Enhancement of SOFC Cathode Electrochemical Performance Using Multi-Phase Interfaces

Dane Morgan, Yueh-Lin Lee  
Department of Materials Science and Engineering  
University of Wisconsin – Madison, WI USA

Stuart Adler, Timothy (TJ) McDonald  
Department of Chemical Engineering  
University of Washington, Seattle, WA USA

Yang Shao-Horn, Dongkyu (DK) Lee  
Department of Mechanical Engineering  
Massachusetts Institute of Technology, Boston, MA USA

14th Annual SECA Workshop  
Sheraton - Station Square, Pittsburgh, PA  
July 23 – 24, 2013
Acknowledgements

External Collaborators
• Michael D. Biegalski, H.M. Christen (Oak Ridge National Laboratory)
• Paul Fuoss, Edith Perret, Brian Ingram, Mitch Hopper, Kee-Chul Chang (Argonne National Laboratory)
• Paul Salvador (Carnegie Melon University)
• Briggs White (NETL)

This material is based upon work supported by the Department of Energy under Award Number DE-FE0009435).
Oxide Heterointerface for SOFC Cathodes

Interface of two oxides: Enhances ORR kinetics by orders of magnitude compared to individual phases\(^1\)-\(^4\)

**LSC-214:** K\(_2\)NiF\(_4\) type
AO-AO-BO\(_2\) stacking, coating

**LSC-113:** ABO\(_3\) Perovskite
(AO-BO\(_2\) stacking)
Cathode Material

Novel Heterostructure Enhances ORR kinetics at 500-600° C

Oxide Heterointerface for SOFC Cathodes

**Interface of two oxides:** Enhances ORR kinetics by orders of magnitude compared to individual phases\(^1-4\)

1. How does this interfacial enhancement work?
2. Can it be extended to XYZ-214/LSCF-113 interfaces?
3. Can we make more active, more stable cathodes with these interfaces?

---

Project Overview

Yang Shao-Horn (MIT)
Present work: LSC-214/LSC-113 and LSC-214/LSCF-113

Dane Morgan (U Wisc.)
Present work: Sr Thermodynamics in LSC, LSCF

Stuart Adler (U Wash.)
Present work: (NLEIS) on LSC$_{113}$, LSCF$_{113}$

Ab initio Energetics Thermokinetic Modeling

NLEIS + Rate modeling, LSC-214/LSCF-113 porous electrodes

LSC-214/LSCF-113 Films

LSC-214
LSCF-113
Overall Conclusions

• LSC$_{214}$ enhances LSCF$_{113}$ (~3x) far less than LSC$_{113}$ (~100x)

• LSCF$_{113}$ has a more stable and Sr rich surface than LSC$_{113}$
  – Supported by aspects of AFM, Auger, DFT, NLEIS

• LSC$_{214}$ changes Sr stability of LSC$_{113}$ more than LSCF$_{113}$ and may enhance LSC$_{113}$ performance by stabilization of Sr rich interface
  – Supported by AFM, Auger, COBRA, DFT
What Are Our Compositions?

- $\text{LSC}_{113} = (\text{La}_{0.8}\text{Sr}_{0.2})\text{CoO}_3$
- $\text{LSCF}_{113} = (\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_3$
- $\text{LSC}_{214} = (\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$
Project Overview

LSC-214/LSCF-113 Films

Yang Shao-Horn (MIT)
Present work: LSC-214/LSC-113 and LSC-214/LSCF-113

Ab initio Energetics
Thermokinetic Modeling

Dane Morgan (U Wisc.)
Present work: Sr Thermodynamics in LSC, LSCF

NLEIS + Rate modeling,
LSC-214/LSCF-113 porous electrodes

Stuart Adler (U Wash.)
Present work: (NLEIS) on LSC_{113}, LSCF_{113}
Surface Exchange Kinetics

- LSC\textsubscript{214} decoration can slightly enhance the surface exchange rate \( (k^q) \) of LSCF.
- LSC\textsubscript{214} decorated LSCF shows comparable \( k^q \) with LSC\textsubscript{214}.
Auger Electron Spectroscopy of LSC\textsubscript{113} and LSC\textsubscript{113/214} on GDC/YSZ (001)

LSC\textsubscript{113}

Pristine

Annealed

LSC\textsubscript{113/214}

Pristine

Annealed

\[ 10 \, \mu m \]

\[ 10 \, \mu m \]

T=550°C

PO\textsubscript{2}=1atm

\( k^g / \text{cm sec}^{-1} \)

Annealing Time / hrs

\[ 10^{-10} \]

\[ 10^{-9} \]

\[ 10^{-8} \]

\[ 10^{-7} \]

Feng et al., JPCL 2013 and D Lee*, YL Lee* et al, Manuscript In Preparation
Sr Occupancy in LSC$_{113}$ Surface

Coherent Brag Rod Analysis (COBRA)

550°C, PO$_2$=1atm

Consistent with DFT (~0.75 Sr)

LSC$_{113}$ has about 0.6-0.8 Sr in top (La,Sr)O [001] layer

Sr Occupancy in LSC$_{214}$/LSC$_{113}$ Interface

Sr in interface and LSC$_{214}$ film and depleted from LSC$_{113}$
Surface Sr Segregation => Enhanced Activity of LSC\textsubscript{113/214}

More active, more stable

**Sr Occupancy in LSCF$_{113}$ Surface**

- **Ab initio** analysis predicts LSCF$_{113}$ (001) AO surface with surface layer Sr conc. 100% is stable.
- Agreement between *ab initio* thermodynamic analysis and the Low Energy Ion Scattering (LEIS) measurement.

\[ \Delta \mu^{eff}_{\text{Fe}(\text{LSCF}_{113})} = -0.24 \text{ eV vs. } \mu^{eff}_{\text{Fe}(\text{Fe}_2\text{O}_3)} \]

Fig. 1. LEIS spectra (3 keV $^4$He$^+$ ions) for LSCF annealed in air for 8 h at various temperatures. Vertical lines indicate theoretical scattering edges for two-body scattering.

Druce SSI 2014

\[ \Delta \mu^{err}_{\text{Sr}(\text{La}_{0.625}\text{Sr}_{0.375}\text{Fe}_{0.75}\text{Co}_{0.25}\text{O}_3)}, \text{ eV} \]

Lee *et al.* in *prep*
Sr Occupancy in LSC\textsubscript{214}/LSCF\textsubscript{113} Interface

Ab initio analysis predicts LSCF\textsubscript{113} more stable vs. Sr reaction with LSC\textsubscript{214} than LSC\textsubscript{113}.

Gadre, PCCP, 2012; Lee et al. in prep
Sr Occupancy in LSC\textsubscript{214}/LSCF\textsubscript{113} Interface

Ab initio analysis predicts LSCF\textsubscript{113} more stable vs. Sr reaction with LSC\textsubscript{214} than LSC\textsubscript{113}
P-band Correlation for SOFC Oxygen Reduction

\[ y = 3.76x + 2.38 \]

\[ R^2 = 0.87 \]

Lee, Rossmeisl, Shao-Horn, Morgan, EES 2011
P-band Correlation Consistent with Interfacial Enhancements

LSC\textsubscript{214}/LSC\textsubscript{113} (100% Sr)

LSC\textsubscript{113} (Sr 62.5%)

LSC\textsubscript{113}

(100% Sr)

10\textsuperscript{-7} - 10\textsuperscript{-10}

10\textsuperscript{-8} - 10\textsuperscript{-9}

10\textsuperscript{-10}

10\textsuperscript{-11}

Relative k\textsuperscript{q} ratio vs base film

Relative bulk O 2p band center shifts vs base film / eV

Annealing Time / hrs

Annealing Time / hrs
Summary

- Coating with LSC$_{214}$ enhances LSC$_{113}$ much more than LSCF$_{113}$.
- Ab initio and COBRA surface stability analysis suggests
  - Unsaturated surface layer Sr content (60~75%) for LSC$_{113}$ within the bulk stability region
  - Saturated Sr content (100%) for LSCF$_{113}$ within the bulk stability region
- LSC$_{214}$ decoration $\rightarrow$ Introduces Sr/La chemical potential perturbation near surface for LSC$_{113}$ more than LSCF$_{113}$
  - Strong thermodynamic driving force (-0.7~-0.9 eV) for Sr$_{La}$ interdiffusion between LSC$_{113}$ and LSC$_{214}$
  - Little thermodynamic driving force for Sr$_{La}$ interdiffusion (-0.2 eV) between LSCF$_{113}$ and LSC$_{214}$
  - Sr segregation with LSC$_{214}$ decoration observed for LSC$_{113}$ but not LSCF$_{113}$, consistent with DFT. May be origin of enhanced performance!
  - Longer-term (10h-70h) surface exchange kinetics may couple with formation of surface Sr secondary phases and surface Sr concentrations making it sensitive to Sr segregation induced by LSC$_{214}$. 
Project Overview

Yang Shao-Horn (MIT)
Present work: LSC-214/LSC-113 and LSC-214/LSCF-113

Dane Morgan (U Wisc.)
Present work: Sr Thermodynamics in LSC, LSCF

Stuart Adler (U Wash.)
Present work: (NLEIS) on LSC$_{113}$, LSCF$_{113}$
Non-Linear Impedance Spectroscopy (NLEIS) on LSC$_{113}$, LSCF$_{113}$

Adler (Univ. Washington)
Electrochemical Measurements

**EIS**
- Current Perturbation
- Voltage Response
- Electrochemical System
- Fourier Analysis
- Harmonic Responses

**NLEIS**
- Current Perturbation
- Voltage Response
- Electrochemical System
- Fourier Analysis
- Harmonic Responses

NLEIS insensitive very sensitive to kinetic/transport and thermodynamic properties
Example: \((\text{La}_{0.8}\text{Sr}_{0.2})\text{CoO}_3\) thin films

Volume-Specific Capacitance (VSC) of LSC thin films vs. pO2 and thickness

Predicted from bulk model (Kawada, et al. JES ’02)
Example: \((\text{La}_{0.8}\text{Sr}_{0.2})\text{CoO}_3\) thin films

NLEIS response of 34 nm LSC-82 thin film vs. pO2

- Results completely inconsistent with bulk thermodynamic properties of LSC-82.
- Hard to rationalize based on any reasonable rate law and properties under the assumption that the film is single phase perovskite with uniform strontium content.
Example: \((\text{La}_{0.8}\text{Sr}_{0.2})\text{CoO}_3\) thin films

Films exhibit Sr stratification both perpendicular and lateral to interface.

SIMS depth profile on 90nm film
Richard Chater and John Kilner, Imperial College

Crumlin, et al. (MIT)
SEM
Example: \((\text{La}_{0.8}\text{Sr}_{0.2})\text{CoO}_3\) thin films

Revised model (T.J. McDonald):

Forward rate law depends on local vacancy defect concentration \((\delta)\) in the surface layer.

\[
\begin{aligned}
\left( L_{\text{SL}} \frac{d\delta_{\text{SL}}}{dt} + L_{\text{bulk}} \frac{d\delta_{\text{bulk}}}{dt} \right) \frac{c_0}{3} &= \frac{-\tilde{i} \cos(\omega t)}{2 F} \\
&- 2\gamma \mathcal{R}_0 \left[ 1 - e^{-\Lambda} \right] - 2(1-\gamma) \mathcal{R}_0 \left[ 1 - e^{-\Lambda} \right]
\end{aligned}
\]

Forward rate law \( \mathcal{R}_0 = k(T)p_{O_2} \delta^2 \) depends on local vacancy defect concentration \((\delta)\) in the surface layer.
Example: $(\text{La}_{0.8}\text{Sr}_{0.2})\text{CoO}_3$ thin films

Dual Surface, Altered Bulk Model

- Capacitance and harmonic response agree well.
- Implies Sr segregation is laterally inhomogeneous.
- $\text{O}_2$-active material for all films has properties of LSC (113) with $x_{s}^{(1)} \sim 0.45$.

Conclusions

Speculation

These films all show precipitation of secondary phases. Could the active material be associated with two-phase saturation/precipitation?
Porous LSCF
• Decreasing $C$ with $p_{O_2}$ reflects loss of vacancies and shorter utilization length.
• Justifies use of 1-D macrohomogeneous model for EIS and NLEIS analysis.
\begin{itemize}
  \item No models fit perfectly, suggesting inhomogeneous properties.
  \item Impossible explain results without increased reducibility of surface relative to bulk (may be due to Sr enrichment at surface)
  \item Transport rates too fast to be consistent with bulk diffusion alone – Implies significant surface diffusion.
  \item Kinetics appear to be 1\textsuperscript{st} order in pO2, and somewhere between 1\textsuperscript{st} and 2\textsuperscript{nd} order in vacancy concentration.
\end{itemize}
Overall Conclusions

• $\text{LSC}_{214}$ enhances $\text{LSCF}_{113}$ ($\sim3x$) far less than $\text{LSC}_{113}$ ($\sim100x$)

• $\text{LSCF}_{113}$ has a more stable and Sr rich surface than $\text{LSC}_{113}$
  – Supported by aspects of AFM, Auger, DFT, NLEIS

• $\text{LSC}_{214}$ changes Sr stability of $\text{LSC}_{113}$ more than $\text{LSCF}_{113}$ and may enhance $\text{LSC}_{113}$ performance by stabilization of Sr rich interface
  – Supported by AFM, Auger, COBRA, DFT
Future Work

• Investigate other 214 decoration candidates to achieve the enhanced surface activity (e.g. (La,Sr)$_2$NiO$_4$, (La$_{0.25}$Sr$_{0.75}$)CoO$_4$)

• Investigate the short- and long-term degradation of LSCF$_{113}$ and LSC$_{214}$/LSCF$_{113}$ and relate to surface properties

• Film growth + Physical characterization (MIT)

• Ab initio stability /reaction energies (Univ. Wisconsin)

• NLEIS + Modeling (Washington Univ.)
Thank you for your attention
Backup for Yang
La$_{0.5}$Sr$_{0.5}$Co$_2$O$_4$ (LSC$_{214}$) decorated LSC$_{113}$ on STO

Z. Feng, Y. Yacoby, W. T. Hong, et al. *JPCL* 2014
Understanding Oxide Surface Chemistry Critical to Activity and Stability

T = 550°C
PO$_2$ = 1 atm

![Graph showing the relationship between annealing time and reaction rate for different oxide compositions. The graph includes data points for LSC$_{113}$, LSCF$_{113}$, LSM$_{113}$, and LSC$_{214}$/LSCF$_{113}$, with a focus on the reaction rate constant $k^q$ in cm sec$^{-1}$.]

D Lee et al., *JPCC submitted*
LSM Decoration Enhances Surface Stability

T=550°C
PO₂=1atm

D Lee et al., JPCC submitted
LSM Decoration Enhances Surface Stability

T=550°C
PO$_2$=1atm

- Mn incorporation into in LSC may drive surface stabilization, enhancing activity and durability.
- Role of Sr unclear.

D Lee et al., JPCC submitted
O₂ electrocatalysis on perovskites at high temperatures

Equation: $y = 3.76x + 2.38$

$R^2 = 0.87$

$T = \sim 1000 \text{ K}$

$P(O_2) = \sim 0.2 \text{ atm}$

Lee, Rossmeisl, Shao-Horn, Morgan, EES 2011
Relative $k^q$ ratio vs base film

$\text{LSC}_{214}/\text{LSC}_{113} \ (100\% \text{ Sr})$

$\text{LSC}_{214}/\text{LSC}_{113} \ (100\% \text{ Sr})$

$\text{LSC}_{113} \ (\text{Sr 62.5\%})$

$\text{LSC}_{113} \ (100\% \text{ Sr})$

Relative bulk O 2p band center shifts vs base film / eV

$10^{\sim}100X$

$k^q / \text{cm sec}^{-1}$

Annealing Time / hrs

$2X$

Annealing Time / hrs
Outline

- Introduction
- Case Studies
  - In situ studies of Solid oxide fuel cell interfaces
  - Layer-by-layer chemical distribution and oxygen disorder in oxides catalysts
- Summary
Crystal Truncation Rod (CTR)

Real Space

- Bulk Single Crystal
- Single layer
- Thin film
- Single crystal substrate

Electron Density (EDY)

Reciprocal Space

- Bulk Bragg points
- Crystal truncation rods

Fourier Transform (FT)

$I(L) \propto |F(L)|^2$

$F(L)$: Structure Factor
CTR and Coherent Bragg Rod Analysis (COBRA)

Real Space

- Thin film
- Single crystal substrate
- Electron Density (EDY)

Reciprocal Space

- Crystal truncation rods
- Bulk Bragg points
- Structure Factor: $T = |T| \exp(i\phi)$

Fourier Transform (FT)

COBRA working principle

1. Reference EDY
2. Compare with CTR Data
3. Calculate the difference
4. Update reference EDY

Output

3D EDY

Information we can obtain

$4 \text{ nm } \text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}/\text{STO(001)}$

LSC_{113} 8020 (4 nm) Model systems: layer-by-layer growth

Annealing was performed at 550 °C with 400 Torr pure O\textsubscript{2} condition for 1 hour.

COBRA results

As-deposited

STO LSC film

Sr Ti particles

Annealed

(0 0 Z) (0.5 0.5 Z)

La/Sr Co

Surface Particle Structure

Electron Density

1-D Structure

Surface Particle Structure

Apical oxygen (O\textsubscript{i}) peaks in film becomes broader and broader
position less coherent to FCC ideal structure

Oxygen Order-Disorder Transition

Sharp change between substrate and film

stronger octahedral distortion

Connections to oxygen electrocatalysis

- Oxygen become more and more disordered $\rightarrow$ stronger octahedral distortion

- Order—Disorder—Order transition $\rightarrow$ interface is important/active for incorporating and diffusing oxygen $\rightarrow$ high ORR activity
Differential COBRA

Energy dependent Atomic scattering factor

Sr depth-dependent distribution, 1st Experimental Evidence!

- Strong depletion of Sr at film/substrate interface \( \rightarrow \) substrate oxygen source
- Particles are Sr rich
- Substrate as O source

Schneider et al, *APL*, 2010
Apical Oxygen Displacement

Sr Inhomogeneity and Apical Oxygen Displacement

Kumah et. al., APL Materials, 2013, 1, 62107

La$^{3+}$ replace Ba$^{2+}$ → electrical field

Sr$^{2+}$ replace La$^{3+}$

DFT: Sr rich coupled w/ oxygen vacancies

Summary: LSC$_{113}$/STO Model System

• **Atomic Structure:**
  Oxygen order—disorder—order transition → Octahedral distortion/rotation and active interface for ORR

  Apical oxygen displacement → Electric fields (intermixing)

• **Chemistry:**
  Inhomogeneous Sr depth dependence →
  1. Octahedral distortion
  2. Substrate as oxygen source
  3. Oxygen vacancy concentration
Outline

- Introduction (materials and COBRA)
- Two Cases
  - La$_{0.8}$Sr$_{0.2}$CoO$_3$ - SrTiO$_3$
  - (La$_{0.5}$Sr$_{0.5}$)$_2$CoO$_{4+\delta}$ / La$_{0.8}$Sr$_{0.2}$CoO$_{3-\delta}$ / STO heterostructured systems
- Summary
2~4 unit cell 
(La\textsubscript{0.5}Sr\textsubscript{0.5})\textsubscript{2}CoO\textsubscript{4+δ} 

~ 3 nm LSC\textsubscript{113} 

5 unit cells 
La\textsubscript{0.8}Sr\textsubscript{0.2}CoO\textsubscript{3-δ} 

~ 2 nm LSC\textsubscript{113} 
~ 5.7 nm LSC\textsubscript{214} 

STO(001) substrate 

• Sr concentrates on 113/214 interface and 214 surface (Sr-rich particles)

• Sr is depleted in 113 bulk film.

• Non-uniformed Sr layer occupation in one LSC$_{214}$ unit cell.

DFT to explain

50% Sr 50% La in each AO layer

Alternating LaO-SrO layer

E₀ = 0 eV (Reference)
E₀ = -0.021 eV/FU (relaxed)
E₀ = -0.037 eV/FU (fixed to STO lat const)

Summary

• Electrochemical Interface is important for Energy Storage and Conversion Systems

• COBRA is unique and sensitive to obtain atomic and chemical information.

• Anomalous Sr distribution is associated with its oxygen deviation (octahedral distortion) and is related to catalytic properties.
Backup for Dane
LSC$_{113}$ and LSCF$_{113}$ Slab model
\[ \Delta \mu_{\text{eff}}^{\text{Fe}}(\text{LSCF}) = 0.0 \text{ eV vs. } \mu_{\text{eff}}^{\text{Fe}}(\text{Fe}_2\text{O}_3) \]

\[ \Delta \mu^{\text{err}}_{\text{Sr}}(\text{La}_{0.625}\text{Sr}_{0.375}\text{Fe}_{0.75}\text{Co}_{0.25}\text{O}_3), \text{ eV} \]

\[ \Delta \mu_{\text{eff}}^{\text{Fe}}(\text{LSCF}) = -0.12 \text{ eV vs. } \mu_{\text{eff}}^{\text{Fe}}(\text{Fe}_2\text{O}_3) \]

\[ \Delta \mu^{\text{err}}_{\text{Sr}}(\text{La}_{0.625}\text{Sr}_{0.375}\text{Fe}_{0.75}\text{Co}_{0.25}\text{O}_3), \text{ eV} \]

\[ \Delta \mu_{\text{eff}}^{\text{Fe}}(\text{LSCF}) = -0.24 \text{ eV vs. } \mu_{\text{eff}}^{\text{Fe}}(\text{Fe}_2\text{O}_3) \]

\[ \Delta \mu^{\text{err}}_{\text{Sr}}(\text{La}_{0.625}\text{Sr}_{0.375}\text{Fe}_{0.75}\text{Co}_{0.25}\text{O}_3), \text{ eV} \]

\[ \Delta \mu_{\text{eff}}^{\text{Fe}}(\text{LSCF}) = -0.36 \text{ eV vs. } \mu_{\text{eff}}^{\text{Fe}}(\text{Fe}_2\text{O}_3) \]

\[ \Delta \mu^{\text{err}}_{\text{Sr}}(\text{La}_{0.625}\text{Sr}_{0.375}\text{Fe}_{0.75}\text{Co}_{0.25}\text{O}_3), \text{ eV} \]
$\Delta \mu_{\text{eff}}^{\text{Fe}}(\text{LSCF}) = -0.0 \text{ eV vs. } \mu_{\text{eff}}^{\text{Fe}}(\text{Fe}_2\text{O}_3)$

$\Delta \mu_{\text{eff}}^{\text{Fe}}(\text{LSCF}) = -0.12 \text{ eV vs. } \mu_{\text{eff}}^{\text{Fe}}(\text{Fe}_2\text{O}_3)$

$\Delta \mu_{\text{eff}}^{\text{Co}}(\text{La}_{0.625}\text{Sr}_{0.375}\text{Fe}_{0.75}\text{Co}_{0.25}\text{O}_3), \text{ eV}$

$\Delta \mu_{\text{eff}}^{\text{Co}}(\text{La}_{0.625}\text{Sr}_{0.375}\text{Fe}_{0.75}\text{Co}_{0.25}\text{O}_3), \text{ eV}$
Backup for Stu
Electrochemical Measurements

**EIS**

- Can separate series rates by timescale.
- Arc resistance related to absolute rates.
- Arc capacitance related to defect concentrations.

**NLEIS**

- Insensitive to absolute rates (scaled out).
- Sensitive to nonlinearities in rate laws.
  - kinetic/transport mechanisms
  - surface thermodynamic properties
  - bulk thermodynamic properties