Enhancement of SOFC Cathode Electrochemical Performance Using Multi-Phase Interfaces

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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)

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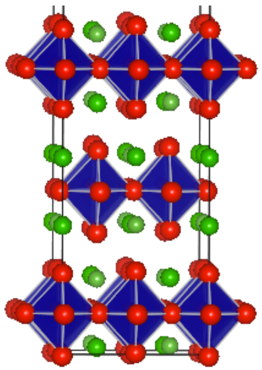
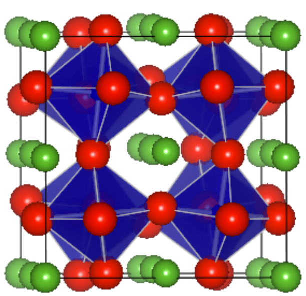
Oxide Heterointerface for SOFC Cathodes

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



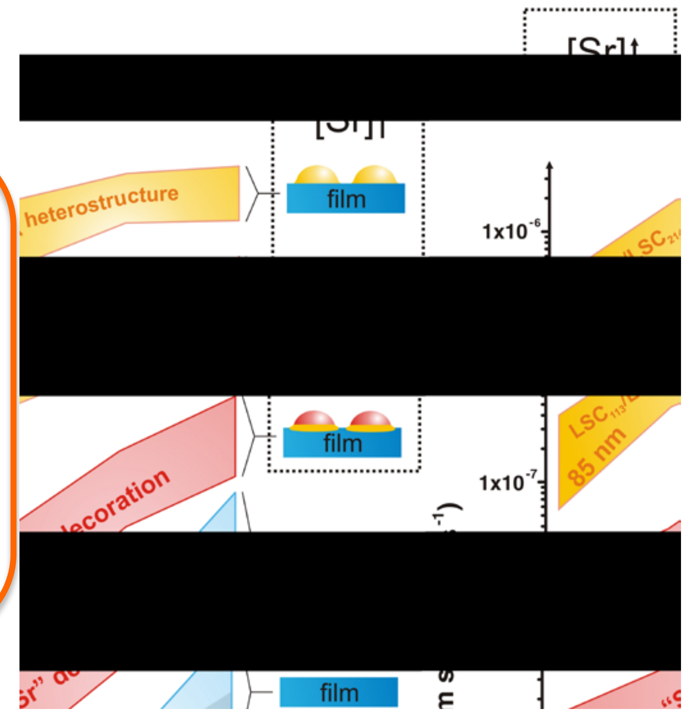
LSC-113: ABO_3 Perovskite
(AO-BO_2 stacking)
Cathode Material

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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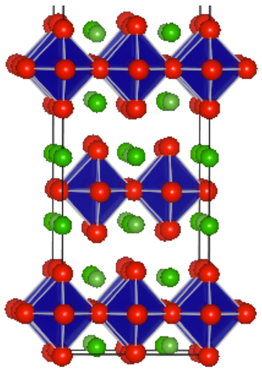

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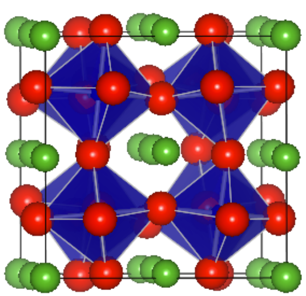

LSC-113: ABO_3 Perovskite
(AO-BO_2 stacking)
Cathode Material

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

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Project Overview

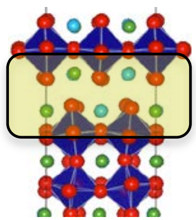
LSC-214/LSCF-113 Films

LSC-214

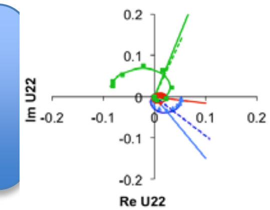
LSCF-113

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

Ab initio Energetics Thermokinetic Modeling



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



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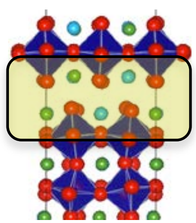

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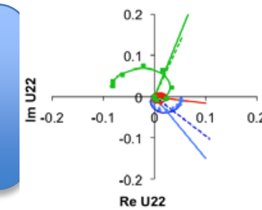

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Start date: 10/1/12 (~9 months completed)

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Milestone 5 – Single phase continuum modeling of LSCF-113 cathodic reaction.

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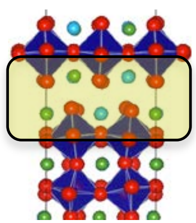

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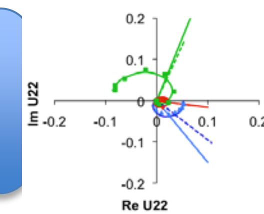

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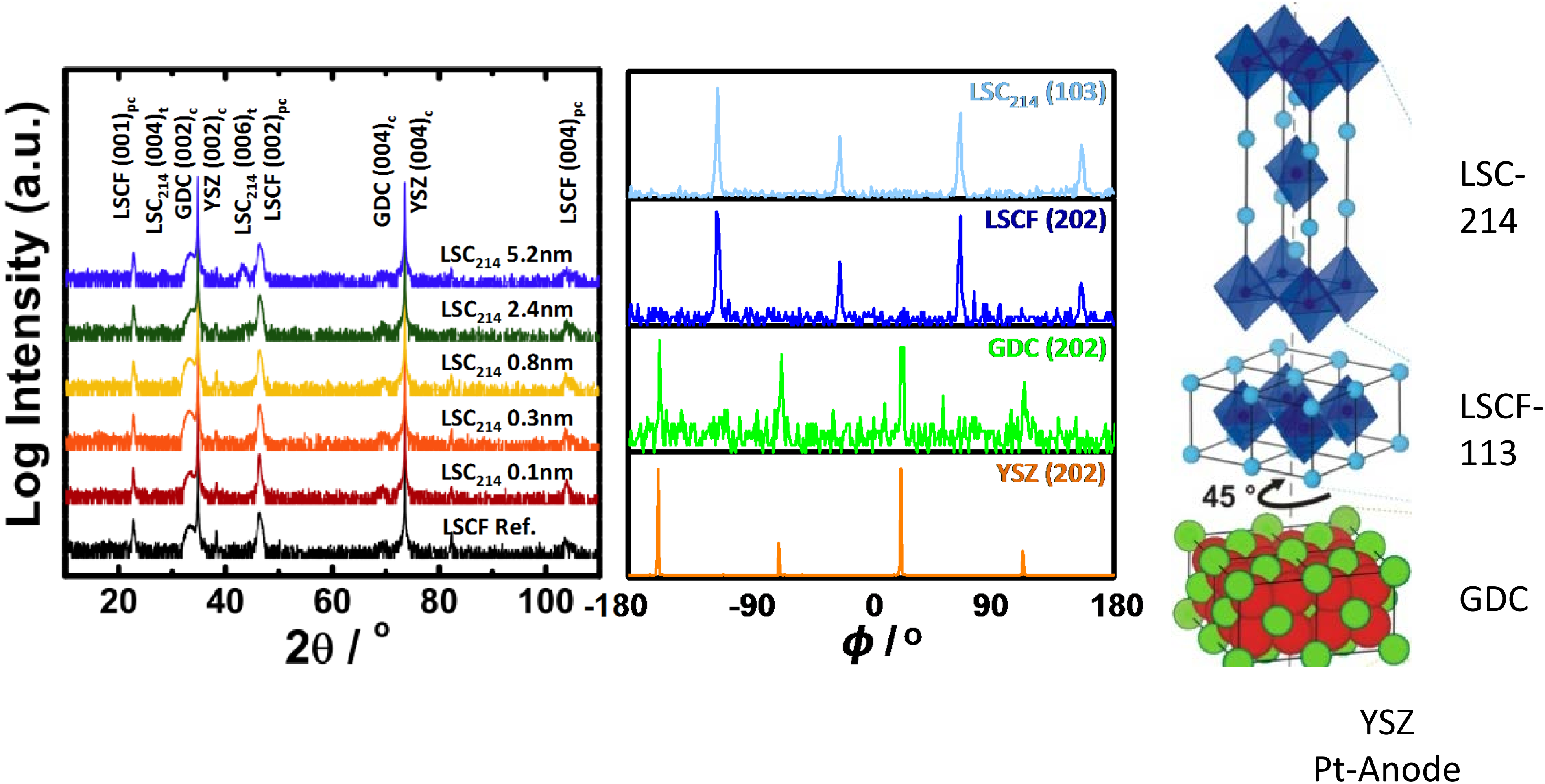
Thin-film Characterization of LSC-214/LSCF-113, LSC-113

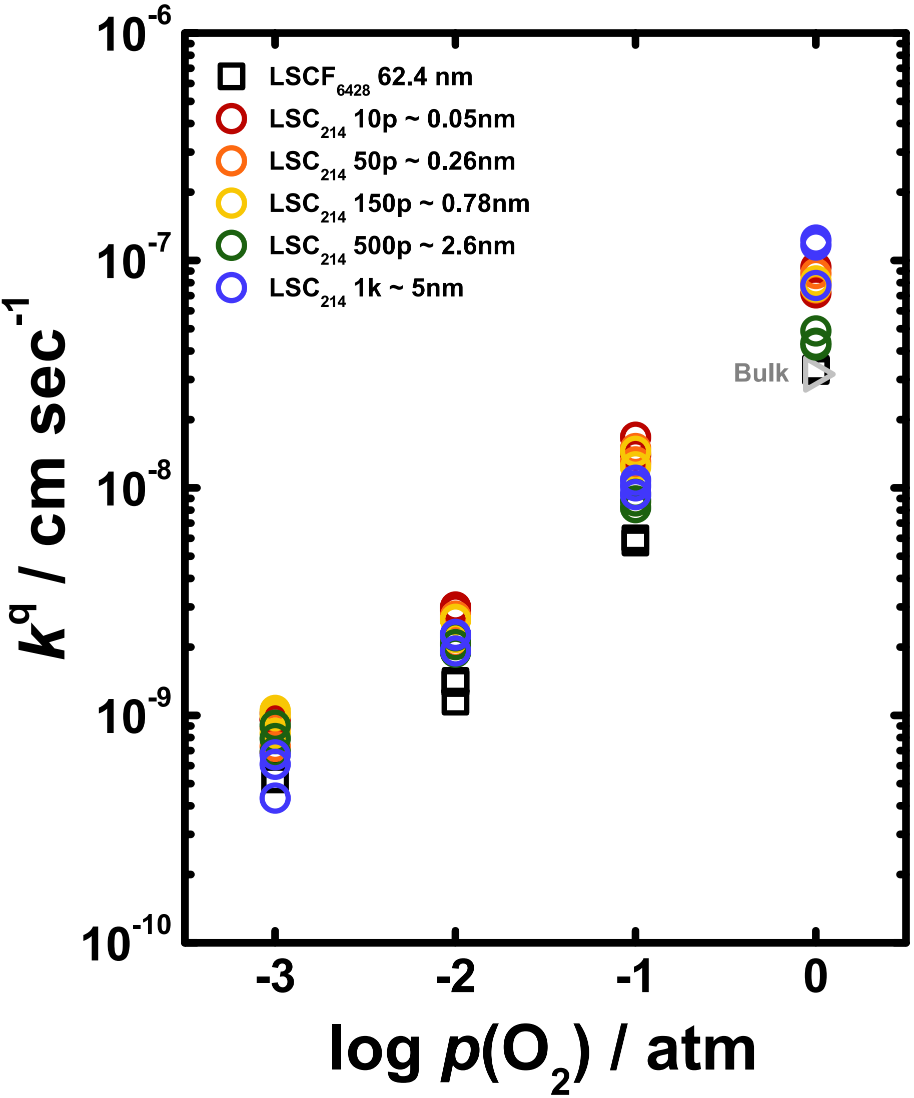
Shao-Horn (MIT)

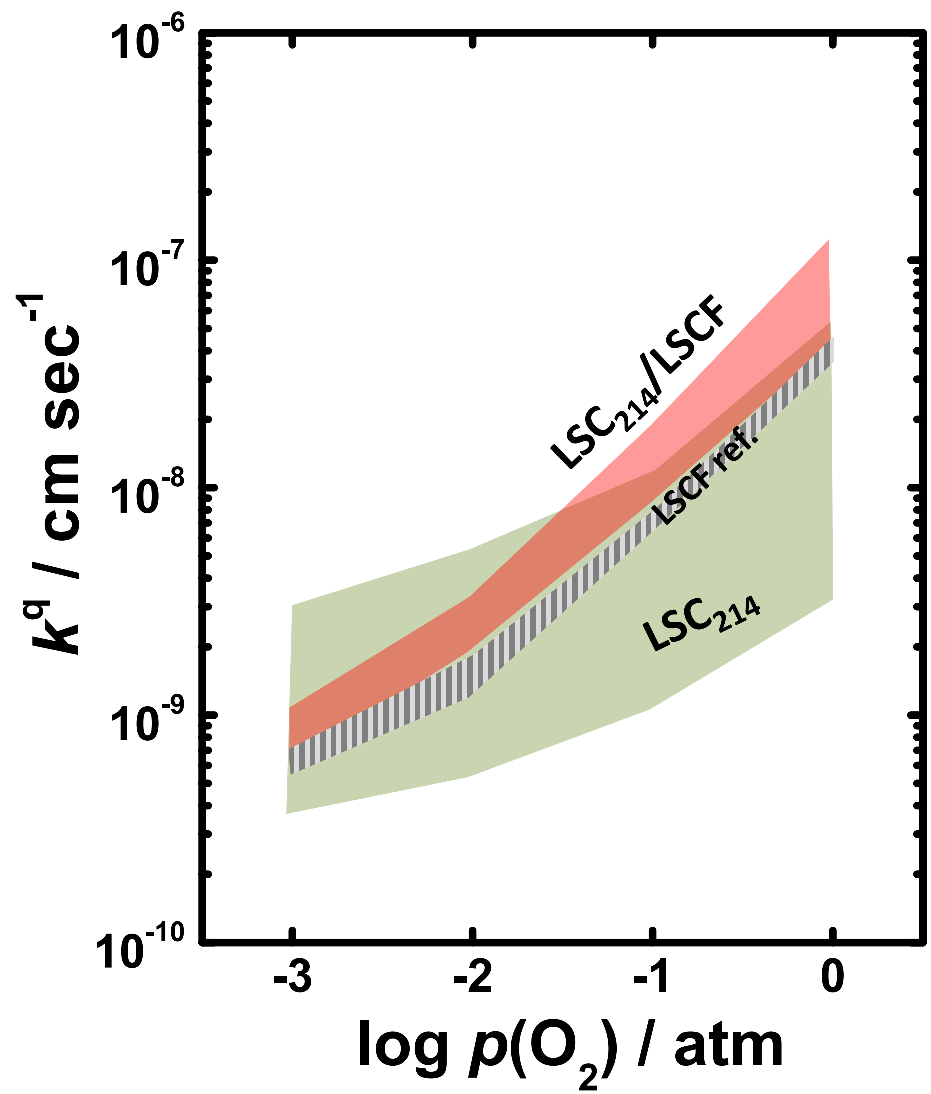
X-ray Diffraction Results



- All films clearly show ***c***-axis-oriented epitaxial thin films
- Off normal XRD shows LSCF unit cell on the GDC with 45^0 rotation

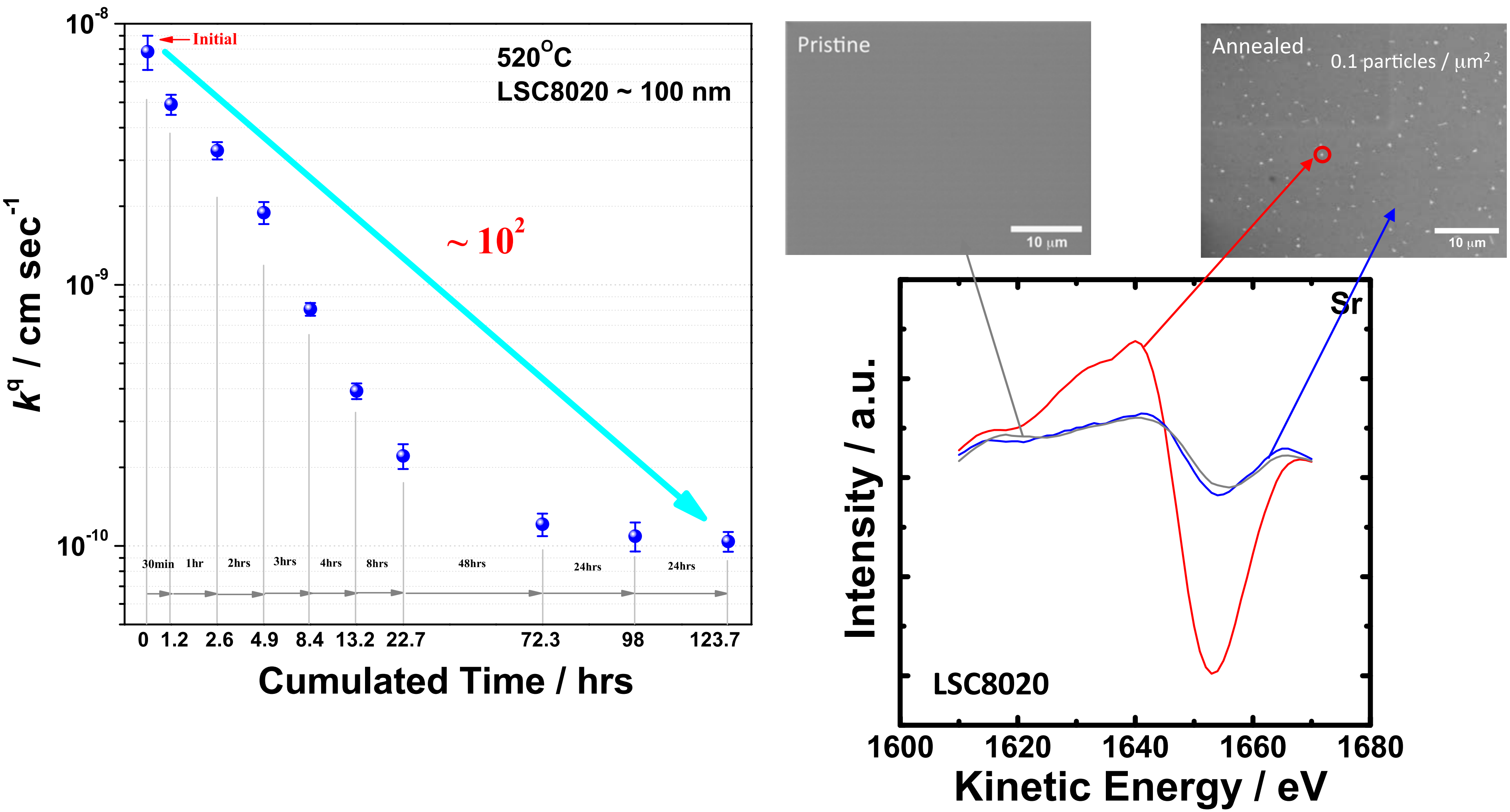
Surface Exchange Kinetics





- ❖ LSC_{214} decoration can slightly enhance the surface exchange rate (k^q) of LSCF
- ❖ LSC_{214} decorated LSCF shows comparable k^q with LSC_{214}

Surface Stability



- ❖ LSC_{113} shows significantly degraded surface activity after long time annealing
- ❖ LSC_{113} shows Sr-enriched particles on the surface after annealing

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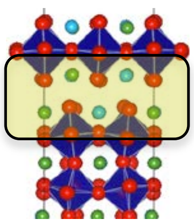

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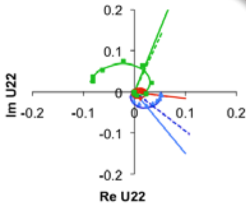

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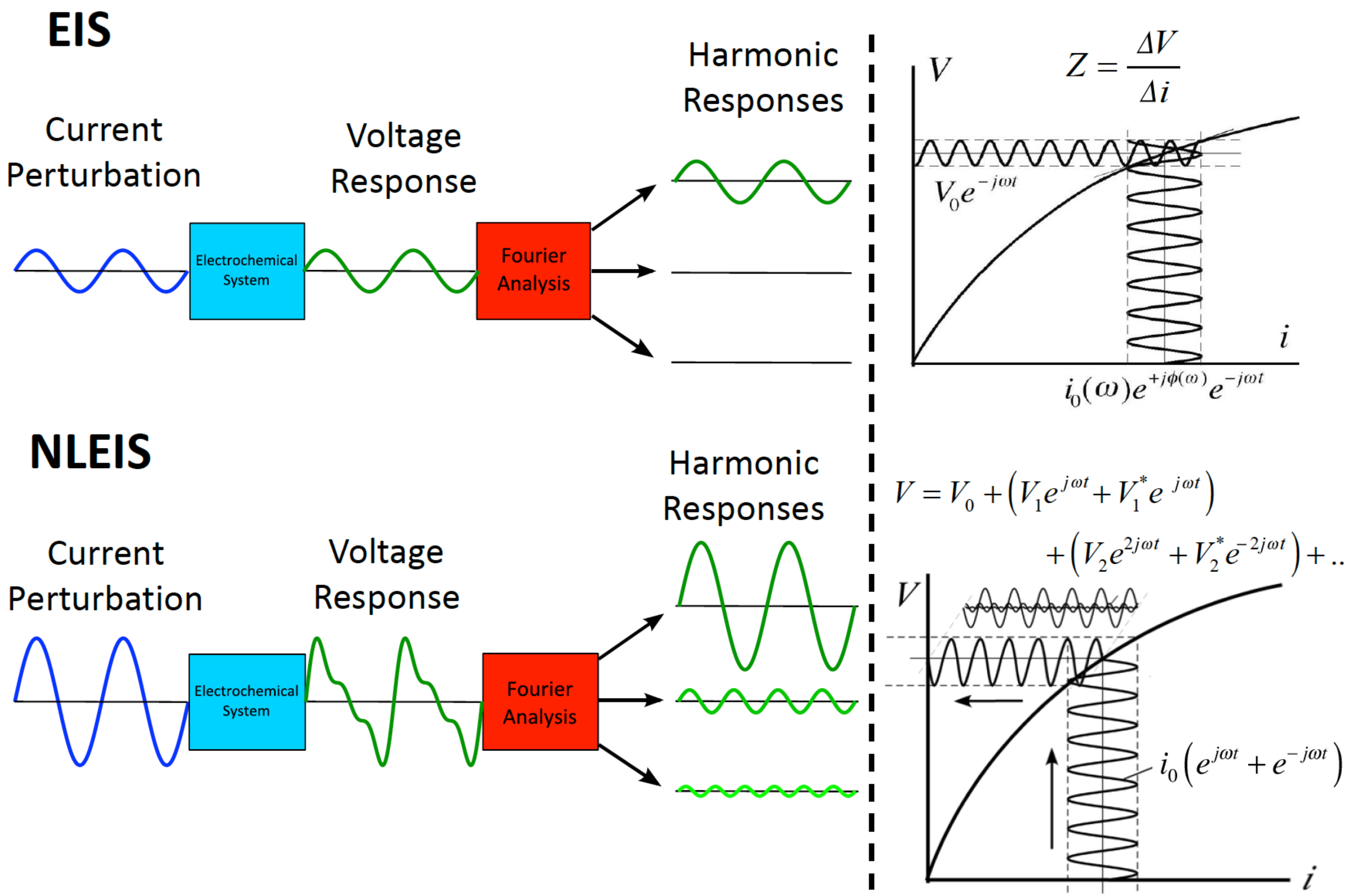
Non-Linear Impedance Spectroscopy (NLEIS) on LSC-113, LSCF-113

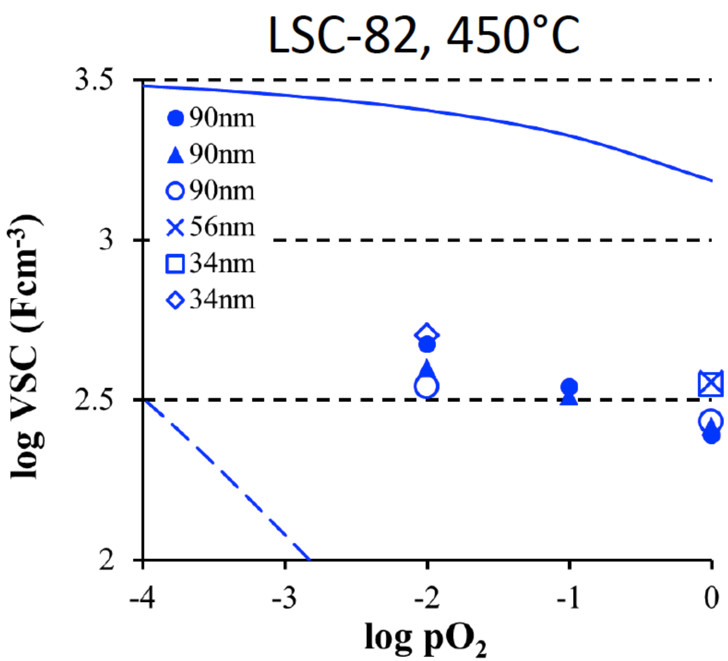
Adler (Univ. Washington)

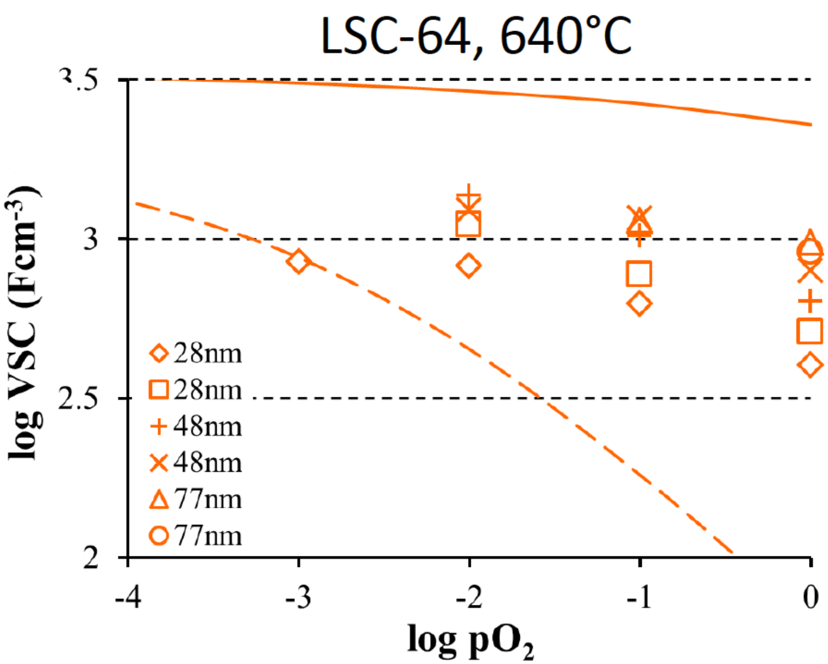
Electrochemical Measurements



NLEIS example: Explaining unusual LSC thin films

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

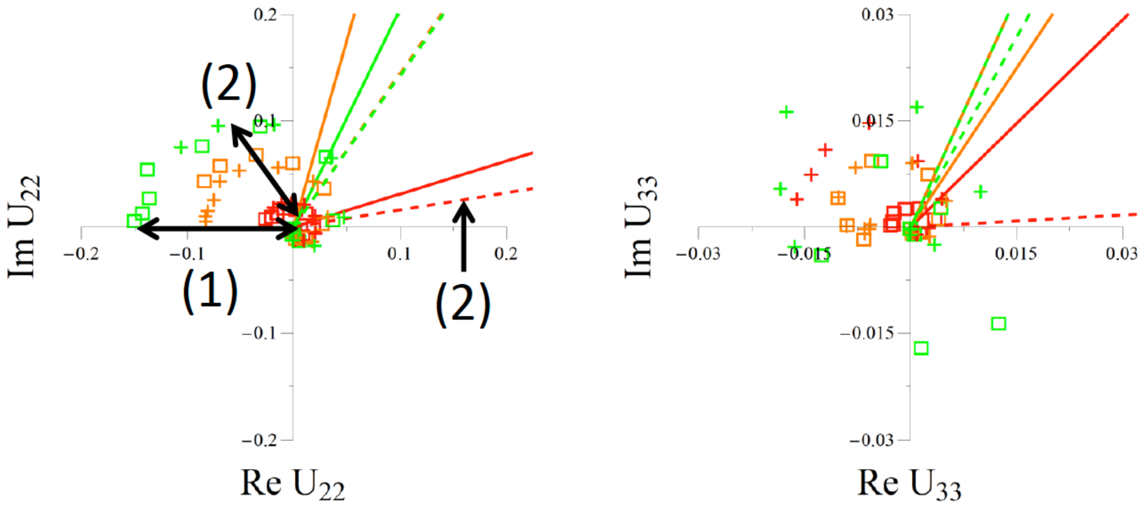




- Enhanced/Suppressed capacitance with LSC-64 like trends
- Large thickness and cell to cell variations

NLEIS on LSC thin films

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



(1) = Thermodynamics of surface and the surface exchange reaction mechanism

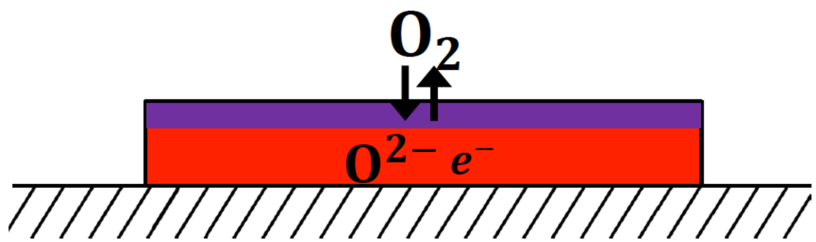
(2) = Thermodynamics of bulk

- 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.

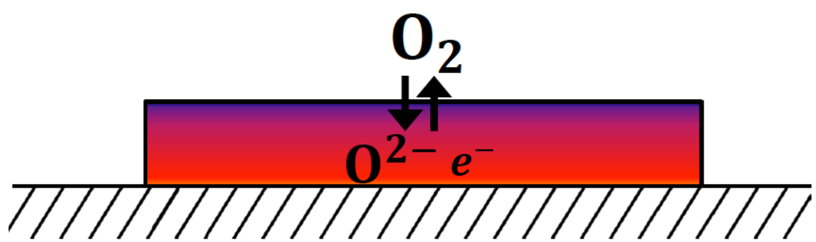
NLEIS on LSC thin films

Film with homogeneous Sr cannot explain NLEIS data!
Explored heterogeneous Sr distributions …

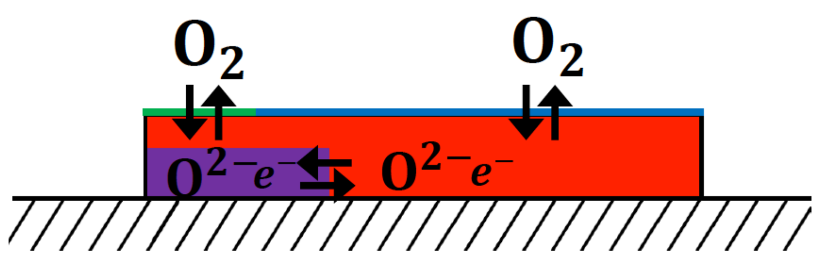
2 Layer Model



Exponential Layer Model



Dual Surface, Altered Bulk Model



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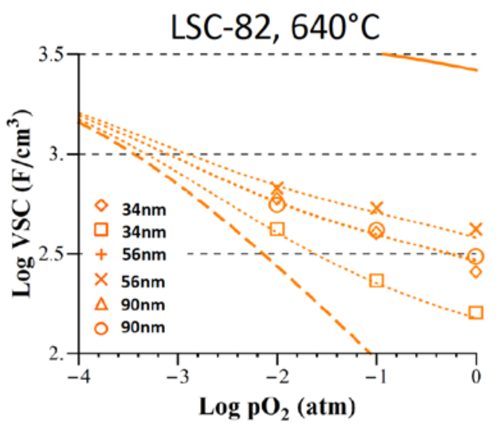
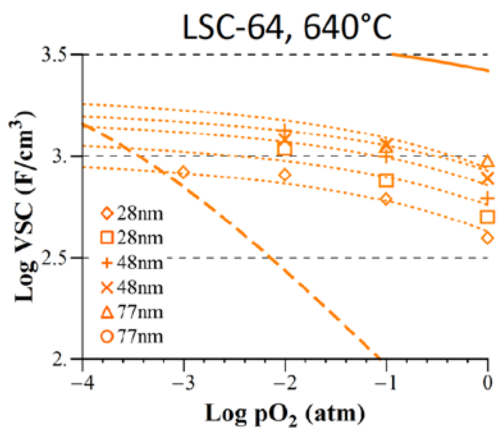
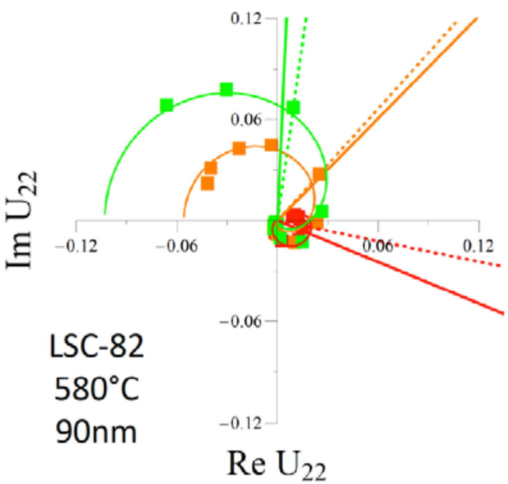
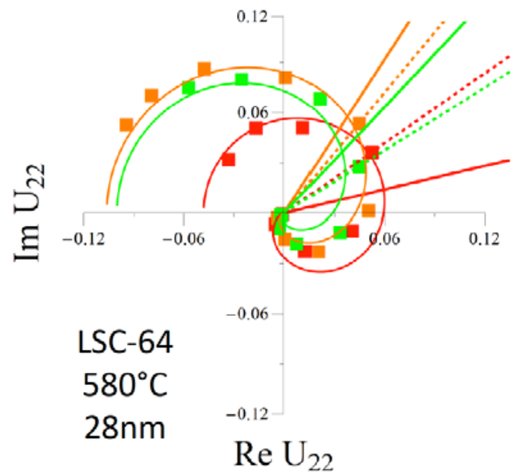








Conclusions

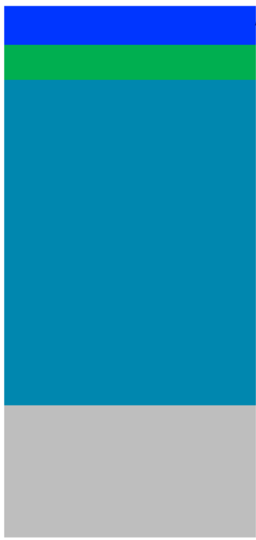
- Capacitance and harmonic response agree well.
- Implies Sr segregation is laterally inhomogeneous.
- O_2-active material for all films has properties of LSC (113) with x ~ 0.45.

Speculation

These films all show precipitation of secondary phases. Could the active material be associated with two-phase saturation/precipitation?

Current Efforts on LSCF

Dense Thin Film Electrode[1]



Mixed Conductor (60nm): $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

Ionic Conductor (60nm): $Ce_{1-x}Gd_{x}O_{2}$

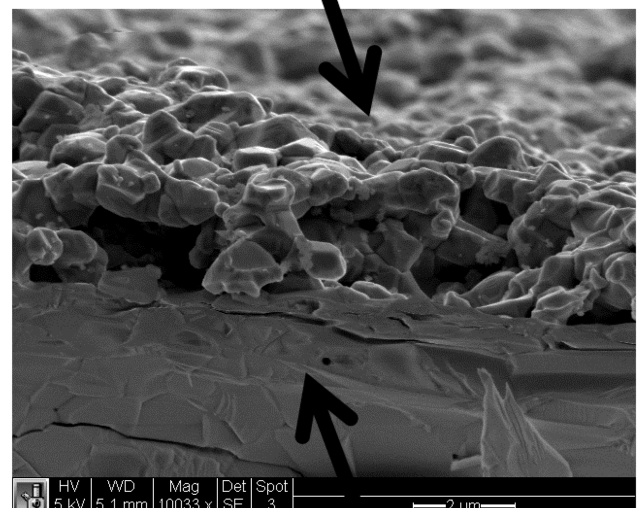
Ionic Conductor: $(Y_2O_3)_x(ZrO_2)_{1-x}$

Electronic Conductor: Pt

- Fabricated with PLD
- ~5mm x 5mm surface

Porous Electrode

Mixed Conductor (2-3 μm): $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$



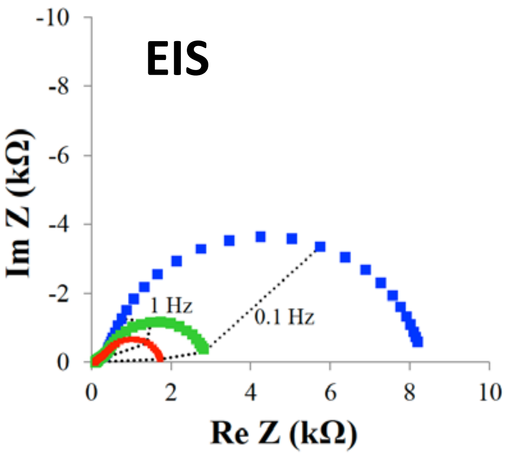
Ionic Conductor (2-3 mm): $Ce_{0.9}Gd_{0.1}O_2$

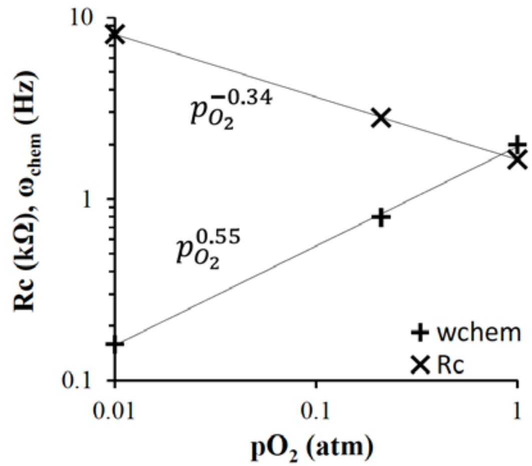
- Relatively low surface area

[1]Sample provided by Paul Fuoss, Argonne National Laboratory

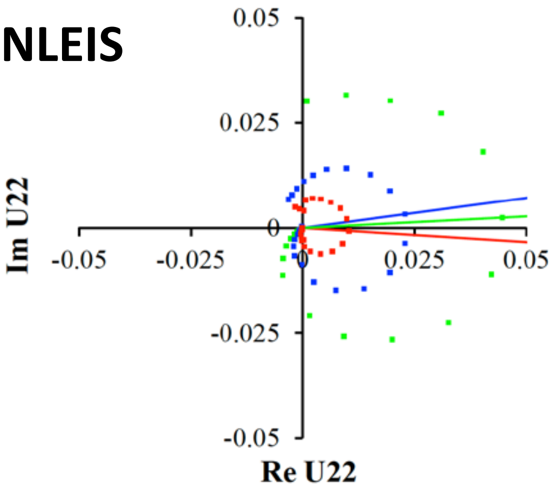
LSCF: Preliminary Results

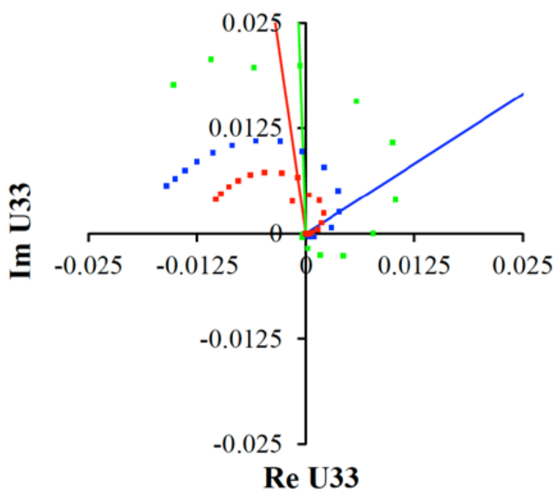
LSCF PLD thin film, 650°C vs. pO2





NLEIS





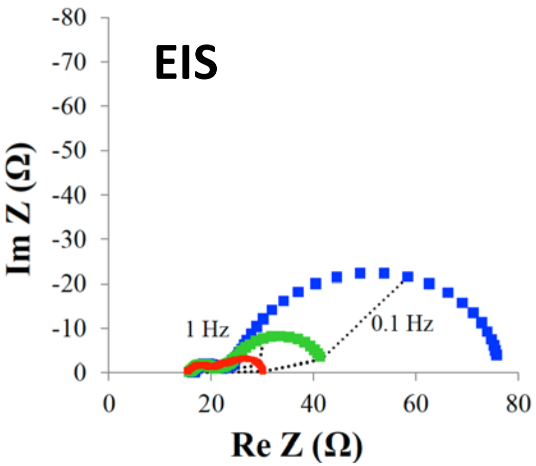
Status

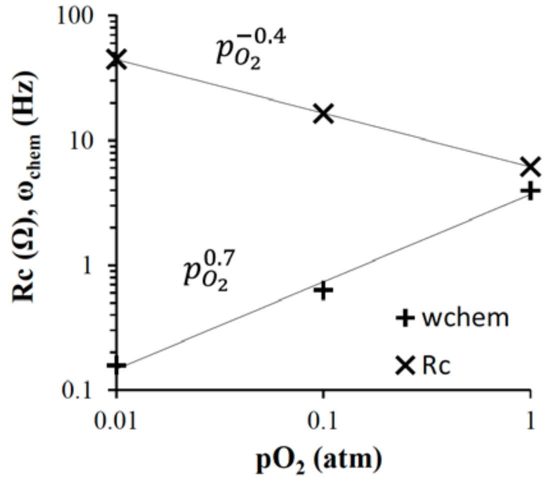
- Stable, well-resolved responses.
- Limited mostly by O_2 exchange with some bulk diffusion.
- Model pending.

LSCF: Preliminary Results

Single-phase Porous LSCF, 750°C vs. pO2

EIS





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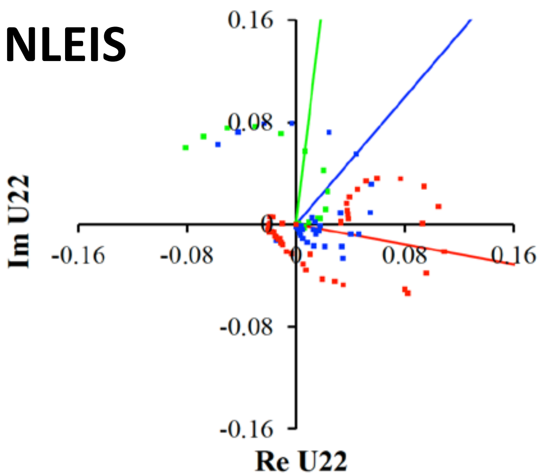

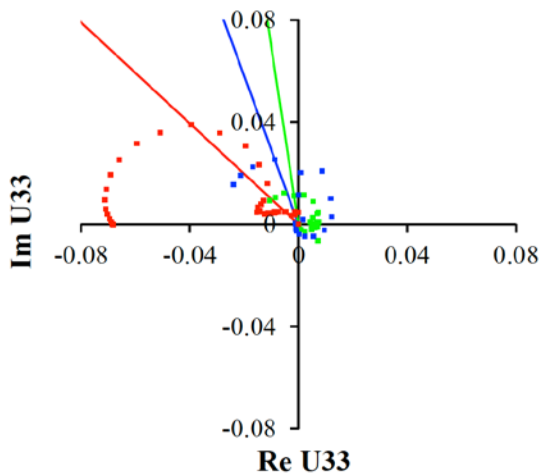

Status

- Over-sintered electrode has poor (but interesting) response.
- Becomes kinetically-limited at low p_{O2} due to small surface area.
- Two features present in EIS and NLEIS. Implies two series processes, both nonlinear.
- Need to optimize fabrication to insure 2nd process is relevant.
- Model pending.

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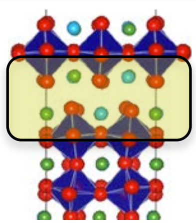

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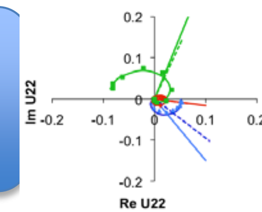

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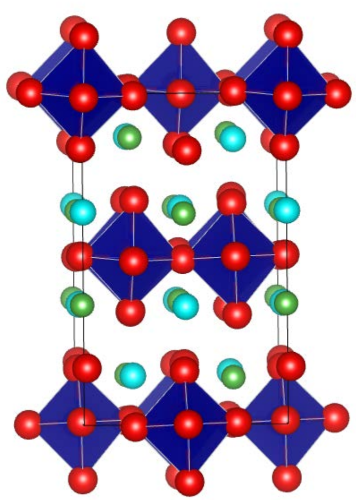
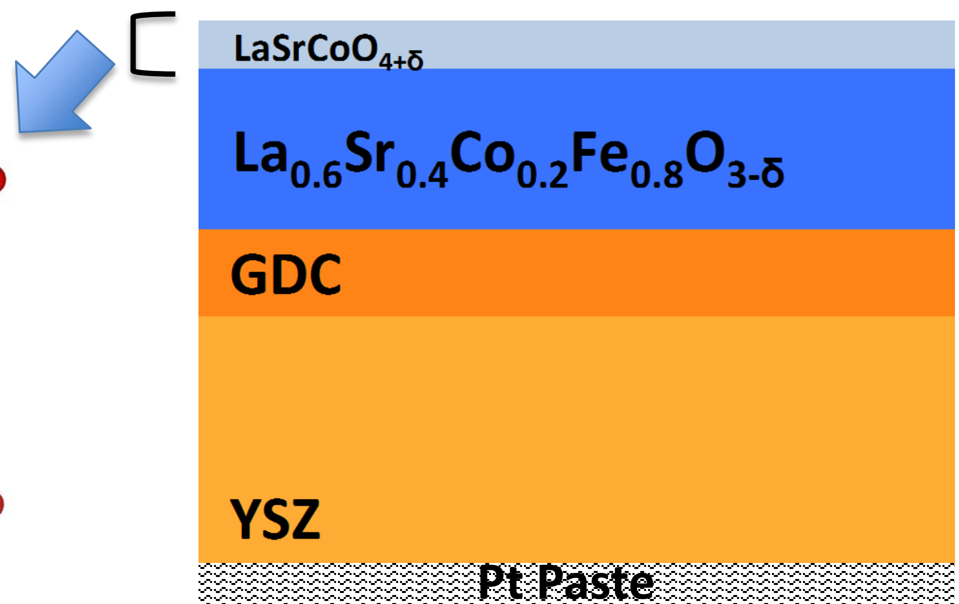
Ab Initio modeling of Defect Chemistry in LSC-214

Morgan (Univ. Wisconsin)

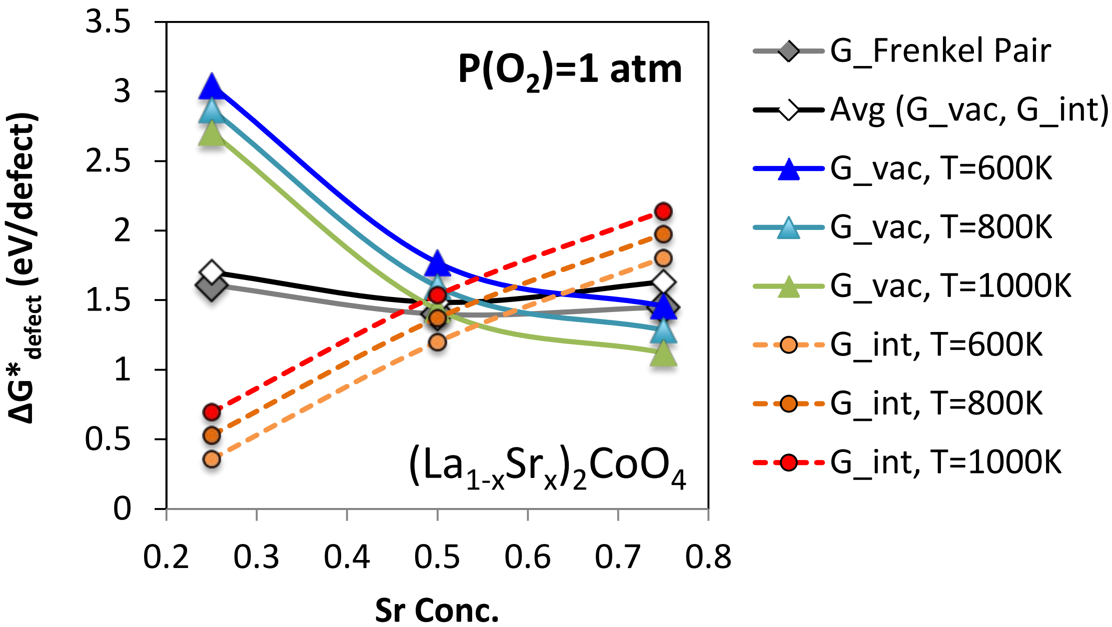
Defect chemistry of $La_{2-x}Sr_xCoO_{4\pm\delta}$

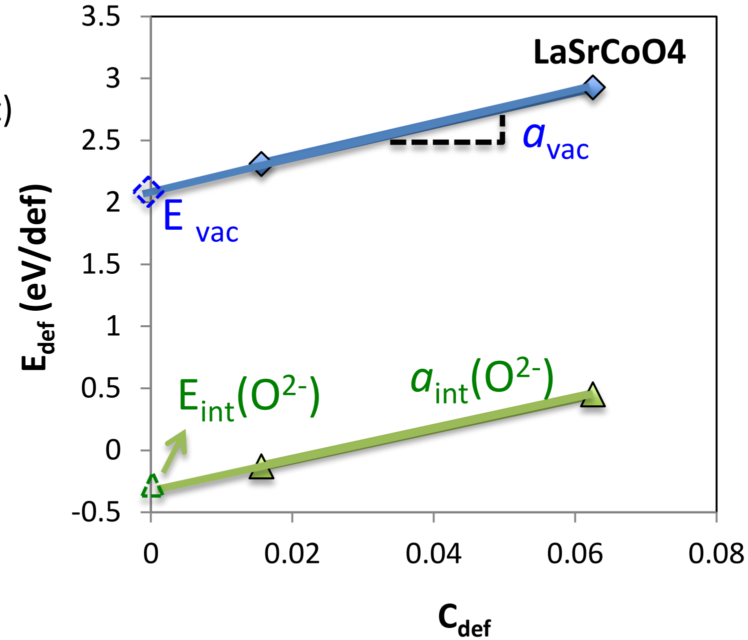
- Bulk defect chemistry of $La_{2-x}Sr_xCoO_{4\pm\delta}$ is less understood that perovksites
  - Both O vac and O int could be active defects for transport and surface reactions
  - Coupling to Sr doping
- Understanding bulk defect chemistry of $La_{2-x}Sr_xCoO_{4\pm\delta}$ as a first step to rationalize fundamental factors that lead to hetero-interface activity enhancement





$(La_{1-x}Sr_x)_2CoO_4$ Defect Energetics

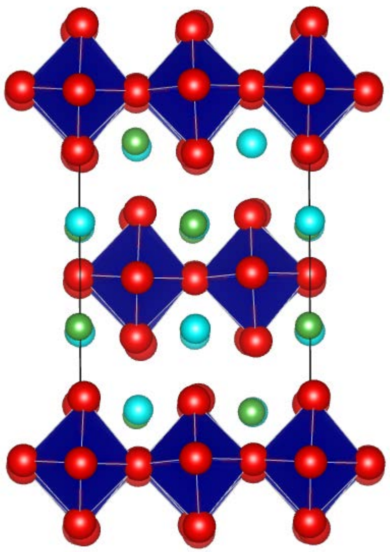




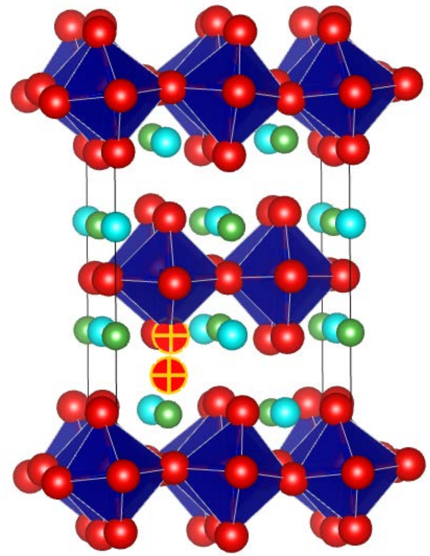
- Crossover of formation free energy of defects at Sr = 0.5 under SOFC conditions
- Strong nonideality (repulsion between same defect type) of defects (~10eV*c)
- Weak interaction between O_{vac}-O_{int}

Two O_{int} configurations in $LaSrCoO_4$

Bulk $LaSrCoO_4$

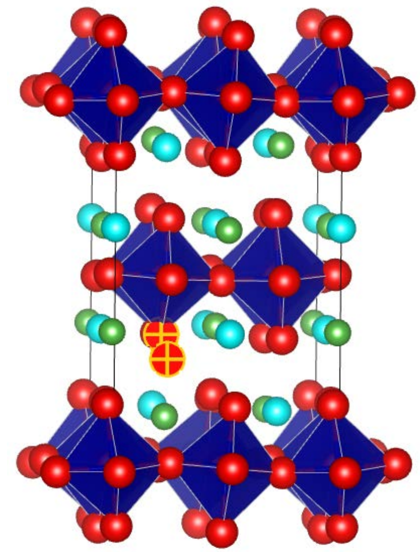


O_{int} config. 1



O-O dist = 2.64 Å

O_{int} config. 2

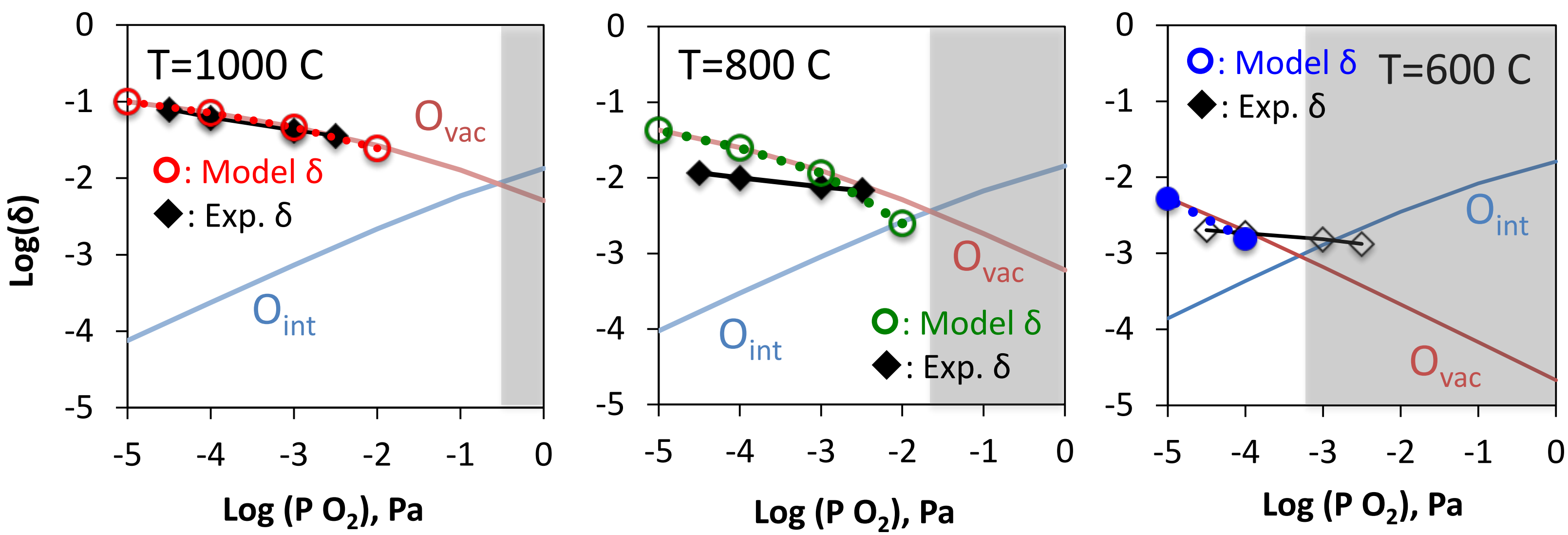


O-O bond = 1.52 Å

- **O_{int} config. 1: O^{2-} ion** in the center of Rocksalt A-site tetrahedra
- **O_{int} config. 2: form peroxide (O_2^{2-})** with lattice O → does not cause Co oxidation
- Relative stability of the two O_{int} species depends on Sr doping conc.
- Have been suggested experimentally in $La_2NiO_{4+\delta}$ (XPS shows no Ni^{3+}) and $La_{2-x}Sr_xCuO_{4+\delta}$ (eg, missing O from tetrahedral site in neutron scattering)

Buttrey JSSC 1988; Jacobson, PRL 1996

(Slight Adjusted) DFT Model Predictions for $LaSrCoO_{4\pm\delta}$



Exp. δ from Vashook, SSI, 2000

- Crossover of O_{int} and O_{vac} concentration vs. $P(O_2)$
- Good agreement with exp. δ at T=1000 C, but deviates at lower T (experimental errors at small defect concentrations?)

Results Summary

- LSC-113/LSCF-214 shows mild enhancement. Difference from LSC-214/LSC-113 may be due to LSC-113 vs. LSCF-113 stability.
- Initial NLEIS on LSCF-113 films and porous electrodes initiated.
- Ab initio studies of LSC-214 shows vacancy/interstitial crossover vs. X_{Sr}, T, and PO_2.

Future Work

- Investigate the surface chemistry, activity, degradation of LSCF-113 and LSC-214/LSCF-113 (why different from LSC-214/LSC-113?)
- Investigate other 214 decoration candidates to achieve the enhanced surface activity

↔

- Film growth + Physical characterization (MIT)
- NLEIS + Modeling (Washington Univ.)
- Ab initio stability /reaction energies (Univ. Wisconsin)

END

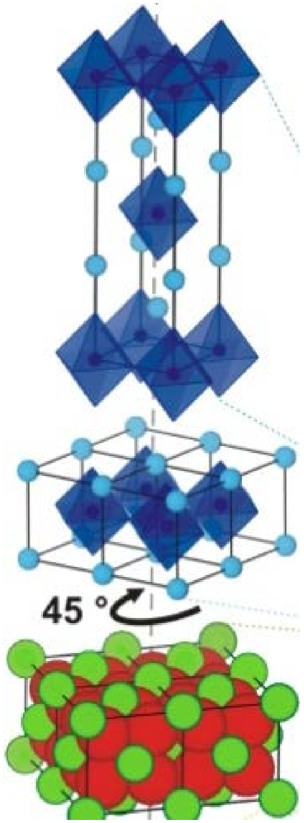
Thank you for your attention

Thin-film Characterization of LSC-214/LSCF-113, LSC-113

Shao-Horn (MIT)

Backup

Surface chemistry greatly influences O_2 electrocatalysis at HT



214

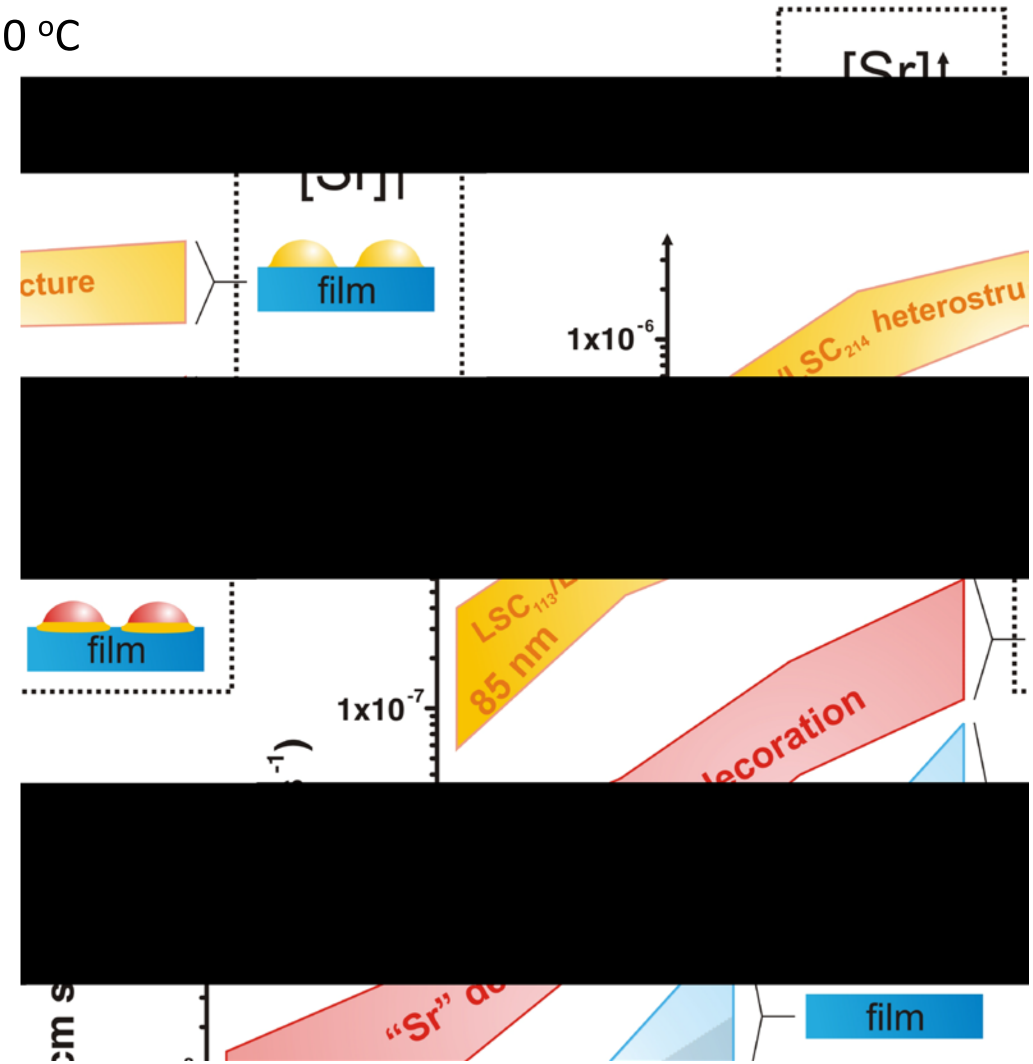
113

GDC

YSZ

Pt-Anode

520 °C



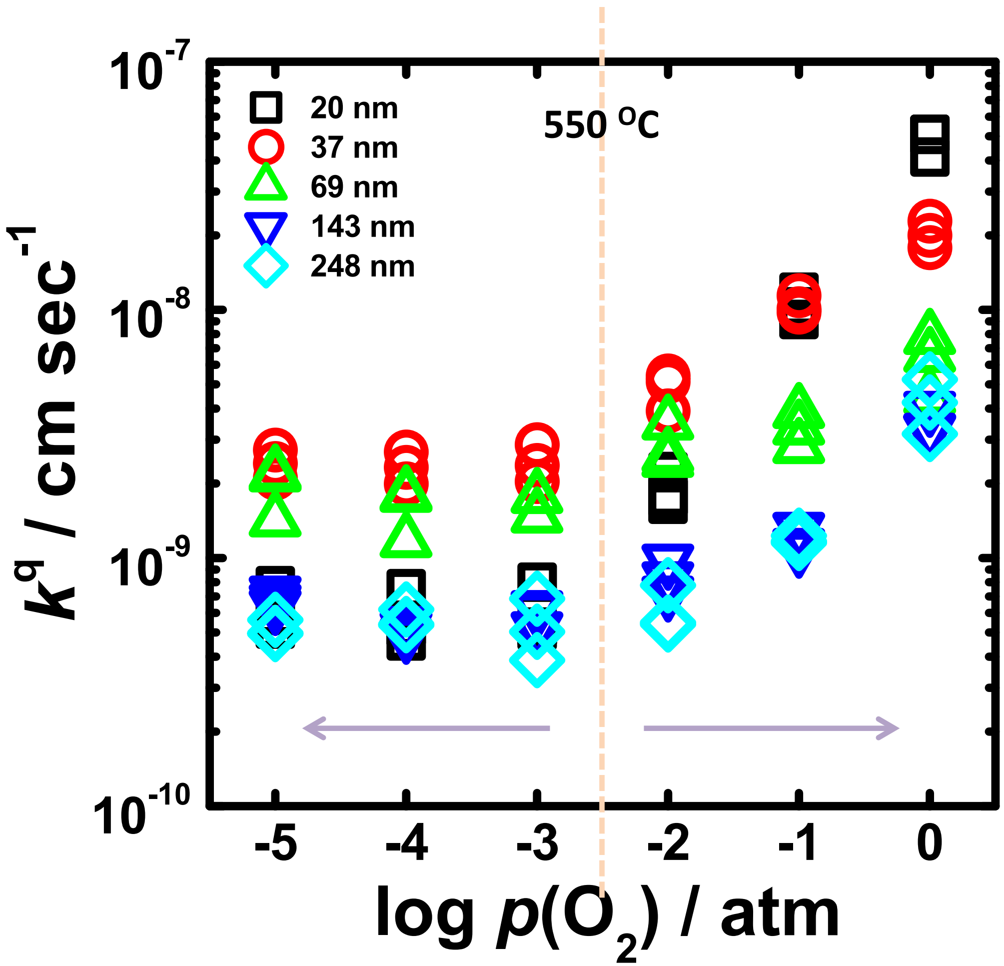
LSC_{113}: $La_{0.8}Sr_{0.2}CoO_{3-\delta}$

LSC_{214}: $(La_{0.5}Sr_{0.5})_2CoO_{4\pm\delta}$

$LSC_{113/214}$: LSC_{214}-decorated LSC_{113}

[1] E. Mutoro et al., Energy Environ. Sci., 2011, 3689–3696, E. J. Crumlin, E. Mutoro et al., JPCL 1, 2010, 3149, [2] G. J. la O' et al., Angew. Chem. Int. Ed. 2010, 49, 5344

Surface Exchange Kinetics



$k^q \propto pO_2^{\,m}$ [1)]

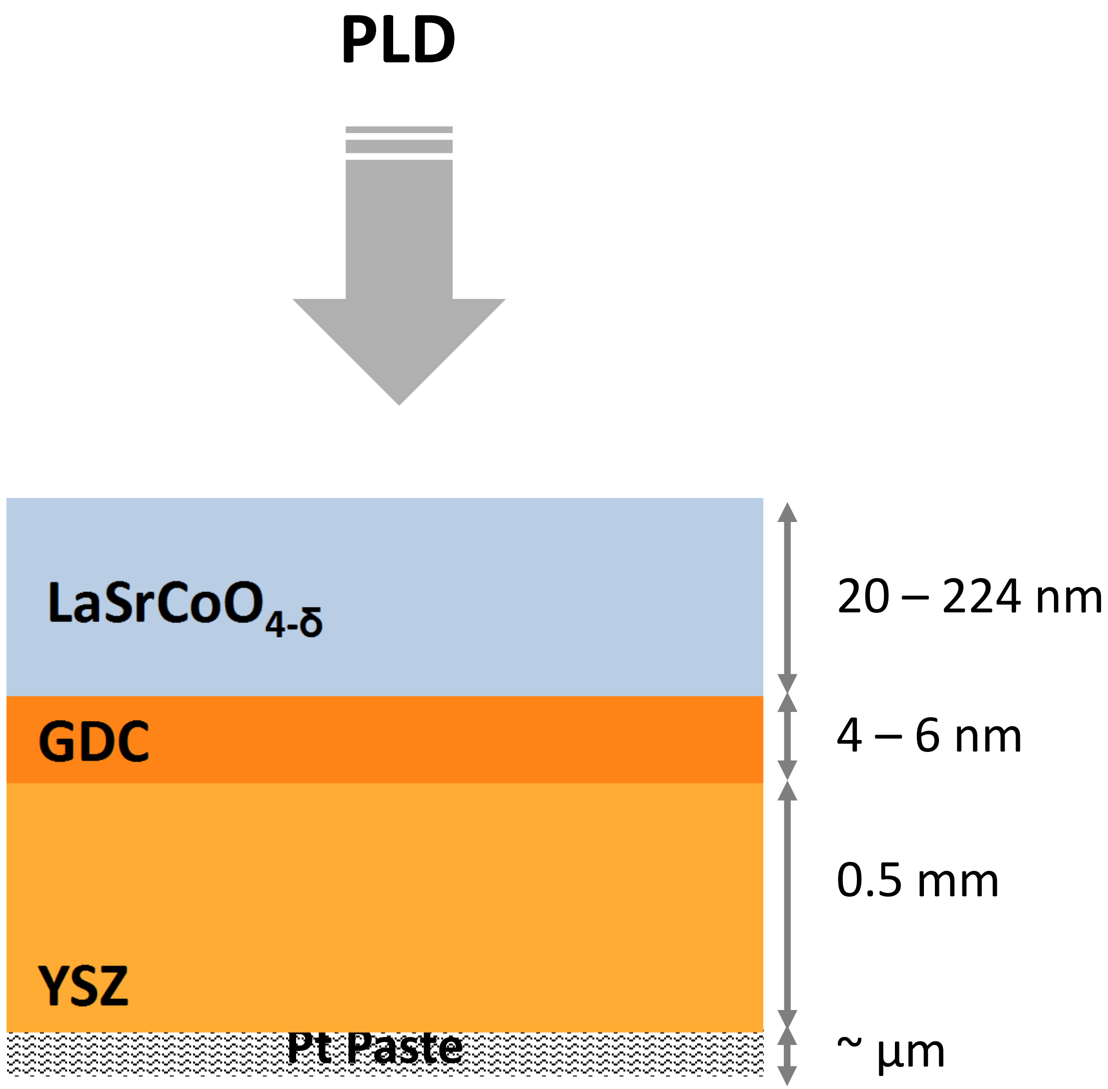
Different m value suggests
Different rate limiting steps

m value	$p(O_2)$ 1atm – 10^{-2}atm	$p(O_2)$ 10^{-3}atm – 10^{-5}atm
20nm	0.7	0
37nm	0.31	0
69nm	0.19	0
143nm	0.31	0
248nm	0.41	0

❖ All films show no change of k^q at low $p(O_2)$ (10^{-3} ~ 10^{-5} atm)

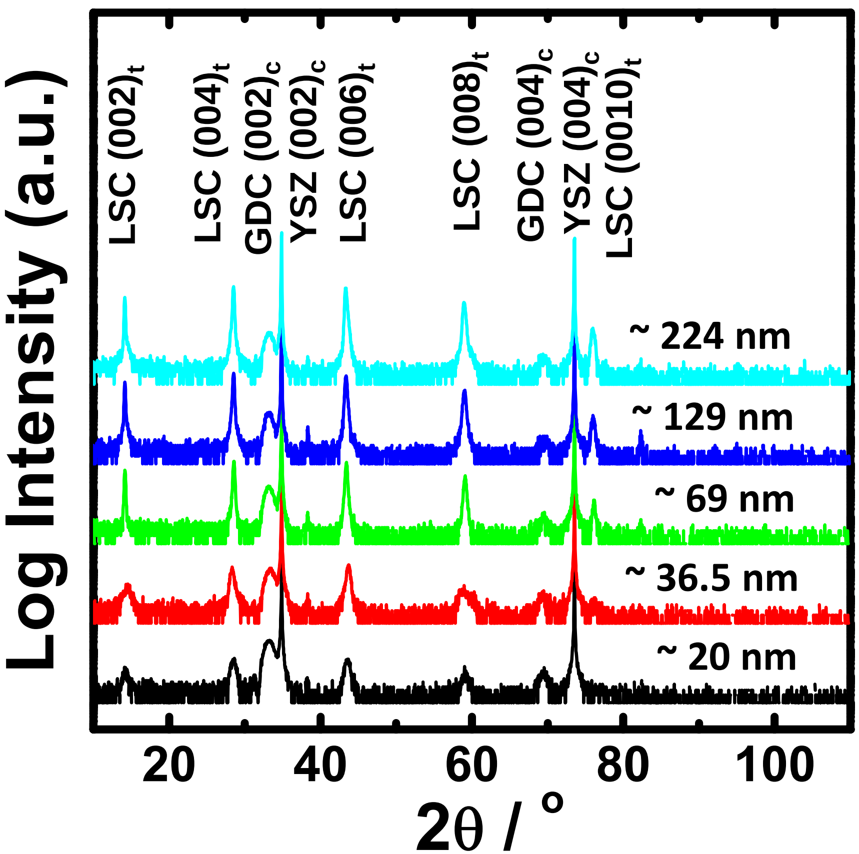
1) De souza, PCCP 2006

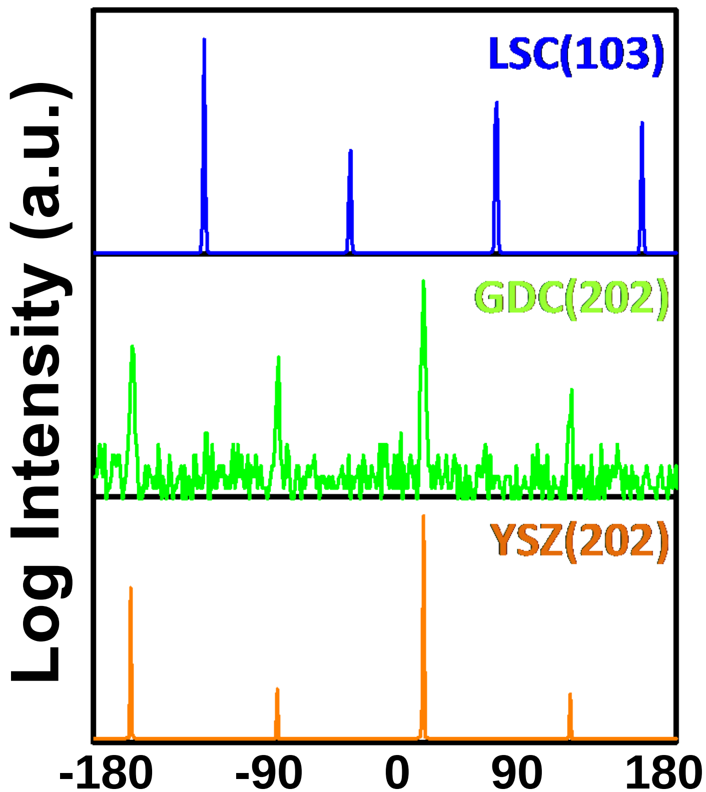
Pulsed Laser Deposition



Pulse (x1000)	Thickness (nm)
1	20
2	36.5
5	69
10	129
15	224

X-ray Diffraction Results

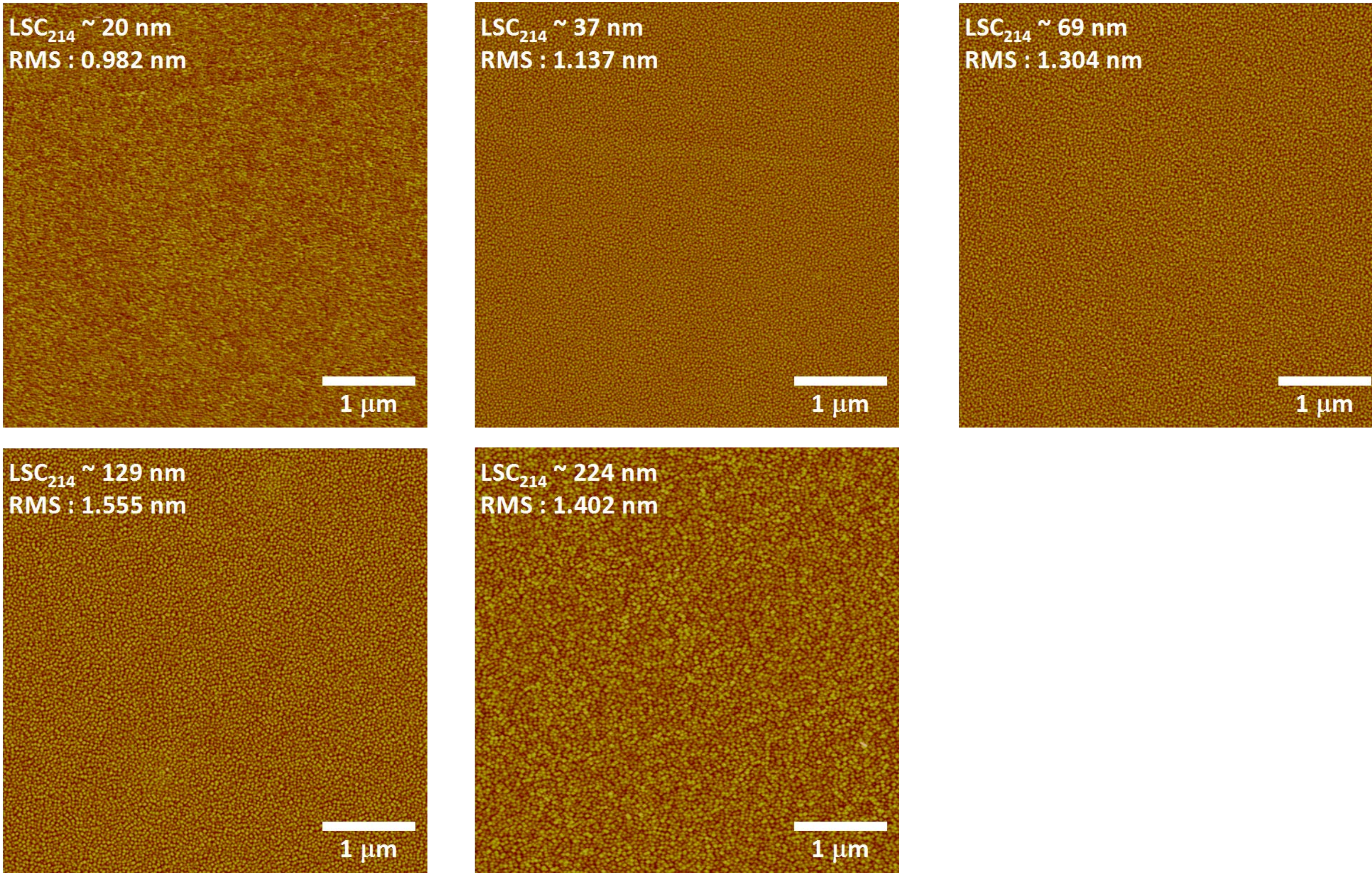




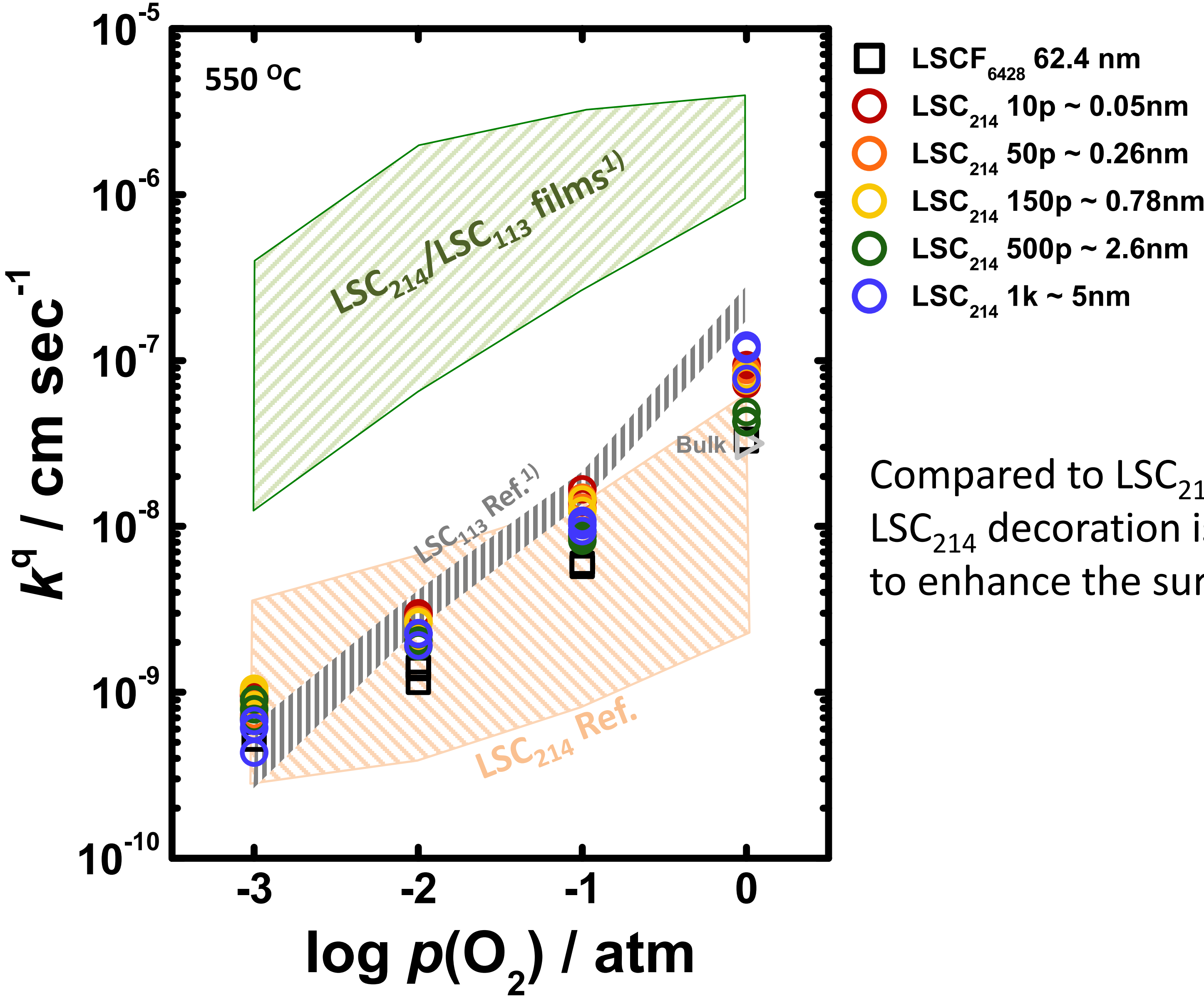
❖ All films clearly show ***c***-axis-oriented epitaxial thin films

❖ Off normal XRD shows LSC unit cell on the GDC with 45^0 rotation

AFM Images (As-deposited)



Comparison with LSC_{214}/LSC_{113}

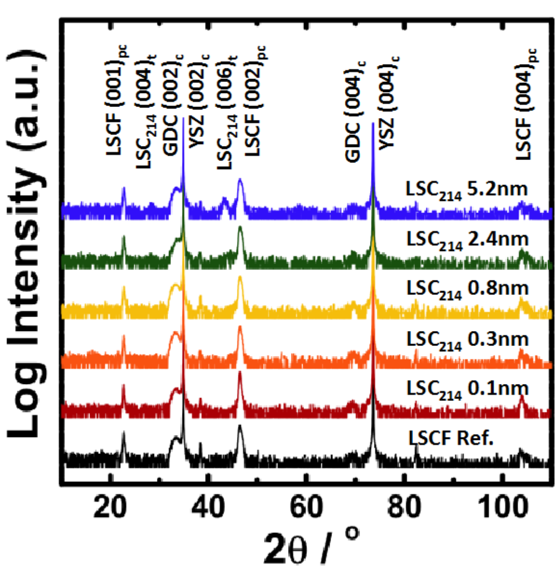


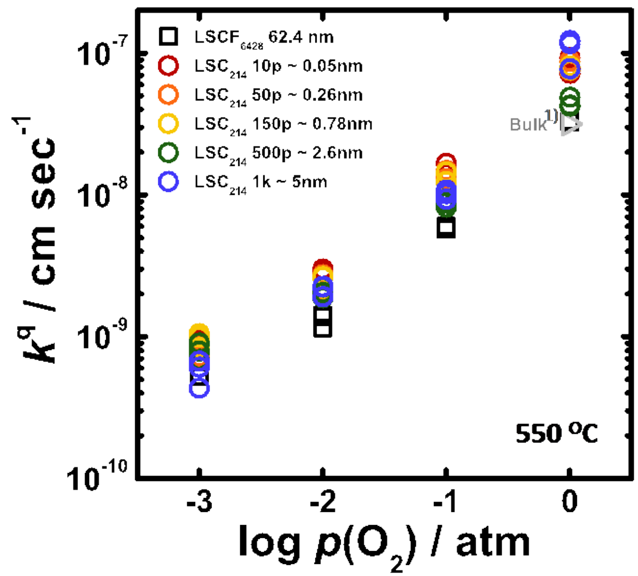
Compared to LSC_{214}/LSC_{113},
LSC_{214} decoration is not much effective to enhance the surface activity of LSCF

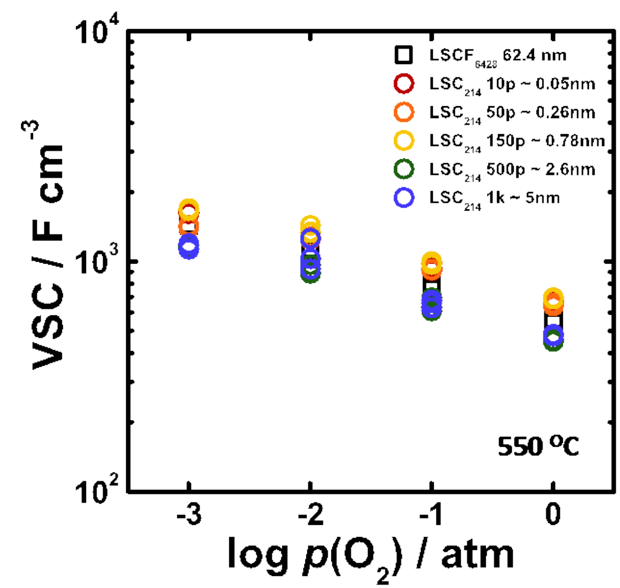
1) Crumlin et al., JPCL (2010)

Summary

- $LaSrCoO_{4-\delta}$ on $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ epitaxial thin films were deposited by PLD
- As-deposited films showed smooth surface (RMS < 0.5 nm)
- LSC_{214} decoration showed slightly enhanced surface activity
- *VSCs* were not significantly changed by LSC_{214} decoration
- Temperature dependent k^q and surface chemistry will be investigated
- More decoration materials (e.g. other A_2BO_4, other ABO_3) need to be investigated

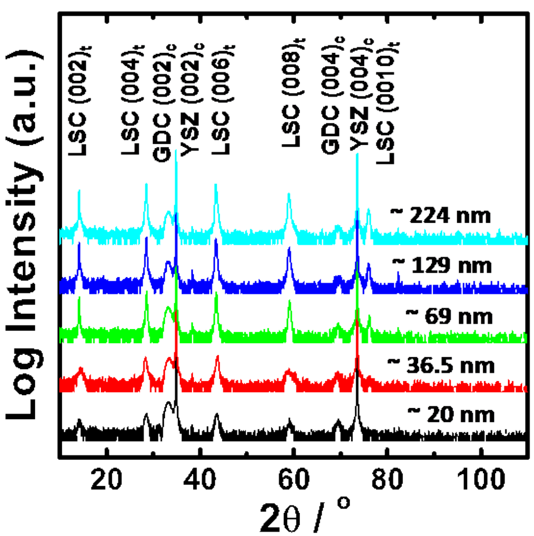


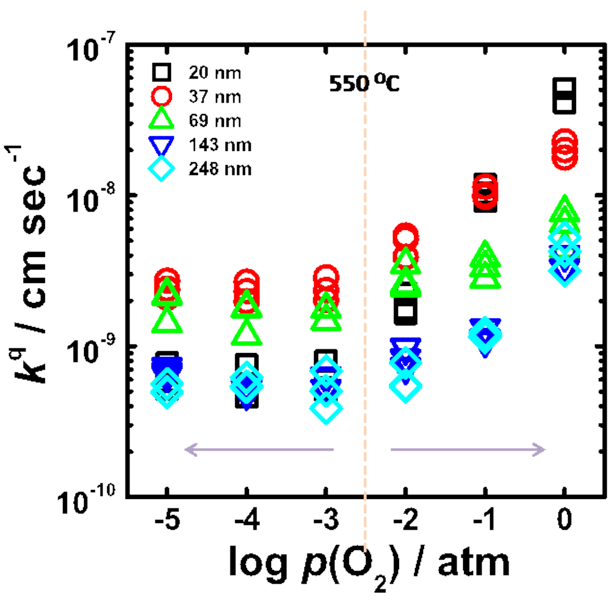


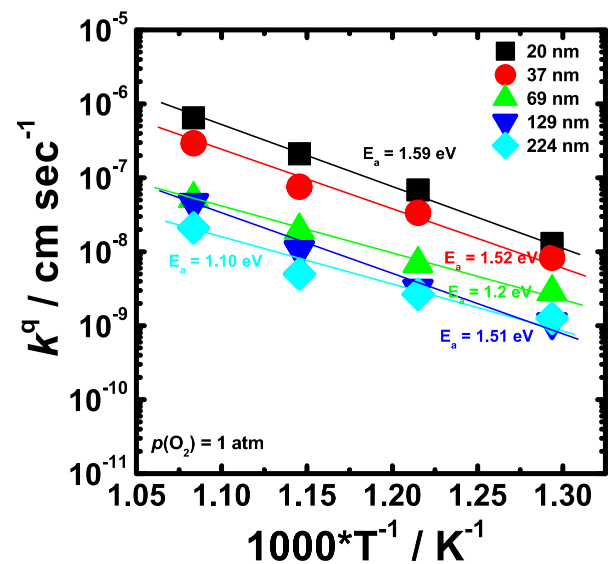


Summary

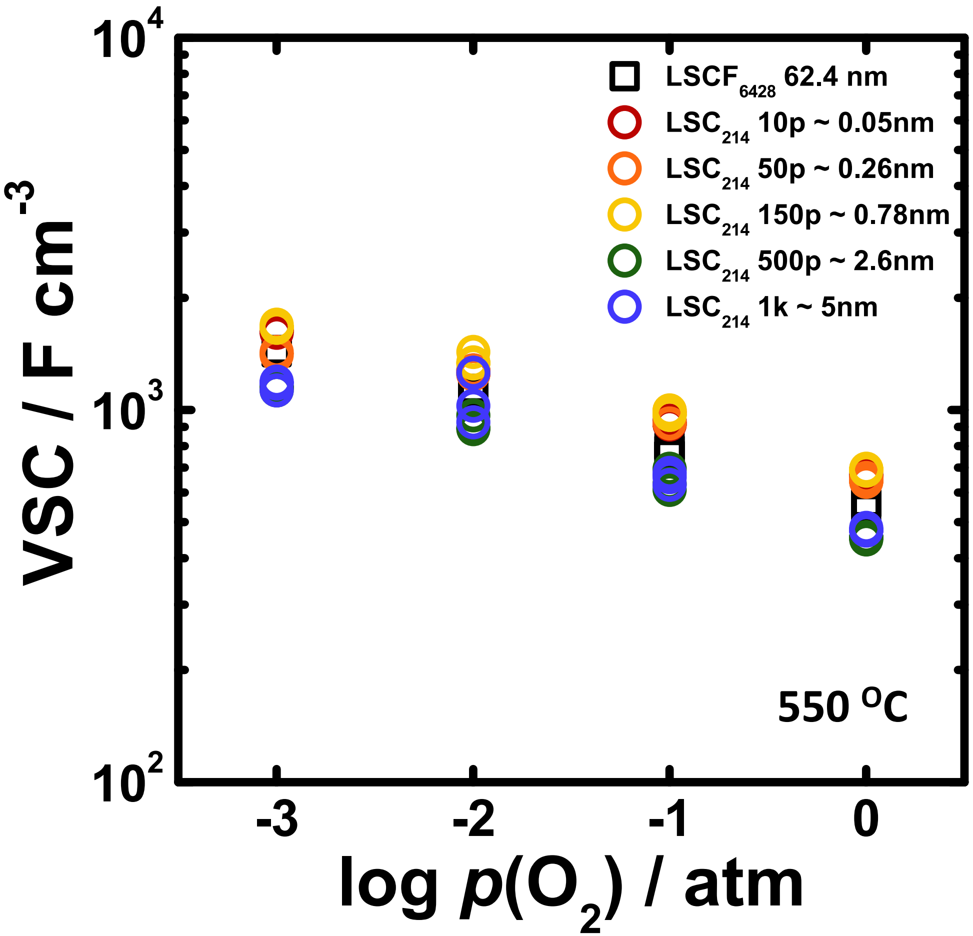
- ❖ $LaSrCoO_{4-\delta}$ epitaxial thin films were deposited by PLD
- ❖ As-deposited films showed smooth surface (RMS < 1.5 nm)
- ❖ All films show not change of k^q at low $p(O_2)$ (10^{-3} ~ 10^{-5} atm)
- ❖ Activation energy was dependent on oxygen partial pressure
- ❖ Surface chemistry of 37nm and 69nm showed not significant difference
- ❖ Defect energetic and surface activity will be more studied







Volume Specific Capacitance



✓ **Volume specific capacitance**

$$VSC = \left(1/V_{\mu electrode}\right)\left((R_{LF})^{1-n}Q\right)^{1/n}$$

Q = non-ideal “capacitance”
n = non-ideality factor

❖ VSCs do not show significant change by LSC_{214} decoration

LSC_{214} Lattice Parameters

	a	c	$\hat{a}$	$\hat{c}$	In-plane strain	Out-of-plane strain
20nm	3.832	12.454	3.811	12.515	0.574	-0.492
36.5nm	3.828	12.467	3.811	12.516	0.457	-0.392
69nm	3.813	12.491	3.808	12.505	0.134	-0.115
129nm	3.806	12.506	3.807	12.503	-0.020	0.017
224nm	3.806	12.512	3.808	12.506	-0.059	0.051

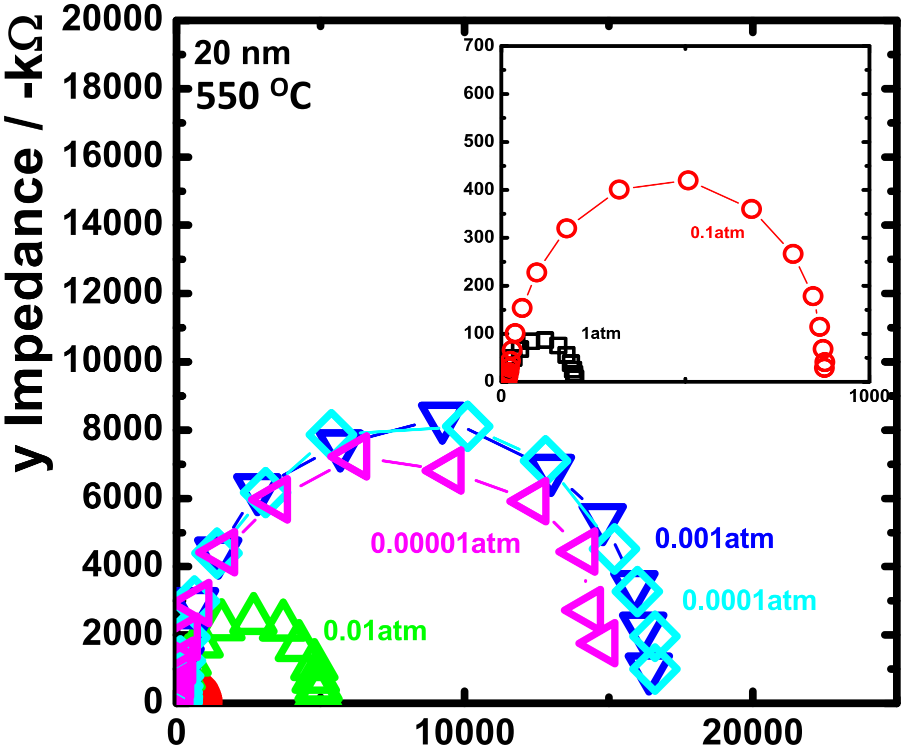
$$\frac{(c-\hat{c})}{\hat{c}} = \frac{-2\nu}{1-\nu}\frac{(a-\hat{a})}{\hat{a}}$$ [1), 2)]

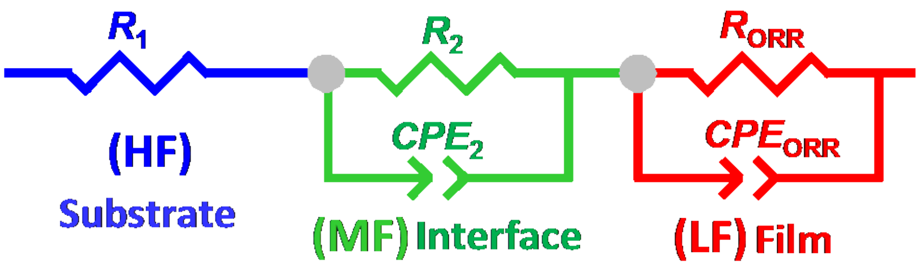
Assuming
1. $\hat{c}/\hat{a} \approx 3.284$ (based on bulk)[3)]
2. $\nu = 0.3$ (perovskite: 0.2 – 0.3)[4)]

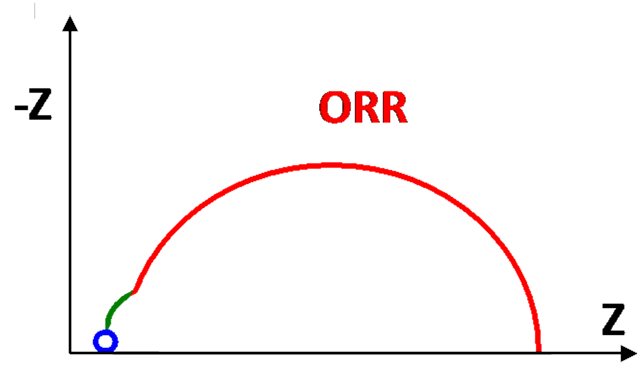
- ❖ In-plane stain decreases as thickness increases
- ❖ Out-of-plane stain increases as thickness increases

1) Crumlin et al., EES, 5 (2012; 2) Christen et al., PRB, 68 (2003); 3) Demazeau et al., Nouv. J. Chim. 3 (1979);
4) Nho et al., APL, 68, (1996)

Nyquist Plot



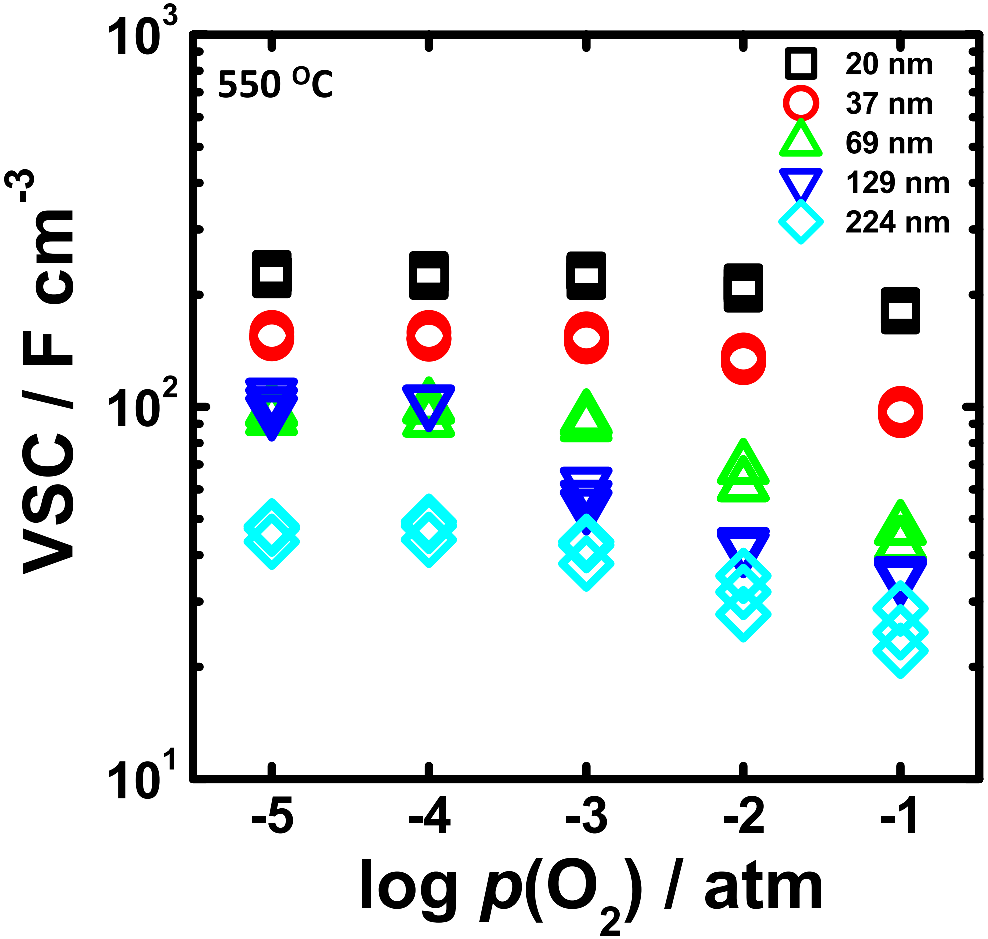




$$k^q = \frac{RT}{4F^2 R_{LF} A_{electrode} C_o}$$ [1, 2]

1) Maier, Phys. Chemistry Ionic Materials, 2004
2) Mizusaki et al., JSSC 1998

Volume Specific Capacitance (*VSC*)



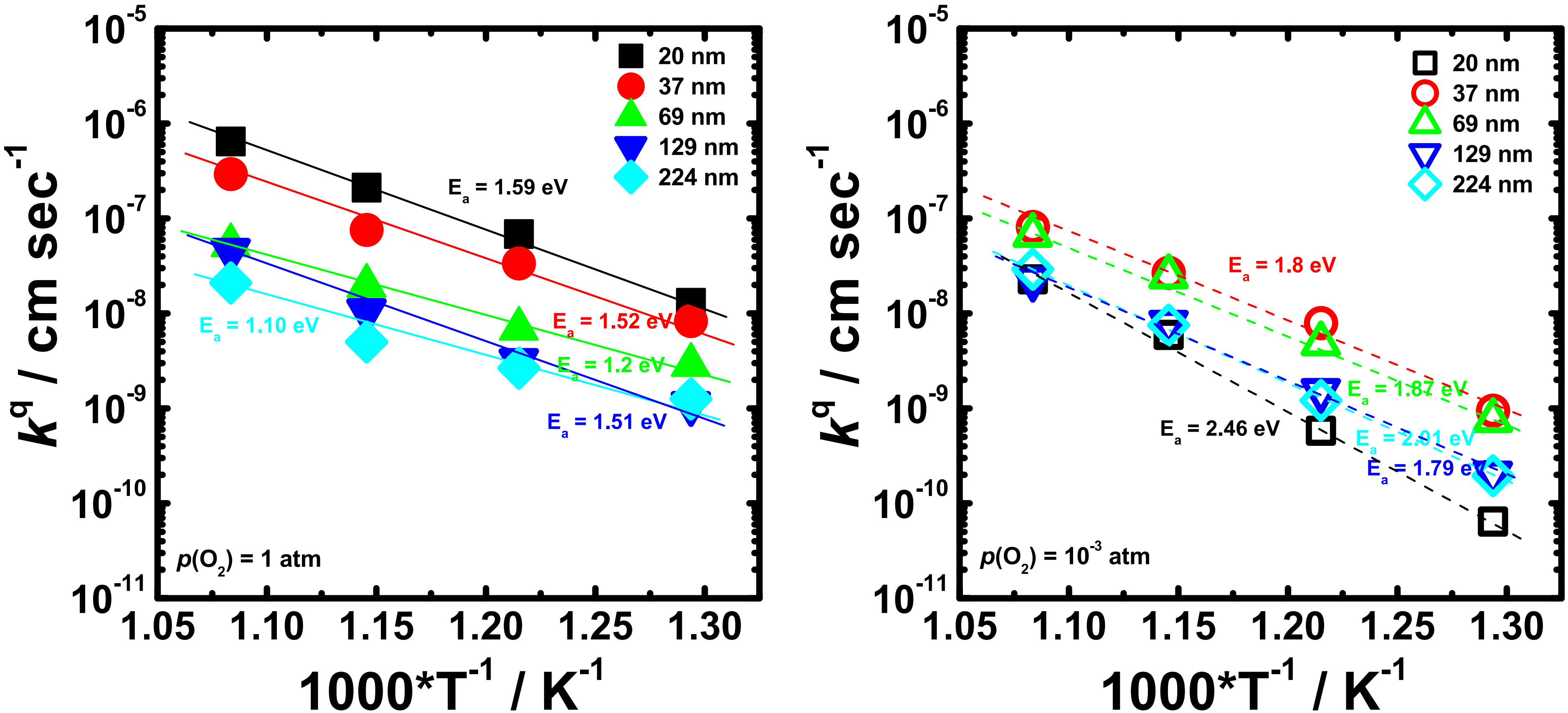
✓ Volume specific capacitance

$$VSC = \left(1/V_{\mu electrode}\right)\left((R_{LF})^{1-n} Q\right)^{1/n}$$

Q = non-ideal "capacitance"
n = non-ideality factor

- ❖ All films show no change of *VSCs* at low $p(O_2)$ ($10^{-3} \sim 10^{-5}$ atm)
- ❖ *VSCs* trend is similar to LSC_{113}, which means vacancy but not interstitial

Activation Energy

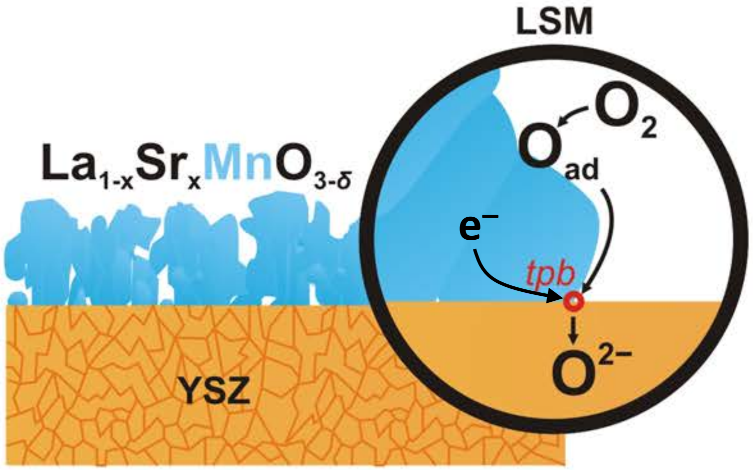


- ❖ At $p(O_2)$ = 1 atm, all films show relatively smaller activation energy
- ❖ At $p(O_2)$= 10^{-3}atm, all films show relatively higher activation energy

Enabling Oxygen Electrocatalysis on Metal Oxides for Energy Storage

Y. Shao-Horn

Oxygen Electrocatalysis on Transition Metal Oxides

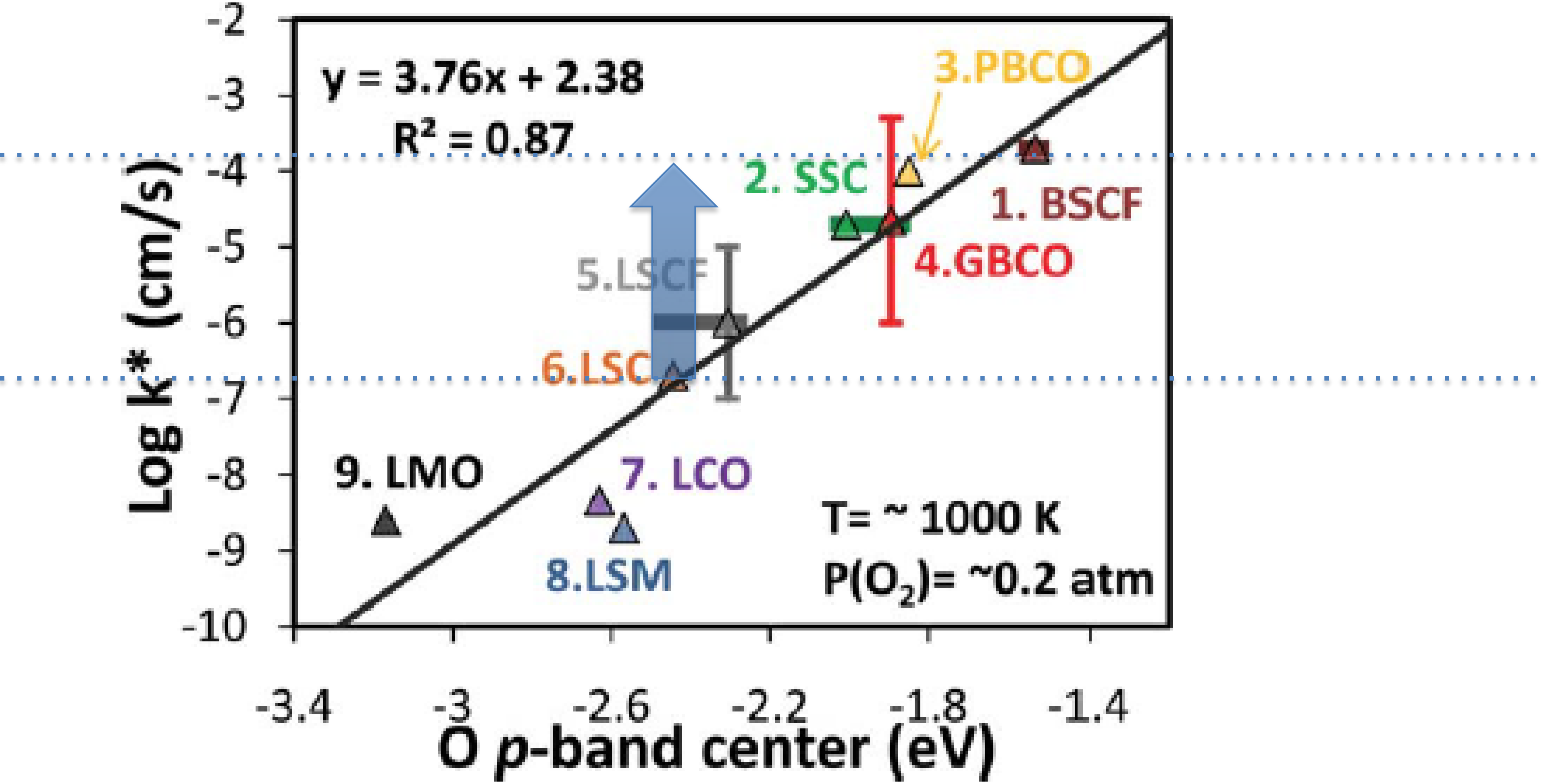


[1] S. B. Adler, Factors Governing Oxygen Reduction in Solid Oxide Fuel Cell Cathodes, Chem. Rev. 2004, 104, 4791,
[2] G.J. la O et al., Catalytic Activity Enhancement for Oxygen Reduction on Epitaxial Perovskite Thin Films for Solid-Oxide Fuel Cells, Angew. Chem. Int. Ed. 2010, 49, 5344.

Preparation of Epitaxial (001)$La_{0.8}Sr_{0.2}CoO_3$ (LSC) Films

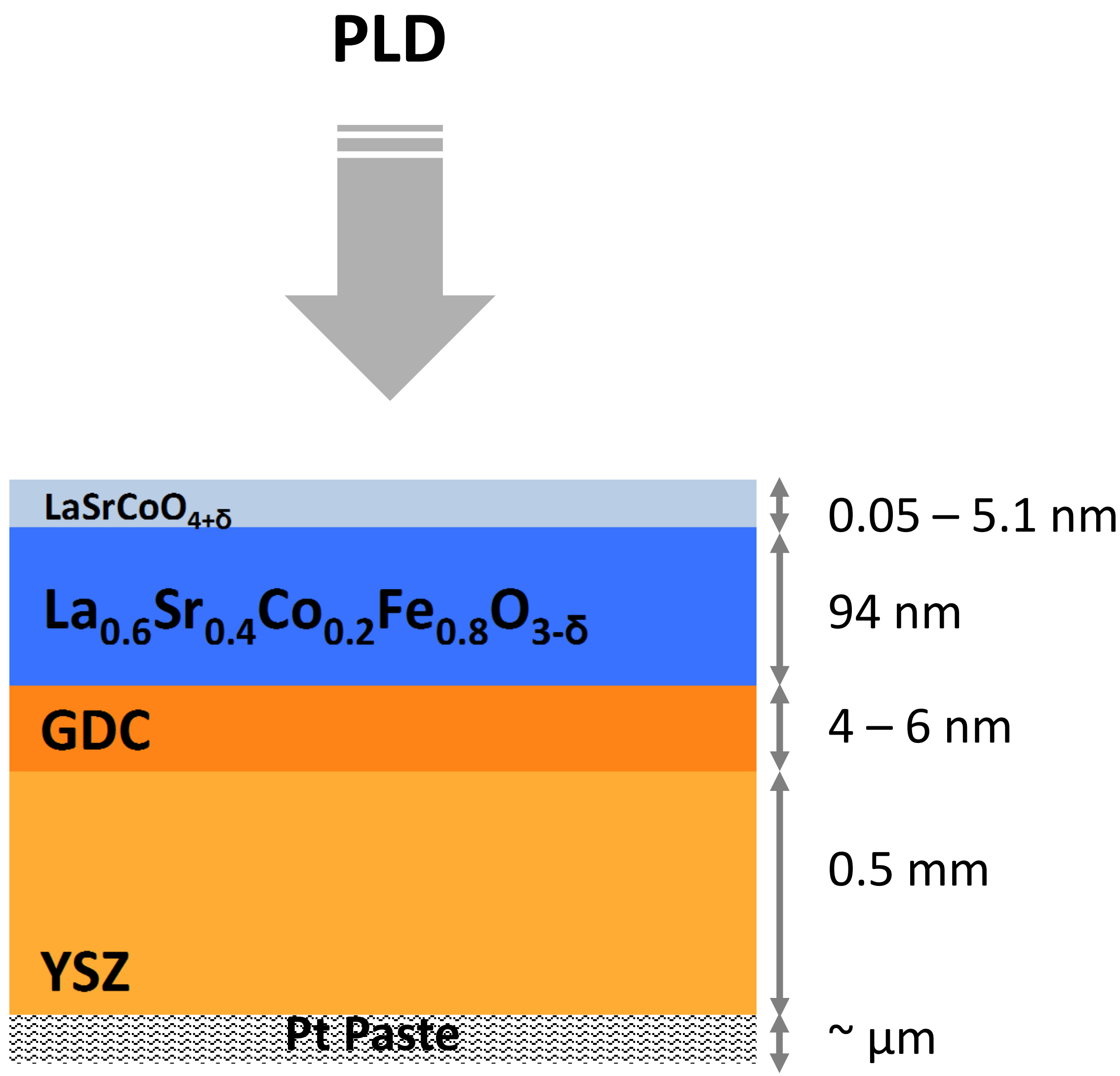
1. $LaSrCoO_{4-\delta}$ / $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

O_2 electrocatalysis on perovskites at high temperatures



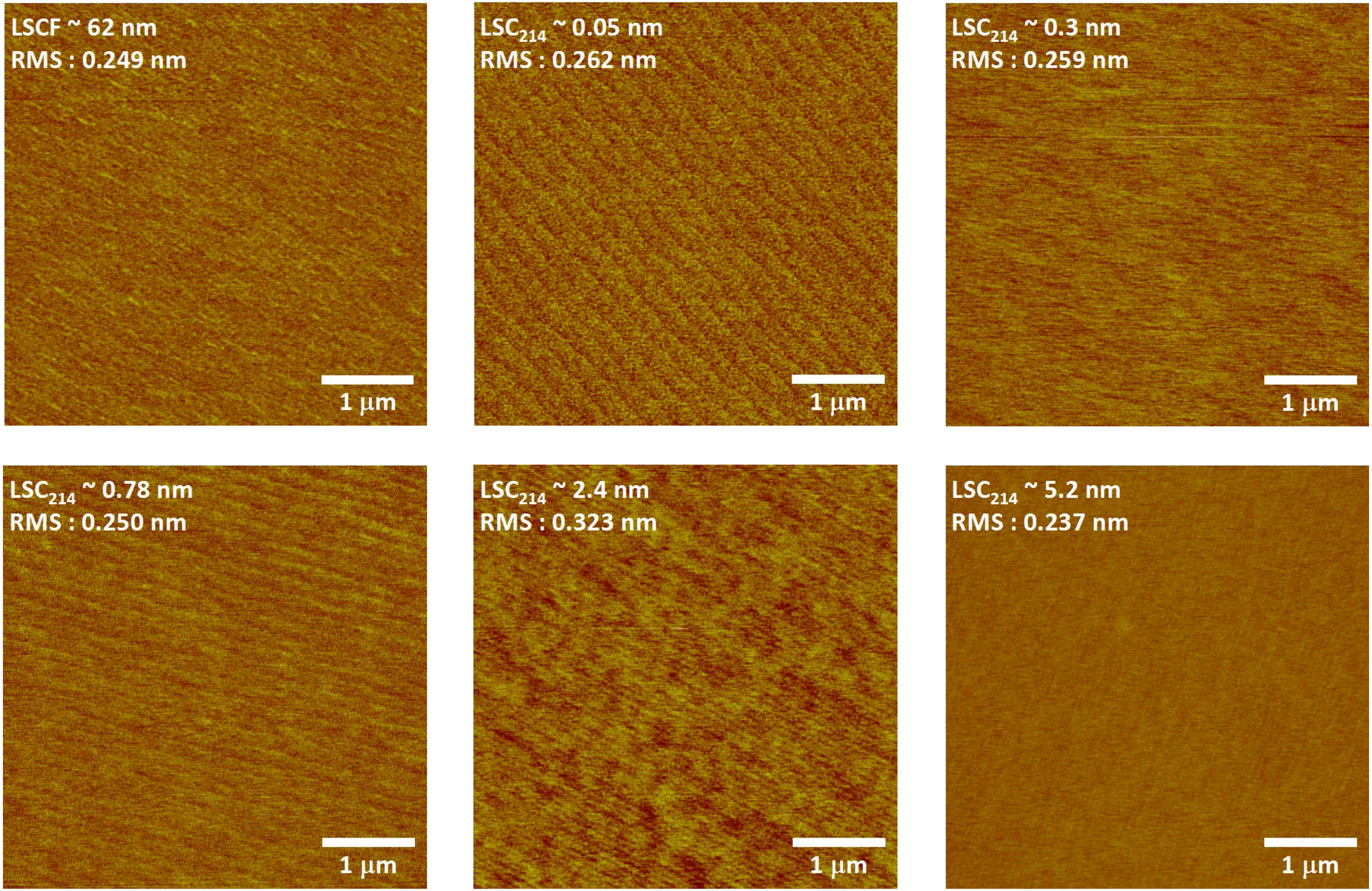
Lee, Rossmeisl and Morgan et al, EES 2011

Pulsed Laser Deposition



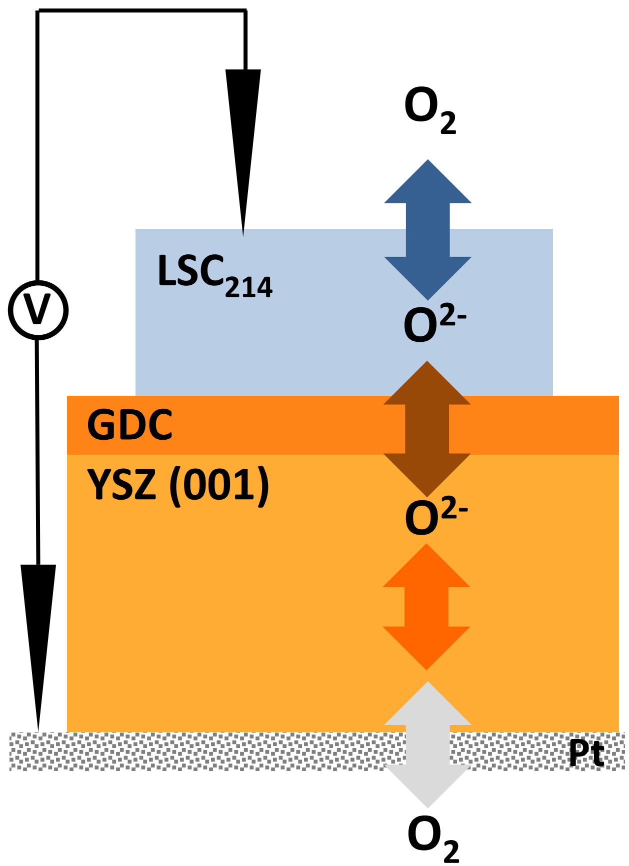
LSC214 pulse	Estimated thickness
10p	0.05 nm
50p	0.26 nm
150p	0.78 nm
500p	2.6 nm
1k	5.1 nm

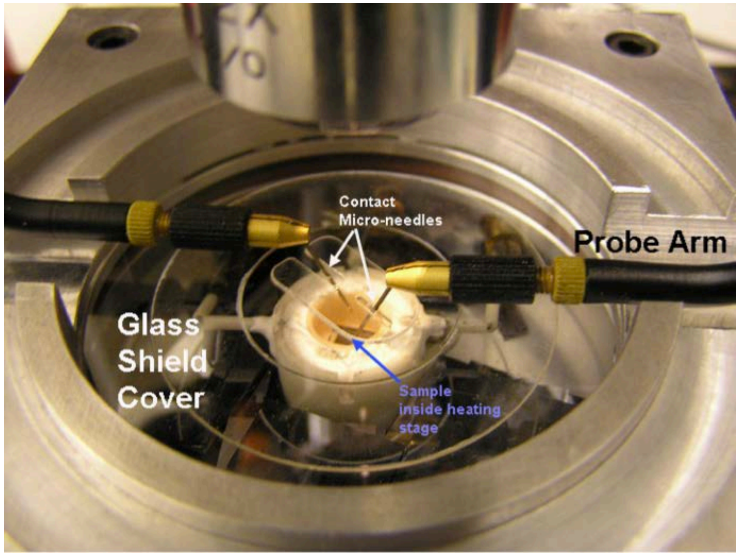
AFM Images (As-deposited)

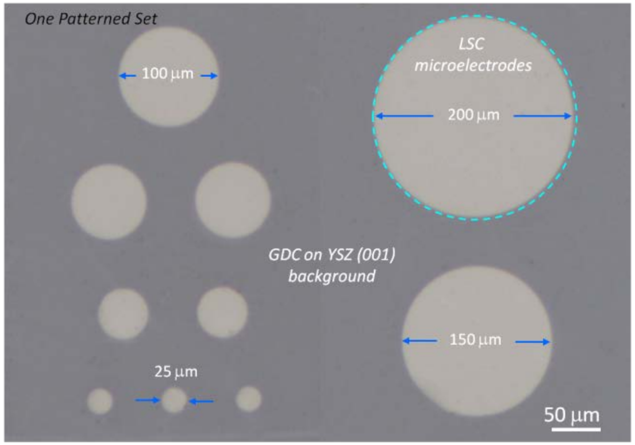


Electrochemical Impedance Spectroscopy

- Temperature = 550 ^{0}C
- pO_2 range = 10^{-3} atm to 1 atm (Ar:O_2 mixture)
- Microelectrode size = 200 μm diameter
- AC amplitude = 10 mV
- DC bias = 0 V

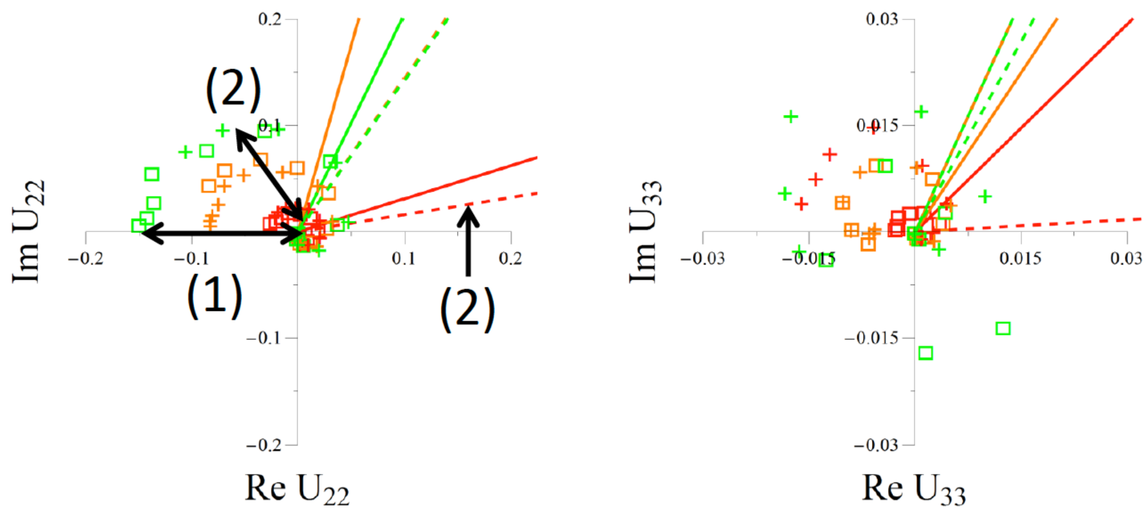






Example: LSC thin films

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

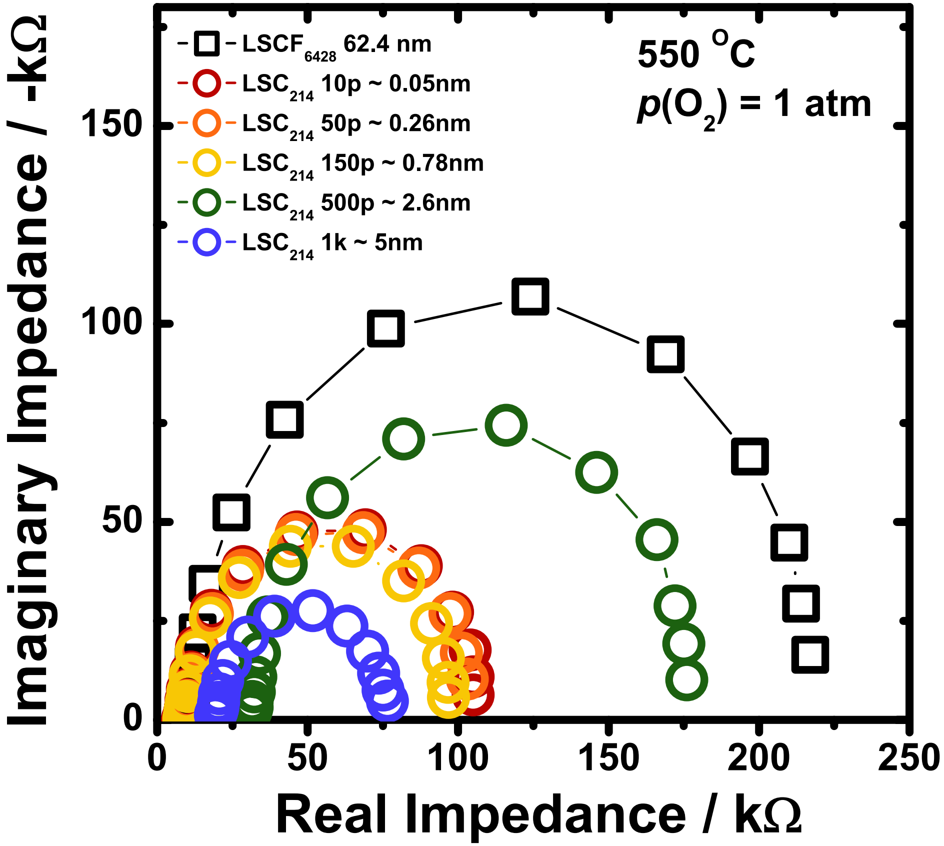


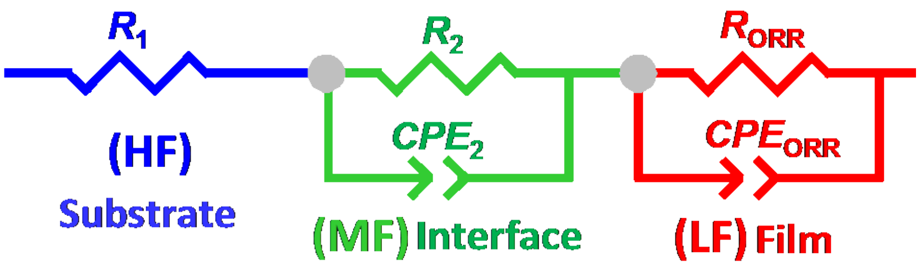
(1) = Thermodynamics of surface and the surface exchange reaction mechanism

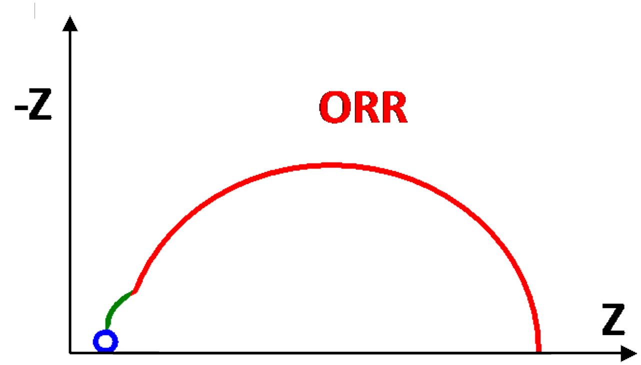
(2) = Thermodynamics of bulk

- 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.

Nyquist Plot







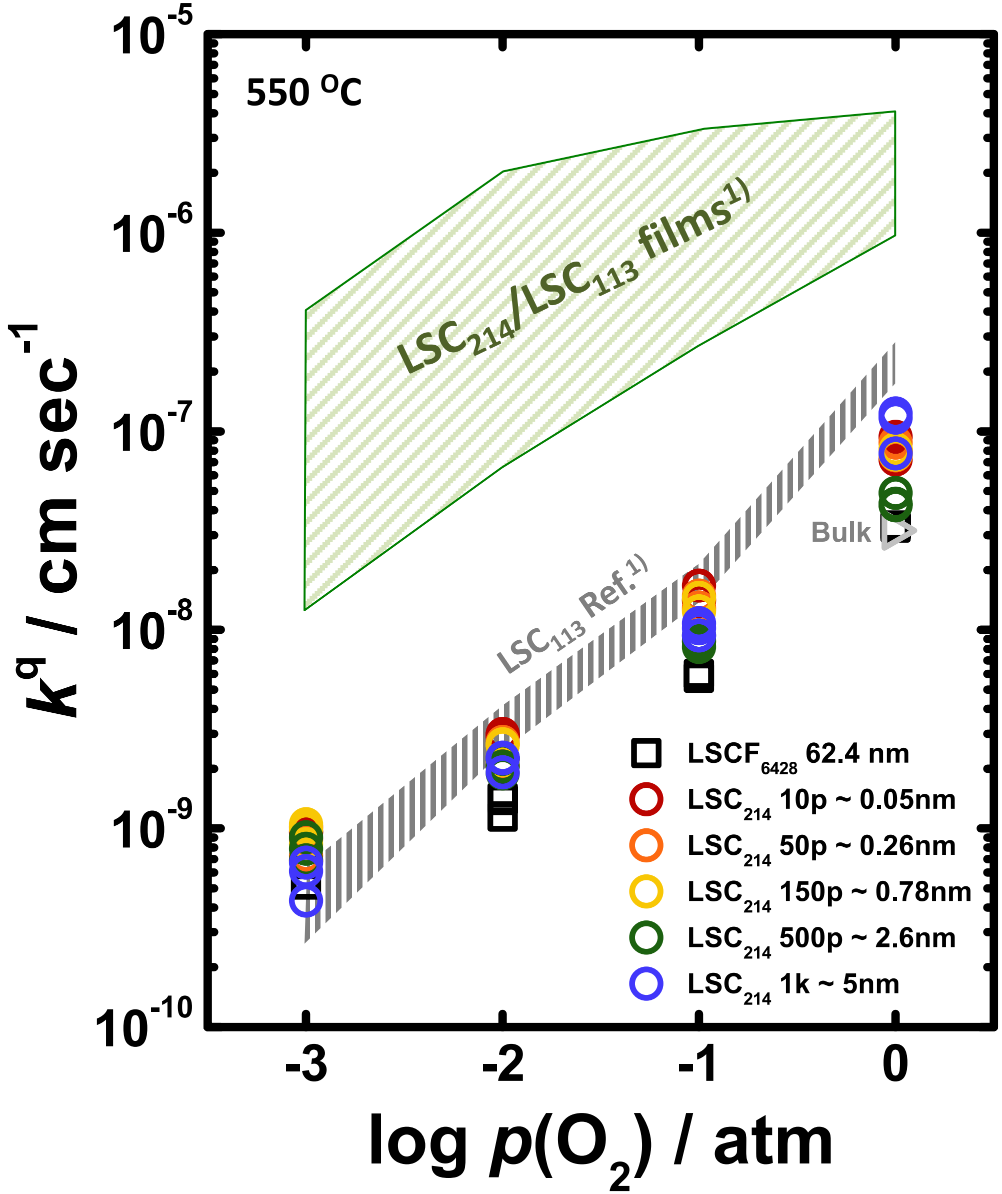
- LF has large pO_2 dependence
- Estimated critical thickness of LSCF[1)] is ~ 9 μm (500 ^{O}C)
- LSCF is governed by **surface exchange limitation**

1) Ramanarayanan et al., Ionic and Mixed Conducting Ceramics III, Vol. 97-24, ElectChem. Soc., NJ, 1997, p. 596.

Non-Linear Impedance Spectroscopy (NLEIS) on LSC-113, LSCF-113

Adler (Univ. Washington)

Comparison with LSC_{214}/LSC_{113}

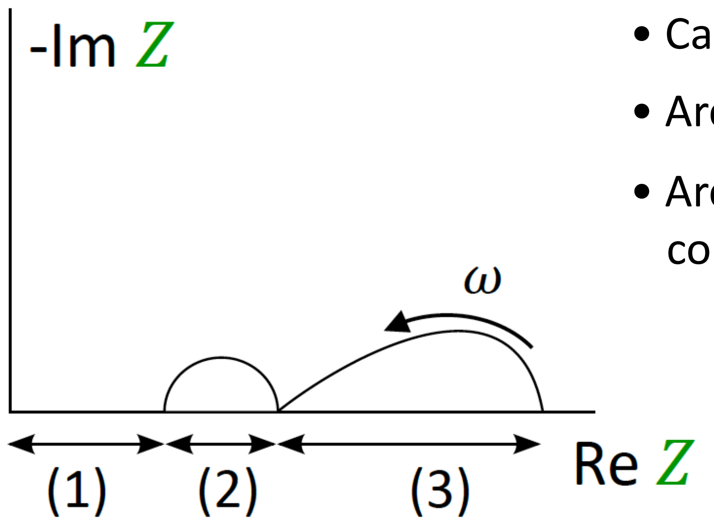


Compared to LSC_{214}/LSC_{113}, LSC_{214} decoration is not much effective to enhance the surface activity of LSCF

1) Crumlin et al., JPCL (2010)

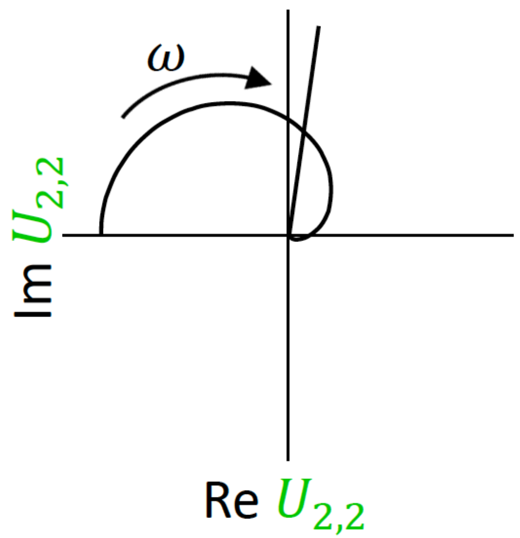
Electrochemical Measurements

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

Ab Initio modeling of Defect Chemistry in LSC-214

Morgan (Univ. Wisconsin)

Backup

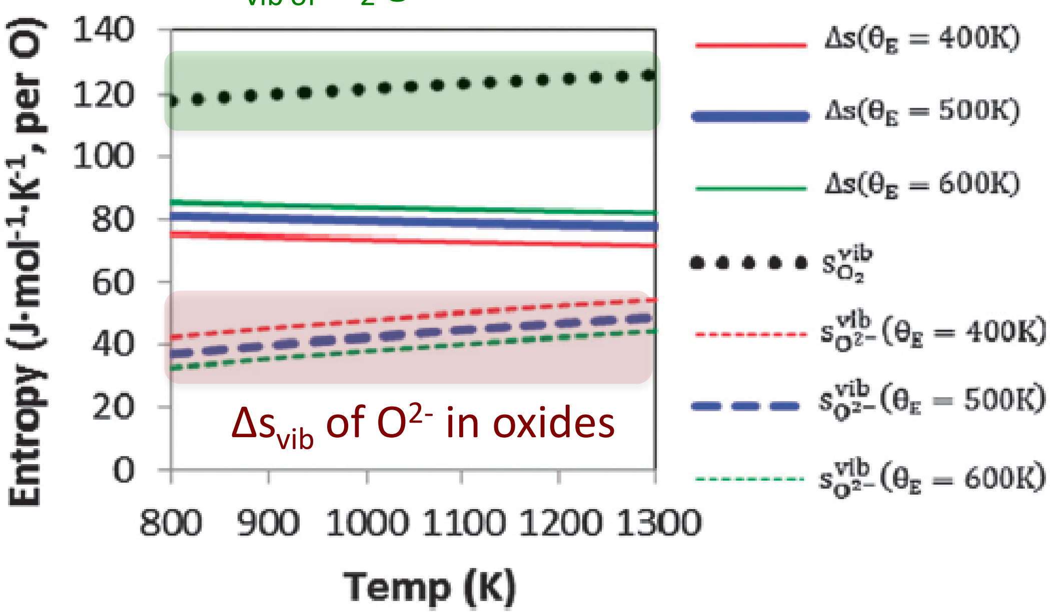
Ab initio based defect thermodynamics

$$\Delta G^*_{defect\ form}(T,\ P_{O_2}) = E^{DFT}_{defect\ form} + a^{DFT}_{nonideal} \cdot c_{defect} \pm \left\{ \left[\frac{1}{2}\left(H^{NIST}_{O_2} - T \cdot S^{NIST}_{O_2}\right) - \left(G_{vib}(O^{2-}_{solid}) - H^{0}_{vib}(O^{2-}_{solid})\right) \right] + \frac{1}{2} \cdot k_b T \cdot ln\left(\frac{P_{O_2}}{P^{0}_{O_2}}\right) \right\}$$

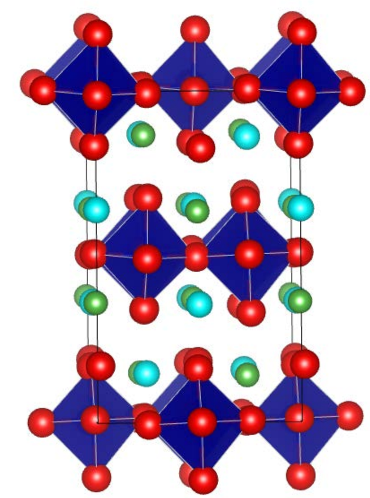
DFT modeling: O_{vac}, O_{int}

Approximate with Einstein Model

$\Delta s_{vib\ of}$ O_2 gas molecule



Δs_{vib} of O^{2-} in oxides



Lee and Morgan PCCP 2012

Literature review for defect chemistry of the RP phases

- Experiment (Neutron diffraction):
  - $La_2CoO_{4+\delta}$: O int, (*Le Toquin Physica B 2000*)
  - $La_2NiO_{4+\delta}$: O int, (*Jorgensen PRB 1989; Paulus, SSS, 2002*)
  - $La_2CuO_{4+\delta}$: O int, (*Chaillout Physica C 1989*)

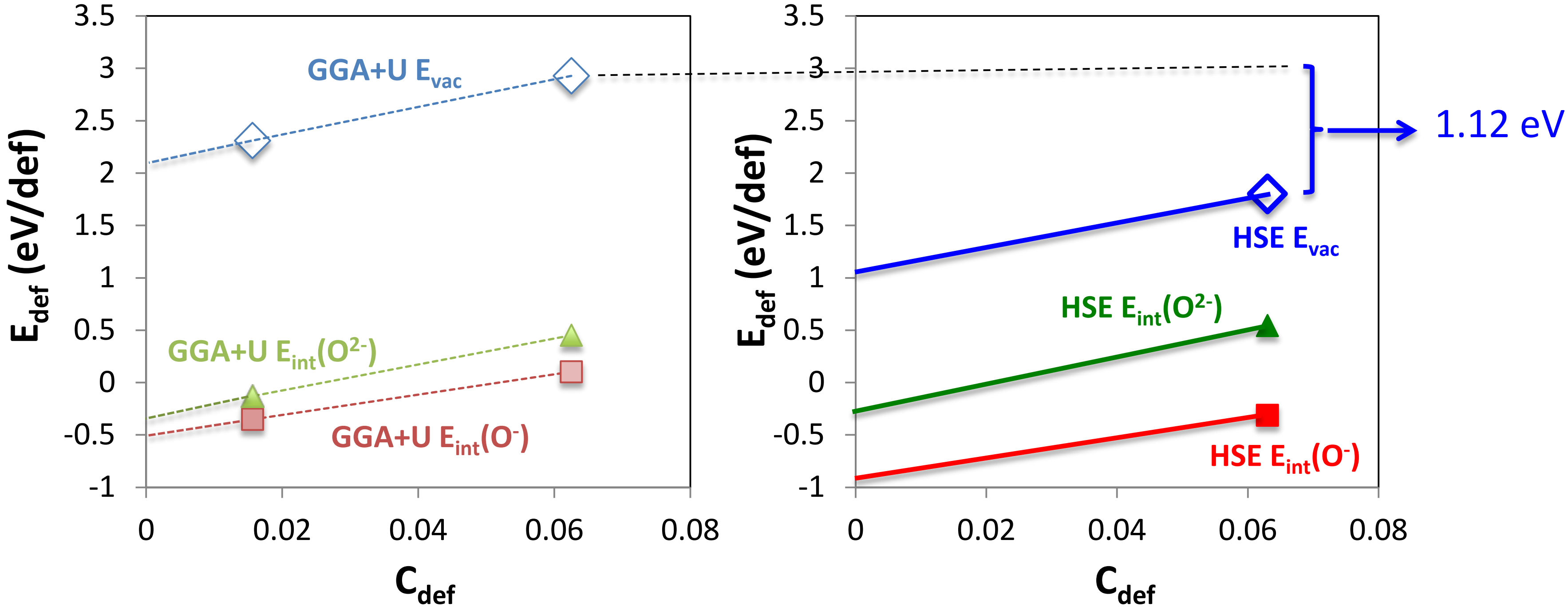
- Defect models suggested or fit to O nonstoichiometry vs T & P(O_2)
  - $La_{2-x}Sr_xCoO_{4\pm\delta}$: O vac for understoichiometry (*Vashook, SSI, 2000*)
  - $La_{2-x}Sr_xNiO_{4\pm\delta}$: O int and O vac; localized and itinerant electron models (*Nakamura SSI 2009*)
  - $La_{2-x}Sr_xCuO_{4\pm\delta}$: O int and O vac; localized and itinerant electron models (*Opila, J Am. Ceram. Soc. 1994*); O int, O vac, La vac, Cu vac, localized and itinerant electron models (*Kanai JSSC 1997*)

- Theoretical Models
  - $La_2CoO_{4+\delta}$: O int, <u>DFT and MD</u> (*Kushima PCCP 2011*)
  - $La_{2-x}Sr_xCoO_{4\pm\delta}$: O int for $x \leq 0.8$and O vac for $x \geq 1.2$, <u>MD</u> (*Tealdi, J Mater Sci. 2012*)
  - $La_2NiO_{4+\delta}$: O int, <u>MD</u> (*Read, JPCB 1999*; *Chroneos, J Mater. Sci. 2010*)

Calculation Methods

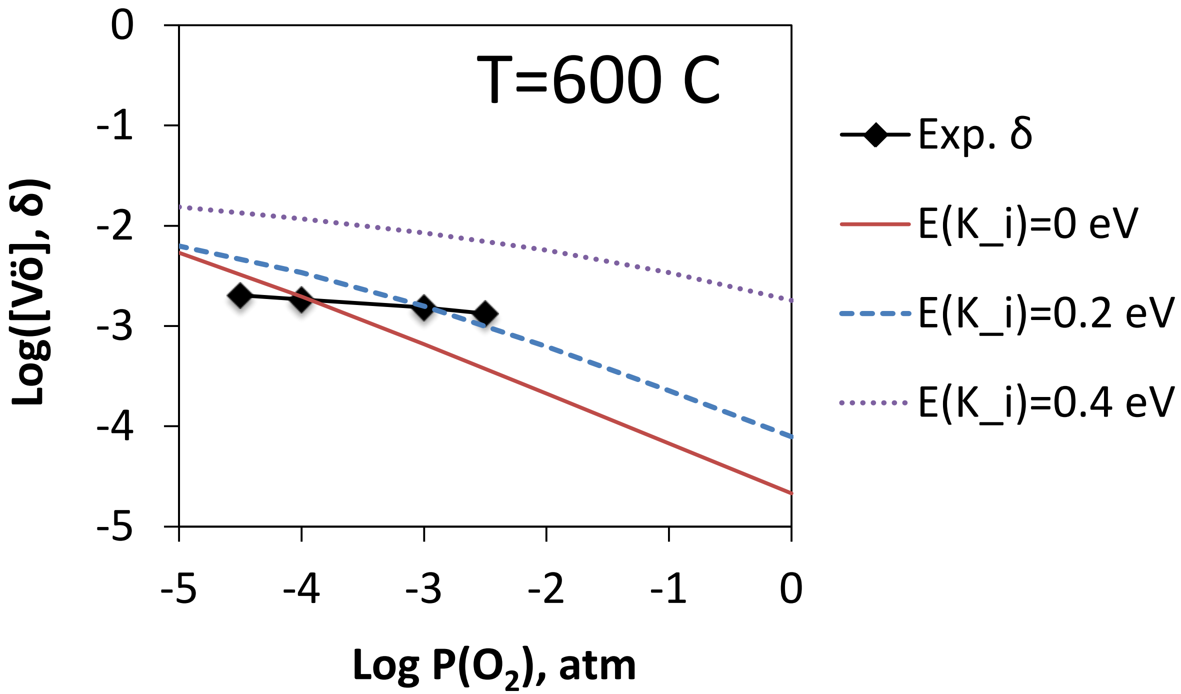
1. Methods:
   - *Ab initio* code: **VASP**
   - Exchange-correlation functions: **GGA+U and hybrids (HSE06)**
   - Cell choices (slab thickness, lateral dimensions): **56-atom supercell for bulk**
   - Thermodynamic models (defect chemisty models, oxygen reference chemical potential): **Defect chemistry model for** ***$(La_{0.5}Sr_{0.5})_2CoO_4$ vs. T and $P(O_2)$***
   - Activation energy approaches (NEB, drag,dimer method): ***NEB***
   - treatment of magnetism (FM, AFM): **FM**
   - treatment of high vs. low-temperature structure: **Use FM for high T**
2. Which properties are being calculated?
   - electronic structures (bands, DOS), defect energetics (O vac, O int, cation vac etc).

$(La_{0.5}Sr_{0.5})_2CoO_4$ Defect Energetics
(GGA+U vs. Hybrid Functional)



- HSE O vac formation energy is ~1 eV lower than GGA+U@U_{eff}=3.3 eV
- Two possible O_{int} configurations in $(La_{1-x}Sr_x)_2CoO_4$ (See next slides)

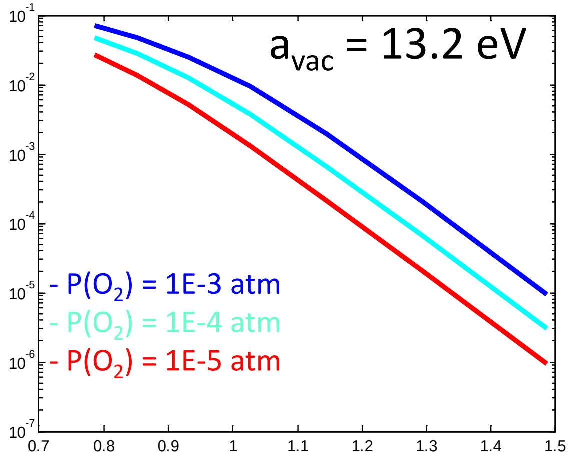
Charge disproportionation energy

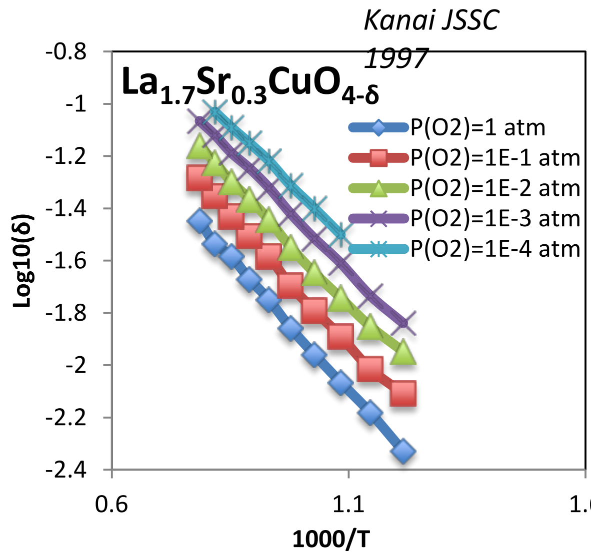


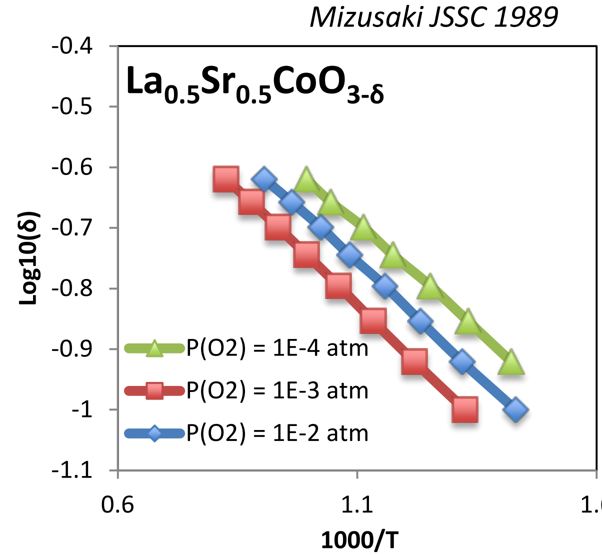
- Adjusting charge disproportionation energy alters low T defect concentration $P(O_2)$ dependence
- Suggests further refinement on the defect (charge) energetics.

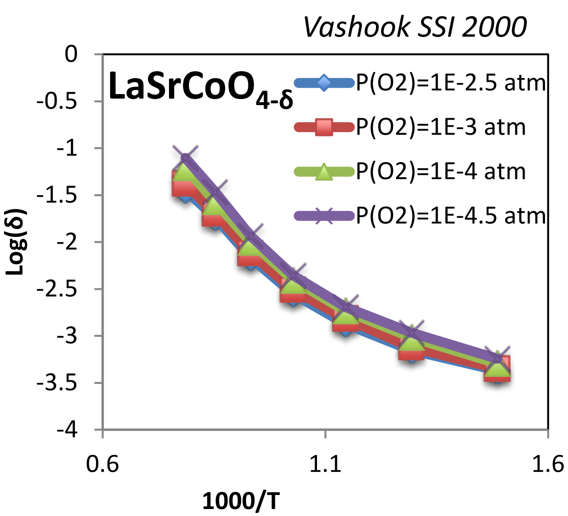
Empirical fit of defect chem. vs. expt

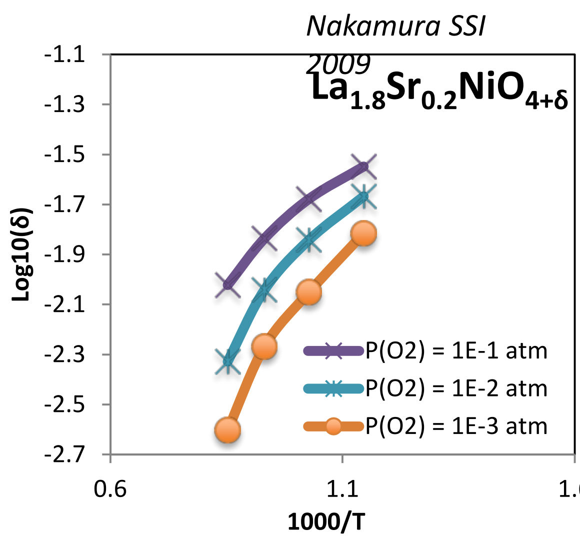
Interacting vacancy model

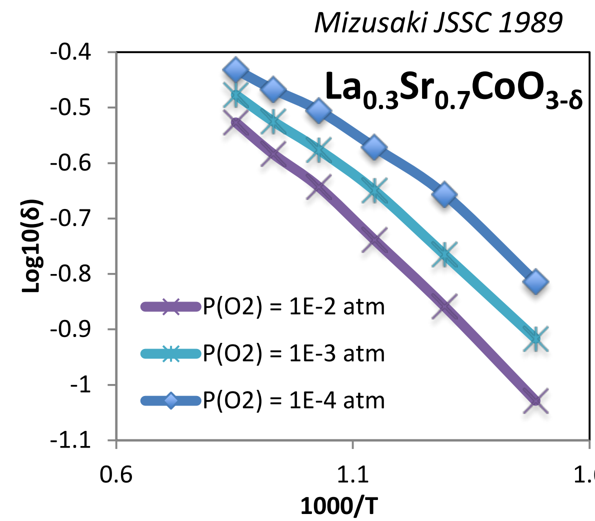






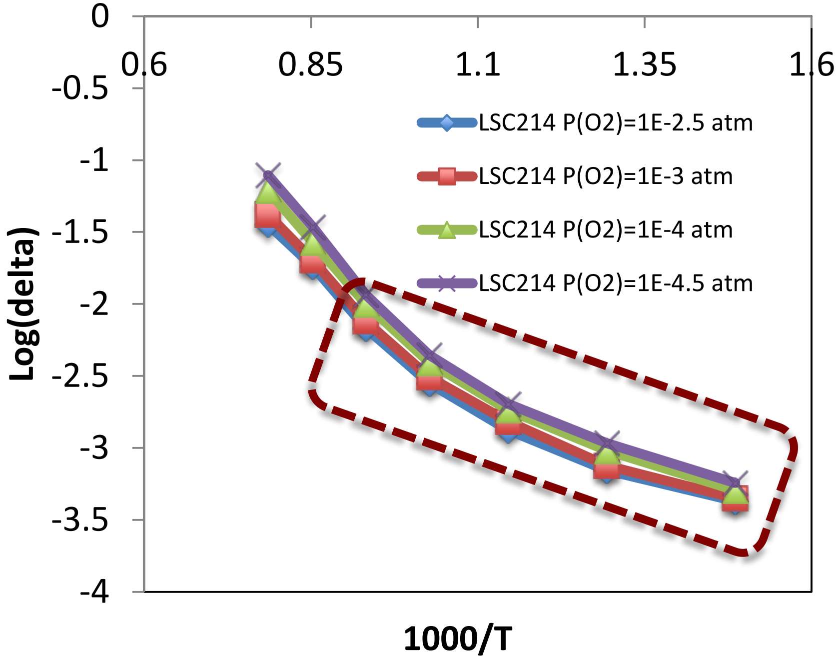


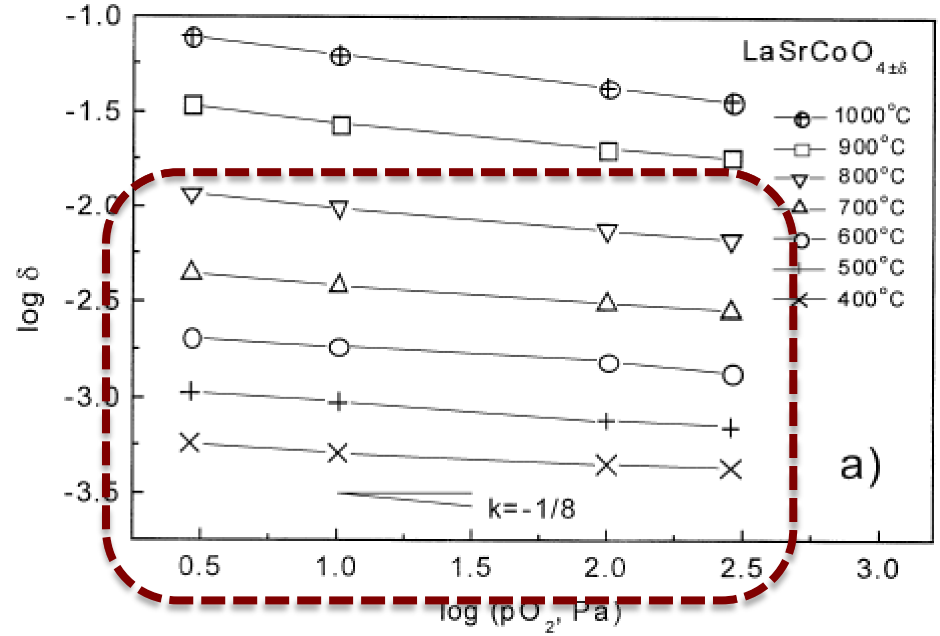




Concerns with the LSC-214 Data

Vashook, et al. SSI, 2000





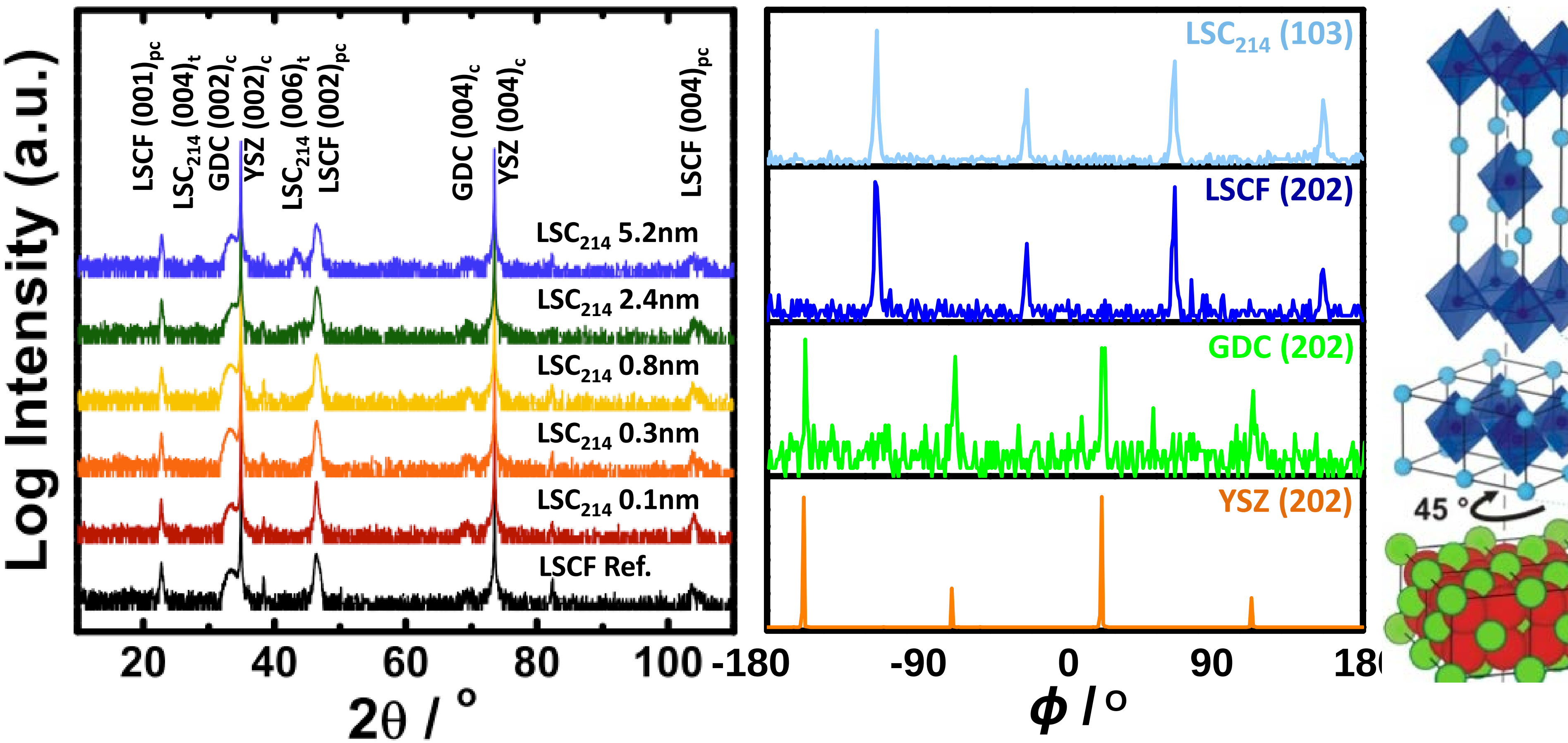
- Convex shape vs. 1/T different than other systems and inconsistent with intuitions, DFT
- <1/2 slopes vs. PO_2 at low defect concentrations different from other systems and inconsistent with intuitions, DFT

Perhaps a problem with low T data.

Focus on high-temperature results.

Trash

X-ray Diffraction Results



❖ All films clearly show ***c***-axis-oriented epitaxial thin films

❖ Off normal XRD shows LSCF unit cell on the GDC with 45^0 rotation

LSC_{113}: $La_{0.8}Sr_{0.}$

LSC_{214}: $(La_{0.5}Sr$

$LSC_{113/214}$: LSC