Enhancement of SOFC Cathode Electrochemical Performance Using Multi-Phase Interfaces

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Acknowledgements

External Collaborators

- Briggs White (NETL)
- Michael D. Biegalski, H.M. Christen (Oak Ridge National Laboratory)
- Paul Fuoss, Edith Perret, Brian Ingram, Mitch Hopper, Kee-Chul Chang (Argonne National Laboratory)
- Zhan Zhang, Christian M. Schlepuetz, Lynette Jirik (ID-33 of Advanced Photon Source)
- Paul Salvador (Carnegie Melon University)

Computing Support

XSEDE — NSF Supercomputing

NERSC — National Energy Research Scientific Computing Center

Center for Nanophase Materials Sciences — Oak Ridge National Laboratory

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NETL, SECA

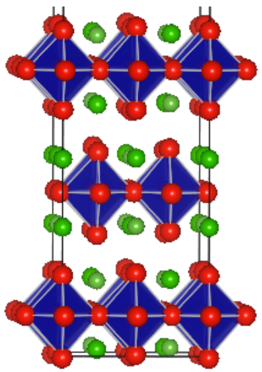
MIT Skoltech Center For Electrochemical Energy Storage

King Abdullah University of Science and Technology

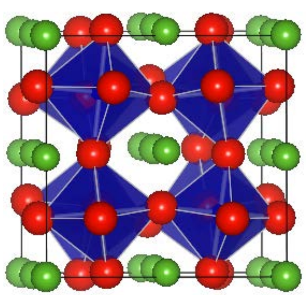
Center for Nanophase Materials Sciences — Oak Ridge National Laboratory

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_2NiF_4 type
AO-AO-BO_2 stacking, coating



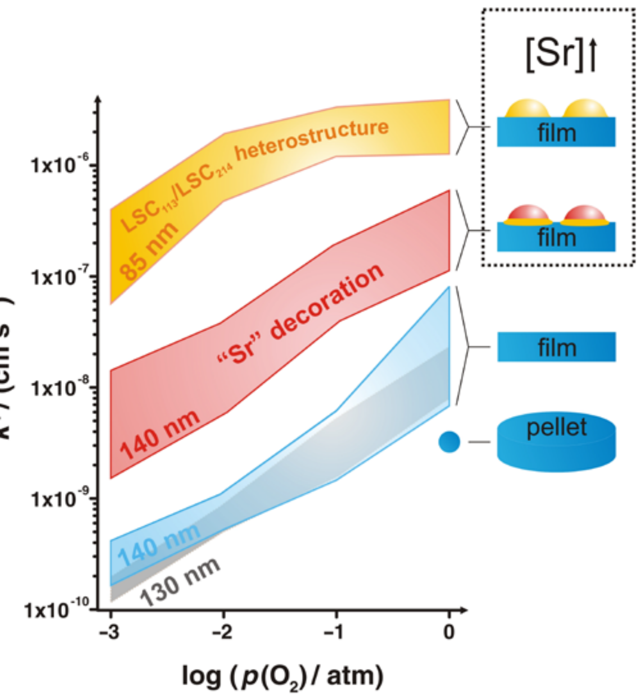
LSC-113: ABO_3 Perovskite
(AO-BO_2 stacking)
Cathode Material

Enhances ORR kinetics at 500-600° C

LSC-214

LSC-113

Novel Heterostructure



[1] E. J. Crumlin, et al., *The Journal of Physical Chemistry Letters, 1, 3149-3155.*
[2] M. Sase, et al., *Journal of The Electrochemical Society, 2008, 155, B793-B797.*
[3] M. Sase, et al., *Solid State Ionics, 2008, 178, 1843-1852.*
[4] K. Yashiro, et al., *Electrochem. Solid State Lett., 2009, 12, B135-B137.*

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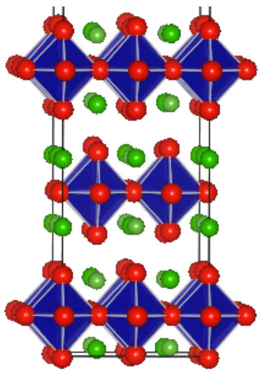

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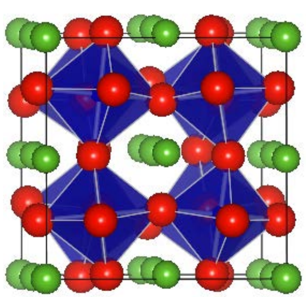

LSC-113: ABO_3 Perovskite
(AO-BO_2 stacking)
Cathode Material

1. **How does this interfacial enhancement work in LSC_{113}?**
2. **Can it be extended to $XYZ_{214}/LSCF_{113}$ interfaces?**
3. **Can we make more active, more stable porous electrodes with these interfaces?**

Completed 33/36 months of project

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Conclusions

1. How does this interfacial enhancement work in LSC_{113}?

   Stabilization of Sr-rich LSC_{113} surface and suppression of Sr-rich precipitation

2. Can it be extended to $XYZ_{214}/LSCF_{113}$ interfaces?

   Yes! $LSC_{214}/LSC_{113}/LSCF_{113}$ enhances $LSCF_{113}$ 10x!

3. Can we make more active, more stable porous cathodes with these interfaces?

   Promising initial results but needs more work with NETL, industry teams, future proposals …

Project Overview

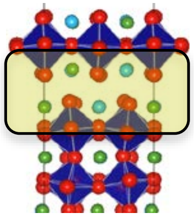
LSC-214/LSCF-113 Films

LSC-214

LSCF-113

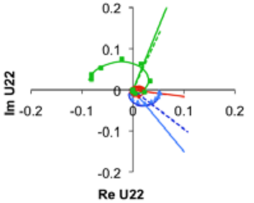
Yang Shao-Horn (MIT)

Ab initio Energetics
Thermokinetic Modeling



Dane Morgan (U Wisc.)

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



Stuart Adler (U Wash.)

Major Activities

- PLD synthesis and physical (SEM, xray, Auger, COBRA) electrochemical (EIS) characterization of LSC_{113}, $LSCF_{113}$, LSC_{214}, LSN_{214}, LSC_{214}/LSC_{113} , $LSC_{214}/LSCF_{113}$, LSN_{214}/LSC_{113}, LSC_{113}-$LSC_{214}/LSCF_{113}$.
- NLEIS, kinetic modeling, degradation testing of oxygen reduction for film/porous electrode LSC_{113} and $LSCF_{113}$.
- Ab initio calculations of defects and Sr segregation in $LaSrMO_4$ (214), LSC_{113}, $LSCF_{113}$, LSC_{214}/LSC_{113}, $LSC_{214}/LSCF_{113}$.

Major Conclusions

- **LSC_{113}:** Sr segregates strongly to surfaces of LSC_{113} but is unstable at these surfaces leading to precipitation and lost performance.
- **LSC_{214}/LSC_{113}:** Has enhanced performance because Sr is gettered by LSC_{214}, which effectively stabilizes Sr-rich LSC_{113} surface and suppresses precipitation.
- **$LSCF_{113}$:** Sr segregates very strongly to surfaces of $LSCF_{113}$ and is relatively stable at these surfaces vs. LSC_{113}.
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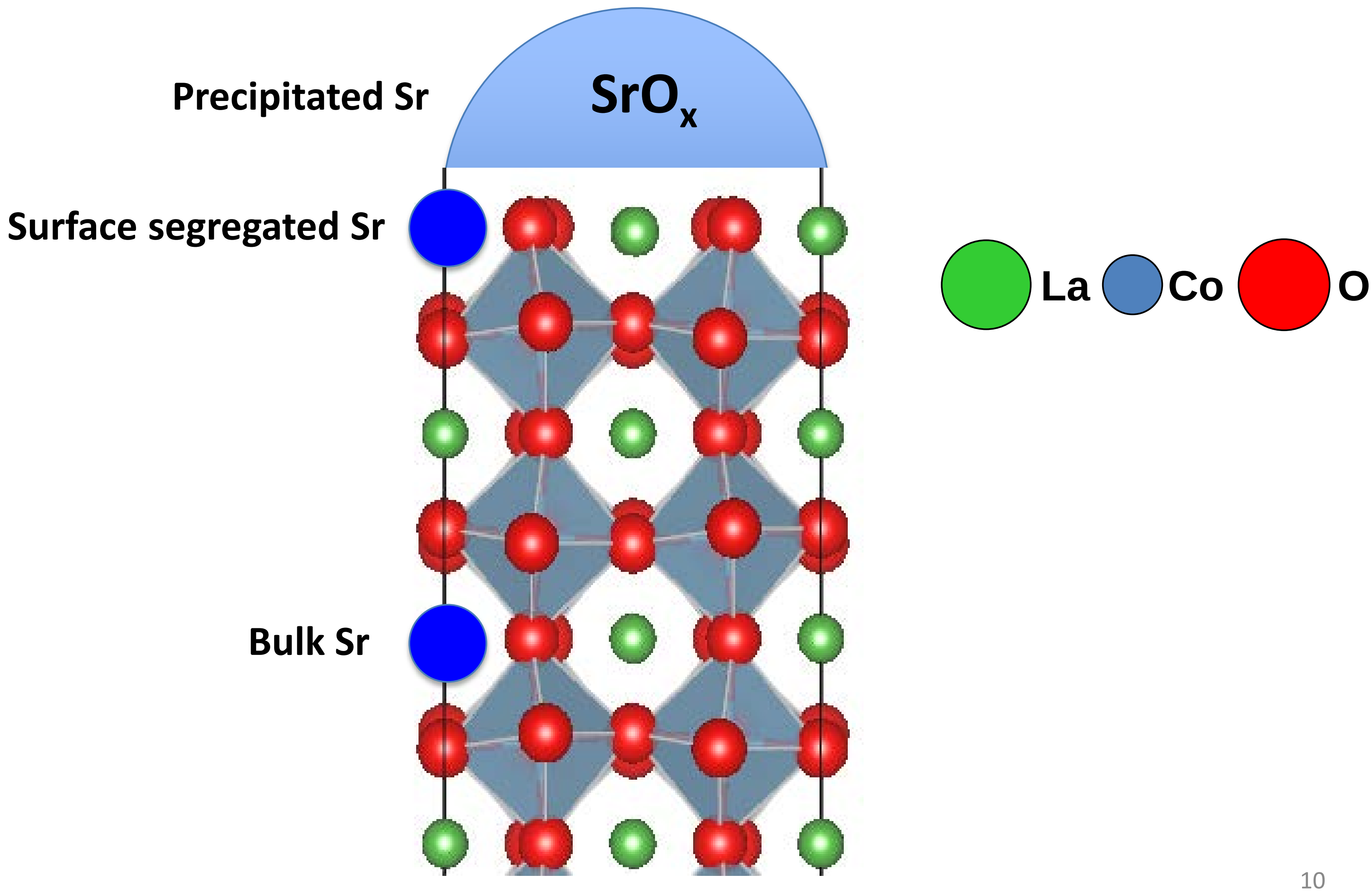
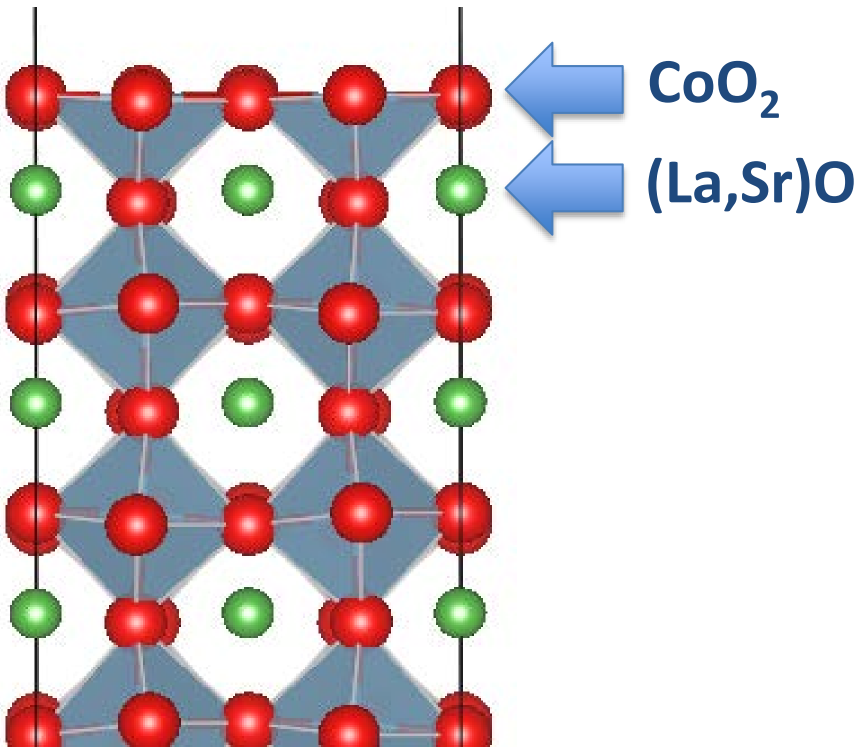
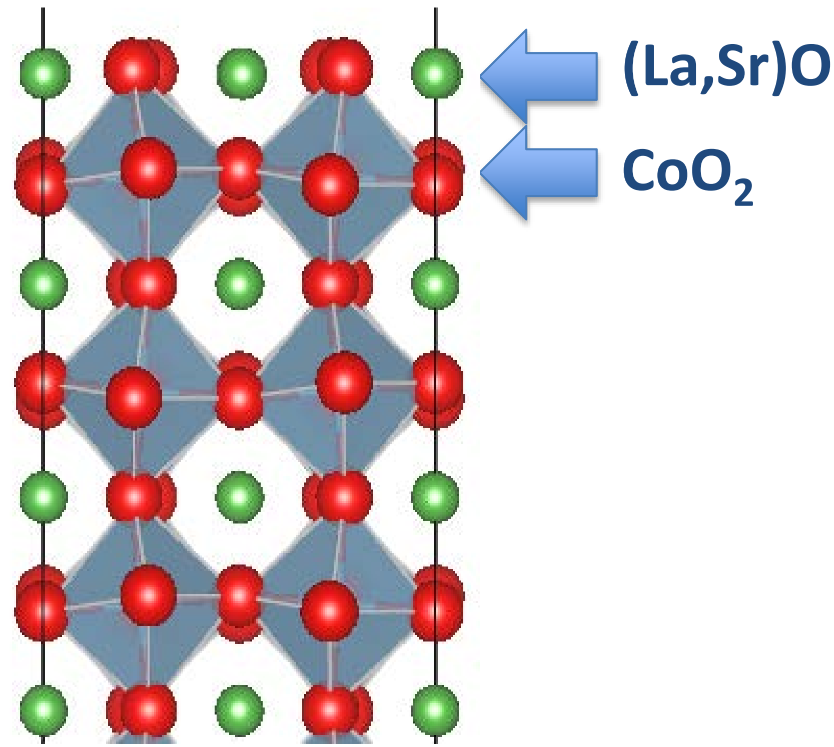
Sr Segregation and Precipitation



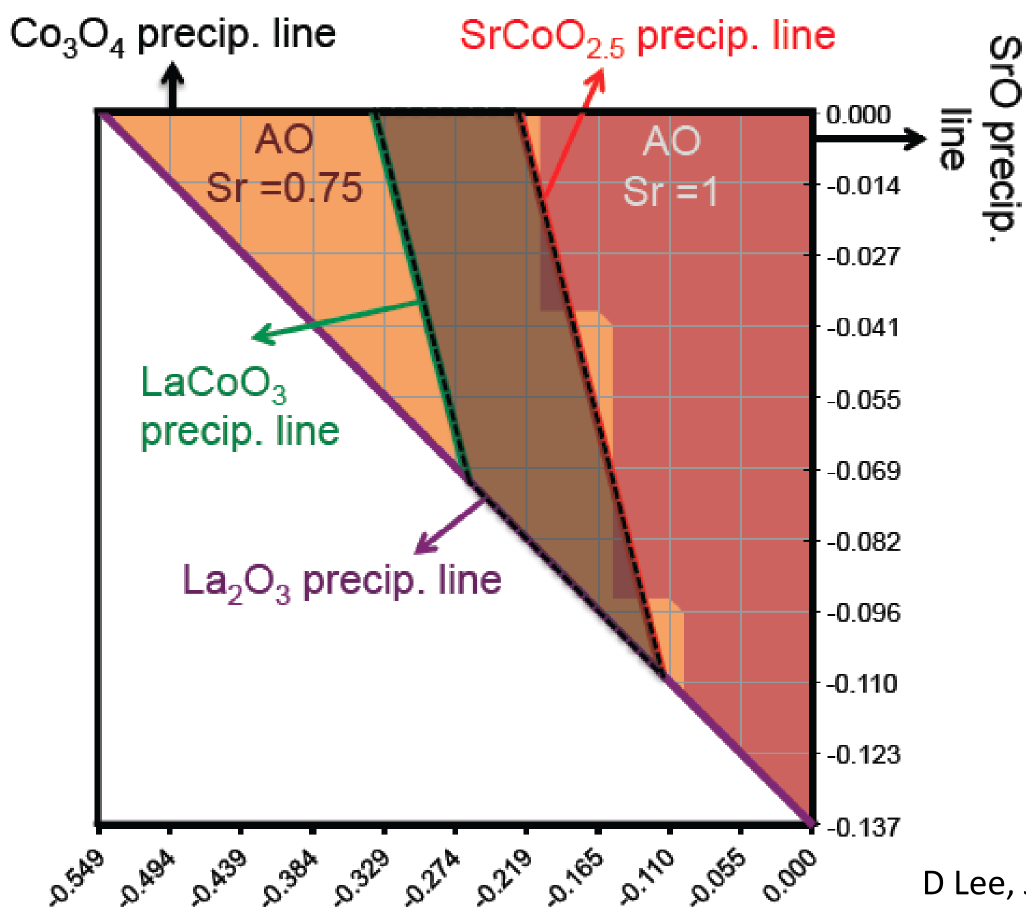
Surface Terminations of (001) $(La,Sr)CoO_3$





What Termination/Segregation is Stable?

(001) $(La_{0.75}Sr_{0.25})CoO_3$, 550°C, 1atm



D Lee, J Mater Chem A 2015

AO surface is stable over CoO_2, and Sr-rich is stable over La-rich.
Consistent with data from Auger spectroscopy, LEIS, COBRA, etc.

What Precipitation is Stable (SEM)?

(001) $(La_{0.80}Sr_{0.20})CoO_3$ 550°C

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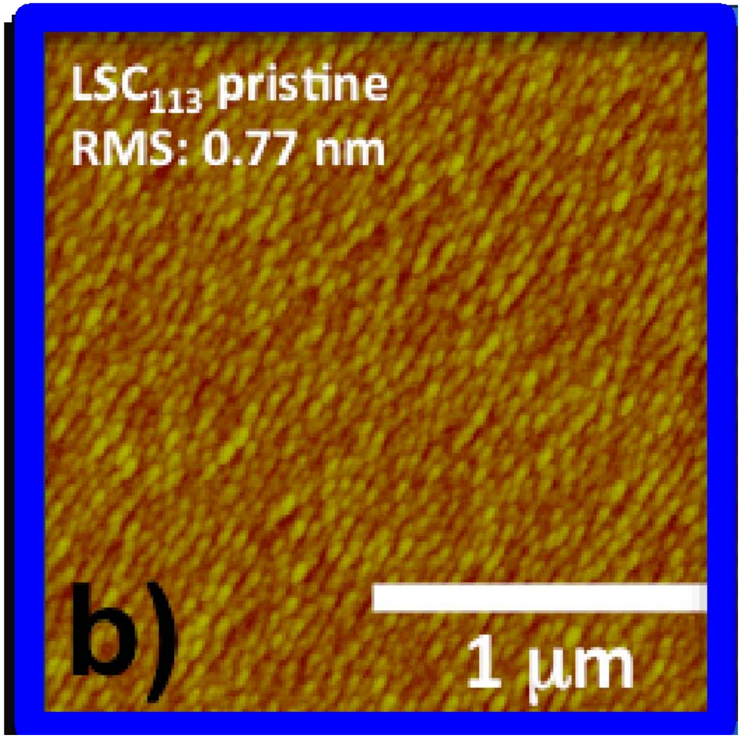
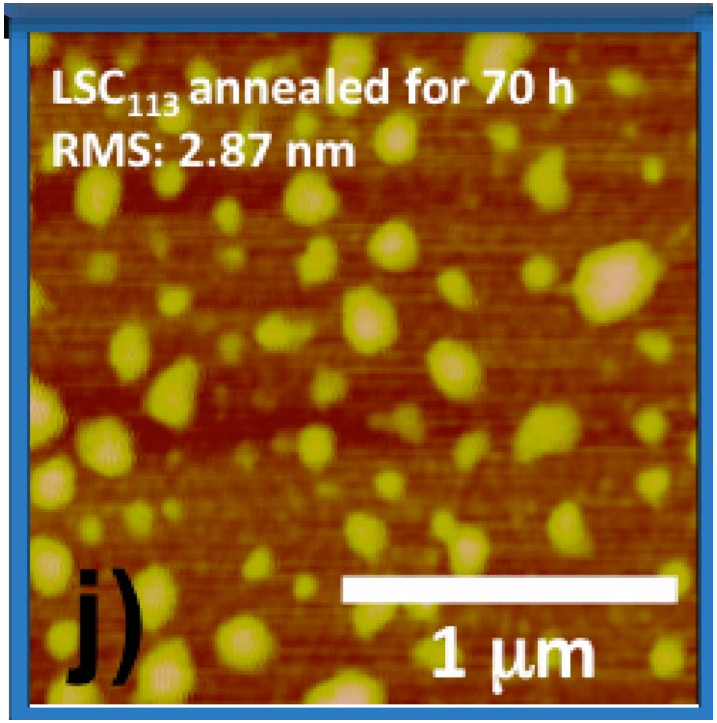


Pristine

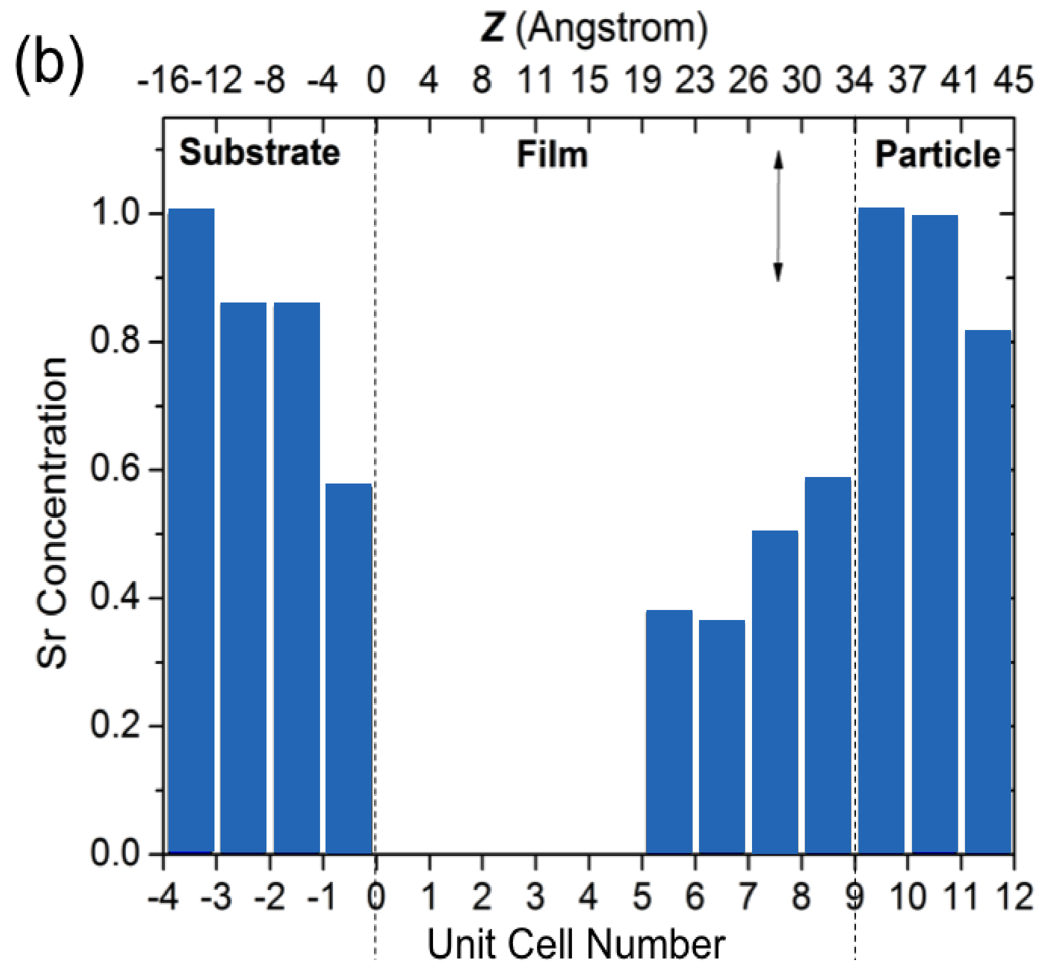


70h Anneal

Surface is unstable with respect to Sr-rich precipitates

What Precipitation is Stable (COBRA)?

(001) $(La_{0.80}Sr_{0.20})CoO_3$



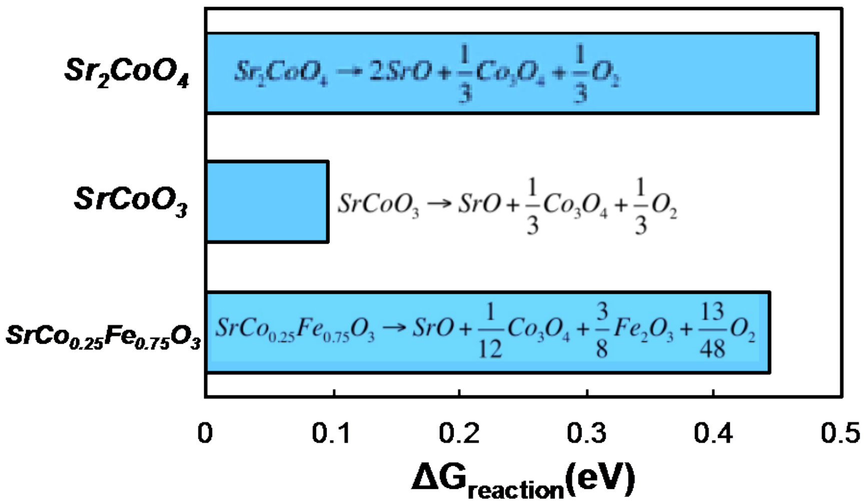
Coherent Brag Rod Analysis (COBRA)

Feng et al., Energy Environ. Sci. 2014;
Feng et al., J Phys. Chem. Lett. 2014

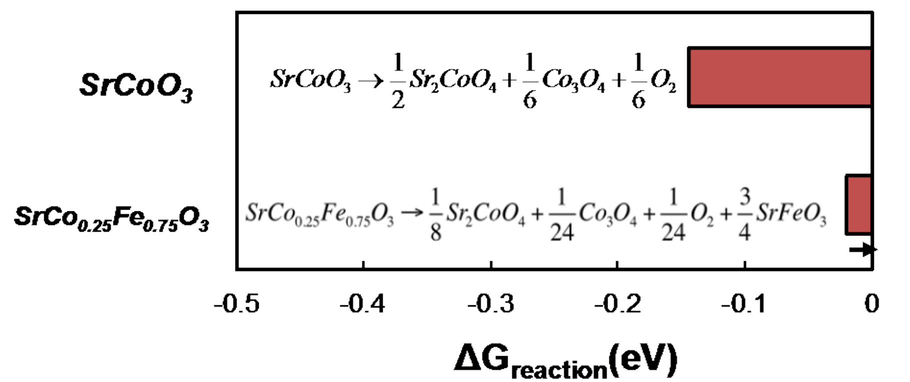
Surface is unstable with respect to Sr enriched precipitates

What Precipitation is Stable (DFT)?

Decomposition to form binary oxides



Decomposition to form RP and Co_3O_4

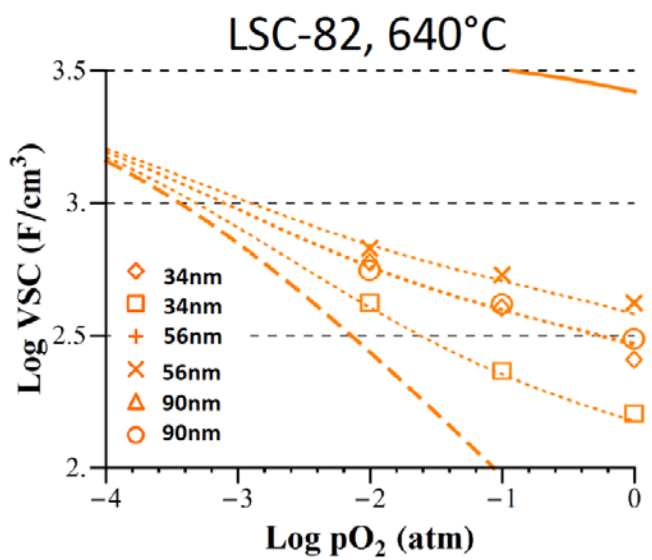


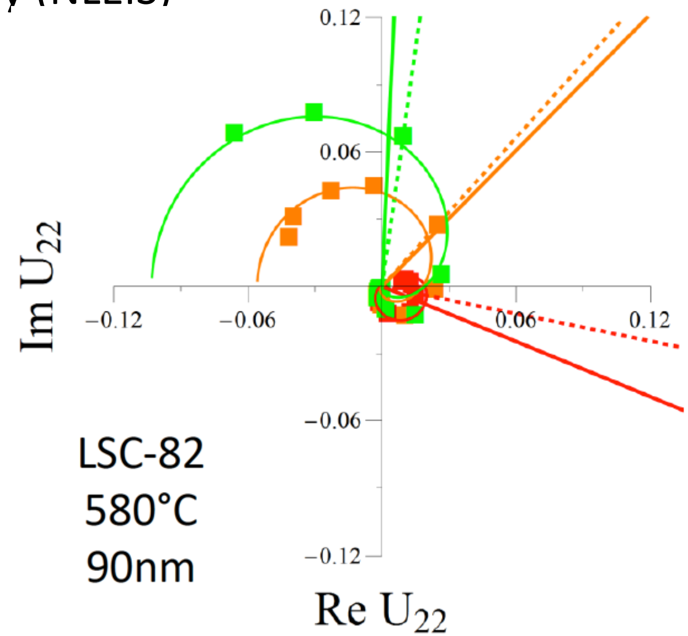
D Lee, Y-L Lee et al., J Mater Chem A 2015

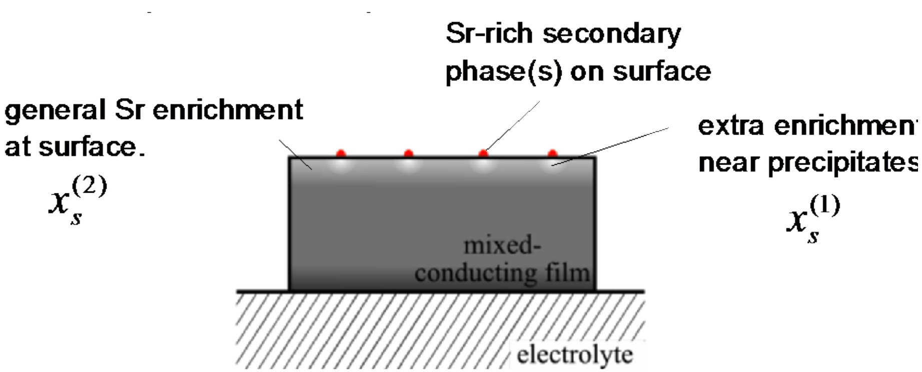
Surface is unstable with respect to Sr enriched precipitates

Further Evidence for Segregation/Precipitation Effects (NLEIS)

Non-Linear Electrochemical Impedance Spectroscopy (NLEIS)







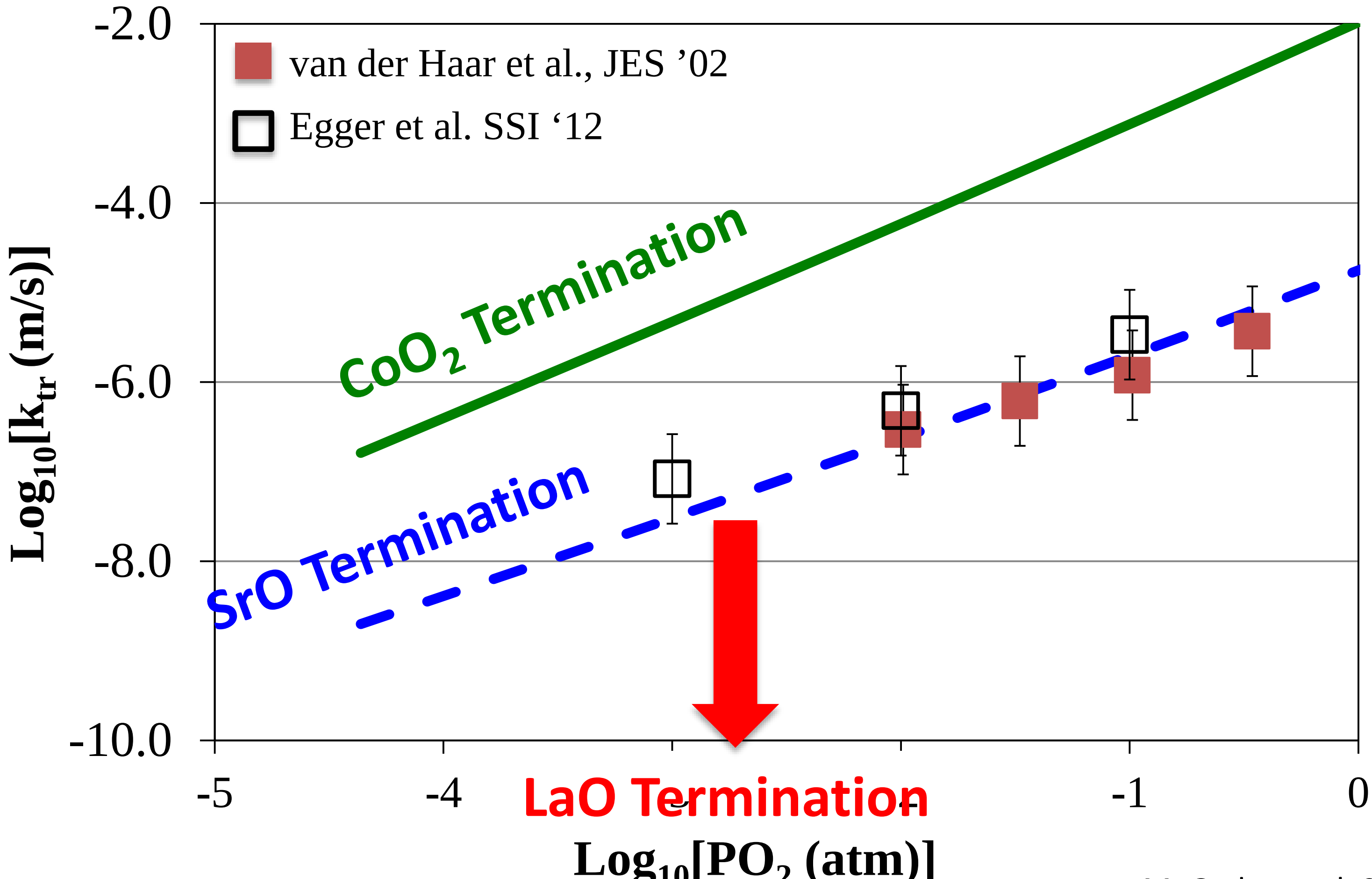
- Excellent agreement with NLEIS data.
- Implies both Sr segregation and lateral Sr inhomogeneity.
- $x_s^{(2)}$ ~0.4 for LSC-82, $x_s^{(1)}$ ~ 0.45.

C. Kreller et al., JES ‘13

What Surfaces are Active?

(001) $(La_{0.5}Sr_{0.5})CoO_3$ 650°C

$$r = -K_{tr}\left(\left[O_O^X\right]-\left[O_O^{X,eq}\right]\right)$$

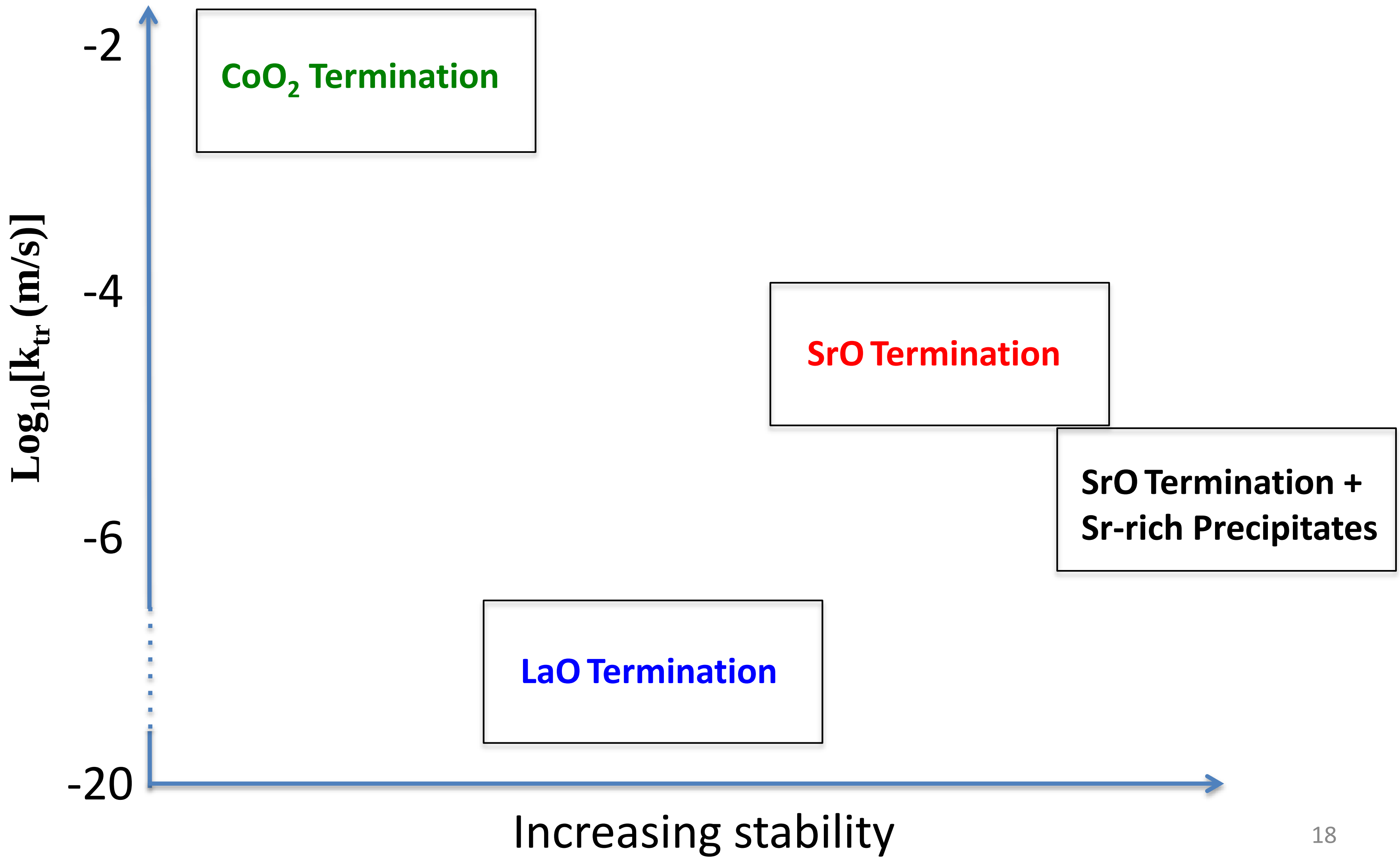


M. Gadre et al, Submitted '15

CoO_2 surface best, SrO next best, LaO surface inactive

Summary of Stability and Activity

(001) $(La_{0.5}Sr_{0.5})CoO_3$ 650°C



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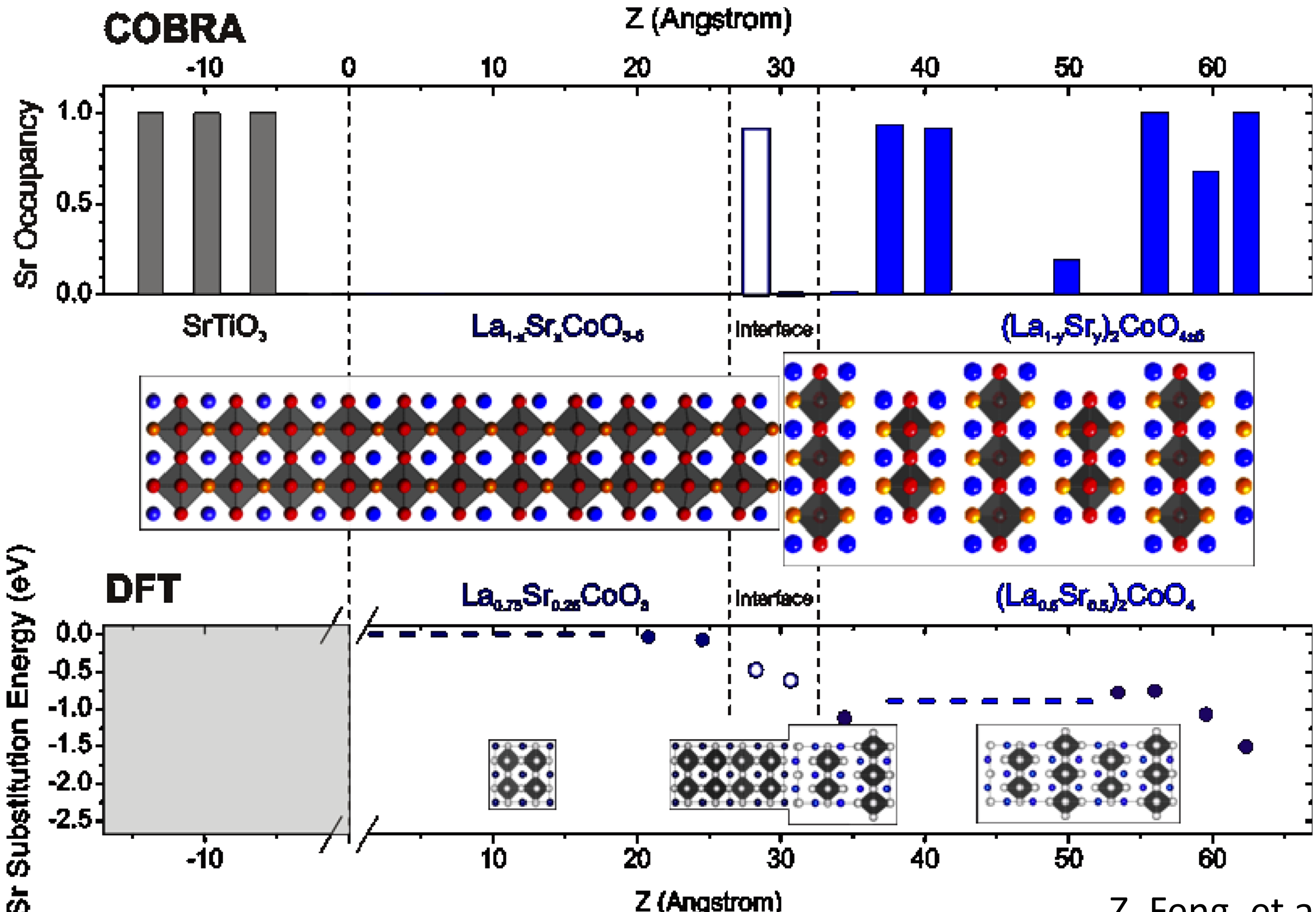
Sr Gettered by LSC_{214} and Stabilized at LSC_{214}/LSC_{113} Interface



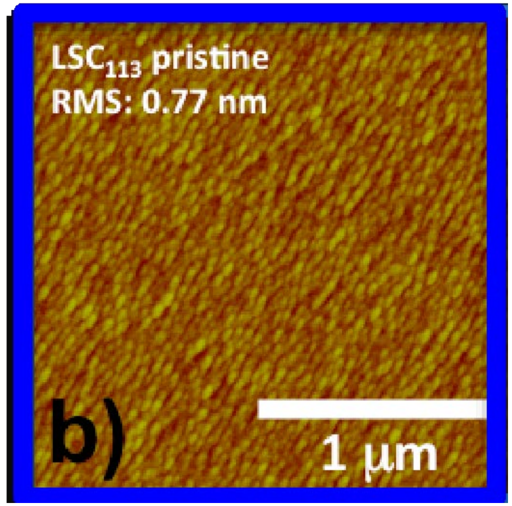
Z. Feng, et al., JPCL ‘14

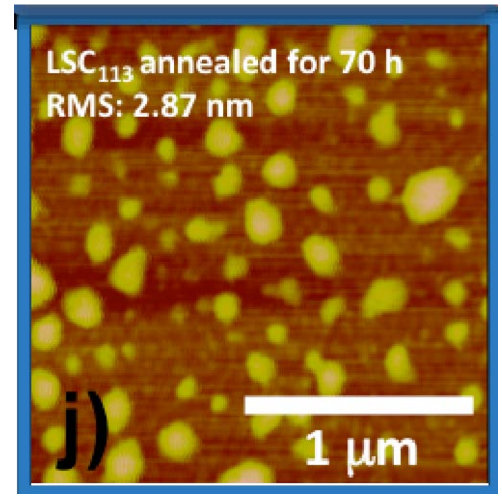
Sr in interface and LSC_{214} film and depleted from LSC_{113}

LSC_{214} Decoration Suppresses Sr-Rich Phase Precipitation

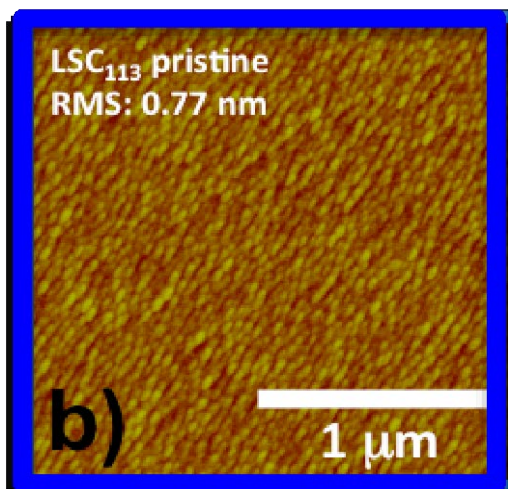
$(LaSr)CoO_4$
$(La_{0.80}Sr_{0.20})CoO_3$
550°C

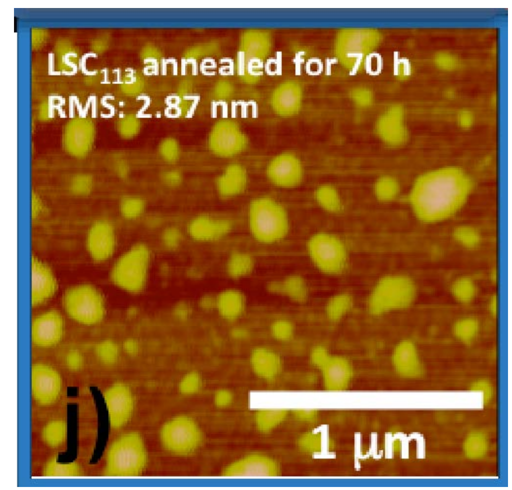
LSC_{113}





LSC_{214}/LSC_{113}





Pristine **70h Anneal**

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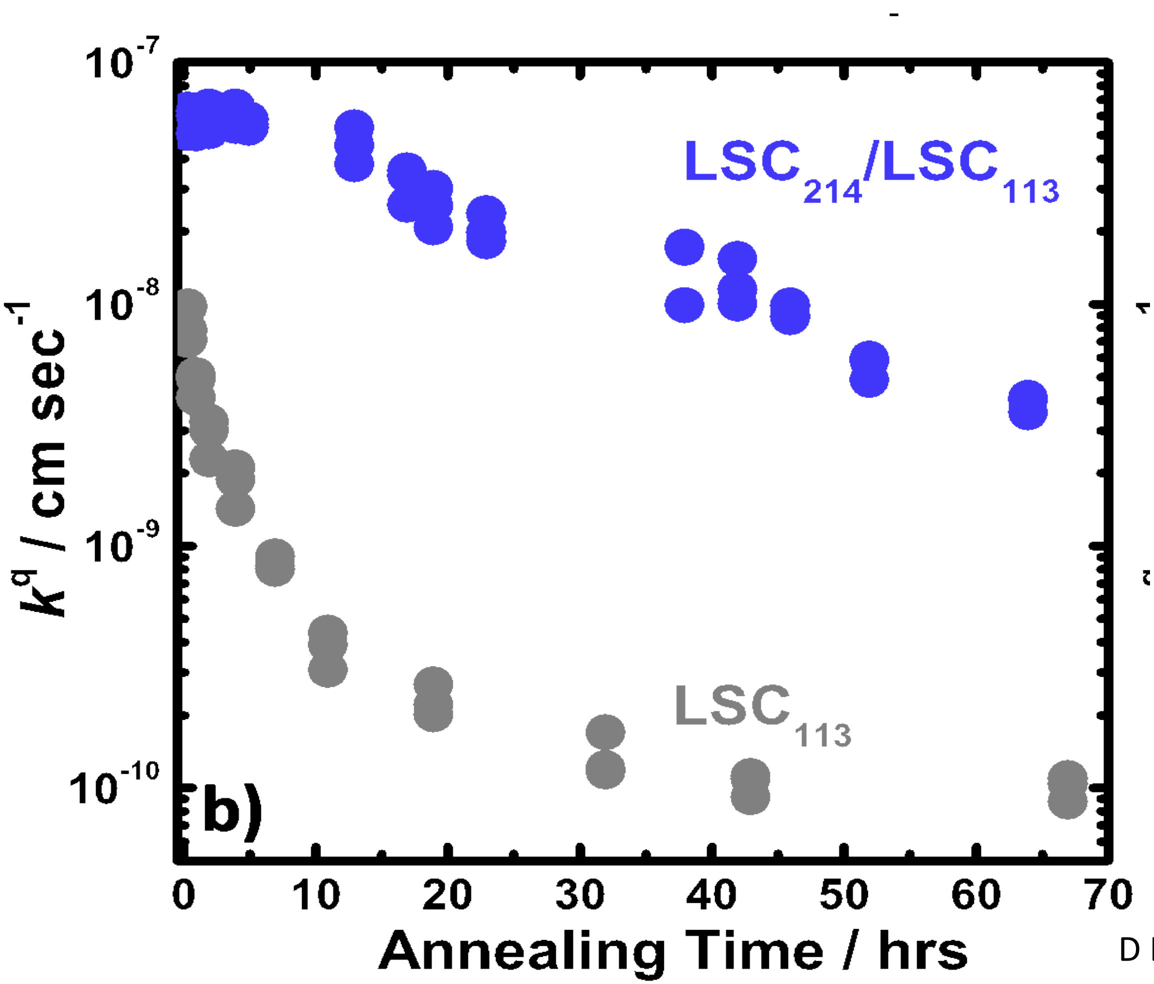
LSC_{214} Decoration Enhances LSC_{113} Activity and Stability

$(LaSr)CoO_4$, $(La_{0.80}Sr_{0.20})CoO_3$ 550°C



D Lee, J Mater Chem A 2015

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(001) $(La_{0.75}Sr_{0.25})CoO_3$, $(La_{0.625}Sr_{0.375})(Co_{0.2}Fe_{0.8})O_3$, 550°C, 1atm

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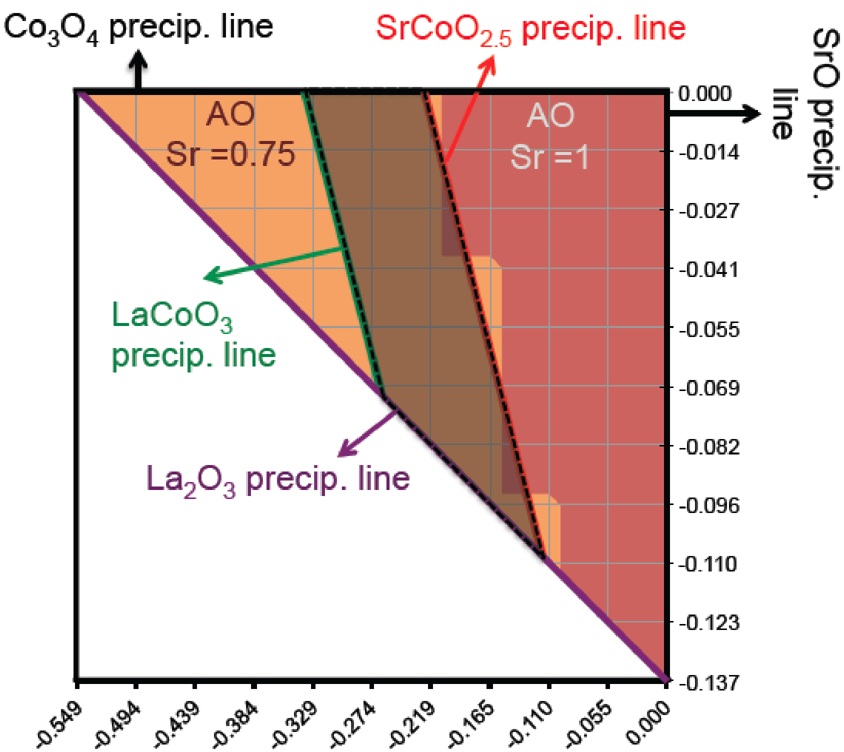
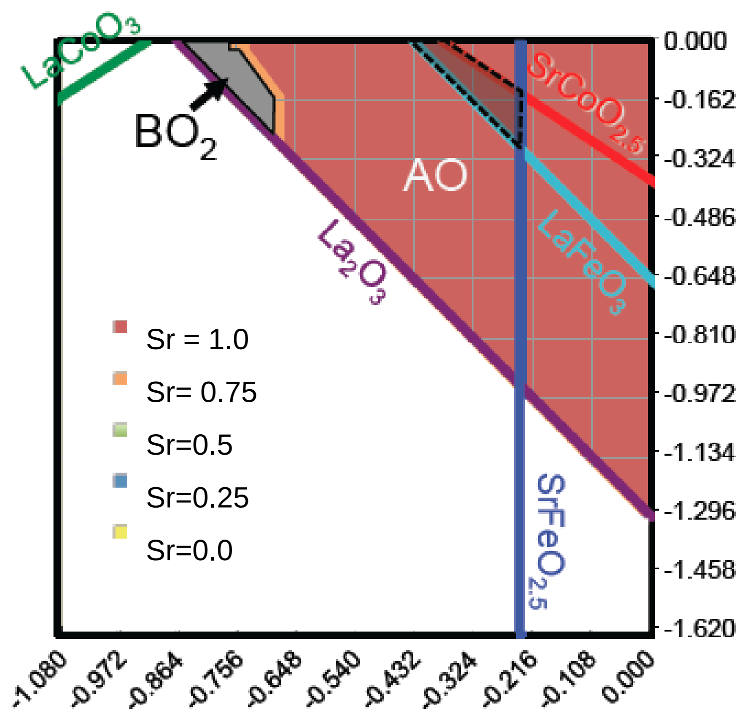
LSC_{113}



$LSCF_{113}$



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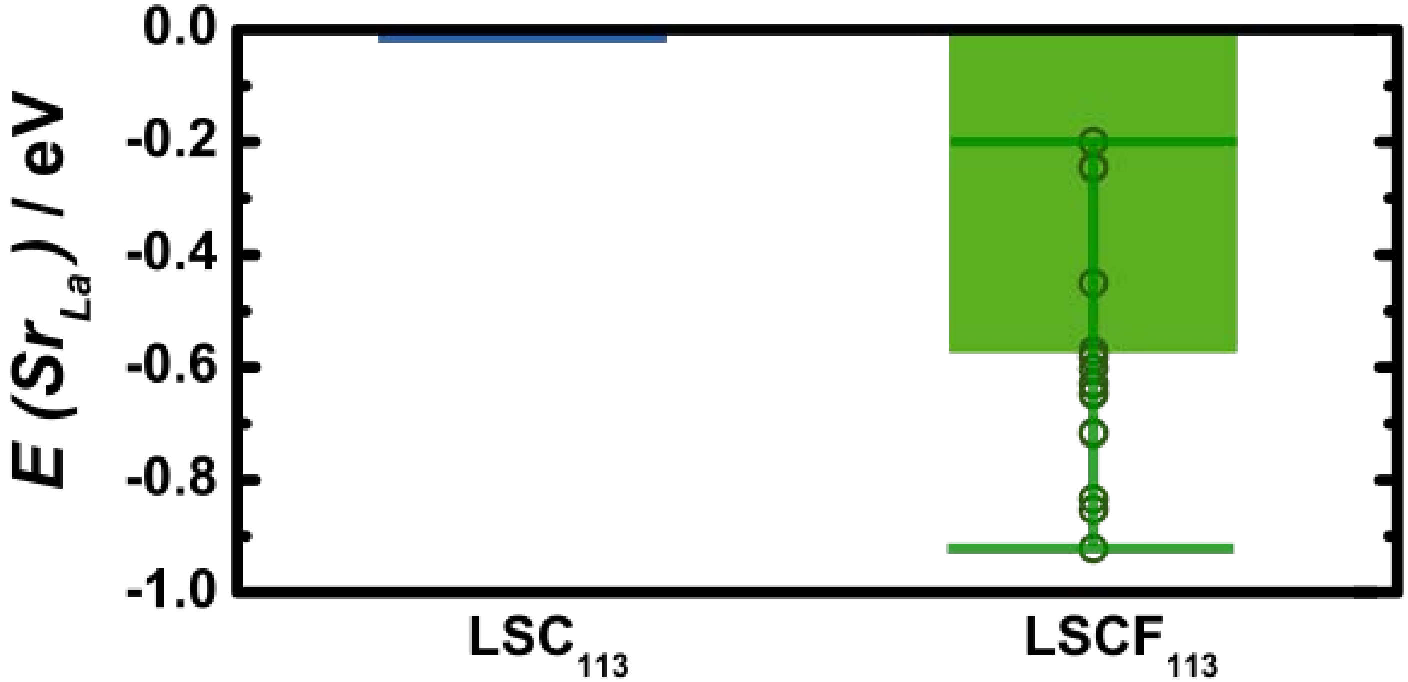
AO surface is stable over CoO_2, and 100% Sr is stable for LSCF, vs. ~75% for LSC. Stronger surface segregation of Sr for LSCF!

Is Sr Stable in LSCF Surface (DFT)?



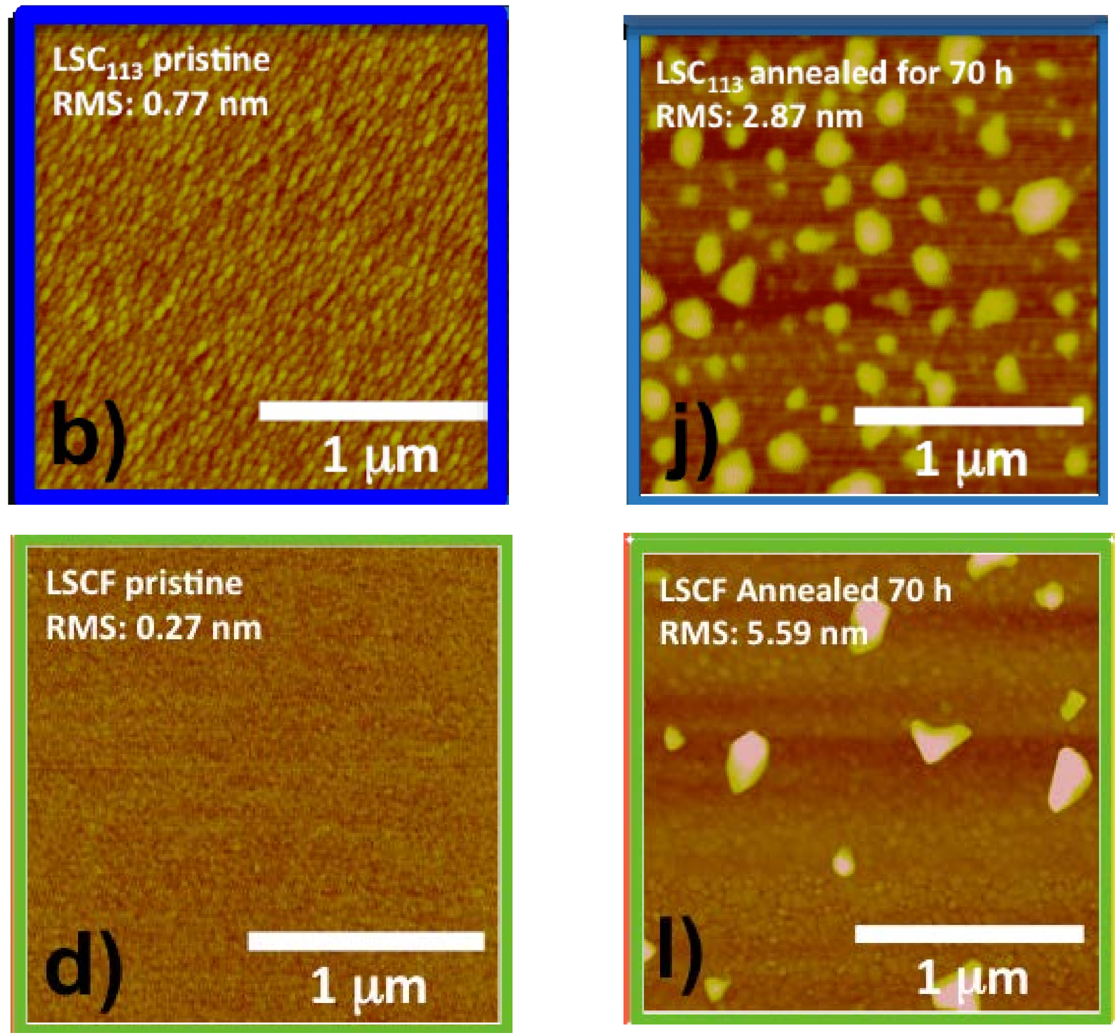
Sr is more stable in Sr-rich LSCF surface than Sr-rich LSC surface

$LSCF_{113}$ Sr-Rich Surface More Stable than LSC_{113}

$(La_{0.80}Sr_{0.20})CoO_3$
$(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$
550°C

LSC_{113}

$LSCF_{113}$



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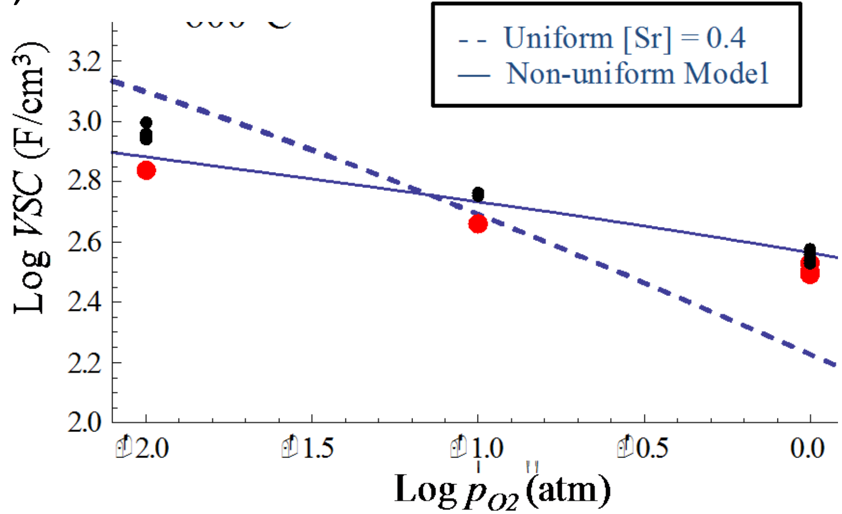
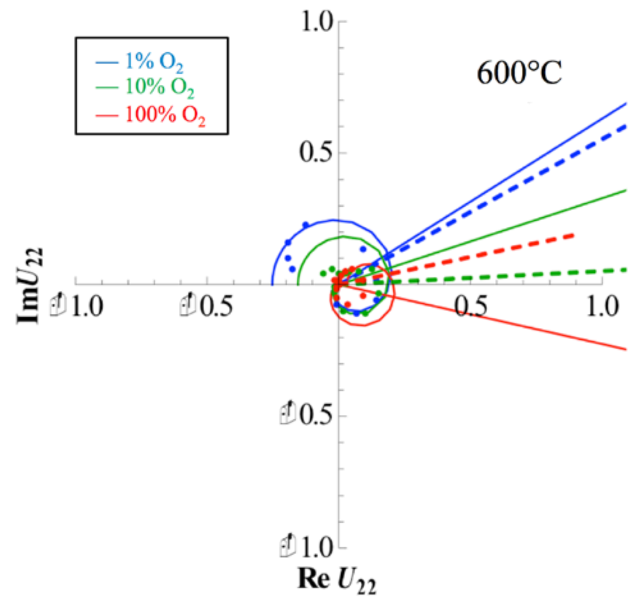
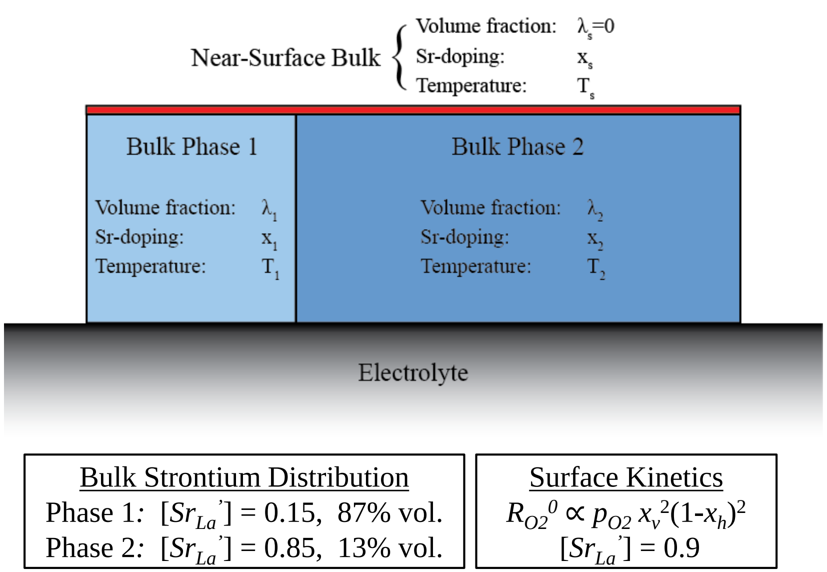
Evidence for Segregation/Precipitation Effects in LSCF (NLEIS)

$(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$
Film, 600°C







- Inhomogeneous thermodynamics needed to fit data
- ~3 nm of Sr-rich phase at surface
- Surface thermodynamics similar to Sr-rich phase
- Total $[Sr_{La}^{'}] < 0.4$ (i.e. possible Sr precipitation)

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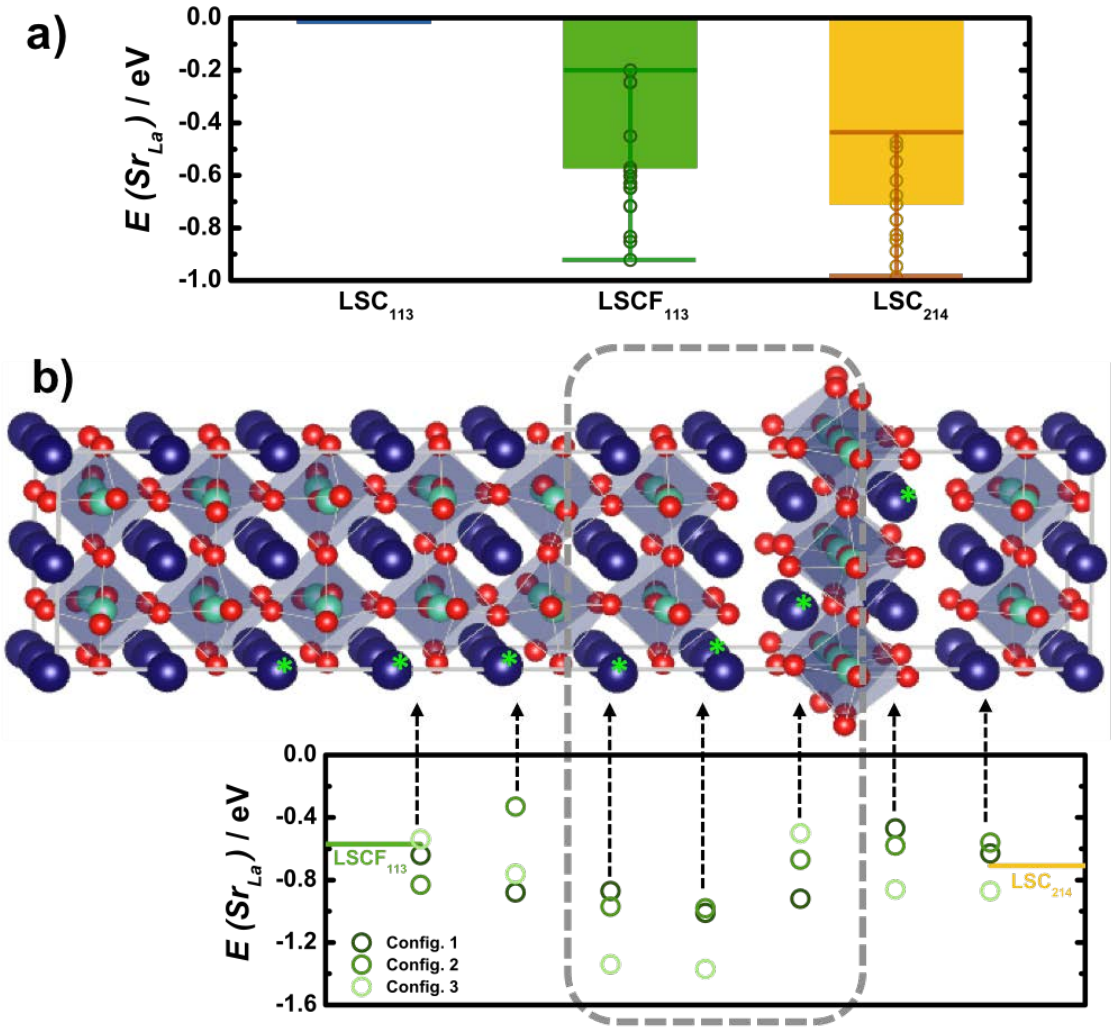
Sr More Weakly Attracted by LSC_{214} form $LSCF_{113}$ Than LSC_{113} (DFT)



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LSC_{214} Decoration Has Little Effect on Sr-Rich Phase Precipitation in LSCF

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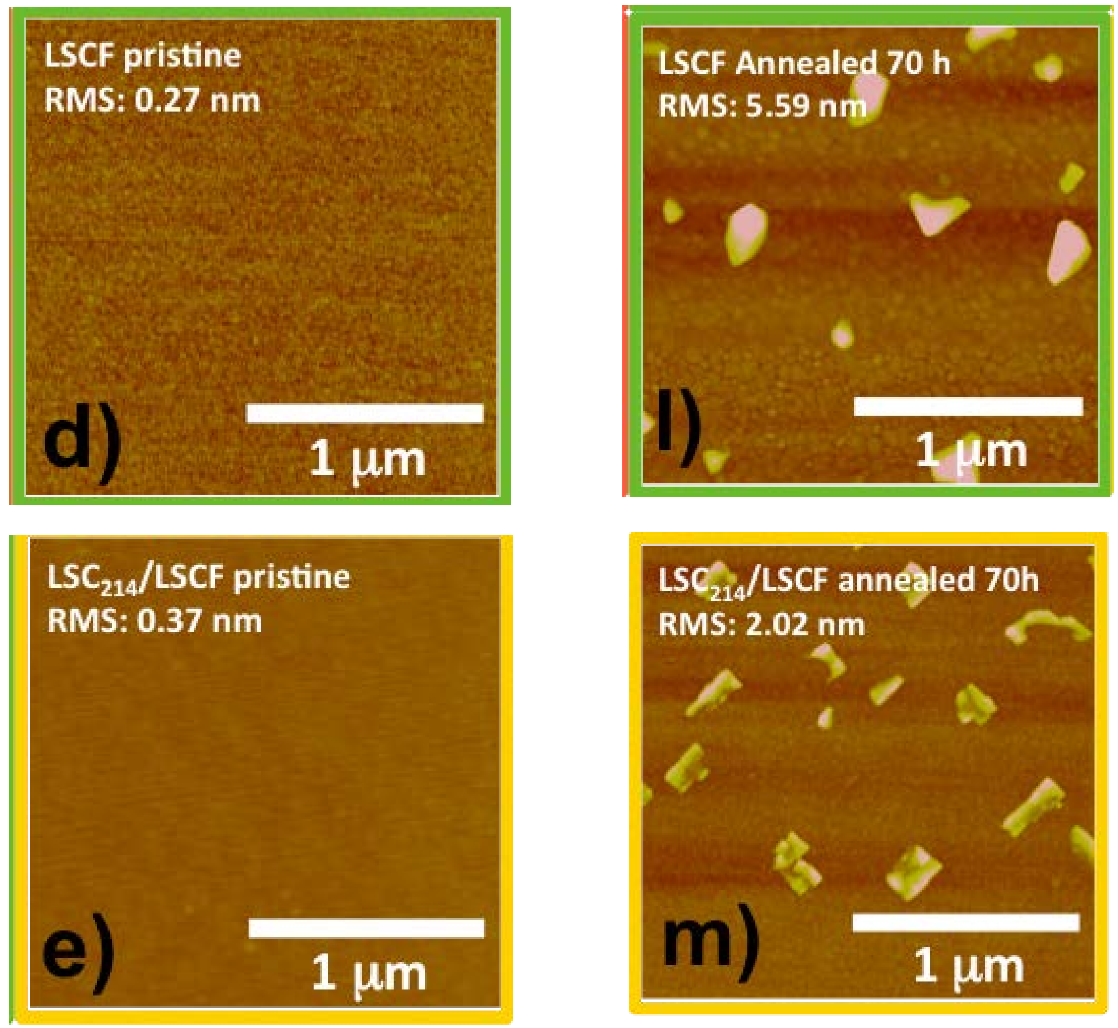
550°C

$LSCF_{113}$

$LSC_{214}/LSCF_{113}$



Pristine **70h Anneal**

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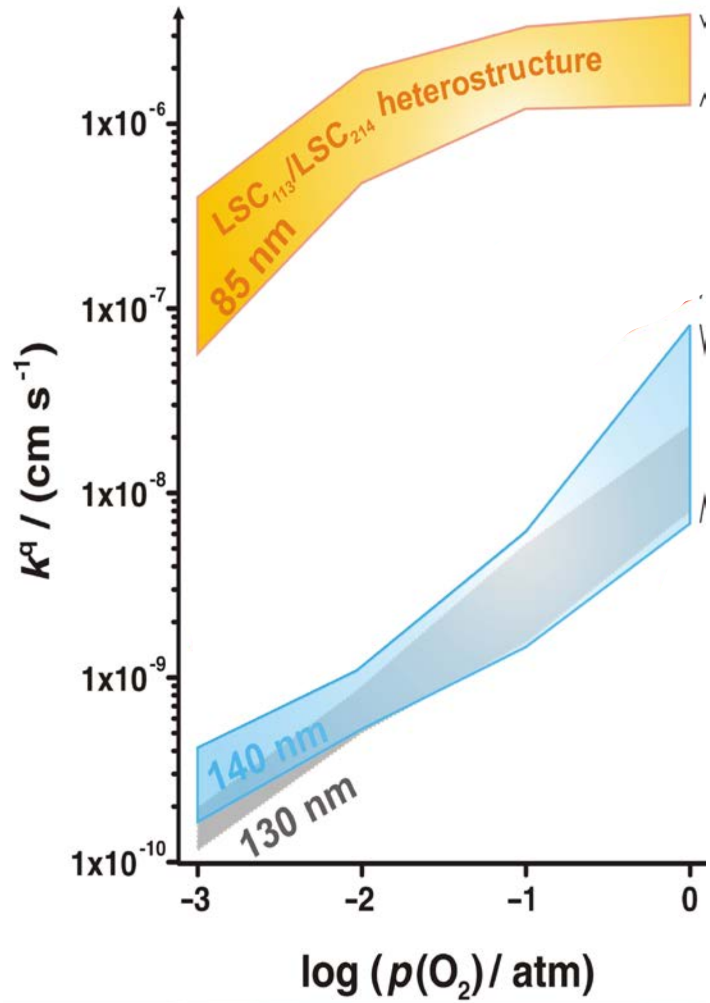
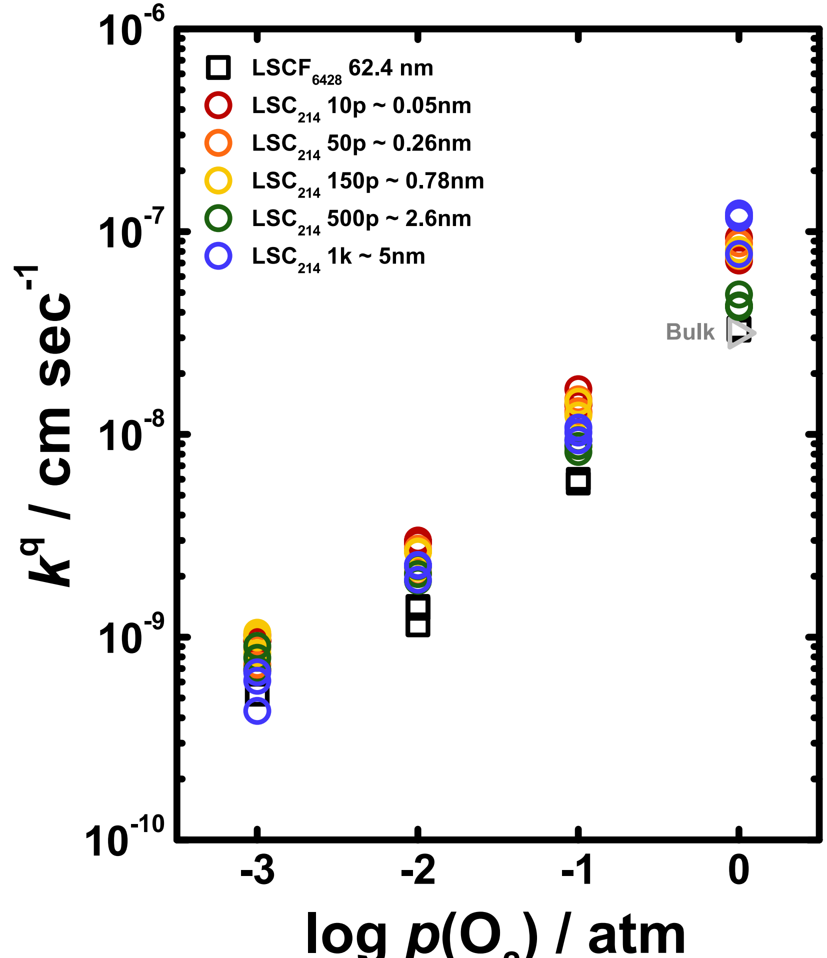
LSC_{214} Decoration Has Little Impact on $LSCF_{113}$ Activity

LSC_{214}/LSC_{113}



$LSC_{214}/LSCF_{113}$



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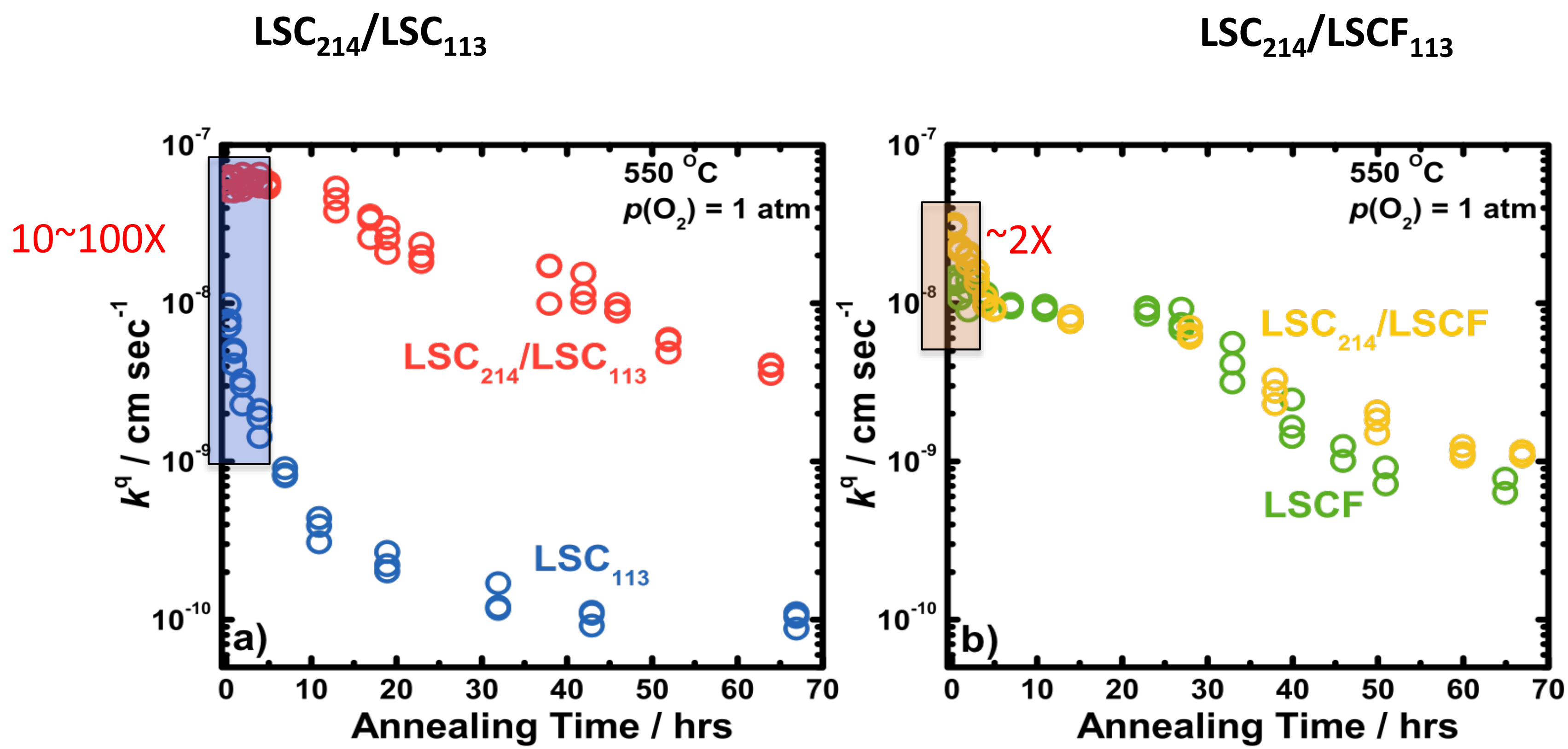
LSC_{214} Decoration Has Little Impact on $LSCF_{113}$ Activity and Stability

$(LaSr)CoO_4$, $(La_{0.80}Sr_{0.20})CoO_3$, $(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$ 550°C



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Major Conclusions

- **LSC_{113}:** Sr segregates strongly to surfaces of LSC_{113} but is unstable at these surfaces leading to precipitation and lost performance.
- **LSC_{214}/LSC_{113}:** Has enhanced performance because Sr is gettered by LSC_{214}, which effectively stabilizes Sr-rich LSC_{113} surface and suppresses precipitation.
- **$LSCF_{113}$:** Sr segregates very strongly to surfaces of $LSCF_{113}$ and is relatively stable at these surfaces vs. LSC_{113}.
- **LSC_{214}/$LSCF_{113}$:** Has little enhanced performance because Sr-rich $LSCF_{214}$ is already fairly stable.
- **LSC_{214}/LSC_{113}/$LSCF_{113}$:** Has enhanced performance due to enhanced activity of LSC_{214}/LSC_{113} on the LSCF.

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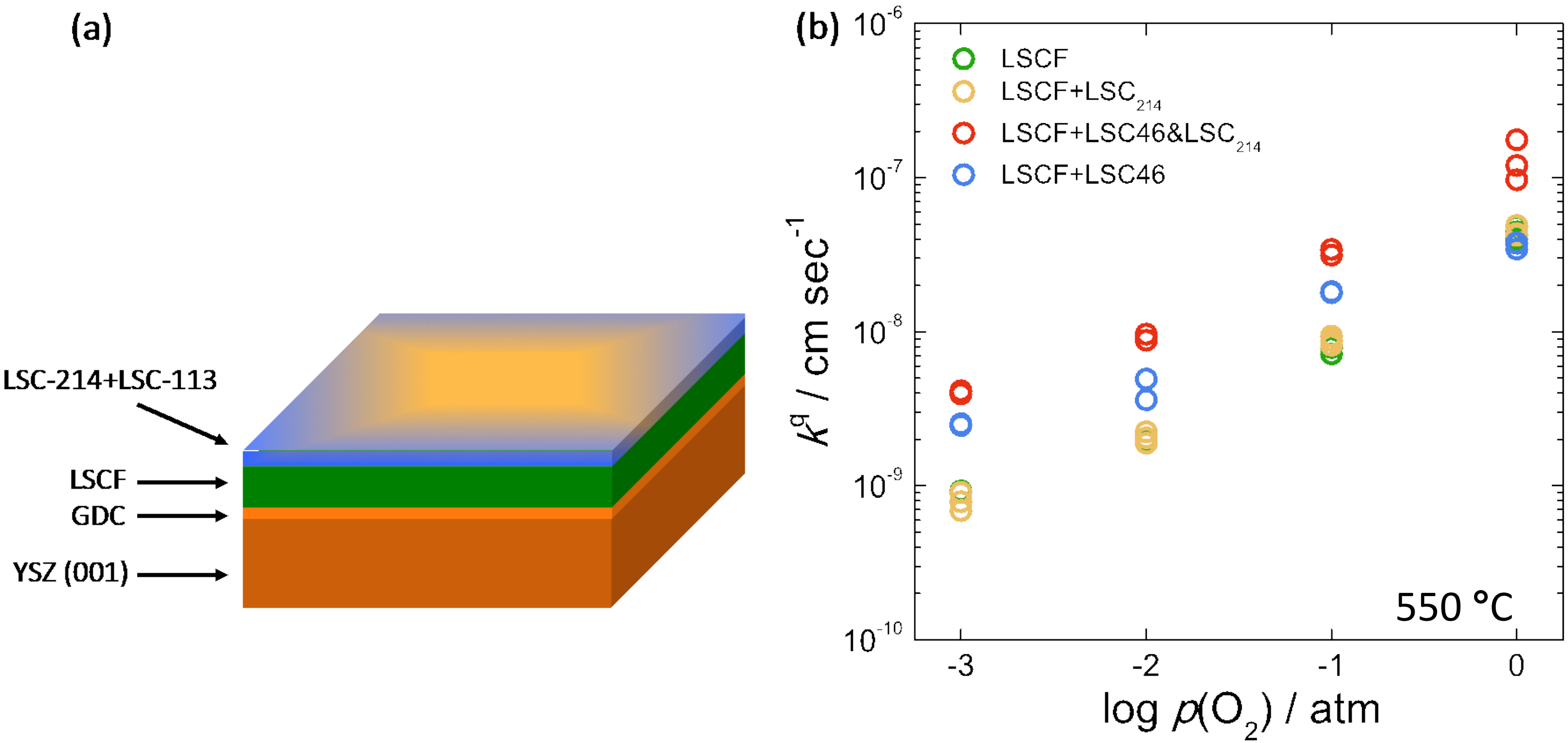
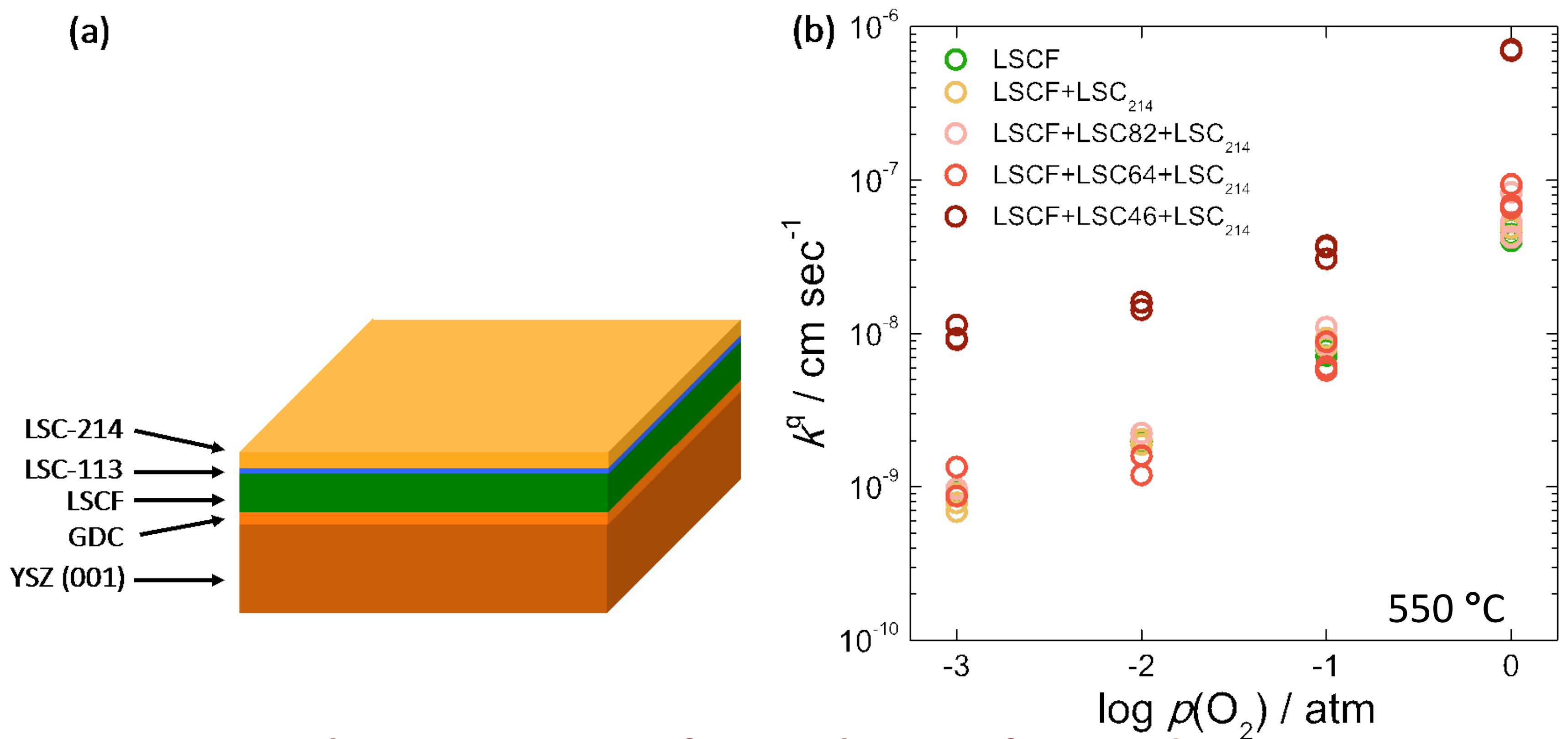
Enhancement from Mixed Single Layer $[LSC_{214}+LSC_{113}]/LSCF_{113}$



- **~10x enhancement in surface exchange of $LSCF_{113}$!**
- **From catalytic ability of $LSC_{214}+LSC_{113}$?**

Enhancement from Double Layer Stacked $LSC_{214}/LSC_{113}/LSCF_{113}$



- **~10x enhancement in surface exchange of $LSCF_{113}$!**
- **From catalytic ability of LSC_{214}/LSC_{113}?**
- Strong Sr dependence (qualitatively consistent with previous observations of Sr being critical) and best for largest Sr content

Conclusions

1. How does this interfacial enhancement work in LSC_{113}?

   Stabilization of Sr-rich LSC_{113} surface and suppression of Sr-rich precipitation

2. Can it be extended to $XYZ_{214}/LSCF_{113}$ interfaces?

   Yes! $LSC_{214}/LSC_{113}/LSCF_{113}$ enhances $LSCF_{113}$ 10x!

3. Can we make more active, more stable porous cathodes with these interfaces?

   Promising initial results but needs more work with NETL, industry teams, future proposals …

END

Thank you for your attention