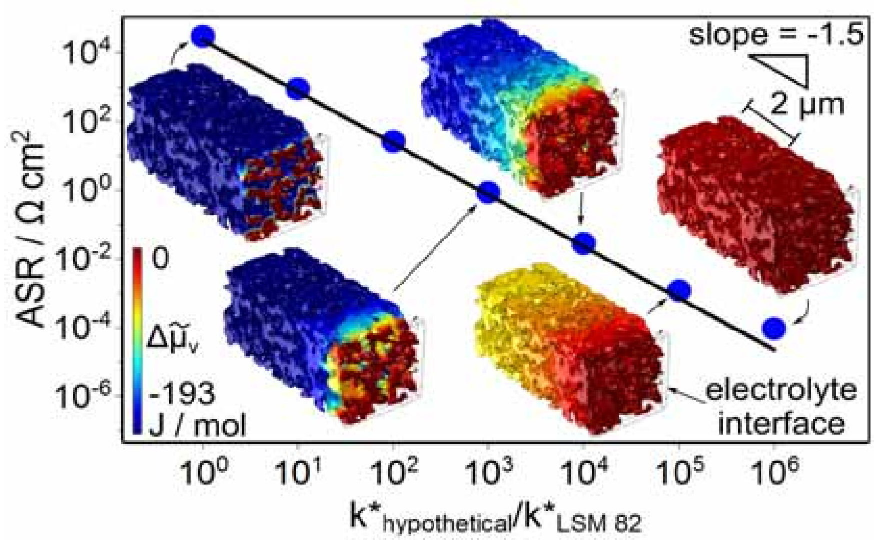
Modelling and Simulation: Quantifying the effects of Microstructure

M. Lynch, W. Chiu, M. Liu, et al., Nano Energy, 2012, accepted.

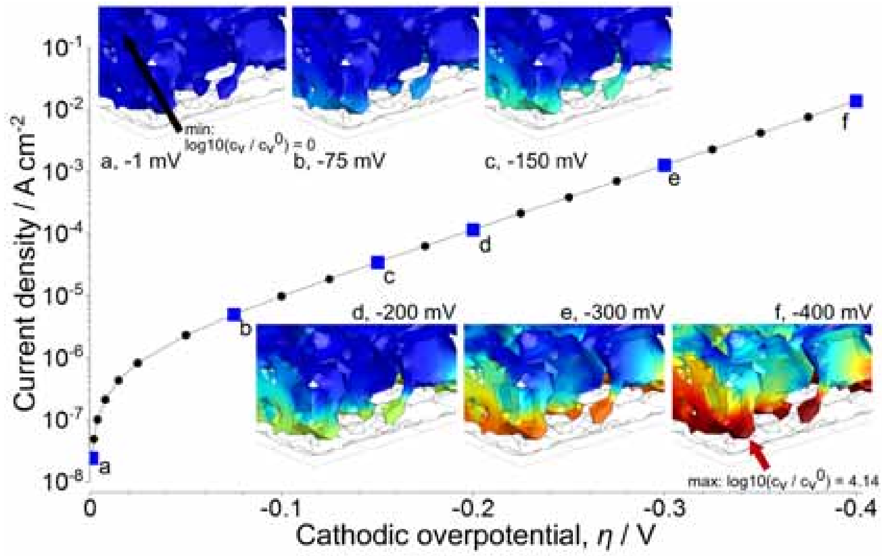
Reconstruction of 3D structure



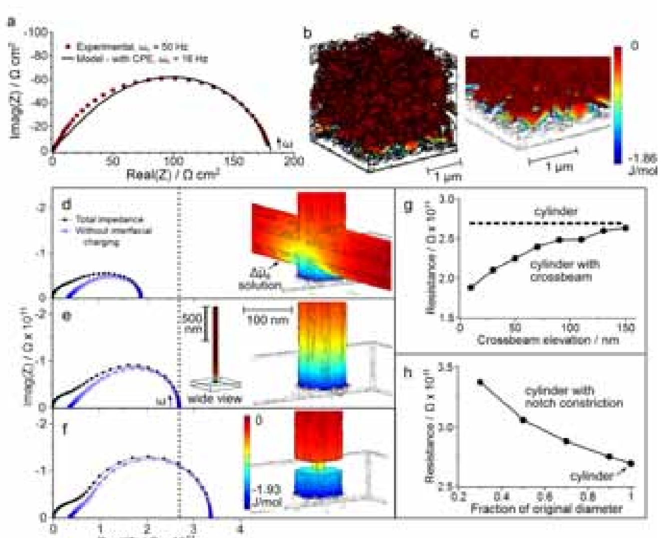
Bulk Pathway Simulations



Effect of DC Polarization



Effect of *Local* Morphology on Performance



Accomplishments to date

- Developed new Mn-based catalysts for infiltration into porous LSCF cathode, demonstrating that several new catalysts offered higher ORR activity than LSM;
- Optimized the LSM infiltration process for commercially available MSRI cells with LSCF cathodes and demonstrated enhanced activity and stability;
- Characterized atomistic & electronic structure of Co, Mn, and Sr in LSCF cathode with/without LSM coating at 850°C annealed for 400 hours using synchrotron-based X-ray absorption spectroscopy (XAS);
- Applied Raman techniques (including SERS) to probing LSM and LSCF films, Cr-containing phases, and other species relevant to cathode degradation (e.g., water, CO_2, and other contaminants).
- Developed models for performance prediction of porous cathodes.

Acknowledgement

Discussions with
Briggs White, Kirk Gerdes, & Jeff Stevenson

DOE-SECA Core Technology Program
Under Grant No. DE-NT0006557.

DOE Basic Energy Science
Energy Frontier Research Center