Project Review for DE-FE32116

U.S. DEPARTMENT OF ENERGY

Heterostructured Cr Resistant Oxygen Electrode for SOECs

WPI

Prof. Yu Zhong
Prof. Songge Yang
Guangchen Liu

West Virginia University

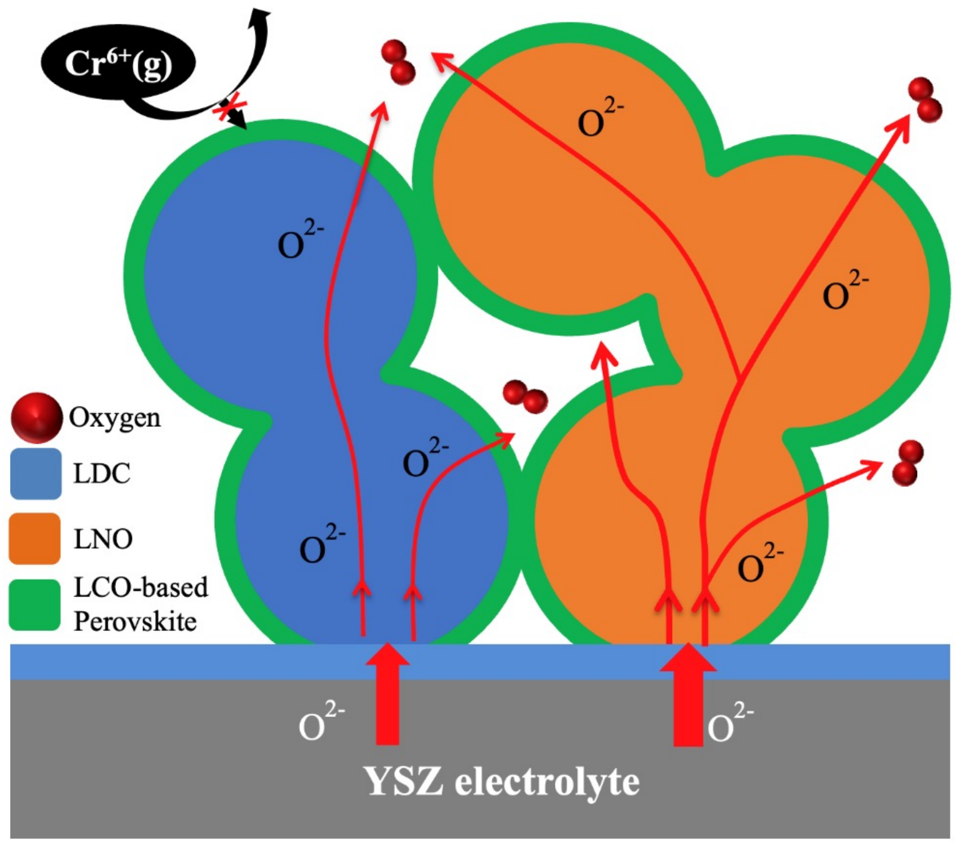
Prof. Xingbo Liu
Prof. Wenyuan Li
Prof. Edward M. Sabolsky
Awa Kalu
Cole Klemstine

April 23, 2024

Outline

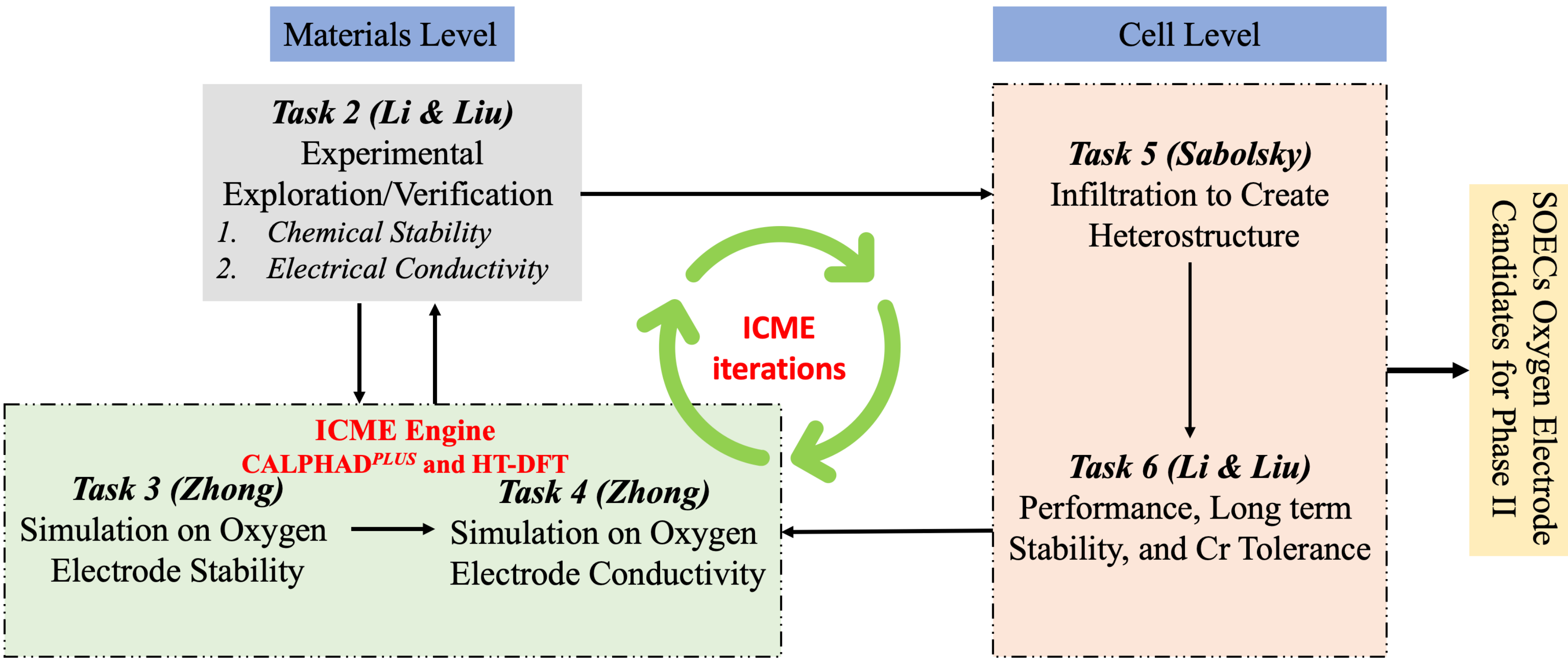
- Proposed Novel La_2NiO_4-$LaCoO_3$ Heterostructure
- Overall Approach & Objectives
- **Updates on the Heterostructure Engineering**
  - **Modification of Perovskite**
  - **Doped LNO**
- Summary and Future Work

Proposed Novel La_2NiO_4-$LaCoO_3$ Heterostructure



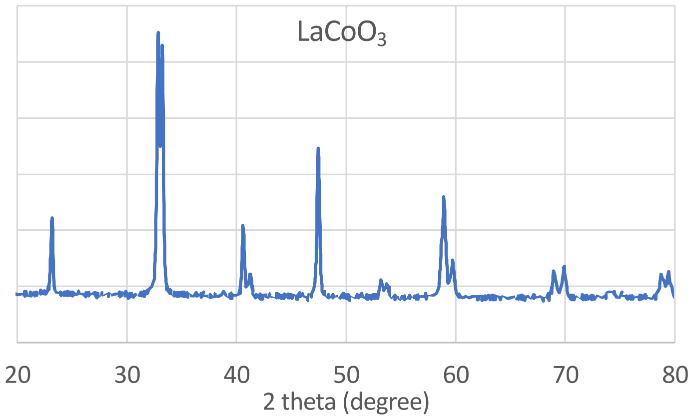
Sr-free, fast O-conducting LNO backbone plus active OER LCO surface coating as Cr-resistant, high performing oxygen electrode

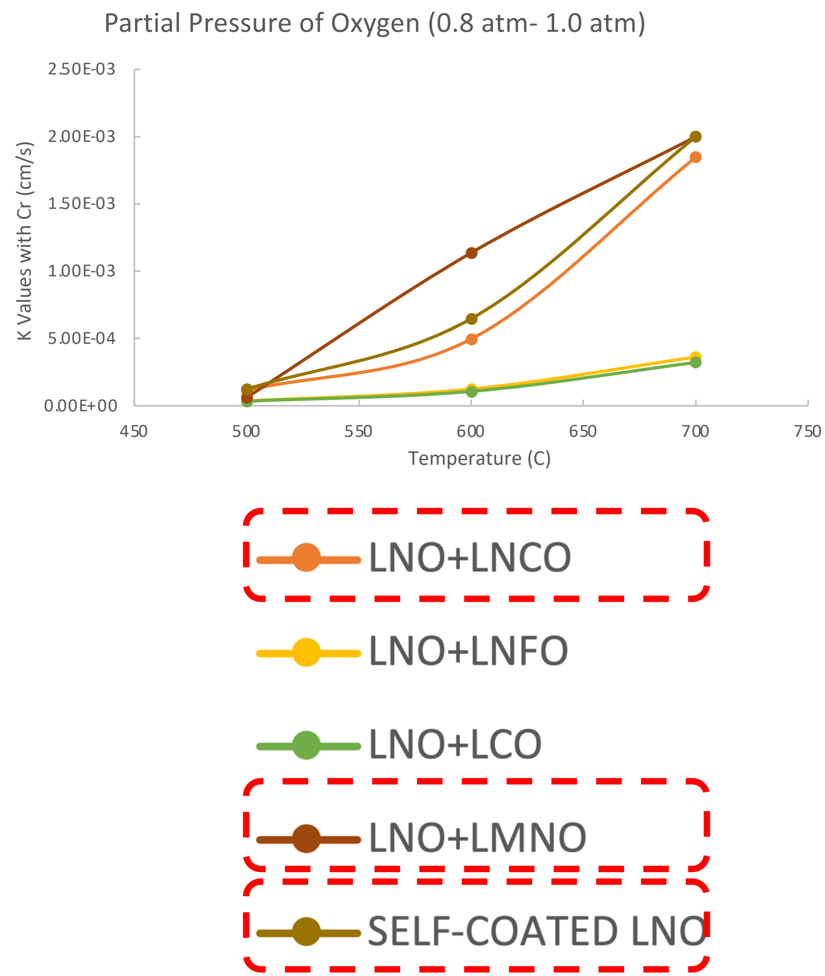
Overall Approach & Objectives

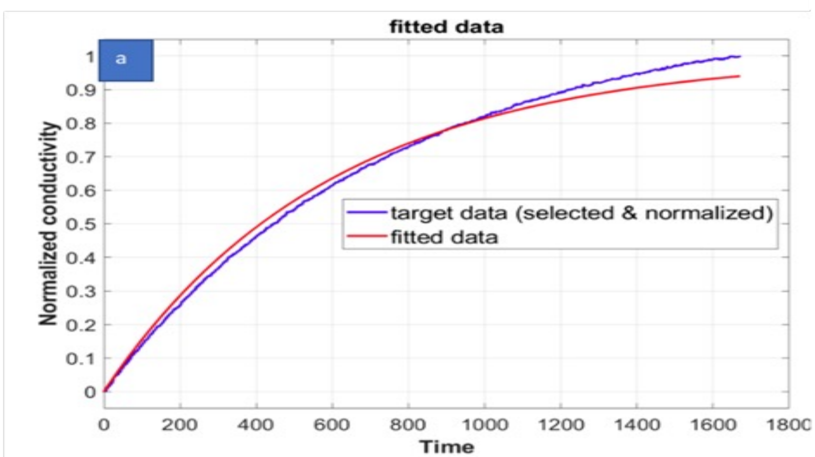


When fully optimized, this oxygen electrode material will target to an INTRINSIC long-term degradation rate of less than 0.3%/1000 hrs at 700^{o}C. By the end of the project, we will reach 1A/cm^2 current density.

Task 2: Experimental exploration and verification







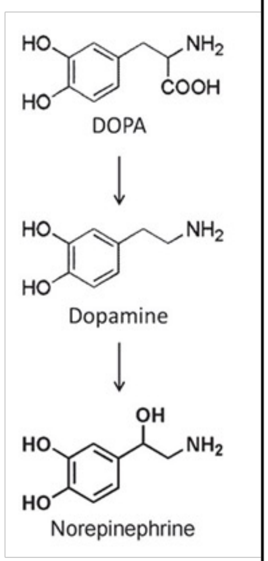
Task 5: Infiltration to Create Heterostructure

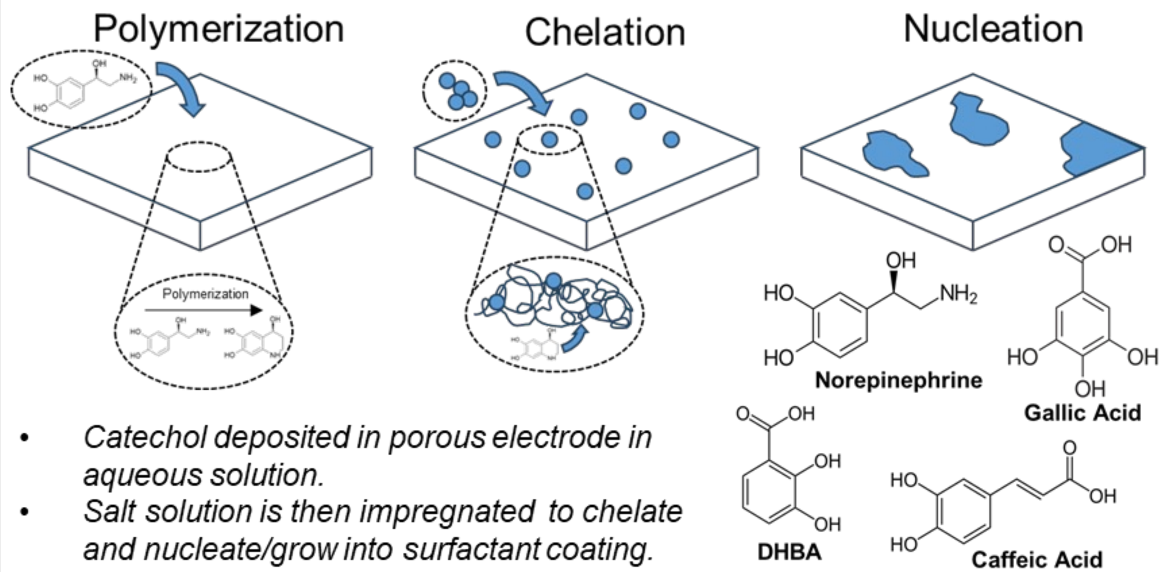
Process Review: Wet-Impregnation of Nano-Catalyst for SOFCs/SOECs

Objective: to deposit full phase binary oxide $LaCoO_3$ (LCO) via controlled deposition throughout a porous structure of the LNO electrode at temperatures ≤ 800 °C.

Proposed Solution: use of poly-norepinephrine and other catechol-like surfactants to properly chelate the complex higher-order nano-oxides in orderly, non-agglomerated fashion.

Bio-inspired catechol adhesive (similar to that on mussel foot) to controllably deposit nano-catalyst.

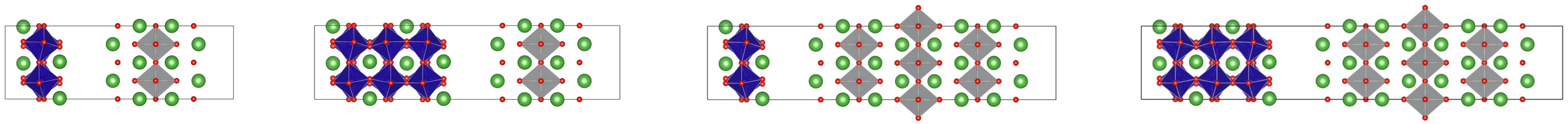




- *Catechol deposited in porous electrode in aqueous solution.*
- *Salt solution is then impregnated to chelate and nucleate/grow into surfactant coating.*

Task 3/4: DFT simulations on Heterostructure

➢Interfacial Energy (VSAP)

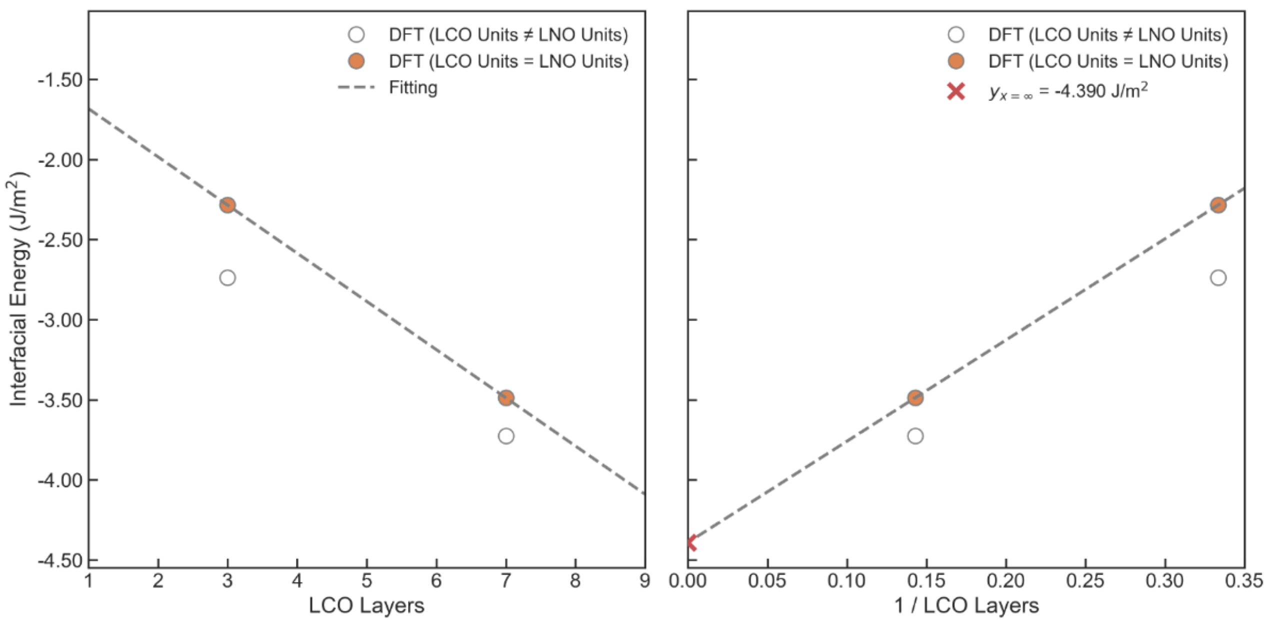


LCO x 1 / LNO x 1
(72 atoms / 3 LCO layers)

LCO x 2 / LNO x 1
(112 atoms / 7 LCO layers)

LCO x 1 / LNO x 2
(128 atoms / 3 LCO layers)

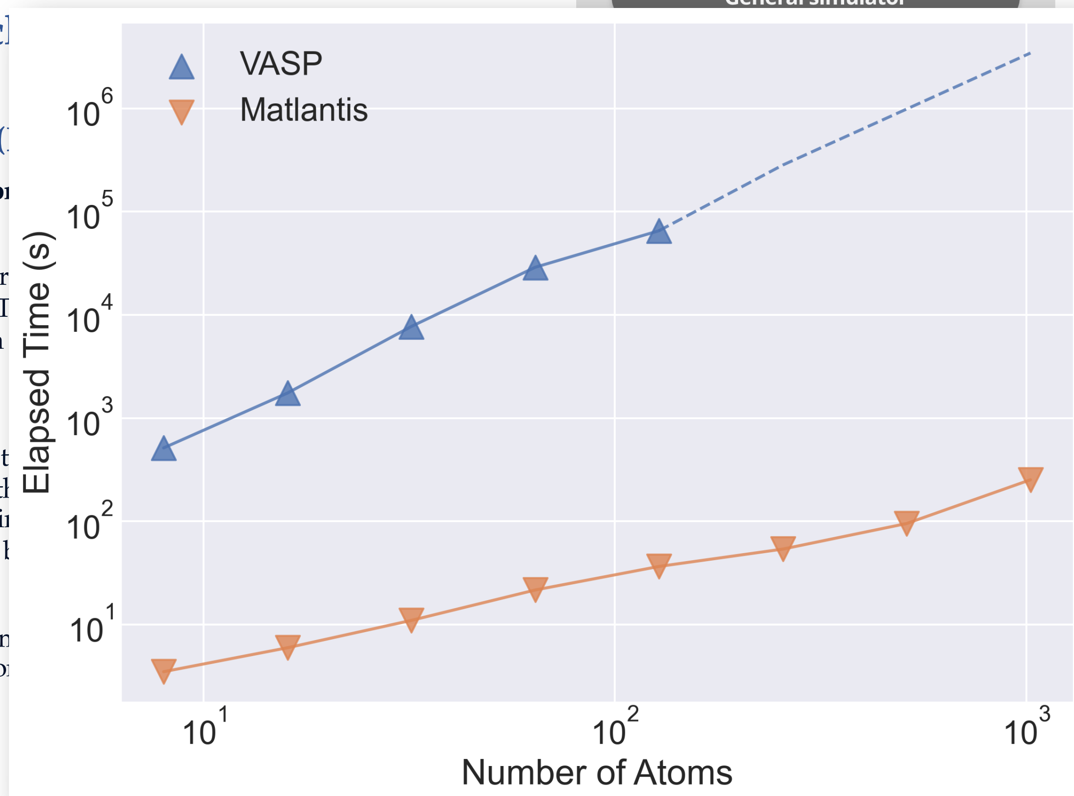
LCO x 2 / LNO x 2
(168 atoms / 7 LCO layers)



Task 3/4: DFT simulations on Heterostructure

➢ MATLANTIS

Matlantis™: Core Tec



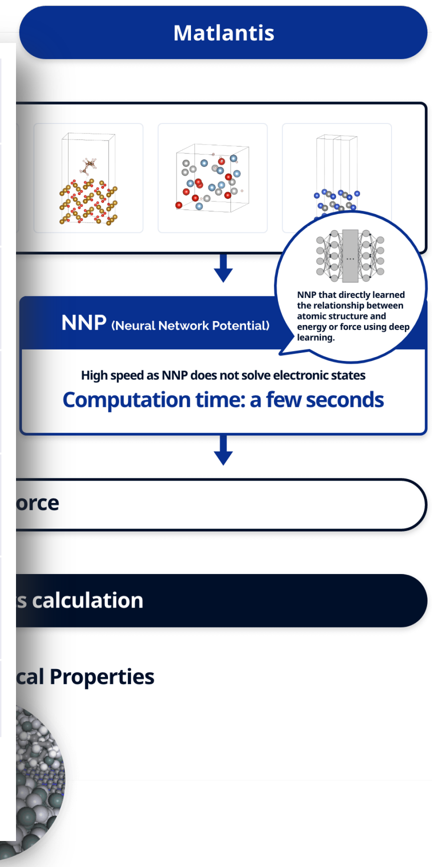
Neural Network Potential (

Significantly accelerates computatio

Matlantis supports large-scale mater various materials at an atomic level. T a neural network potential (NNP) in into a conventional atomic simulator.

Conventional physics-based atomist high-cost calculations for solving t calculations thanks to the deep learni data necessary for simulating atomic

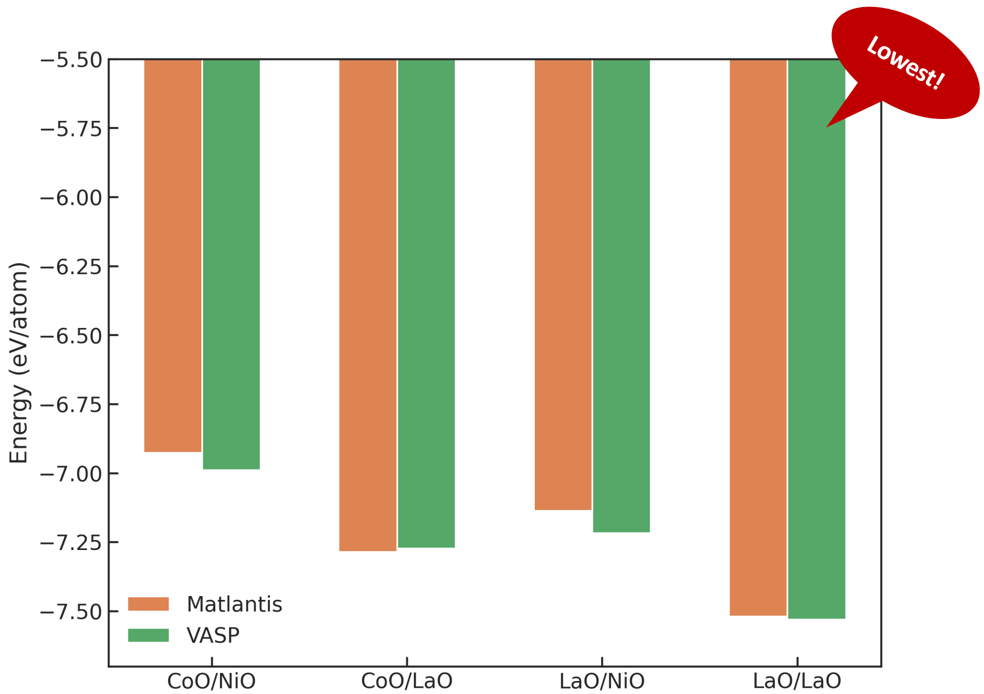
This allows researchers to quickly sir systems with relatively low calculatio



Task 3/4: DFT simulations on Heterostructure

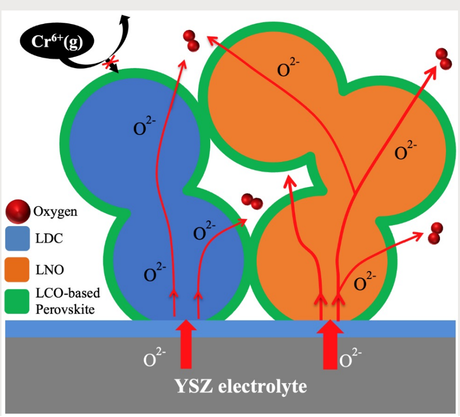
➢ Benchmark Test

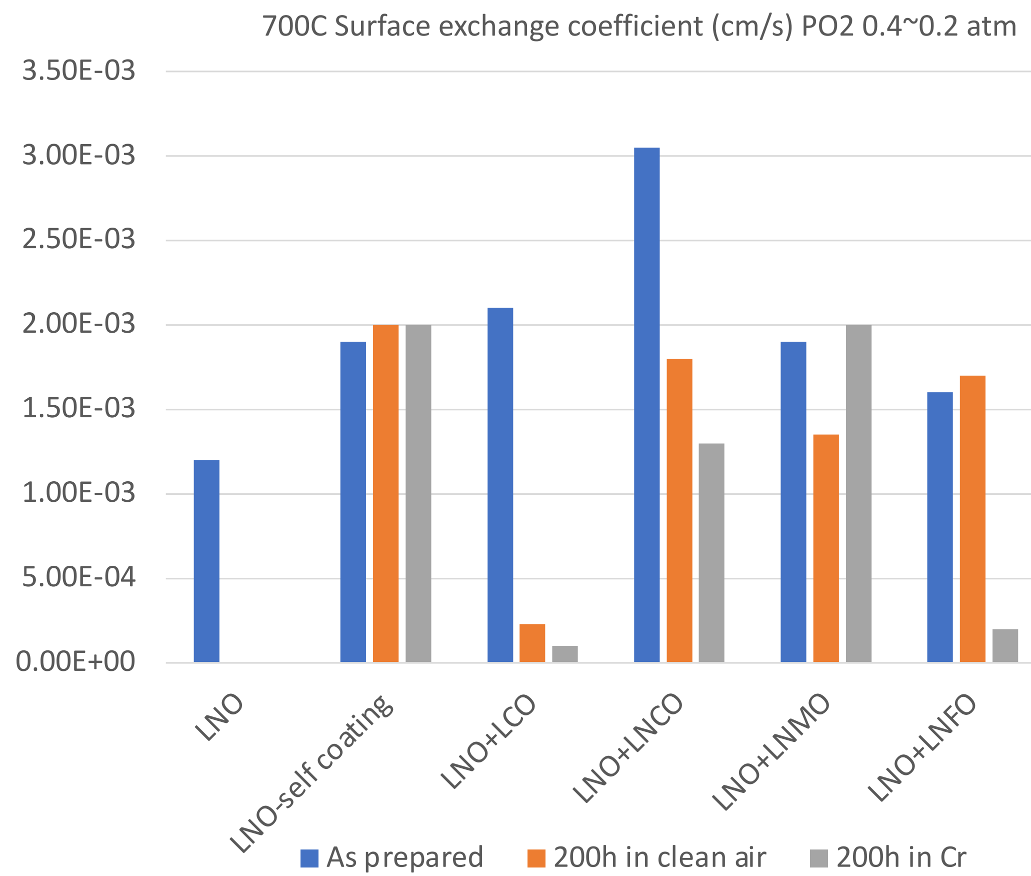
	VASP (eV/atom)	Matlantis (eV/atom)	Difference (%)
LCO	-7.1144	-7.1919	1.08
LNO	-7.4458	-7.2785	2.25



Two Research Directions for the Heterostructure Engineering

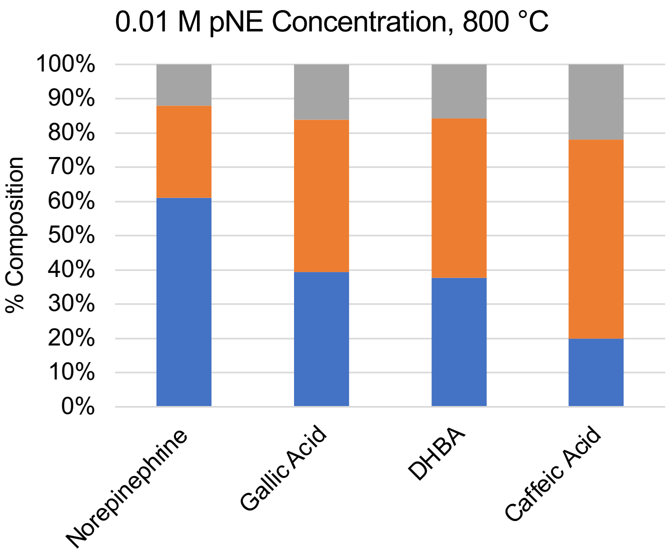
- Make modification of LCO perovskite
  - Regular doping
  - HEPs
- Doping of LNO

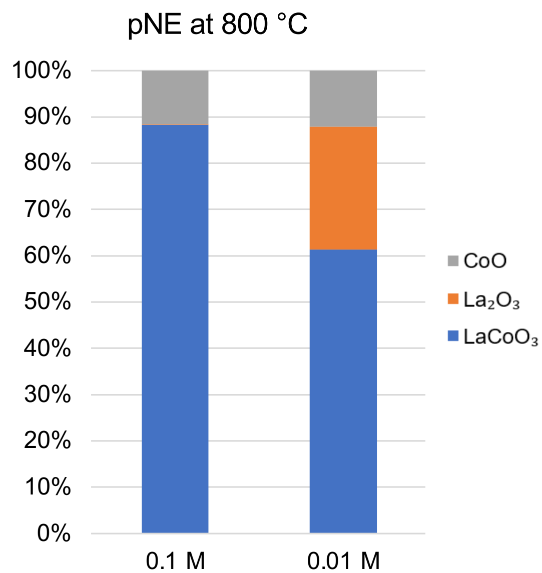


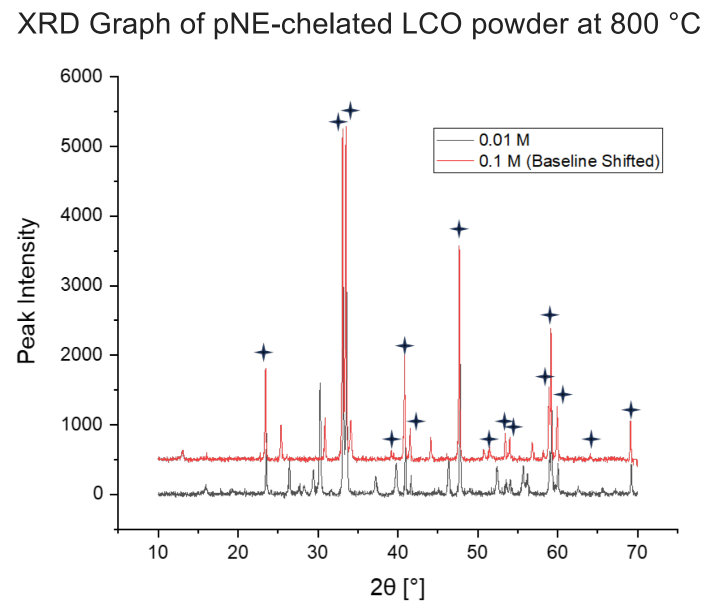


Infiltration Evaluation of Heterostructured Surface (pure/doped LCO)

Lanthanum Cobaltite Deposition Study: XRD Phase Purity Powder Study of LCO





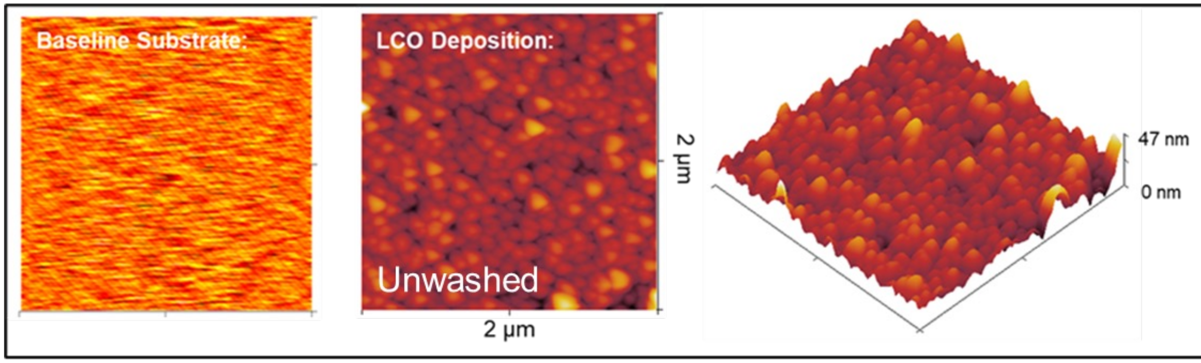


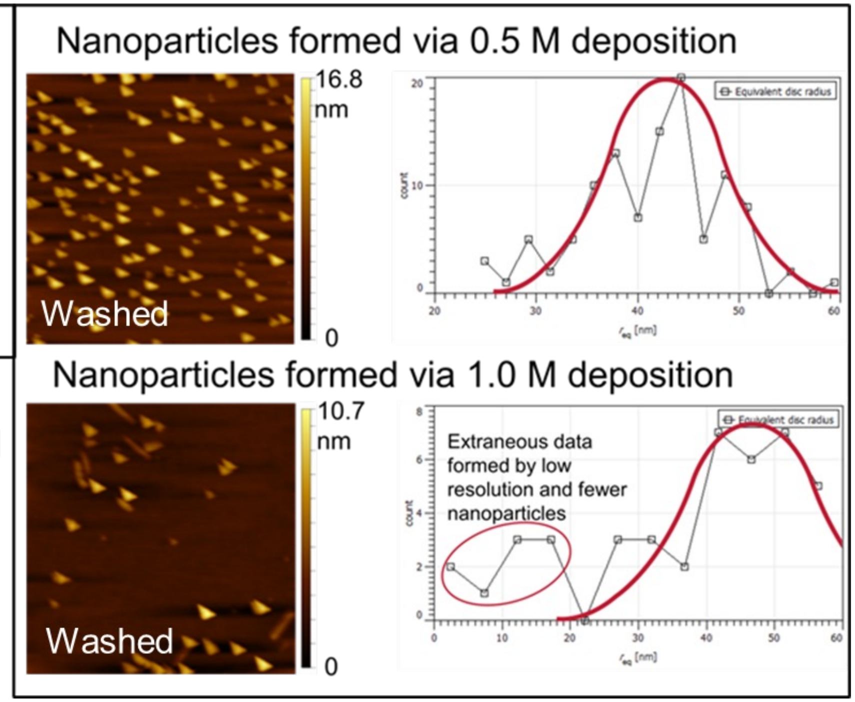
- pNE was best performing chelating agent, with maximum phase purity of 88%
- 800 °C was the lowest temperature necessary for high phase purity
- Without any surfactant, LCO phase was only identified around 10%

Infiltration Evaluation of Heterostructured Surface (pure/doped LCO)

Lanthanum Cobaltite Deposition Study: AFM Analysis of Single Crystal YSZ Deposition

Atomic force microscopy maps of $LaCoO_3$ on YSZ single-crystal substrates were gathered for statistics about particle coverage



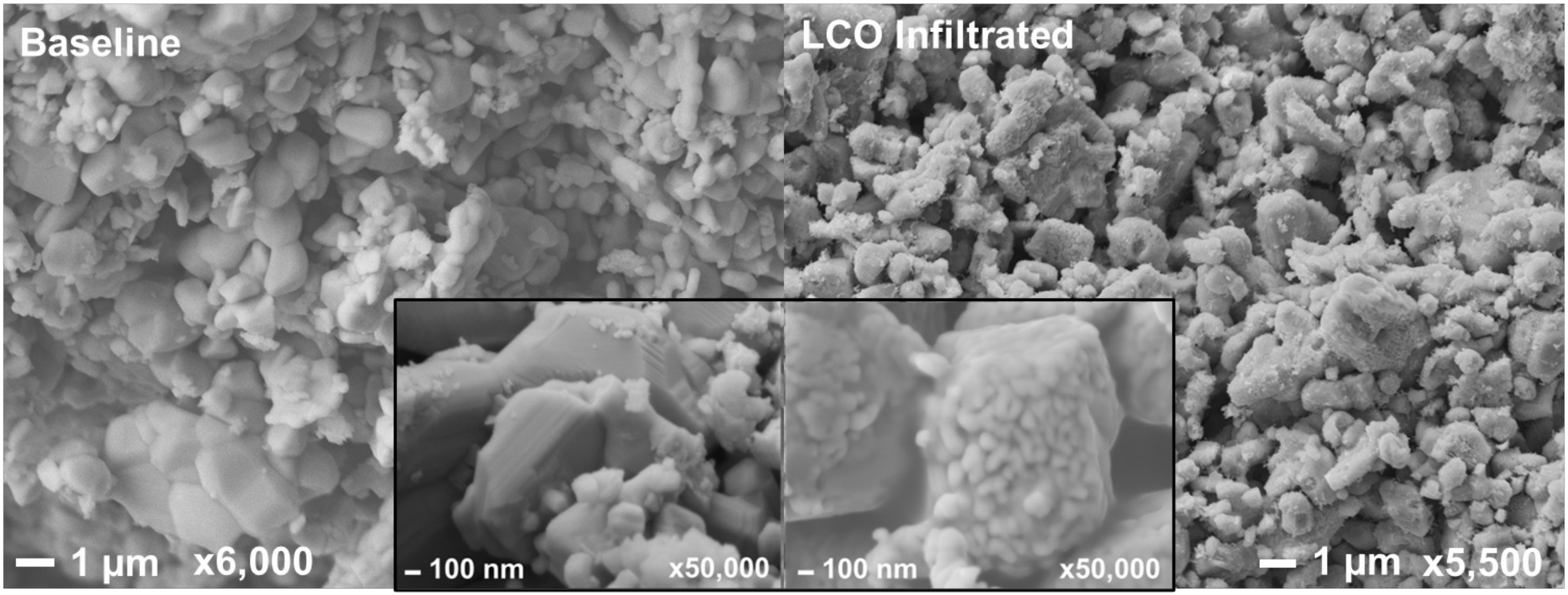


Results:

- Unwashed samples showed interconnected network, what would be typical in-situ
  - ➢ RMS Roughness (rq): 1.25371 nm
  - ➢ Kurtosis (rku): 2.61714
- Washed samples used to calculate typical particle radii, ~40 nm, and showed a normal distribution of particle sizes

Infiltration Evaluation of Heterostructured Surface (pure/doped LCO)

In-situ SOEC Deposition Studies: Scanning Electron Microscopy

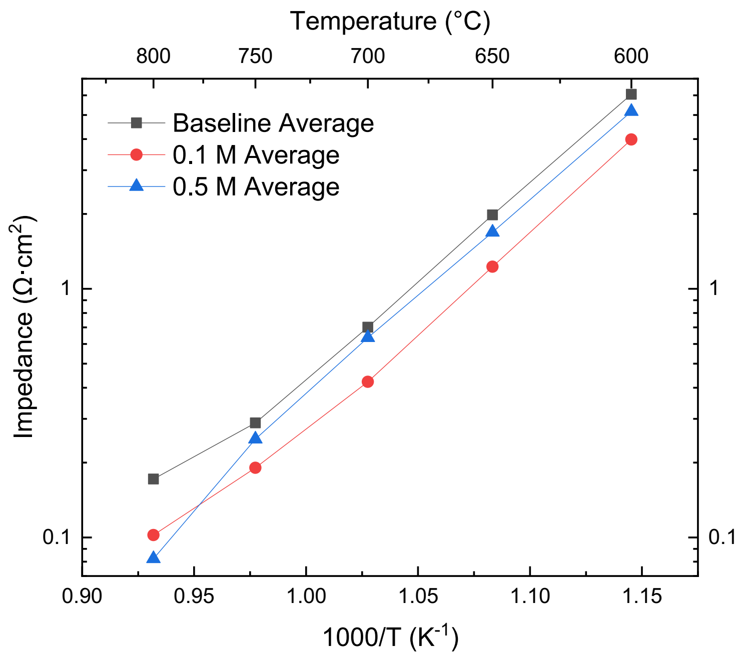


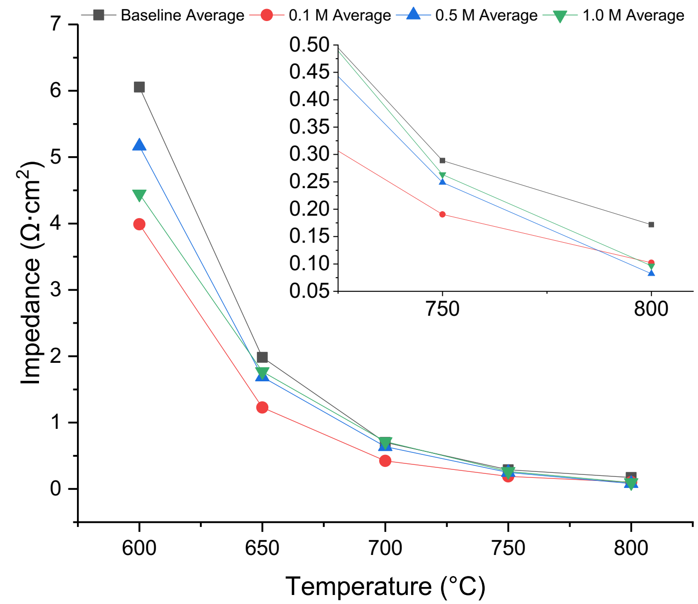
LCO-infiltrated cells were expected to show a nanoparticle structure based on other works of this kind

- Nanofilm structure with connected particles seen across all surfaces, similar to nanoparticles

Infiltration Evaluation of Heterostructured Surface (pure/doped LCO)

In-situ SOEC Deposition Studies: Electrochemical Impedance Spectroscopy





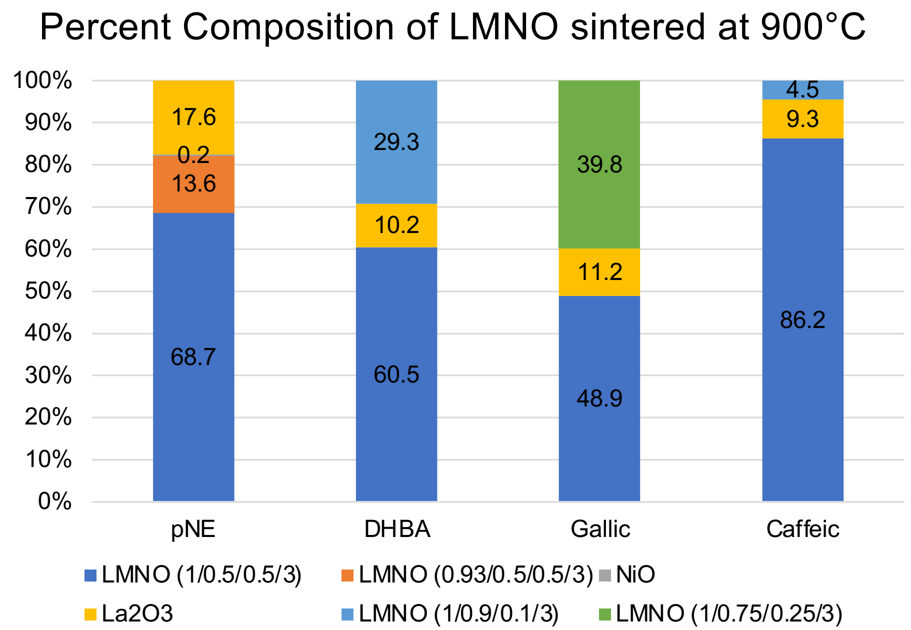
- 0.5 M performed best at 800 °C in all time ranges
- 0.1 M performed significantly better at temperatures at and below 750 °C

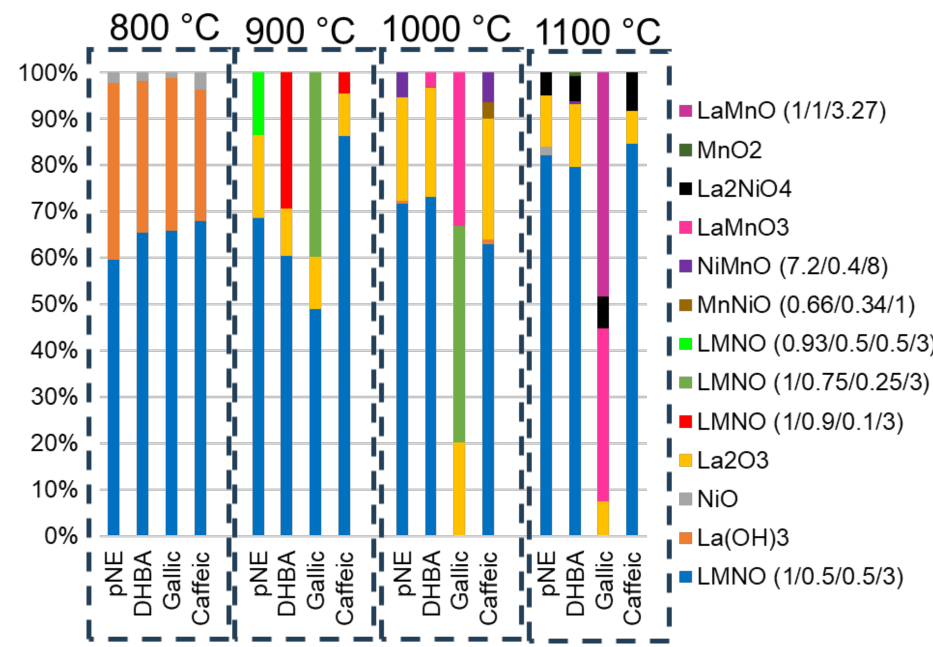
Important to note that these cells are not fully optimized, serving more as a comparative study to show impact of LCO coating on performance

- In this sense, the best performing cells showed a threefold improvement over baseline, non-coated LNO

Infiltration Evaluation of Heterostructured Surface (pure/doped LCO)

Ternary Coatings: XRD Phase Purity Powder Study of LNMO

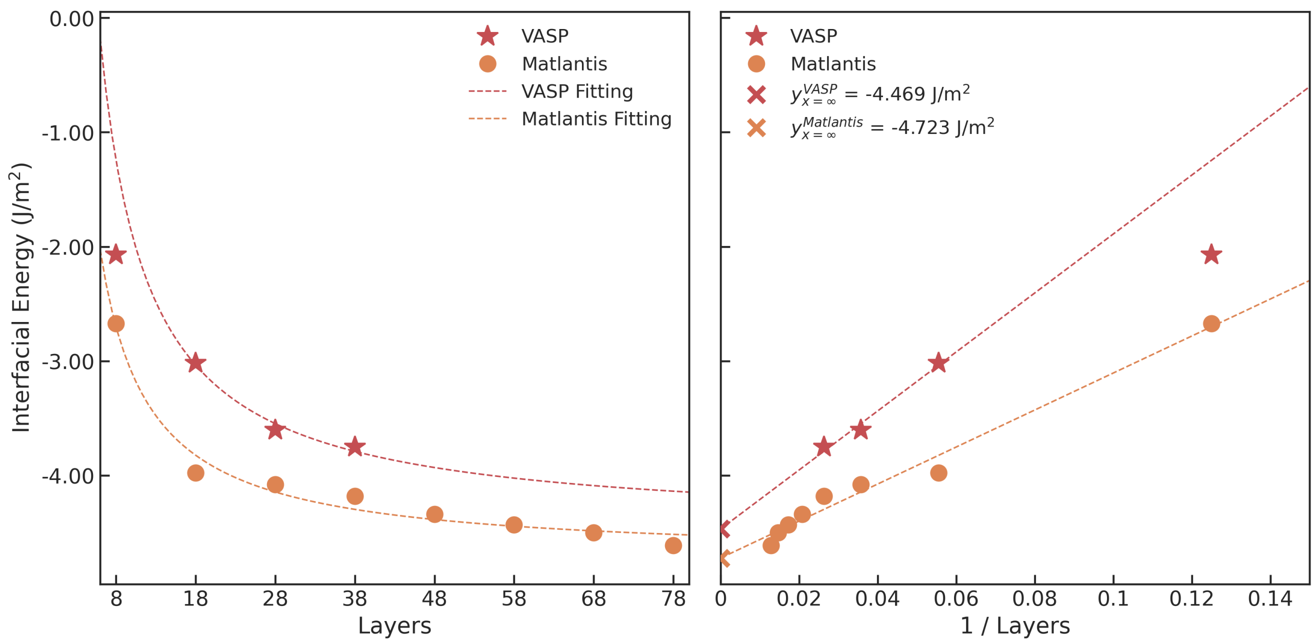




- LNMO [$La(Ni_{0.5}Mn_{0.5})O_3$] solution combined with all surfactants sintered at different temperatures and run through Rietveld analysis to determine phase composition of resultant powder
- Phase purity neared at sintering temperature of 1100 °C by all powders except gallic acid
- Caffeic acid performed best at 900 °C, with 86.2% purity

DFT Simulations on Heterostructure Interfacial Energy

	LCO * 1 / LNO * 1	LCO * 2 / LNO * 2	LCO * 3 / LNO * 3	LCO * 4 / LNO * 4	LCO * 5 / LNO * 5	LCO * 6 / LNO * 6	LCO * 7 / LNO * 7	LCO * 8 / LNO * 8
LCO Layers	8	18	28	38	48	58	68	78
Total Atoms	72	168	264	360	456	552	648	744
Time (VASP/Matlantis)	10h+/1min+	16h+/2min+	19h+/4min+	28h+/6min+	-/8min+	-/9min+	-/11min+	-/12min+

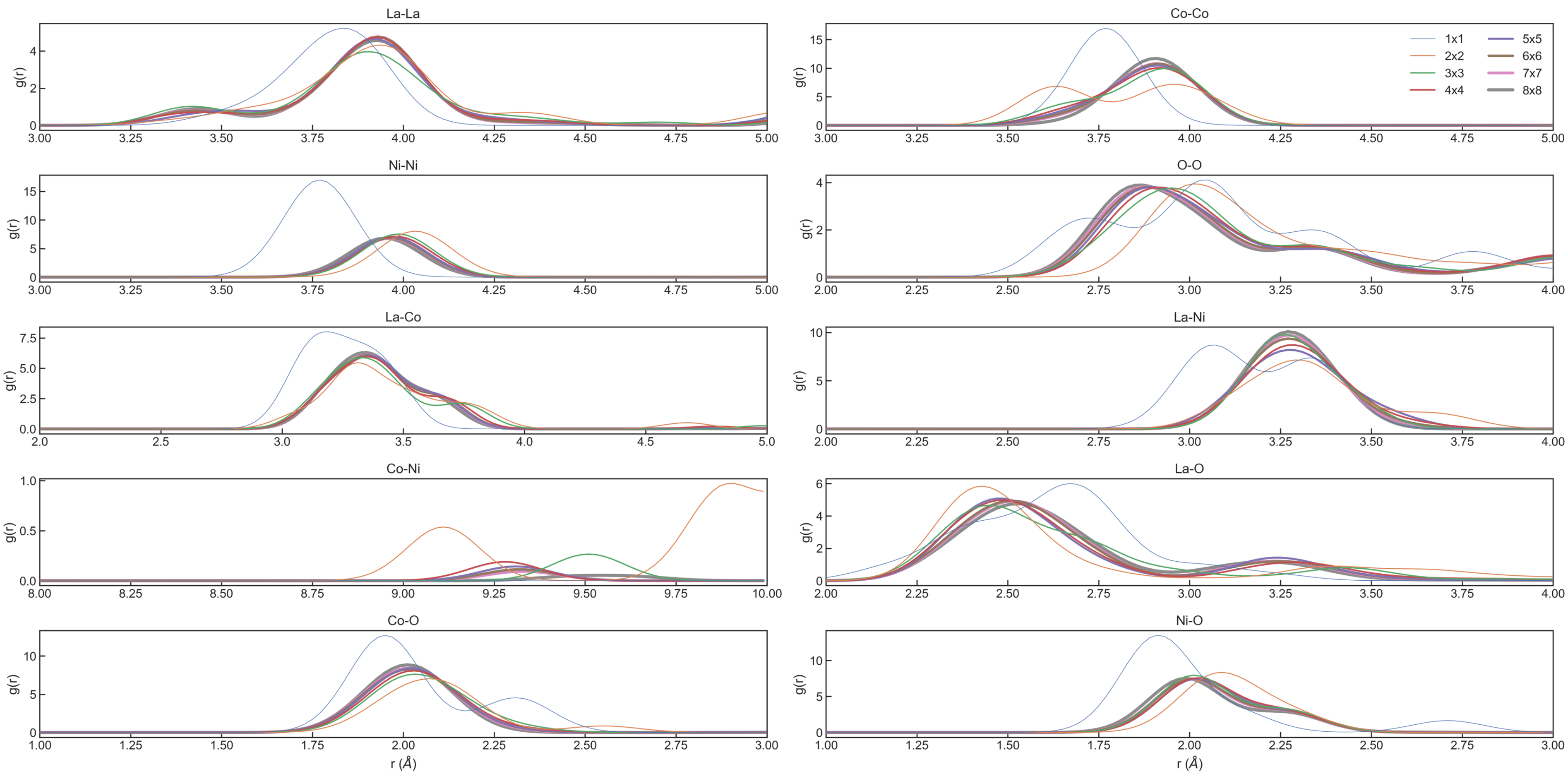


DFT Simulations on Heterostructure Interface Structure

MATLANTIS

➢ Interfacial Structure

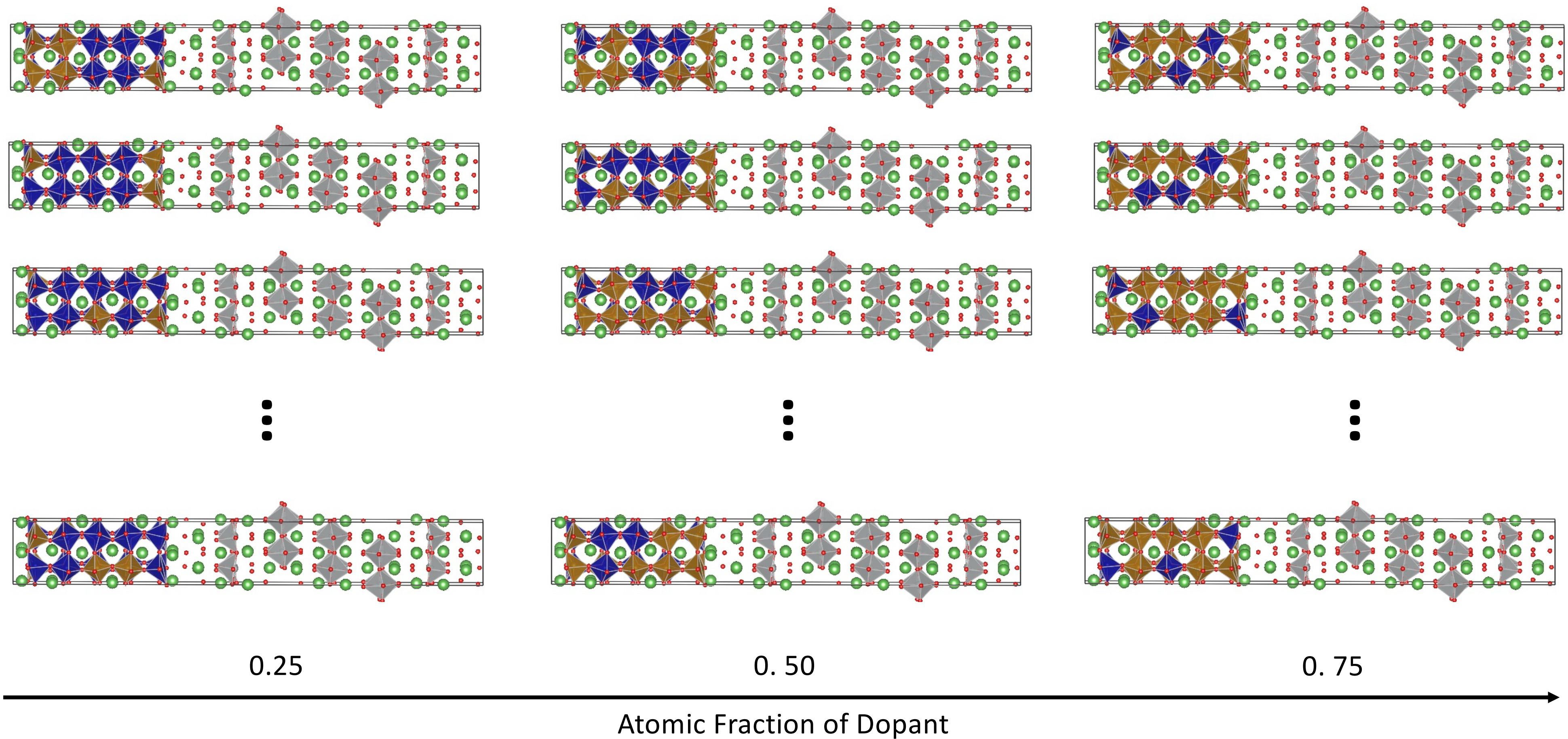
No significant changes after 3x3!



Construction of the Doped Heterostructure

➢ Doping Method (Random Sampling)

Using 3x3 interface: LNO+$LC_{1-x}M_xO$ (M: Fe; Ni; Mn)

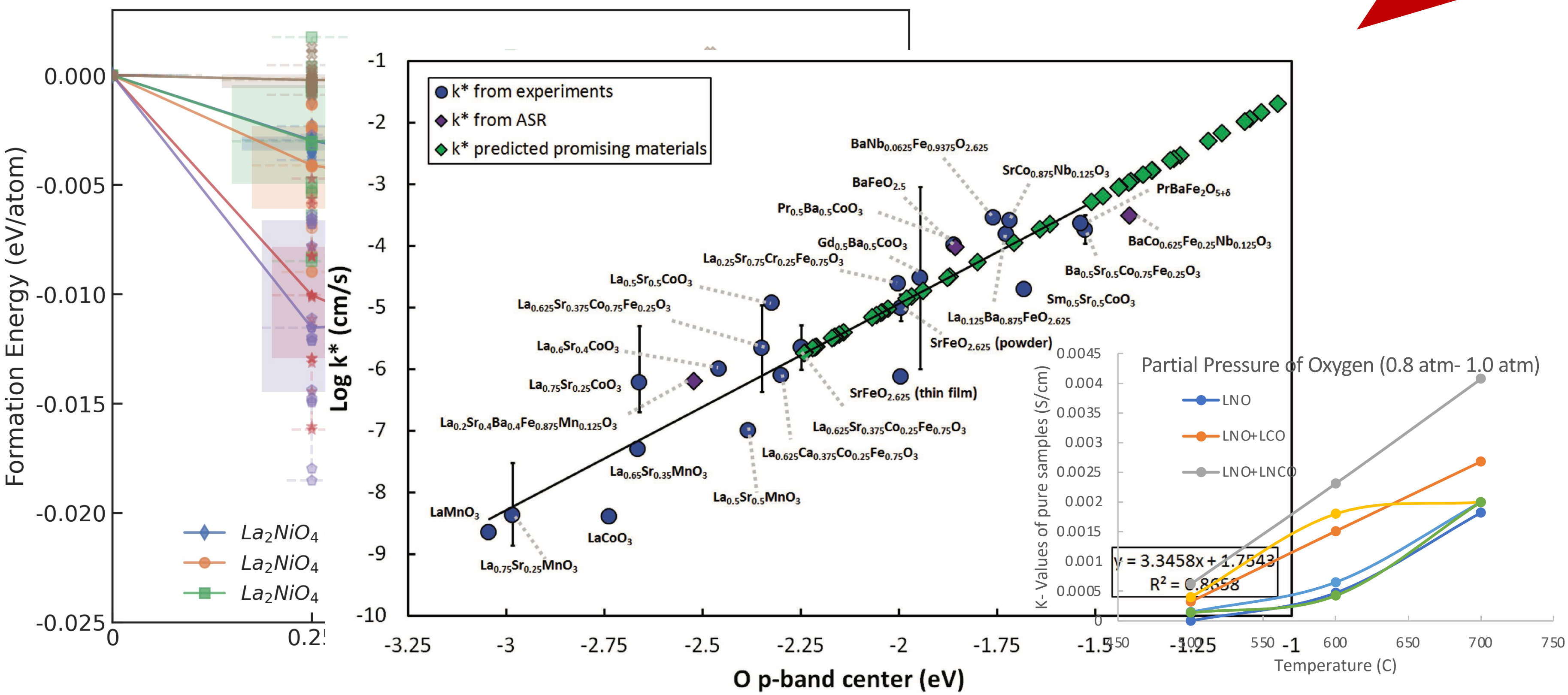


Heterostructure Stability vs. Conductivity (doped LCO)

MATLANTIS

➢ **Dopant Effect on Stability (Fe, Ni, Mn)**

Less stable -> Higher conductivity

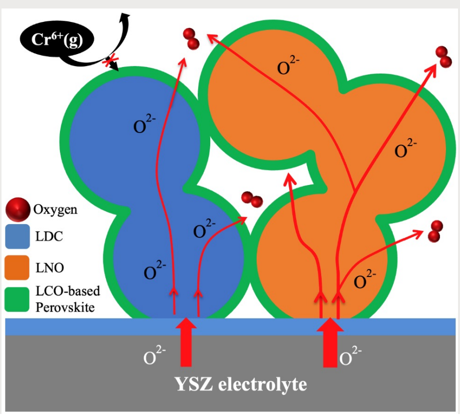


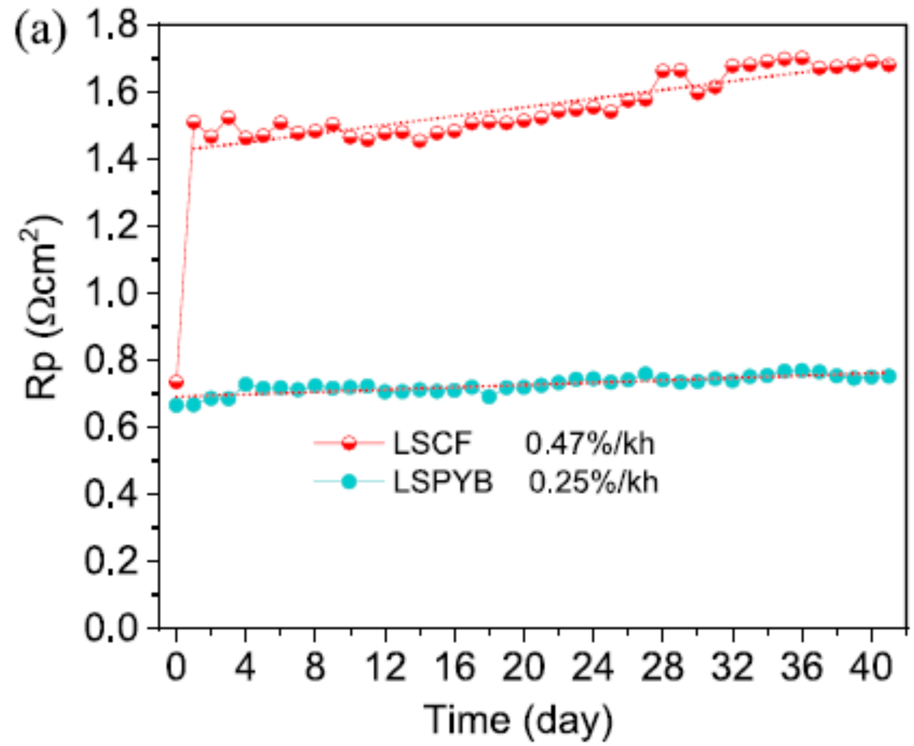
Stability: LNO+LNFO>LNO+LNMO>LNO+LCFO>LNO+LCNO>LNO+LCMO>LNO+LFMO   ***K-Values: LNO+LCNO>LNO+LNMO>LNO+LNFO***

Jacobs, Ryan, Tam Mayeshiba, John Booske, and Dane Morgan. "Material discovery and design principles for stable, high activity perovskite cathodes for solid oxide fuel cells." *Advanced Energy Materials* 8, no. 11 (2018): 1702708.

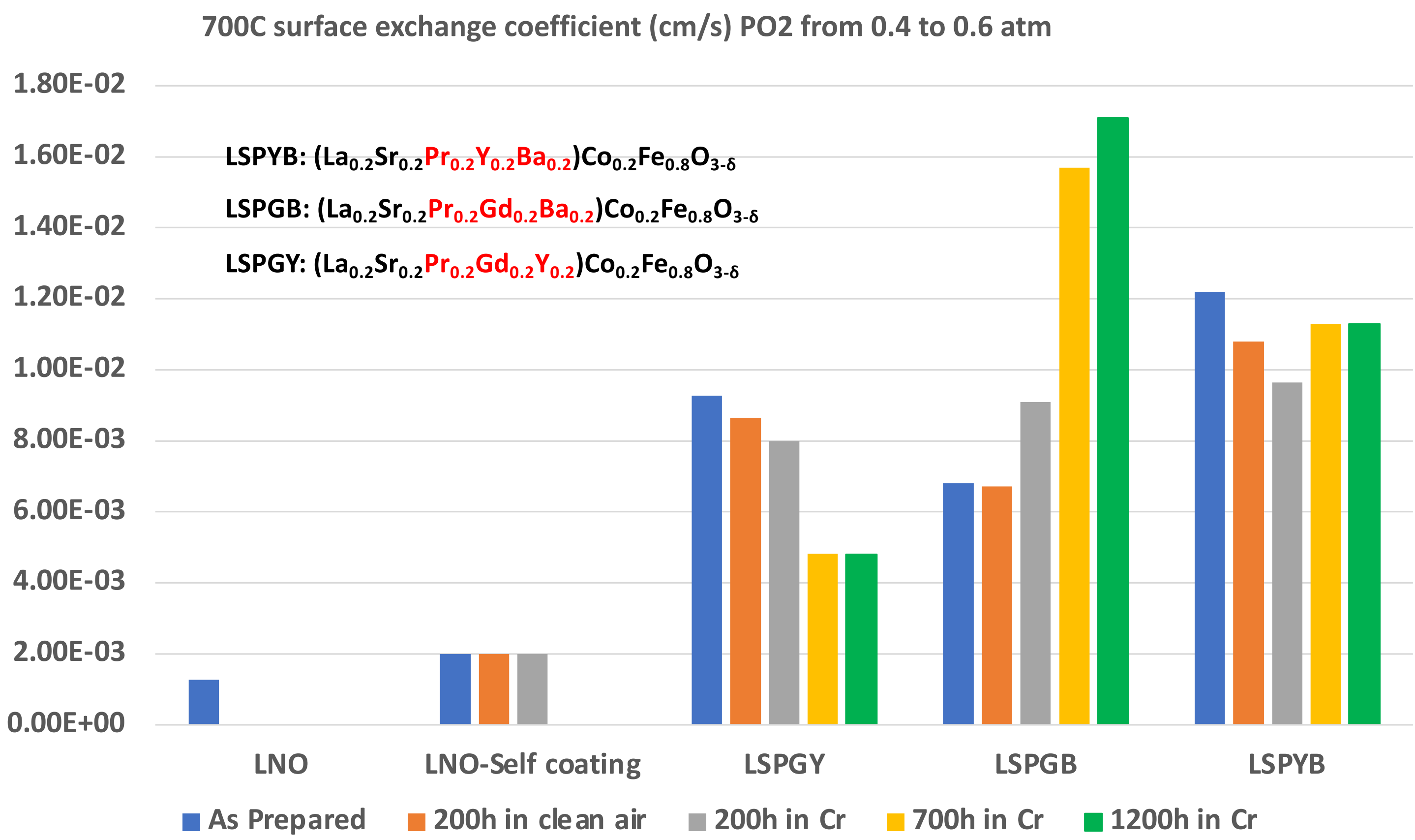
Two Research Directions for the Heterostructure Engineering

- Make modification of LCO perovskite
  - Regular doping
  - HEPs
- Doping of LNO





Experimental exploration and verification



Initial Performance:
LSPYB>LSPGY>LSPGB

long-term exposure to Cr:
LSPGB>LSPYB> LSPGY

Infiltration Evaluation of HEPs (LSPYB)

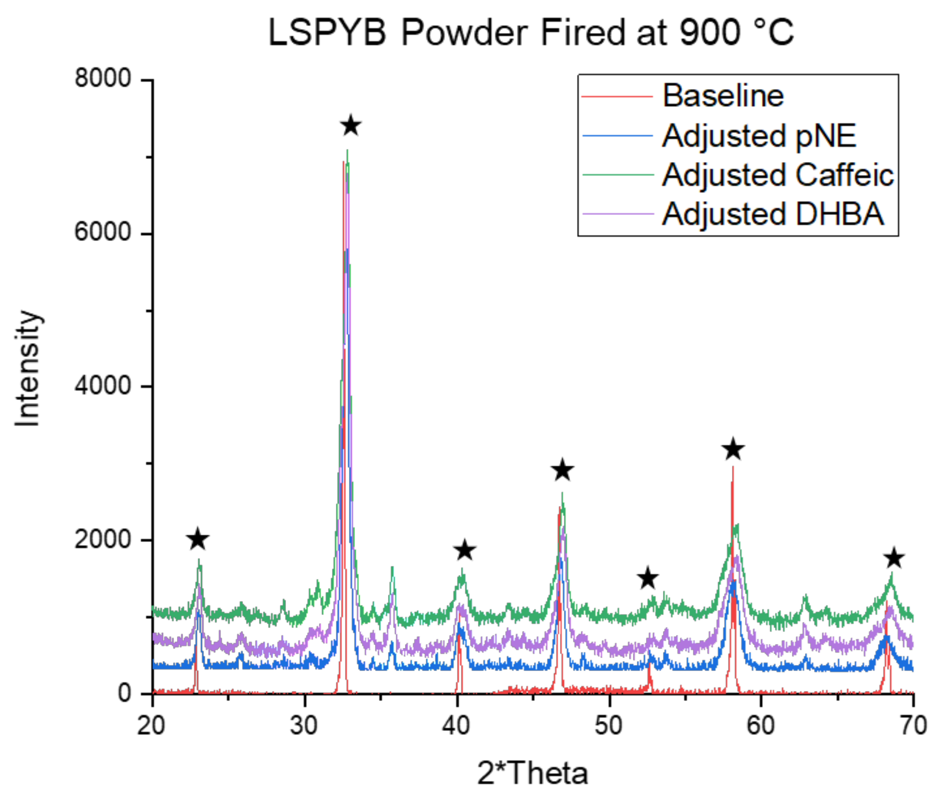
Ternary and High-Entropy Coatings: XRD Phase Purity Study of LSPYB

LSPYB and other HEP's were found as candidates

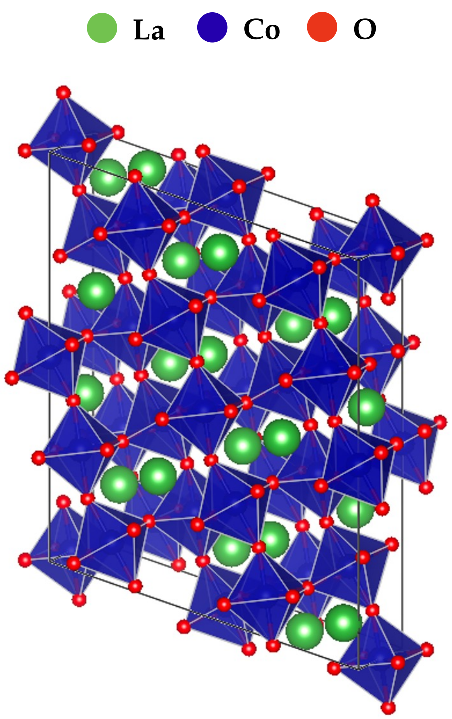
- Powder study was completed for LSPYB
- Unable to complete Rietveld analysis due to lack of data for HEP's in database
  - Performance of surfactant determined by peak intensity of extra phases
- Least amount/smallest intensity of extra peaks shown by pNE
- Most amount/greatest intensity of extra peaks shown by caffeic acid

Results:

- pNE chosen as the surfactant of choice to deposit LSPYB and other high-entropy ceramics thanks to its performance in this data
- Lowest temperature for highest phase purity was determined to be 900 °C.



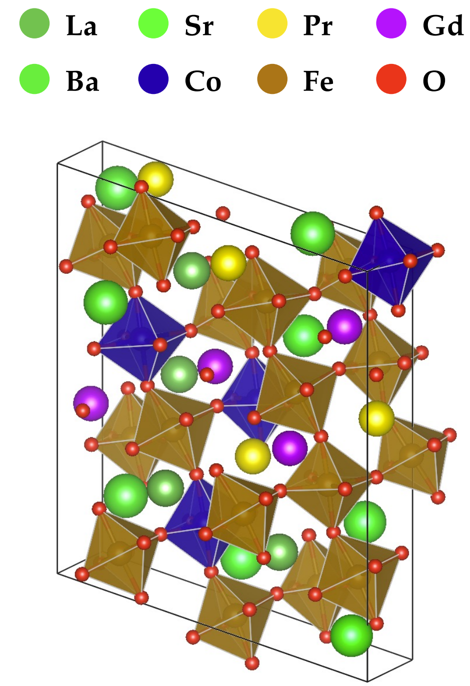
Contruction of HEP Supercell



$LaCoO_{3-\delta}$

Atoms	Energy (eV/atom)
100	-7.1921

SQS Method



$(La_{0.2}Sr_{0.2}Pr_{0.2}Gd_{0.2}Ba_{0.2})Co_{0.2}Fe_{0.8}O_{3-\delta}$

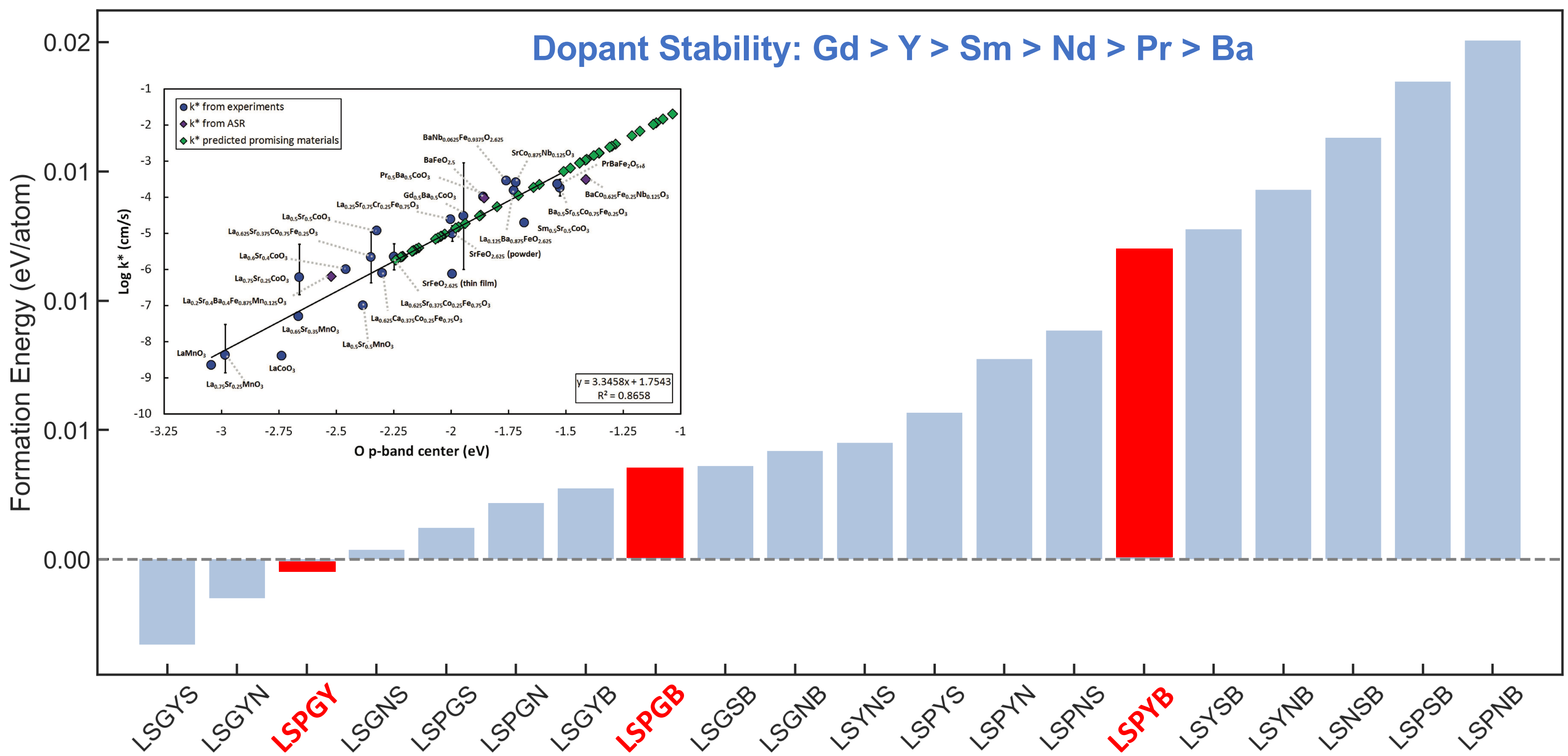
Atoms	Energy (eV/atom)
100	-7.3228

HEP Stability vs. Conductivity

➢ HEPs: Stability

$(La_{0.2}Sr_{0.2}A_{0.2}B_{0.2}C_{0.2})Co_{0.2}Fe_{0.8}O_{3-\delta}$

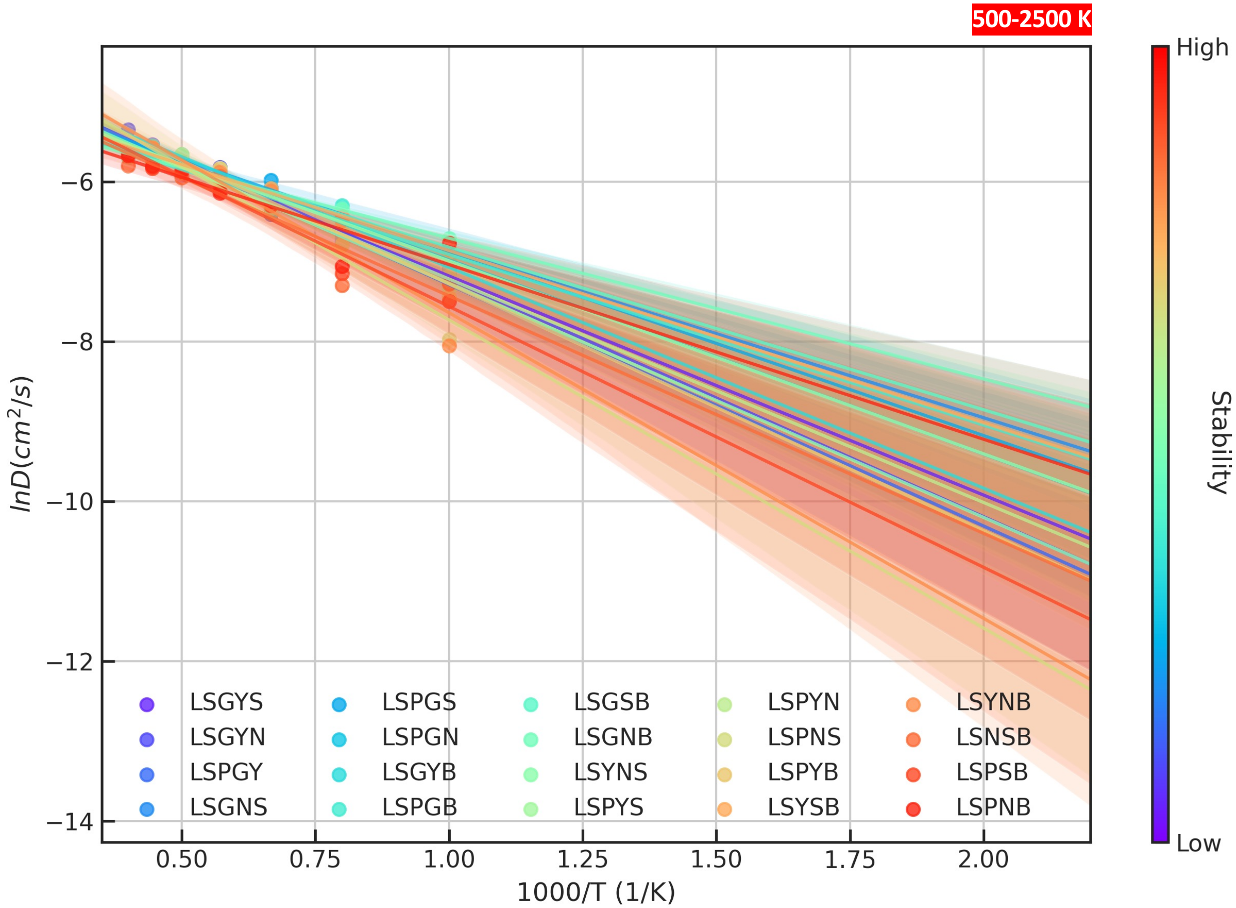
Symbol (A, B, C)	P	G	Y	N	S	B
Element	**Pr**	**Gd**	**Y**	**Nd**	**Sm**	**Ba**

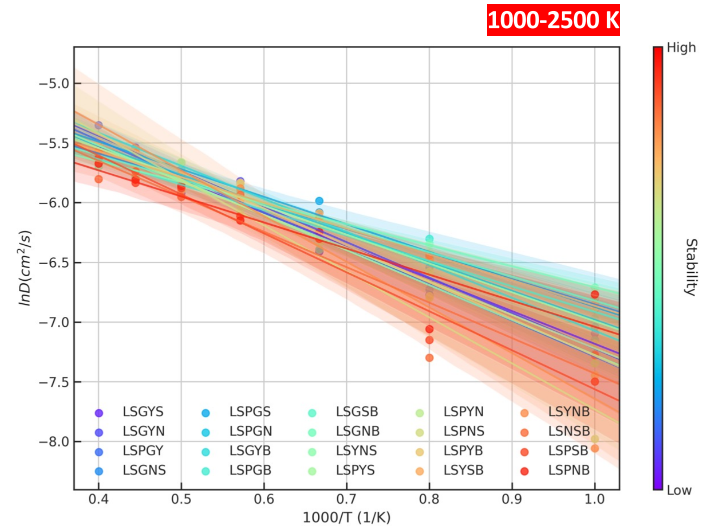


HEP Stability vs. Conductivity

MATLANTIS

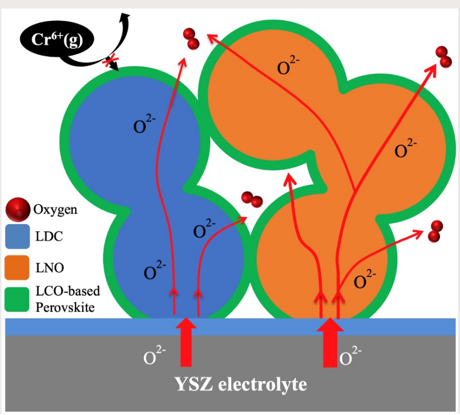
➢ HEPs: Conductivity (Oxygen Vacancy: 1.67 %)

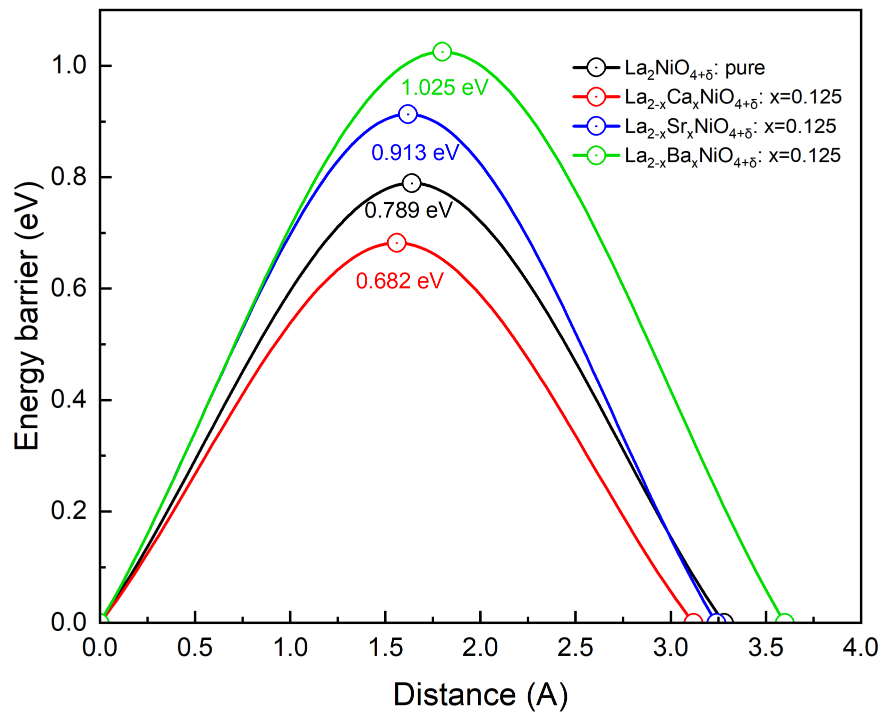




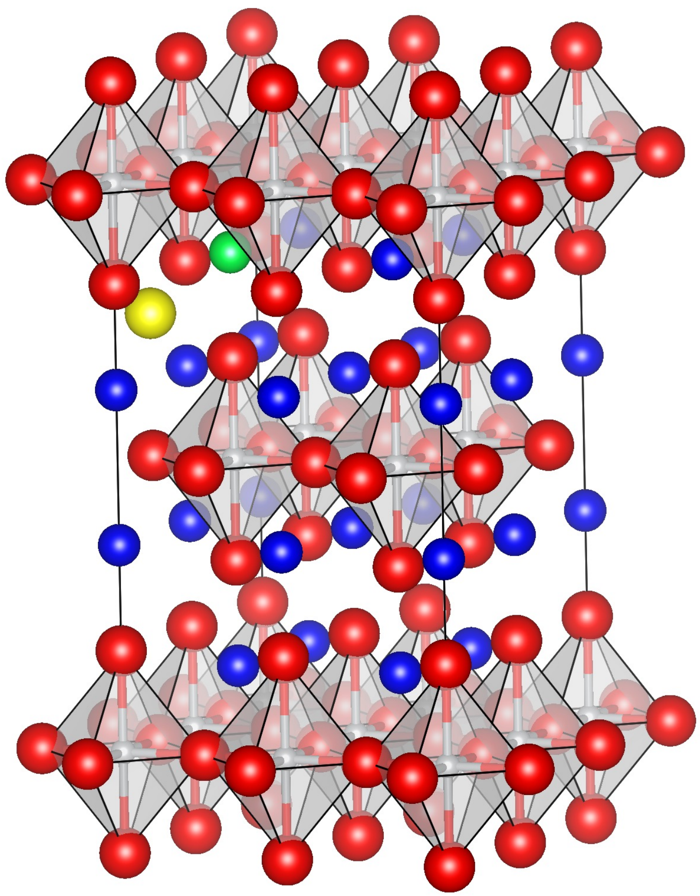
Two Research Directions for the Heterostructure Engineering

- Make modification of LCO perovskite
  - Regular doping
  - HEPs
- Doping of LNO

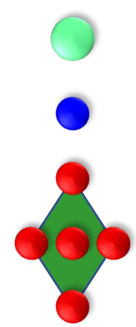




Diffusion for Doped $La_2NiO_{4+\delta}$ R-P Phase



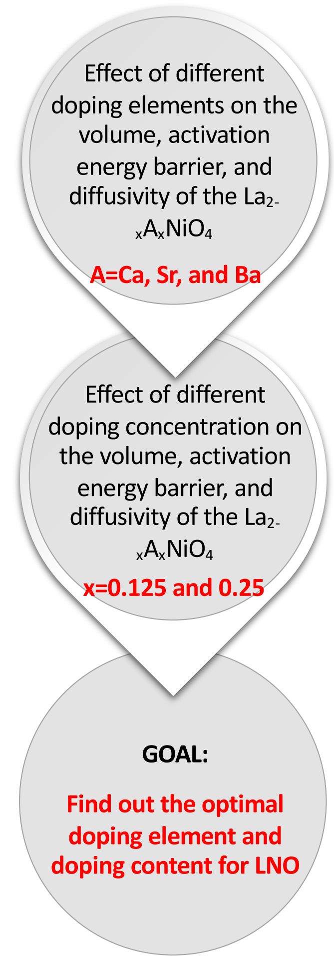
$La_{2-x}A_xNiO_{4+\delta}$ phase



Dopants A (Ca, Sr, Ba)

La

NiO_6 octahedral

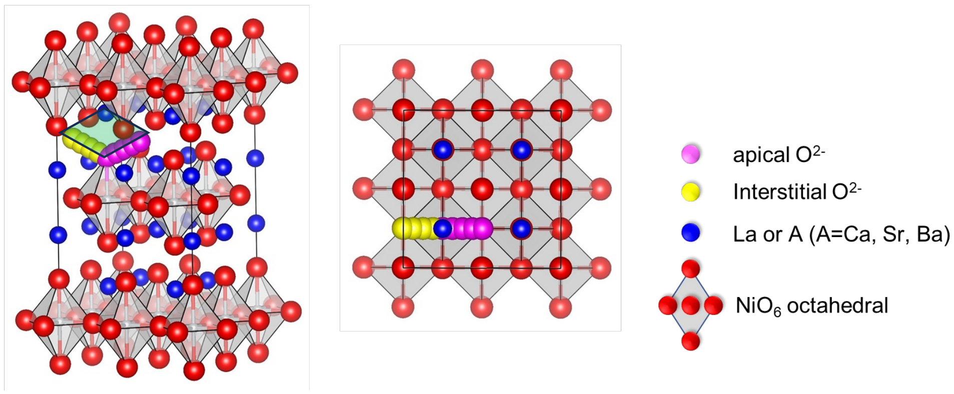


Objective of the work

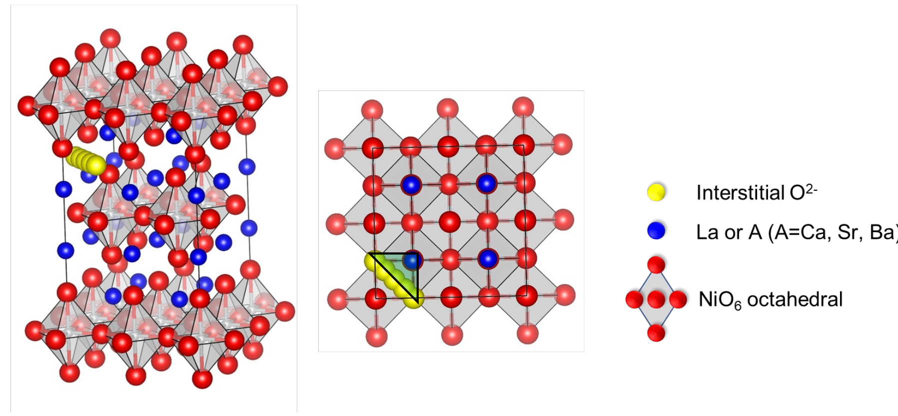
Diffusion Path for Doped $La_2NiO_{4+\delta}$ R-P Phase

➢ Diffusion Paths and Scenarios

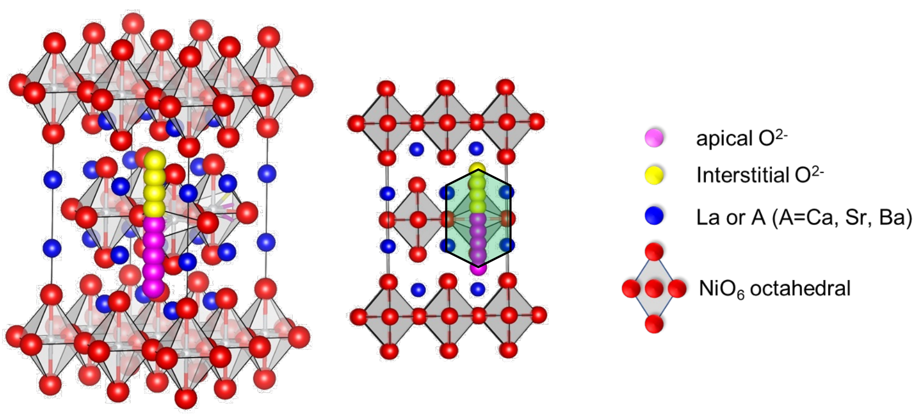
Path 1: Interstitialcy mechanism (ab plane)

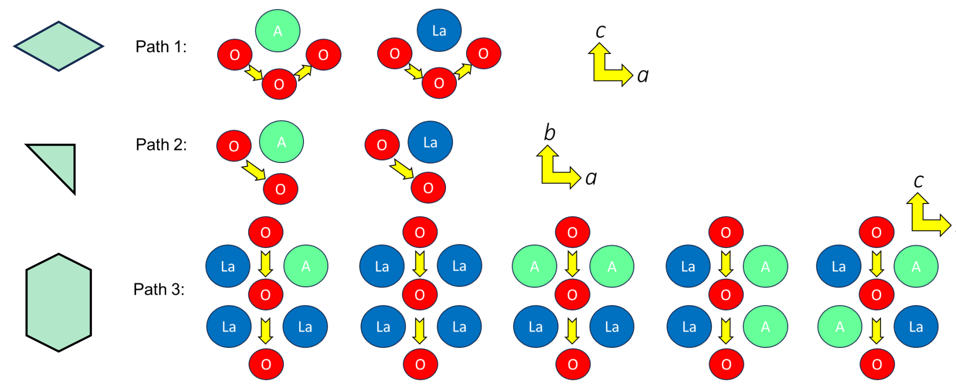


Path 2: Direct interstitial diffusion (ab plane)

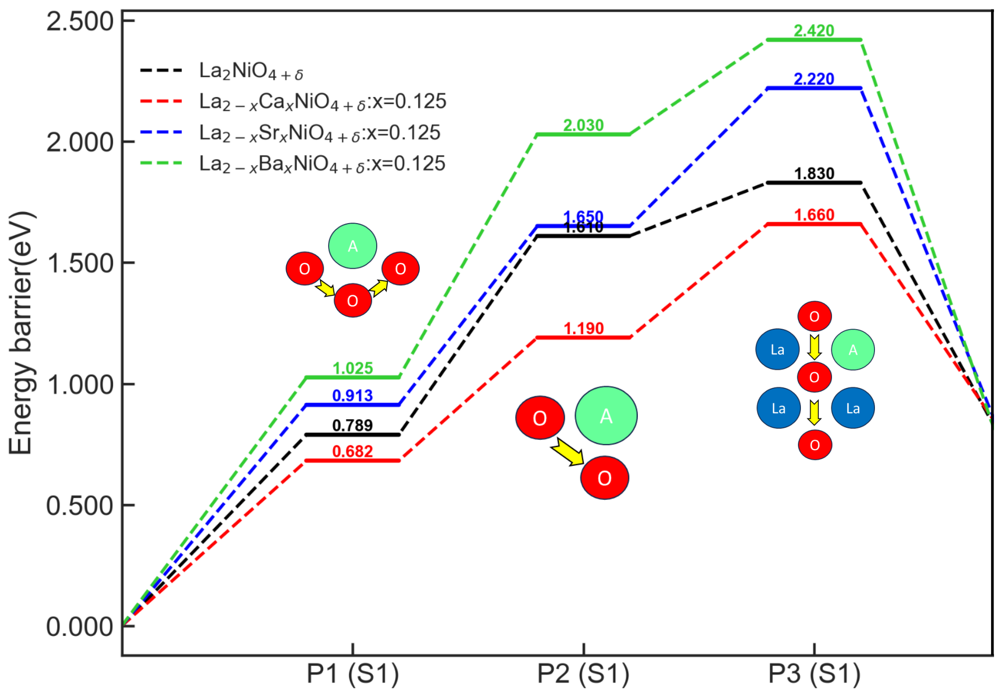


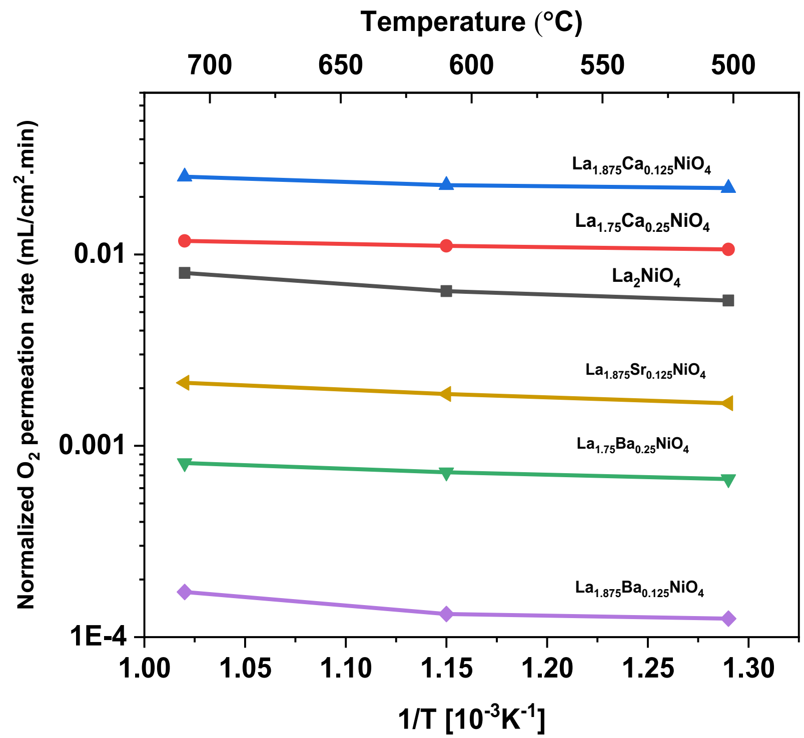
Path 3: Interstitialcy diffusion (c axis)



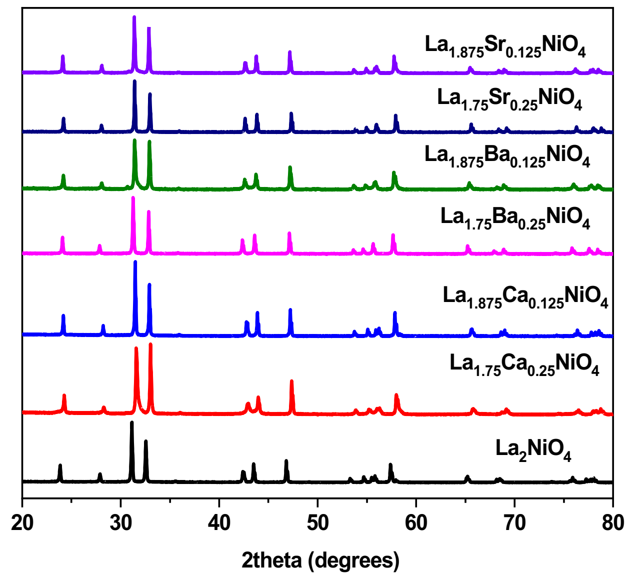


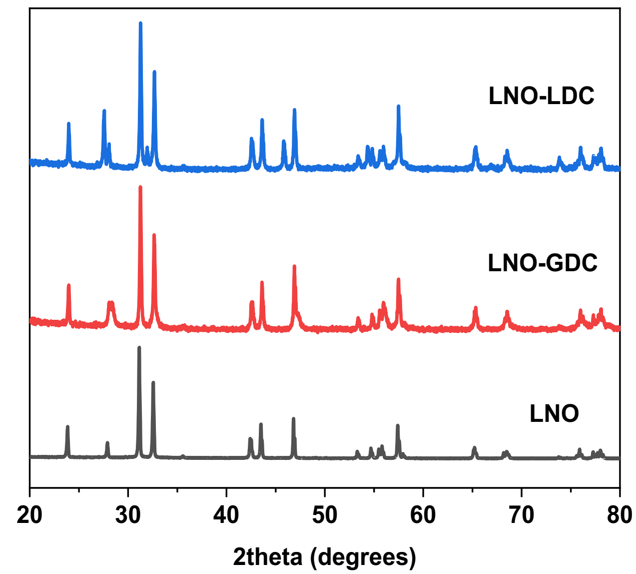
Energy Barriers vs. O2 Permeation





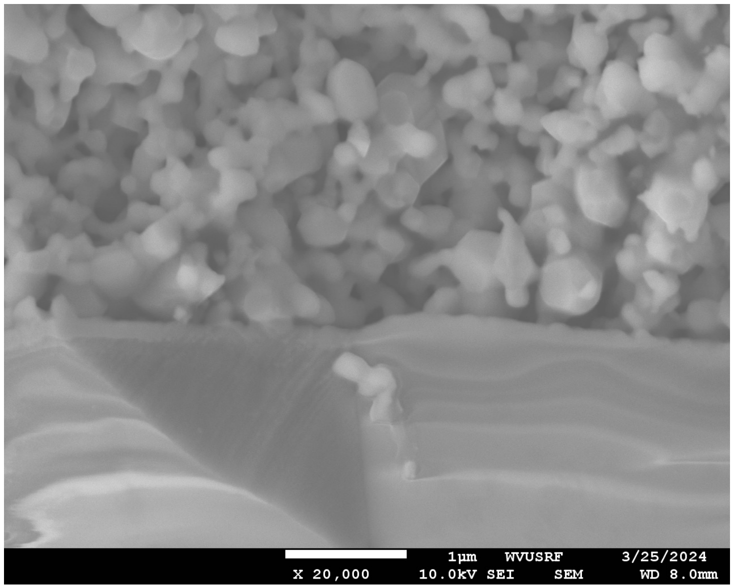
Investigation of Doped LNO electrode



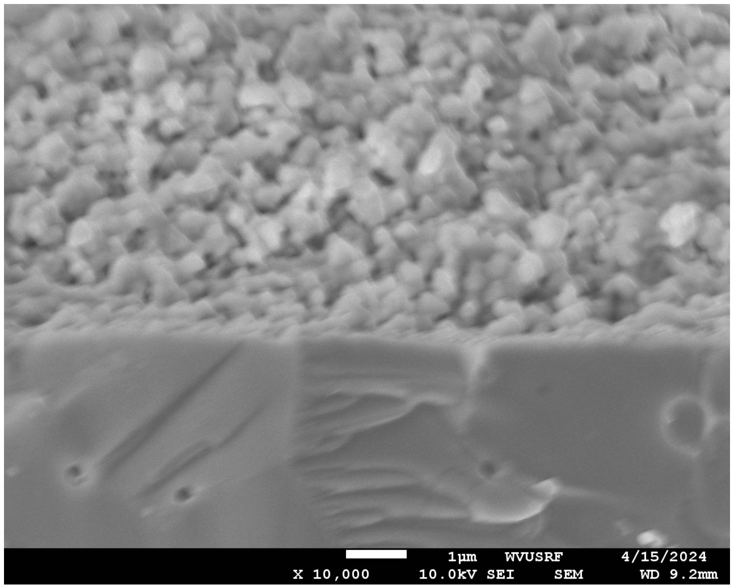


- Different doped LNOs were synthesized to improve the electronic conductivity, enhance the mechanical strength, and offer improved resistance to Cr-related degradation
- Each pattern matches the K_2NiF_4 structure, indicating that pure R-P phase is obtained for all nickelate samples explored

Electrode-Electrolyte Interface



Cross-sectional view of LNO-LDC (8:2) electrode and GDC interfaces

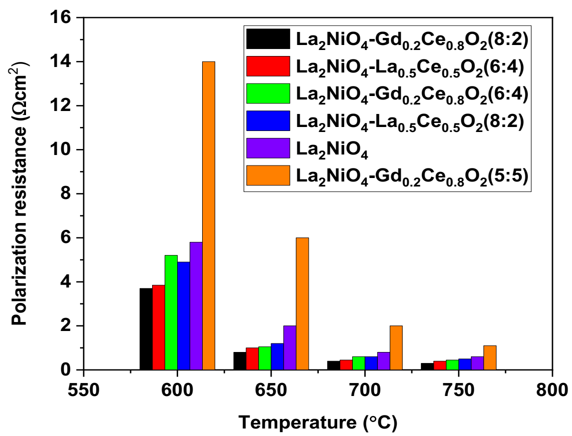


Cross-sectional view of $La_{1.75}Ca_{0.25}NiO_4$-$Gd_{0.2}Ce_{0.8}O_2$ (8:2) electrode and GDC interfaces

The bond between the electrodes and GDC is good

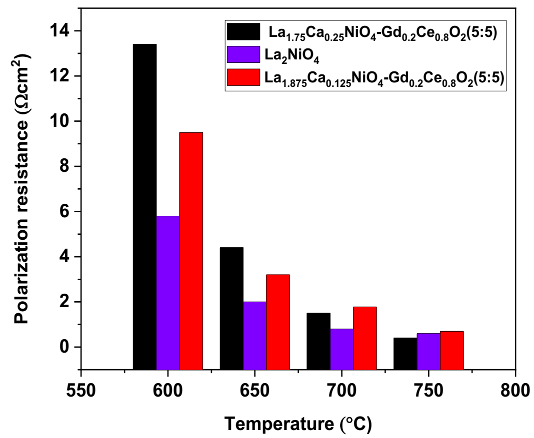
Performance of Doped LNO

Pure LNO and different ratios of LDC and GDC



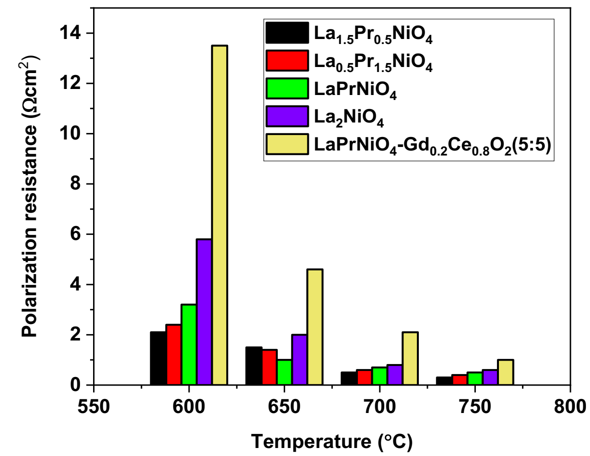
- The best-performing oxygen electrode in this category is **LNO-GDC (8:2)**
- The worst electrode is **LNO-GDC (5:5),** where the **LNO** is even better in performance

Pure LNO and different ratios of Ca-doped LNO and GDC



- At lower temperatures, the LNO backbone has the best performance
- When the temperature was raised to 750 ^{o}C, the Ca-doped LNO **($La_{1.75}Ca_{0.25}NiO_4$-$Gd_{0.2}Ce_{0.8}O_2$)** improved a lot

Pure LNO and different Pr/La ratios



- We got the best electrode material when the amount of La was more compared with the Pr: **$La_{1.5}Pr_{0.5}NiO_4$**
- The worst electrode is **LPNO-GDC (5:5)**, where the **LNO** is even better in performance

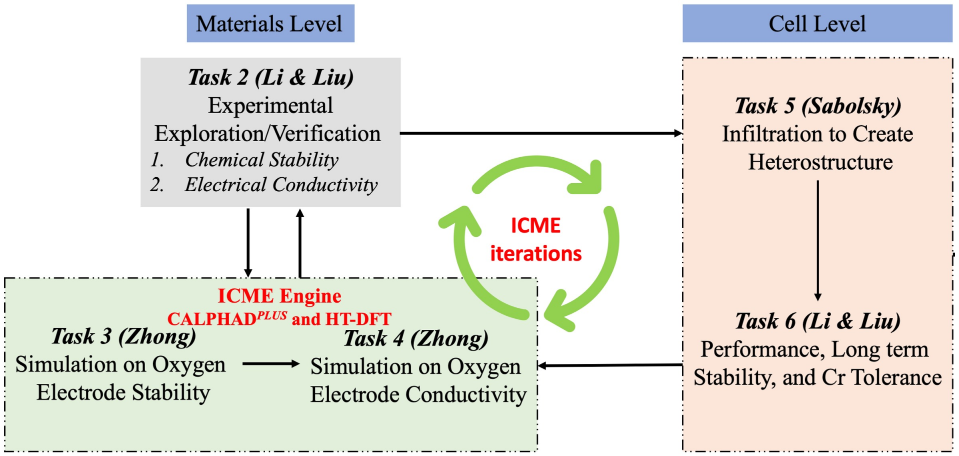
Overall, the composites that were mixed with GDC in the ratio of 5:5 tend to reduce the performance of the electrode materials

Summaries

- The prediction of perovskites (doped LCO + HEPs) stability vs. conductivity has good agreement with experimental observation
- The prediction of the doped r-p phase conductivity has a good agreement with exp observation
- HEP (LSPGB) shows even better performance with the exposure of Cr
- Ca and Pr doped LNO shows very high conductivity
- Infiltration has been successfully applied with the challenging Doped LCO and HEPs.

Next Steps

- Explore the Cr's impact to the HEPs performance
- Further testing on the doped LNO and HEPs nano-coating with symmetrical cells
- Finalize the electrode candidates
- Cell test including Long term degradation performance



Thank You!

Thanks to funding support from DOE (DE-FE0032116) and the Program manager Andrew O'Connell