# Heterostructured Cr Resistant Oxygen Electrode for SOECs

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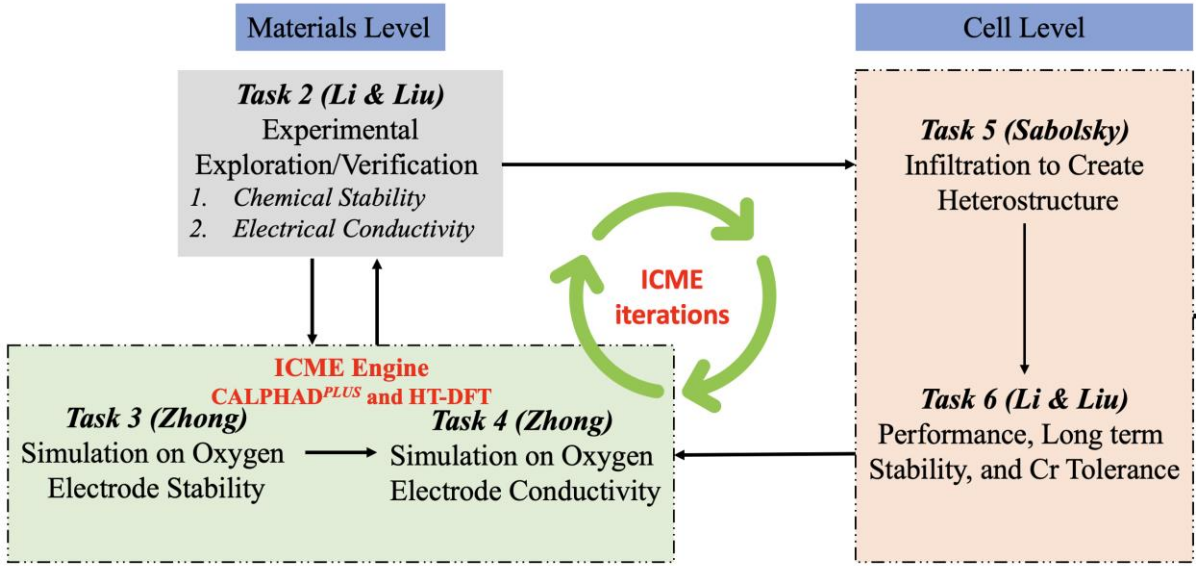
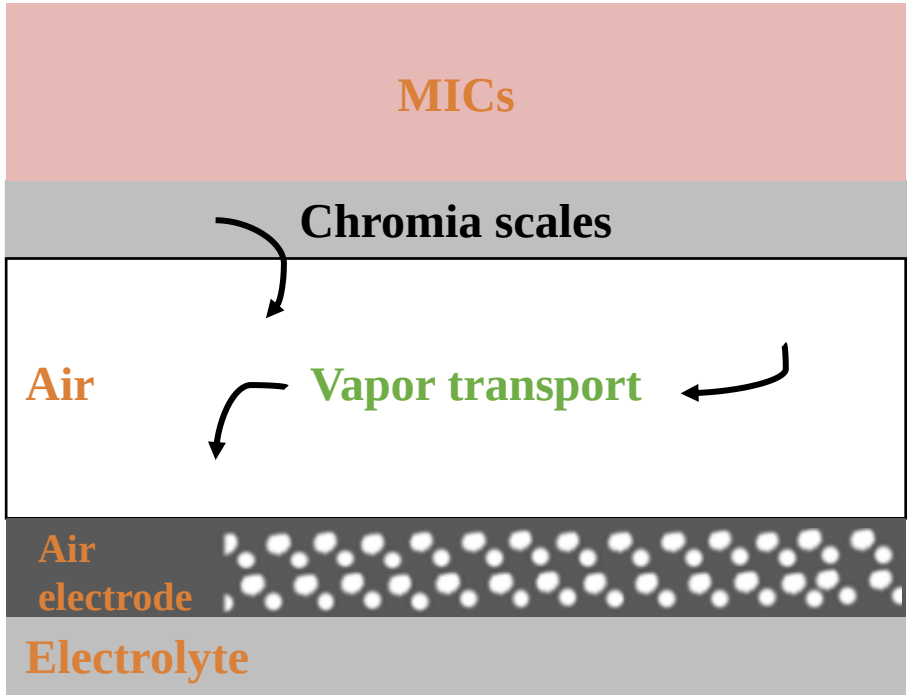
# Outline

- Background
- Proposed novel $La_2NiO_4$-$LaCoO_3$ heterostructure
- Critical Factors to consider
- Overall Approach & Objectives
- **Updates on Tasks**
  - Experimental exploration (Task #2)
  - Simulation (Tasks #3&4)
  - Infiltration (Task #5)

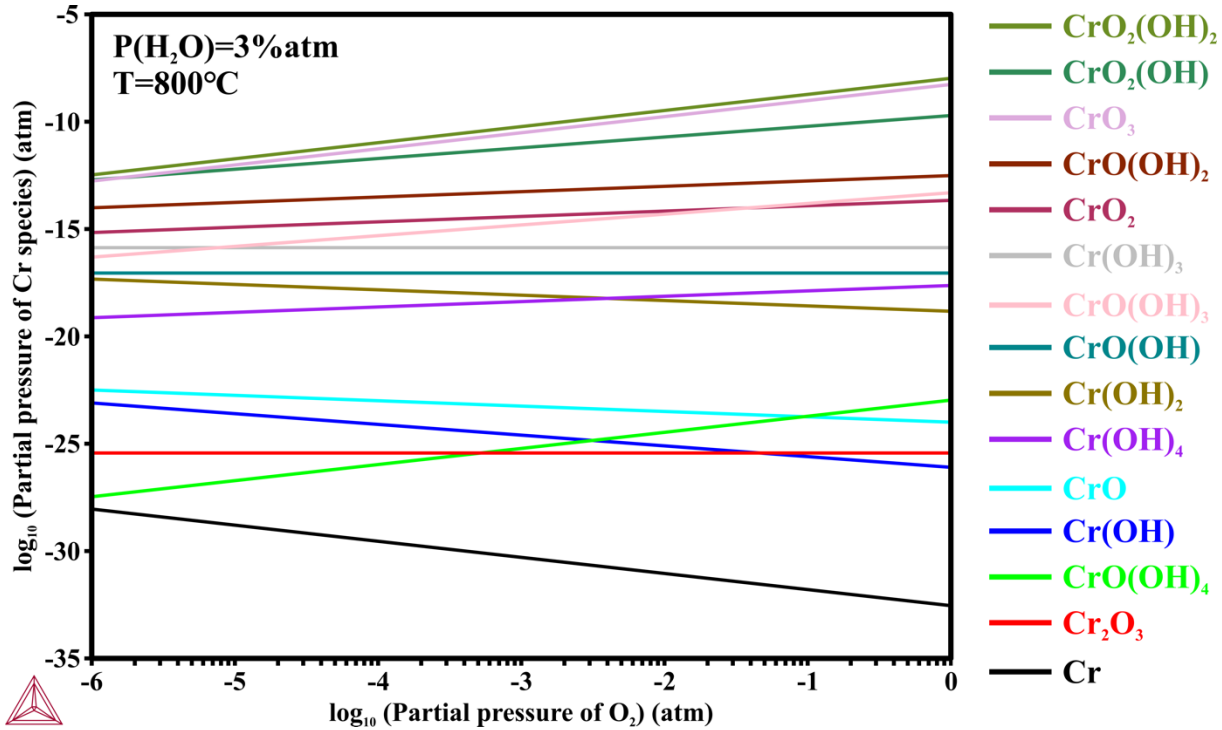


# Background: Cr in SOC Stack

Cr from metallic part in the stack




High $P_{O2}$ in SOEC lead to increased $P_{Cr}$ relative to SOFC




$$SrO + CrO_3(g) \rightarrow Cr - Sr - O(nuclei)$$

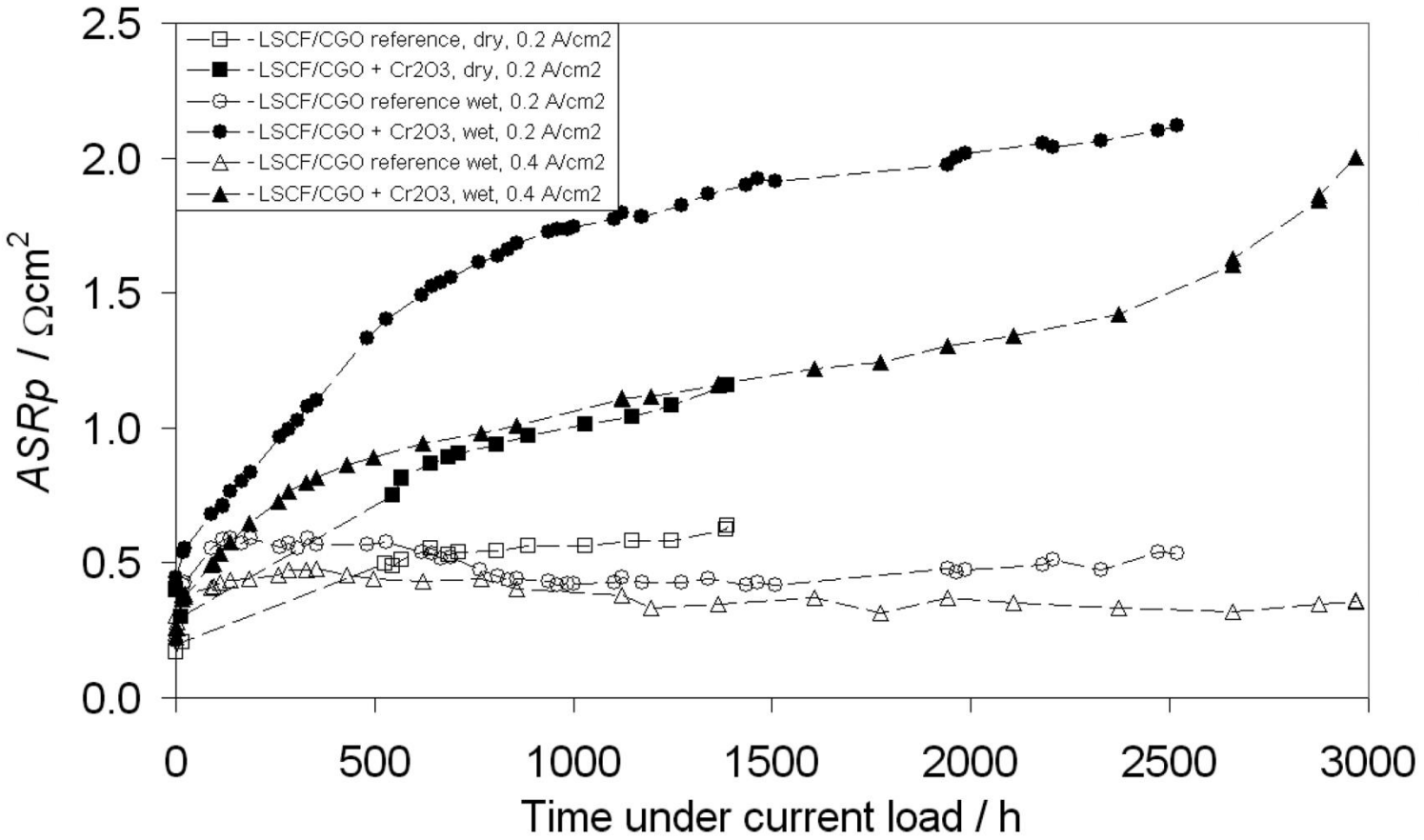
$$Cr - Sr - O(nuclei) + CrO_3(g) \rightarrow Cr_2O_3(s)$$

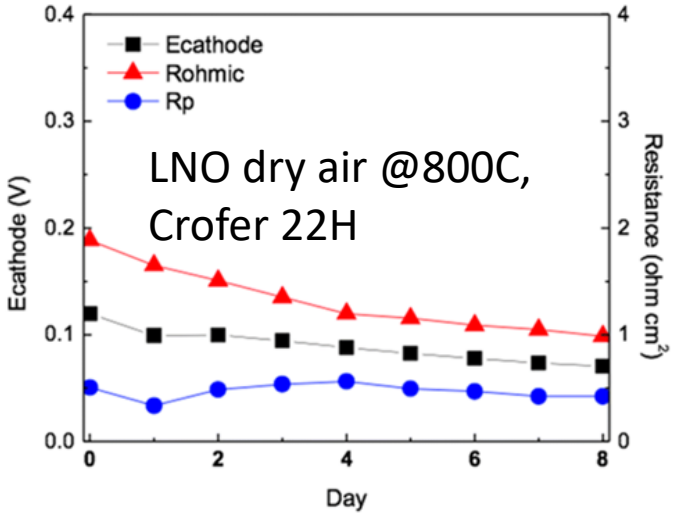
$$Cr - Sr - O(nuclei) + SrO + CrO_3(g) \rightarrow SrCrO_4(s)$$

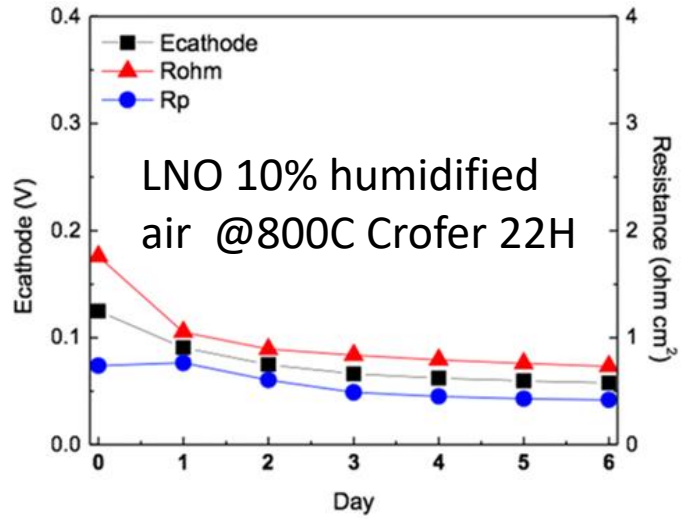
Alkaline-earth element - Sr is the triggering factor

# Background: Cr to Poison Benchmark LSCF

Fast degradation of LSCF benchmark
in presence of Cr source @750C



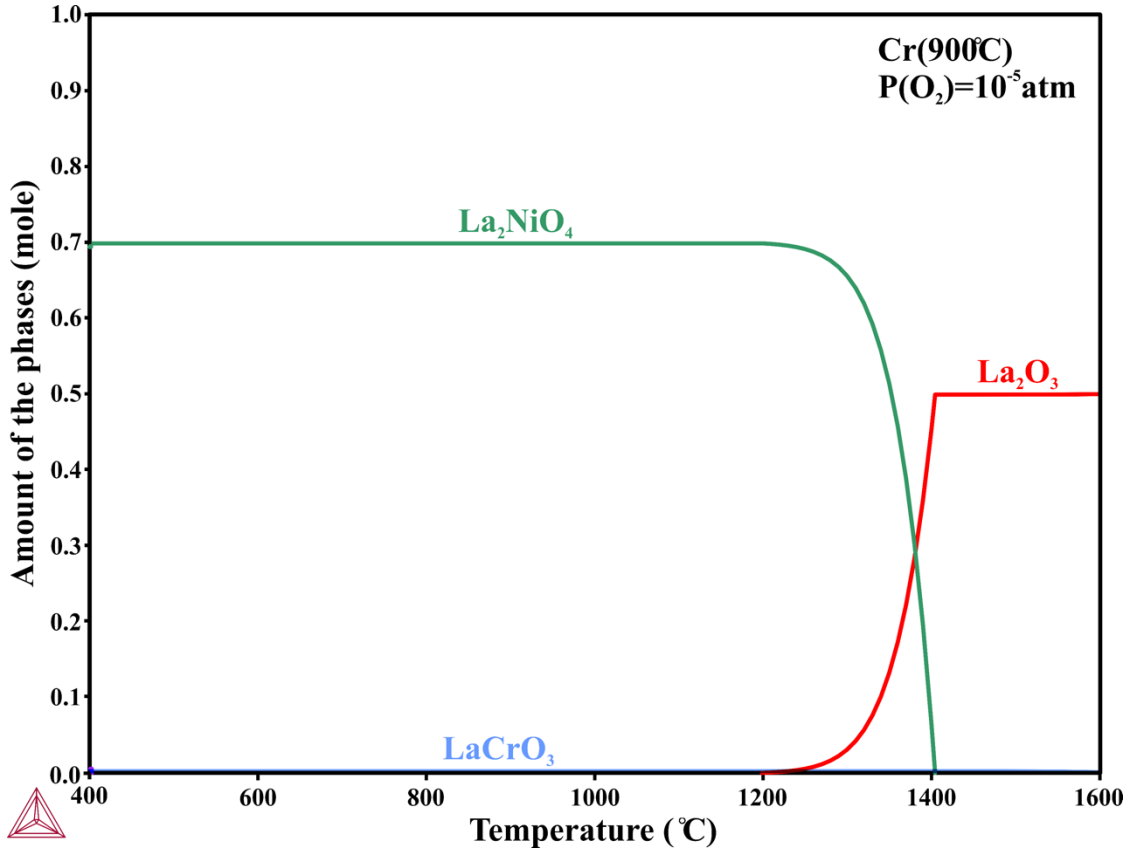



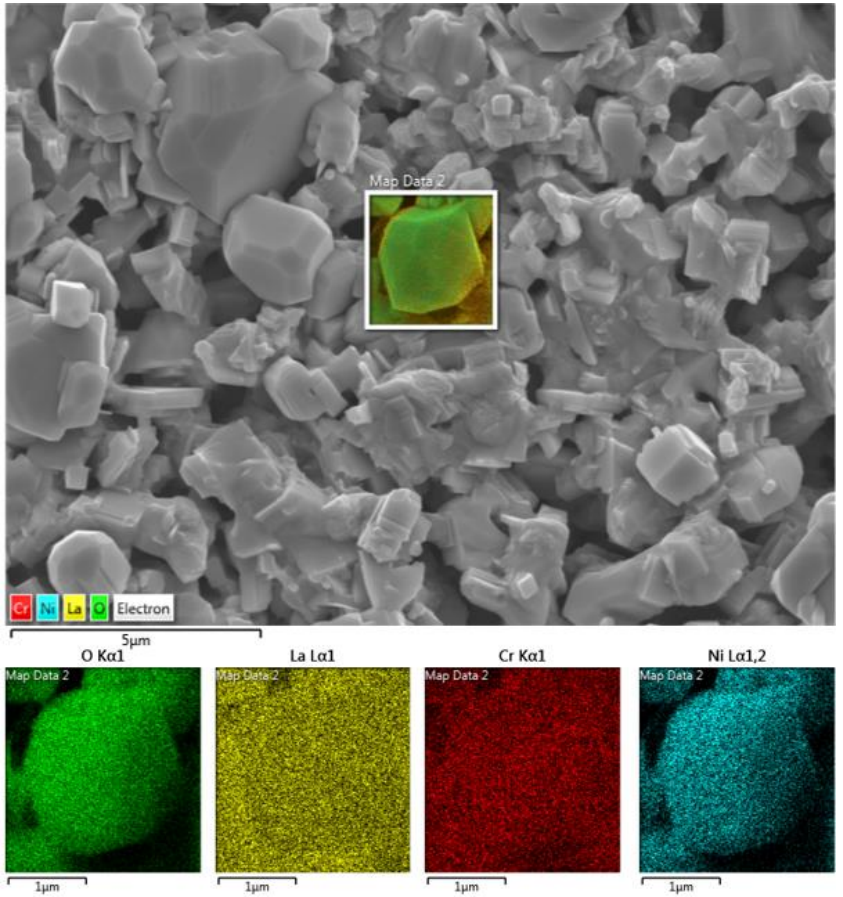

Promising short-term LNO tolerance to Cr

FUEL CELLS 09, 2009, No. 6, 823–832
*JOM* **volume 71**, pages3848–3858 (2019)

# Previous Results From WPI on $La_2NiO_4$

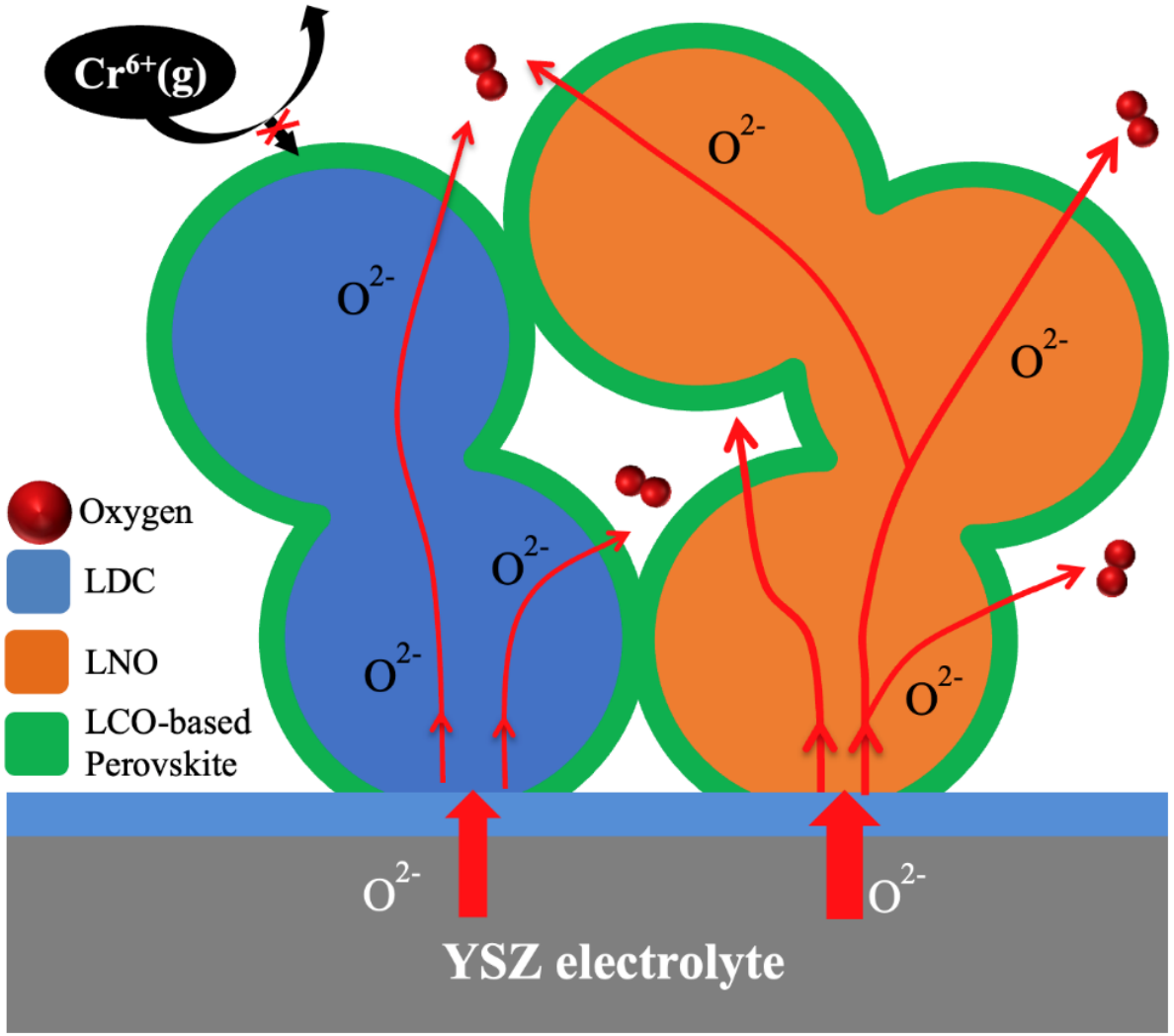



LNO is stable with the exposure to Cr




No apparent secondary phase formation

# Proposed Novel $La_2NiO_4$-$LaCoO_3$ Heterostructure

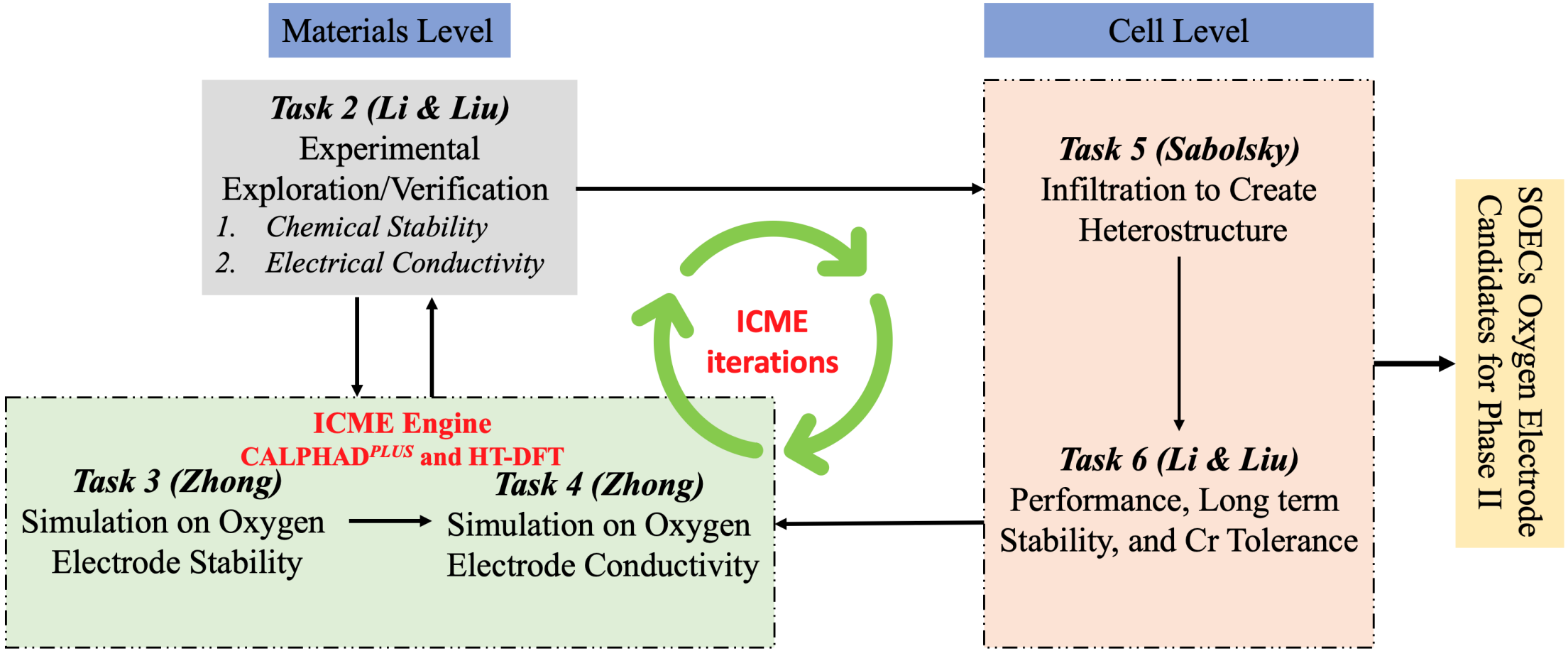



Sr-free, fast O-conducting LNO backbone plus active OER LCO surface coating as Cr-resistant, high performing oxygen electrode

# Critical Factors to consider

- ***CF1. Cr Resistance:*** *It is well known that Sr is the main reason for the Cr poisoning due to the formation of $SrCrO_4$. The new oxygen electrode candidate should not have Sr;*
- ***CF2. Oxygen Ionic Conductivity:*** *R-P phases and perovskites have totally different oxygen ionic conduction mechanisms. Dopant choice and interface engineering is needed to achieve excellent bulk conductivity and interfacial ion exchange;*
- ***CF3. Interfacial Stability:*** *The infiltration with LCO-based perovskites will introduce the interfaces with LNO and LDC barrier layer respectively. Dopant choice is needed to control the bulk and interfacial phase stabilities;*
- ***CF4. Long-Term Degradation Mechanism:*** *Accelerated test will be carried out to simulate the long-term degradation performance. However, it is imperative to validate the accelerated test mechanism is identical to which under the real operation conditions.*

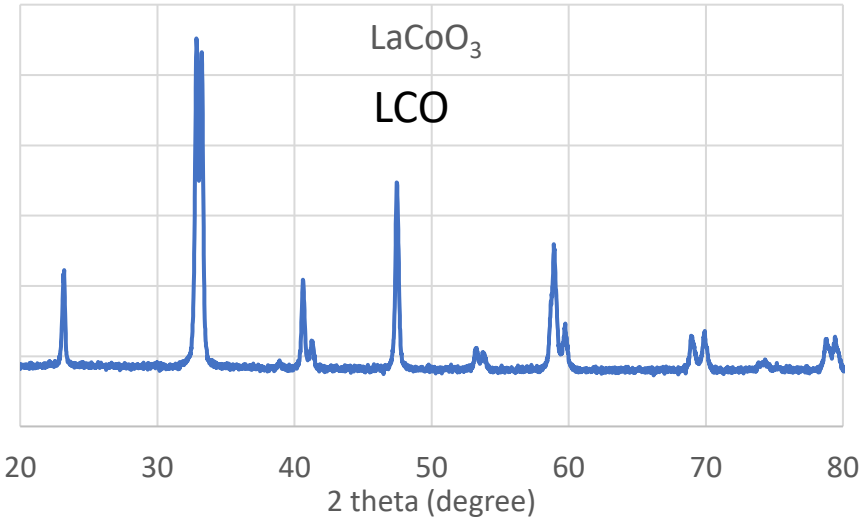
# Overall Approach & Objectives

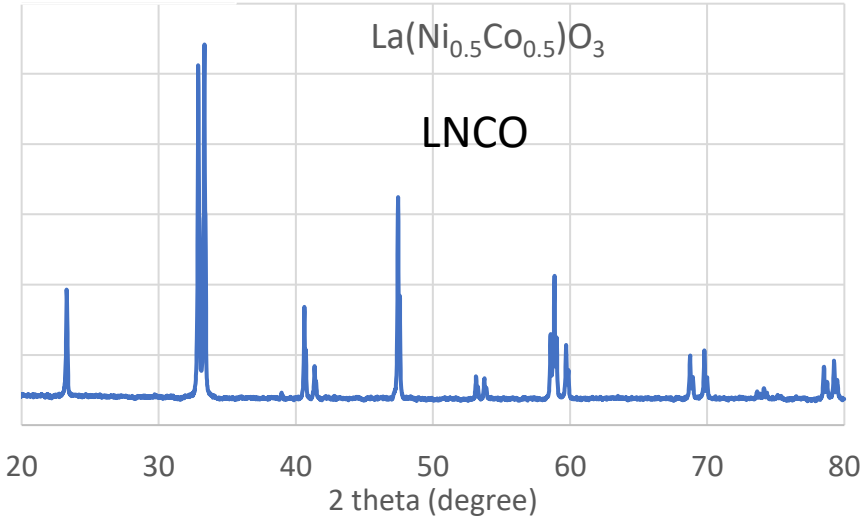


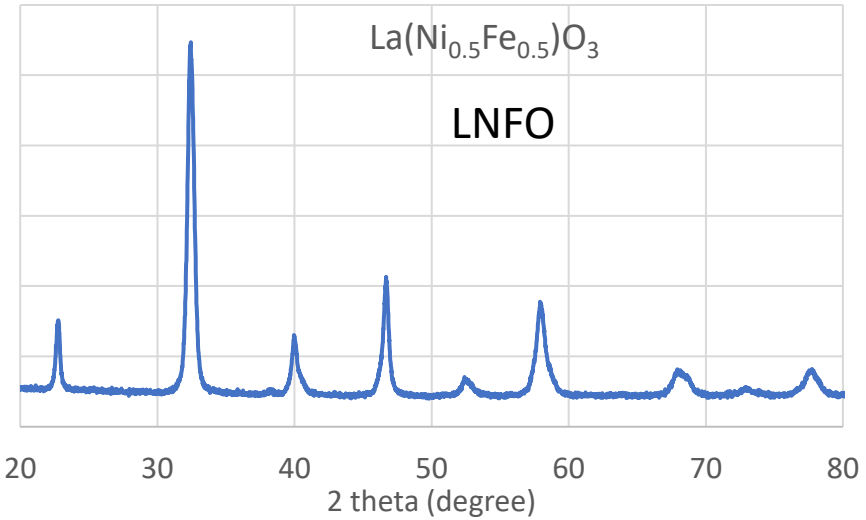

When fully optimized, this oxygen electrode material will target to an INTRINSIC long-term degradation rate of less than 0.3%/1000 hrs at 700°C. By the end of the first year, it is expected to reach the 0.8A/cm$^2$ current density at 1.4V applied potential. By the end of the project, we will reach 1A/cm$^2$ current density.

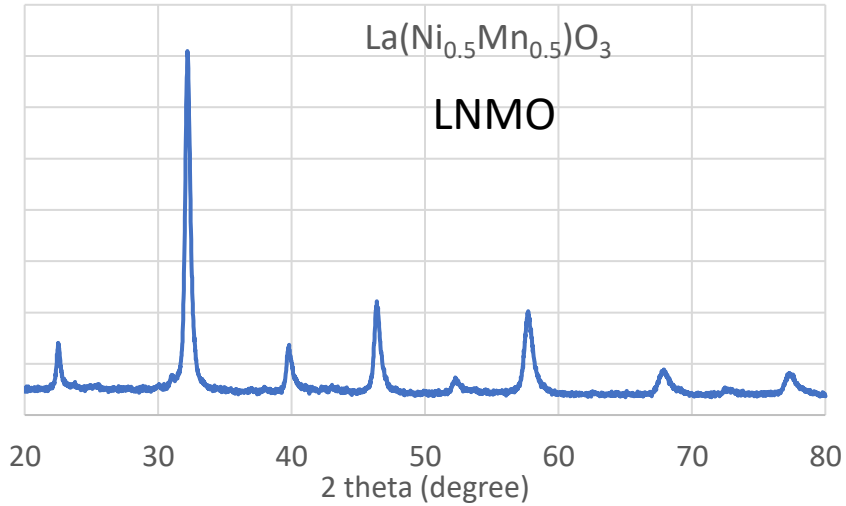
# Task 2: Experimental exploration and verification

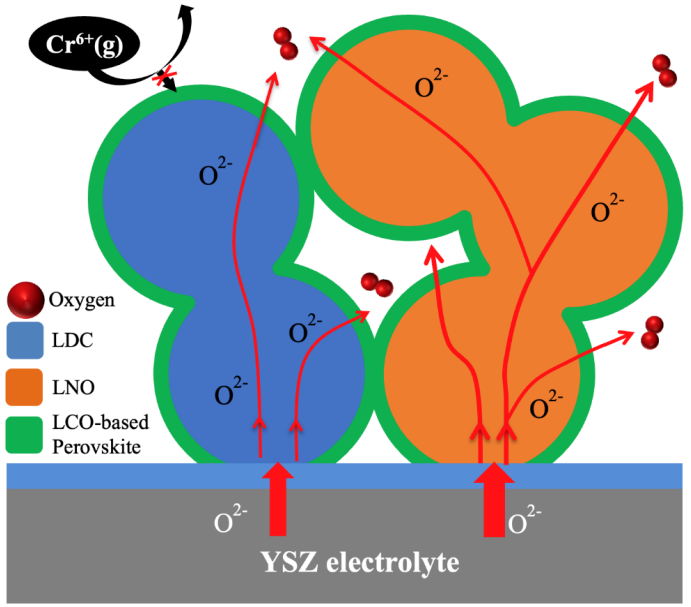
Synthesis of Sr-free perovskite surface coating materials



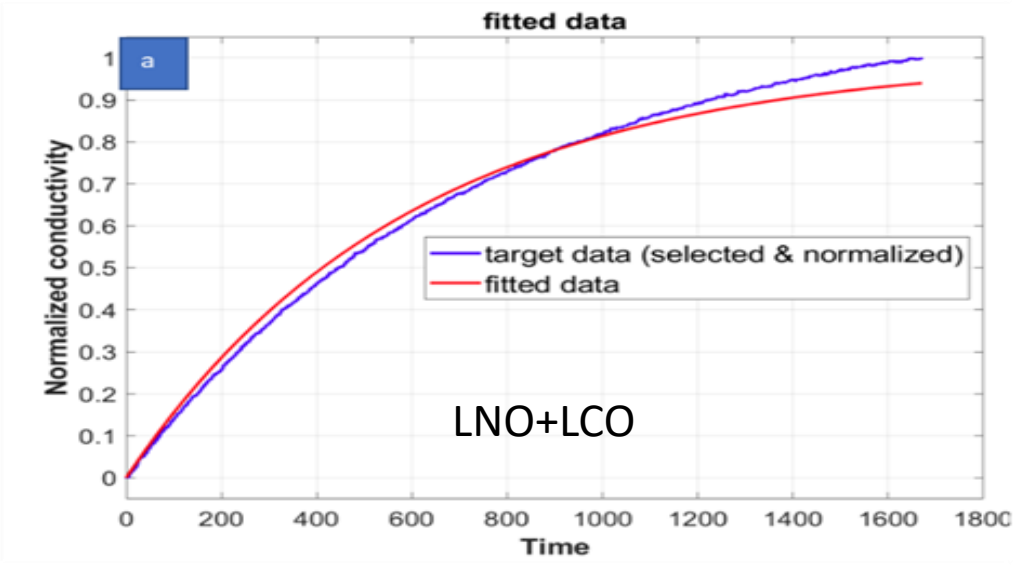



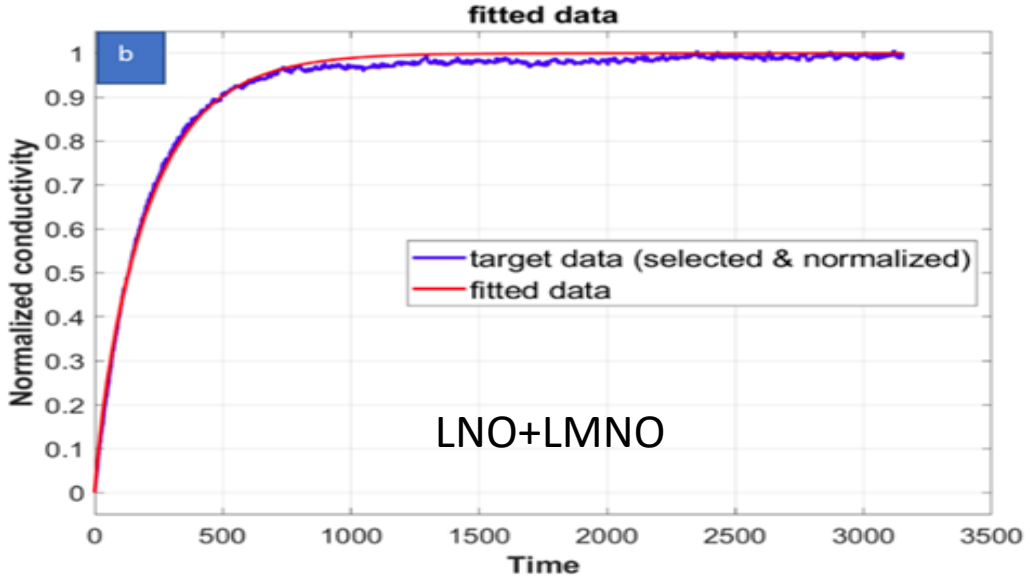



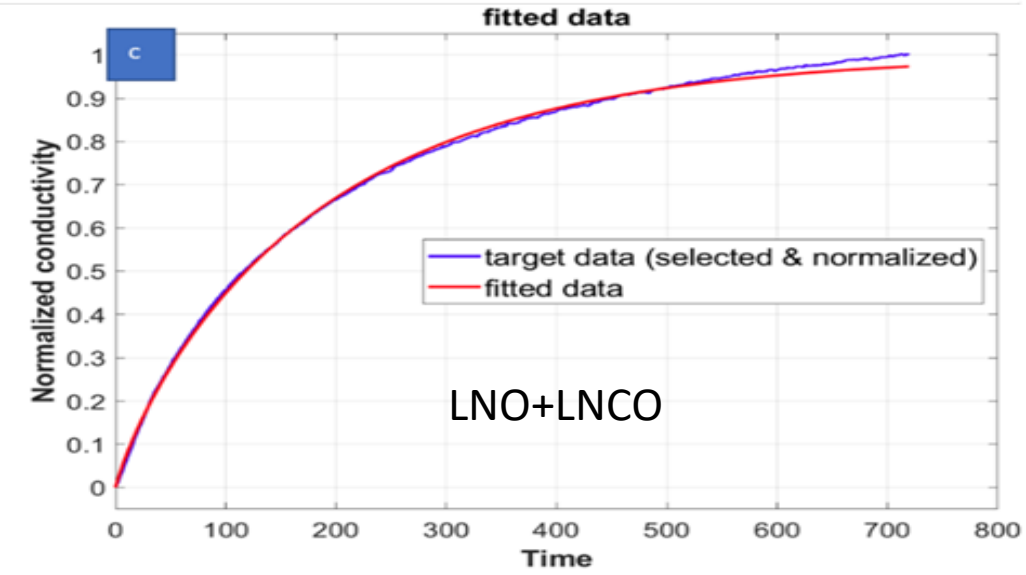

Pure phase achieved for each perovskite material at 800C

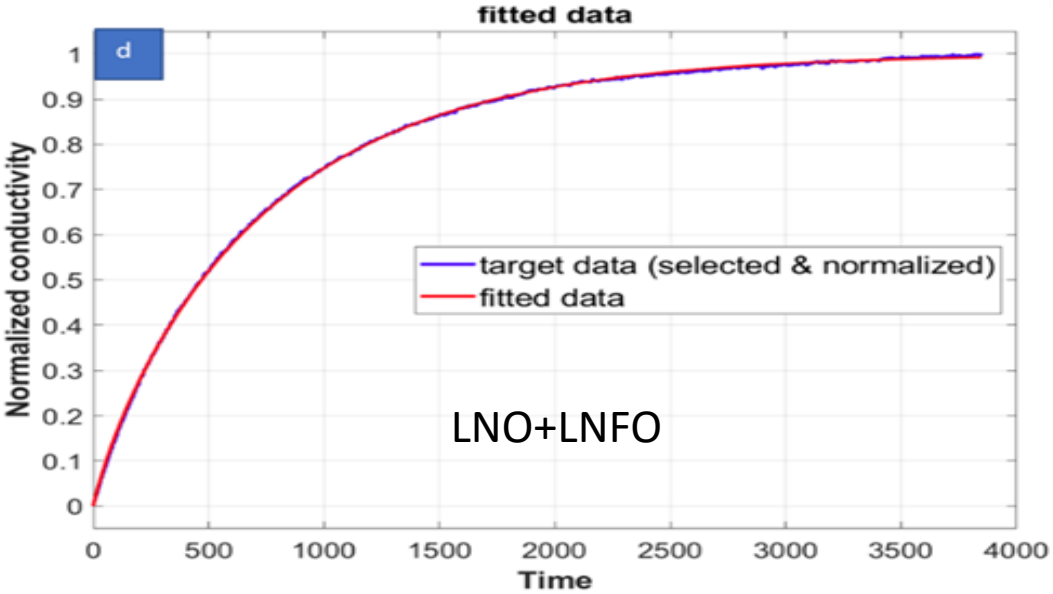
# Task 2: Experimental exploration and verification

Fittings for samples with Heat: for 0.8atm-1.0atm at 600°C



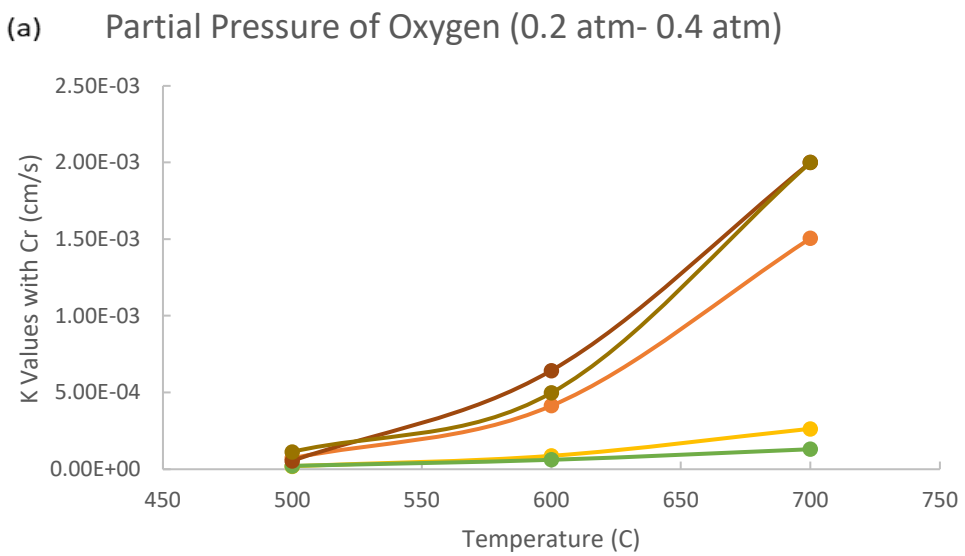



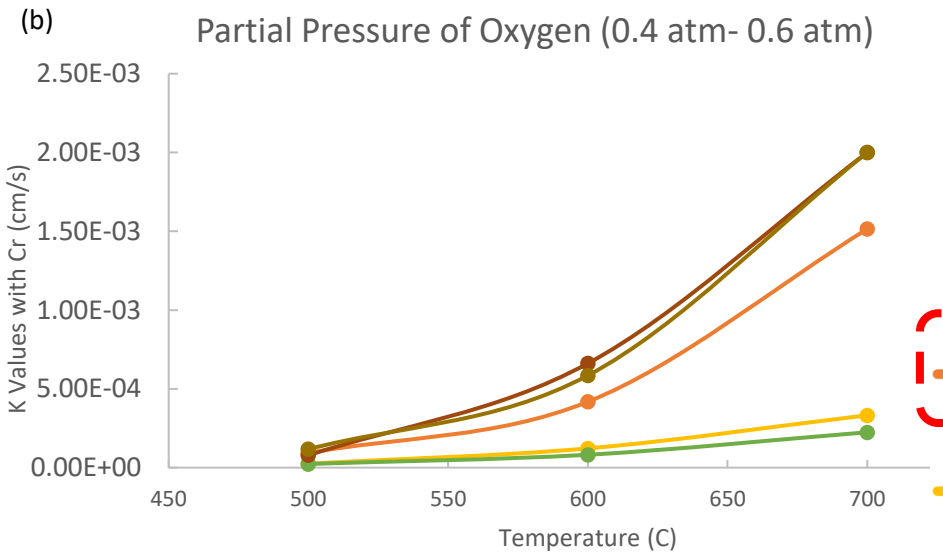



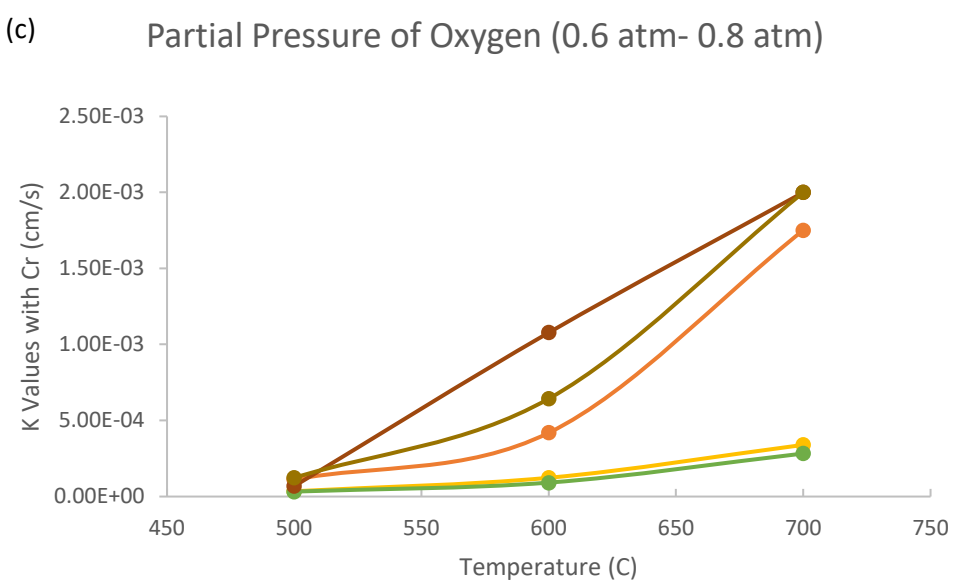



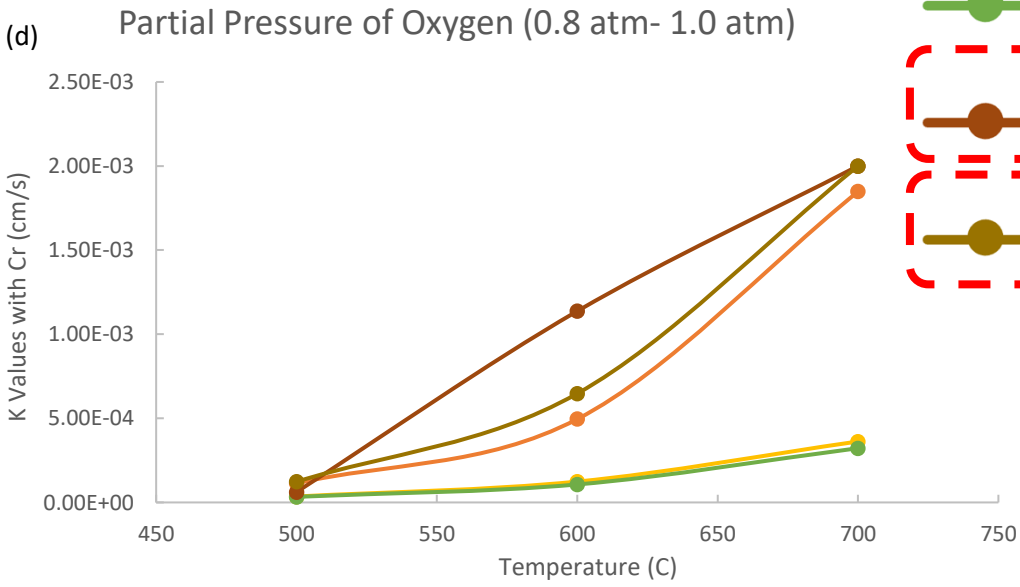
# Task 2: Experimental exploration and verification

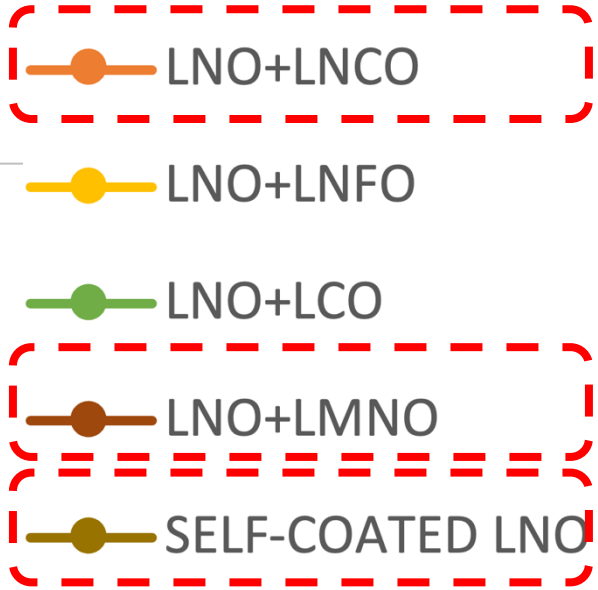
K-Values for samples **with Cr** at different Oxygen partial pressure and varying temperatures



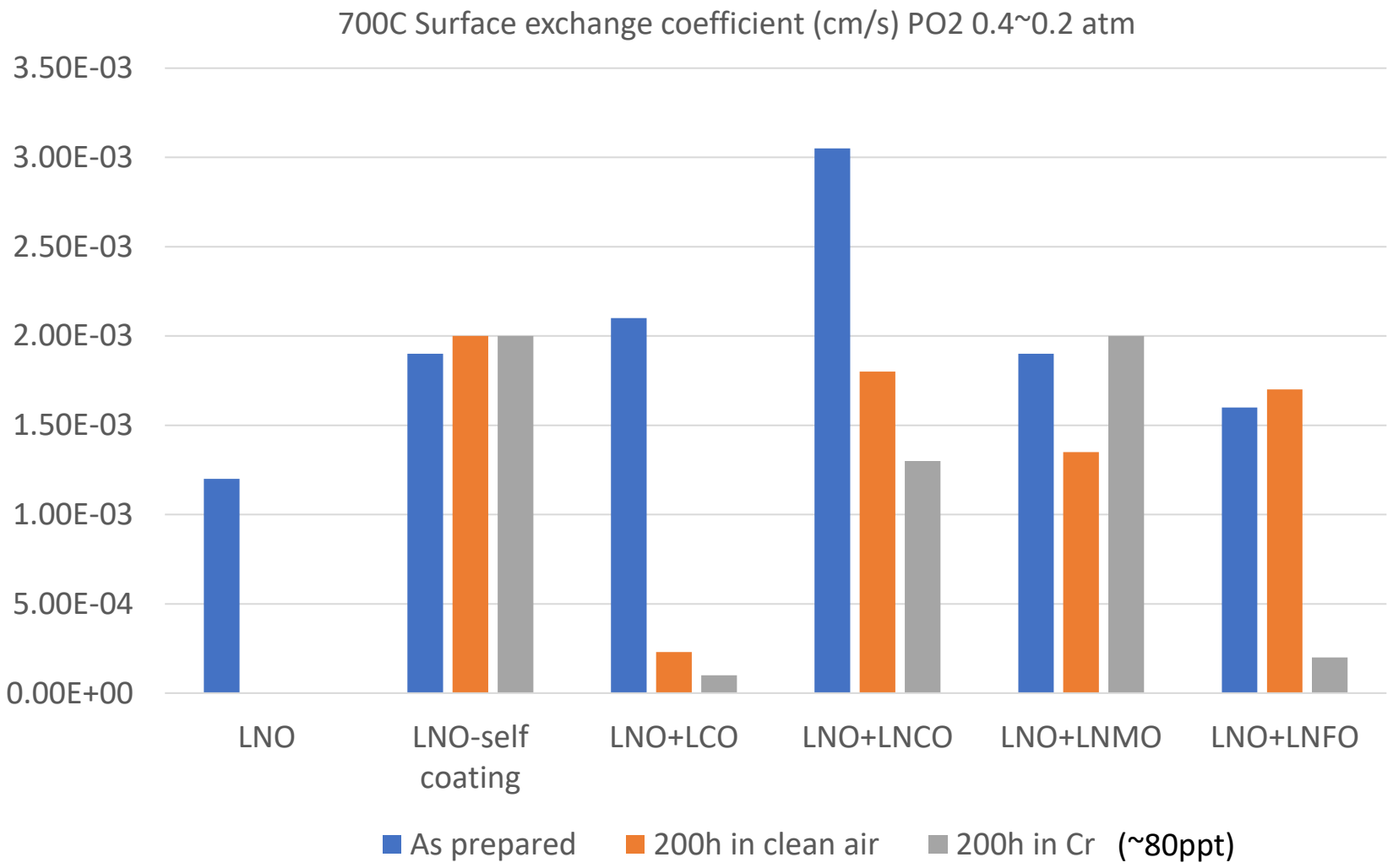



# Task 2: Experimental exploration and verification

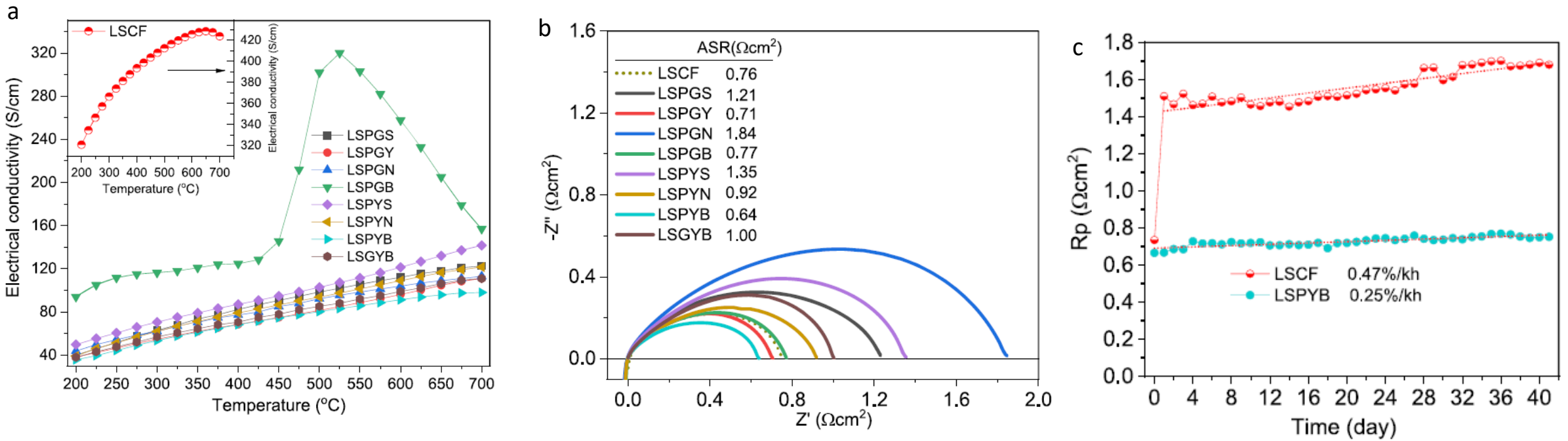



Initial high surface oxygen exchange, but largely lost to thermal treatment

# Task 2: Experimental exploration and verification

## High Entropy Perovskites (HEP) were explored

a: Electrical conductivities of HEP samples and LSCF; b: Polarization resistance of HEPs and LSCF cathodes measured in air at 700°C;
c: Long-term stability of HEP LSPYB and LSCF toward Cr poisoning




**High-Entropy Perovskite as a High-Performing Chromium-Tolerant Cathode for Solid Oxide Fuel Cells**

Zhongqiu Li, Bo Guan, Fang Xia, Jiuyuan Nie, Wenyuan Li, Liang Ma, Wei Li, Lingfeng Zhou, Yi Wang, Hanchen Tian, Jian Luo, Yan Chen, Matthew Frost, Ke An, and Xingbo Liu

LSPGS $(La_{0.2}Sr_{0.2}Pr_{0.2}Gd_{0.2}Sm_{0.2})(Co_{0.2}Fe_{0.8})O_3$ LSPYS $(La_{0.2}Sr_{0.2}Pr_{0.2}Y_{0.2}Sm_{0.2})(Co_{0.2}Fe_{0.8})O_3$

LSPGY $(La_{0.2}Sr_{0.2}Pr_{0.2}Gd_{0.2}Y_{0.2})(Co_{0.2}Fe_{0.8})O_3$ LSPYN $(La_{0.2}Sr_{0.2}Pr_{0.2}Y_{0.2}Nd_{0.2})(Co_{0.2}Fe_{0.8})O_3$

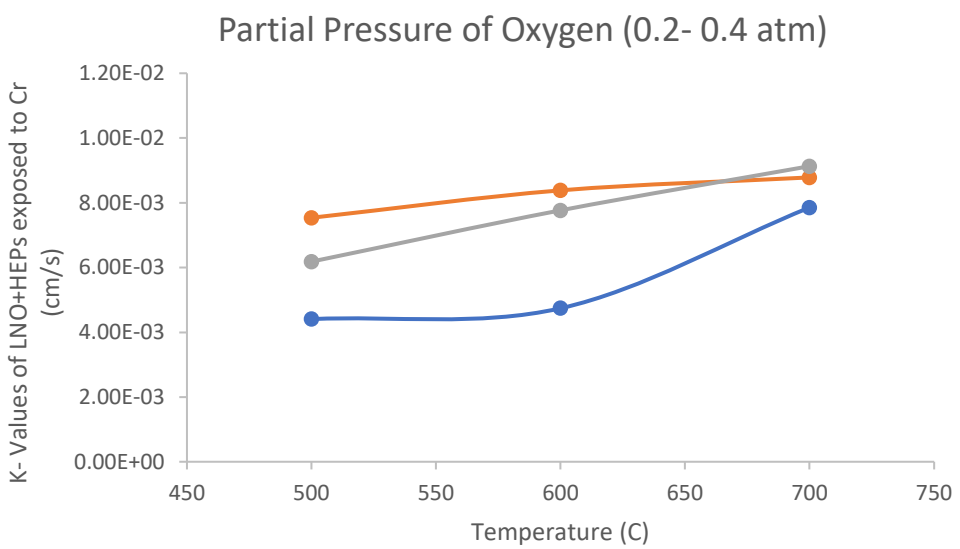
LSPGN $(La_{0.2}Sr_{0.2}Pr_{0.2}Gd_{0.2}Nd_{0.2})(Co_{0.2}Fe_{0.8})O_3$ LSPYB $(La_{0.2}Sr_{0.2}Pr_{0.2}Y_{0.2}Ba_{0.2})(Co_{0.2}Fe_{0.8})O_3$

LSPGB $(La_{0.2}Sr_{0.2}Pr_{0.2}Gd_{0.2}Ba_{0.2})(Co_{0.2}Fe_{0.8})O_3$ LSGYB $(La_{0.2}Sr_{0.2}Gd_{0.2}Y_{0.2}Ba_{0.2})(Co_{0.2}Fe_{0.8})O_3$

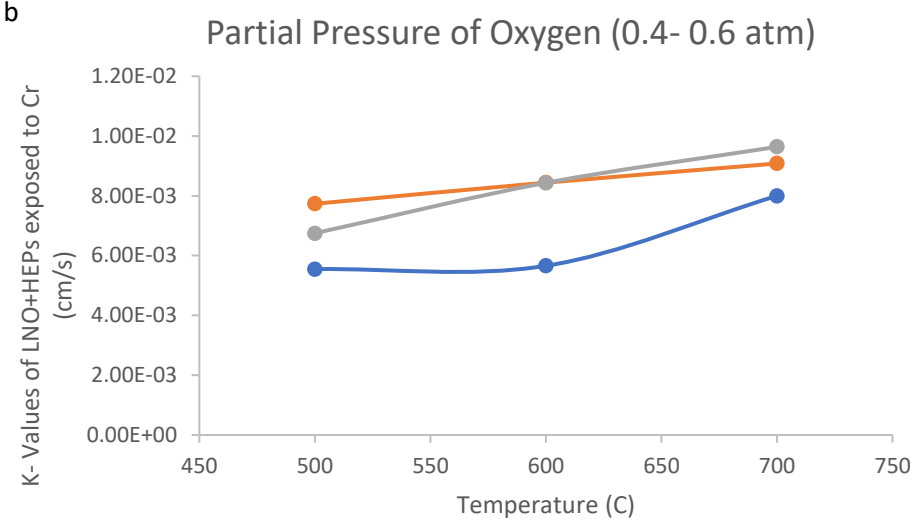
# Task 2: Experimental exploration and verification

K-Values for samples **with Cr** at different Oxygen partial pressure and varying temperatures

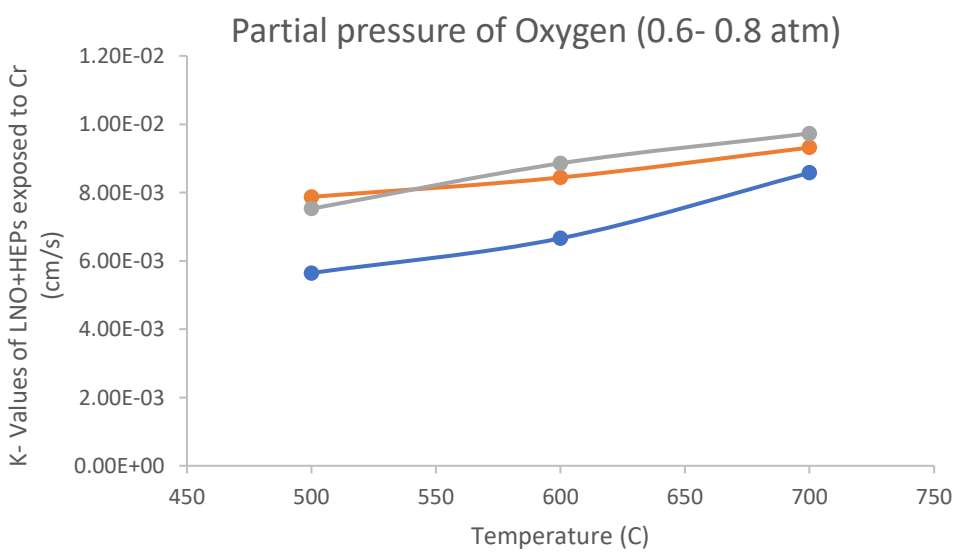
a




b




c

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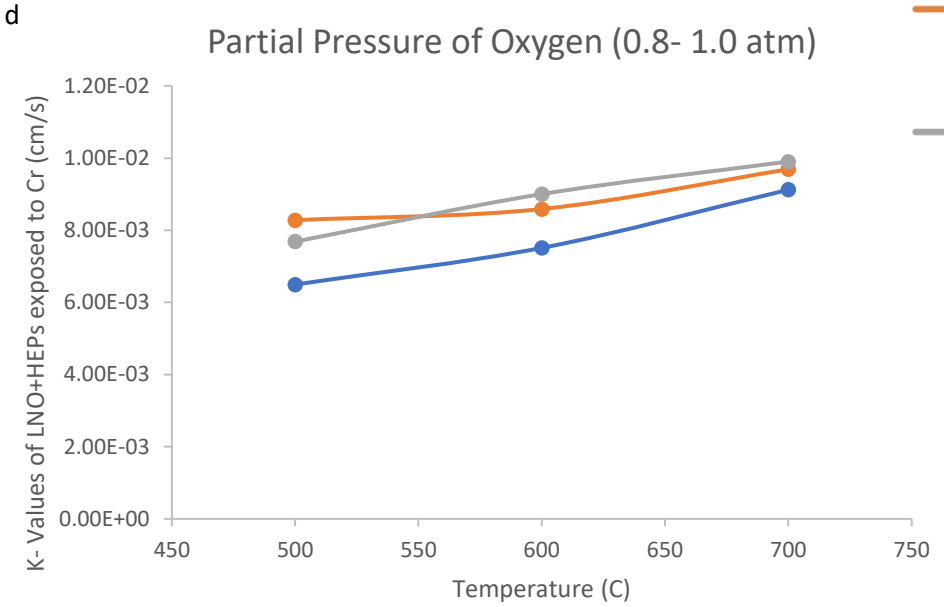
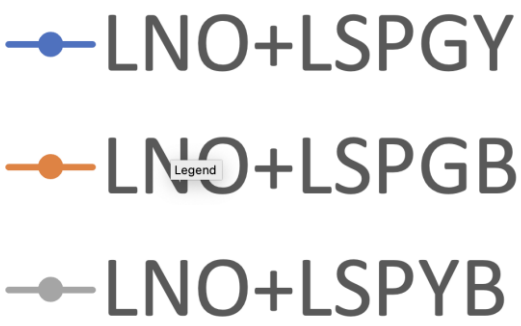
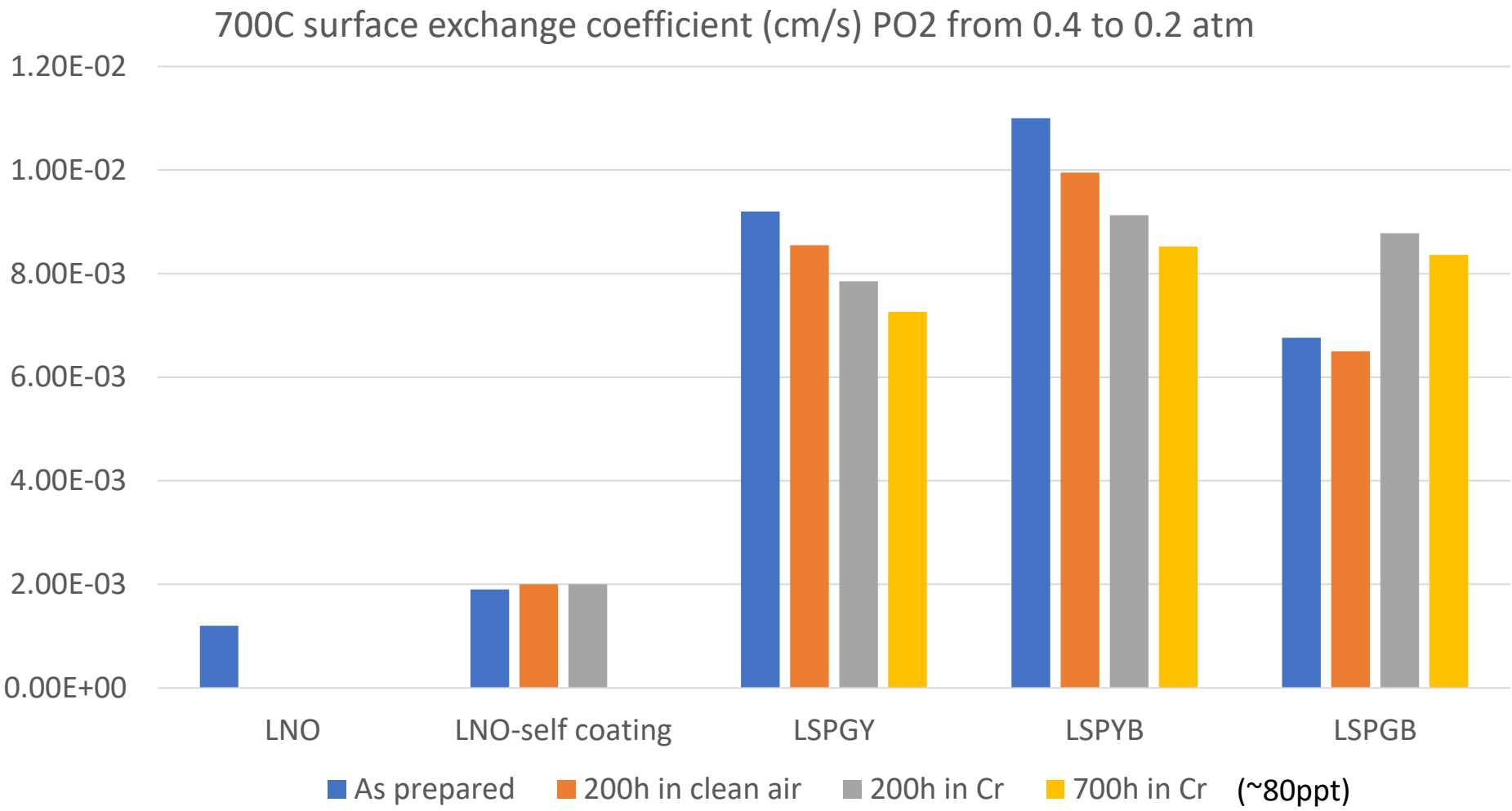


# Task 2: Experimental exploration and verification




Abrupt enhancement upon surface exchange by HEP coating
Better resistance to heat and Cr

# Task 2: Experimental exploration and verification

## Summary:

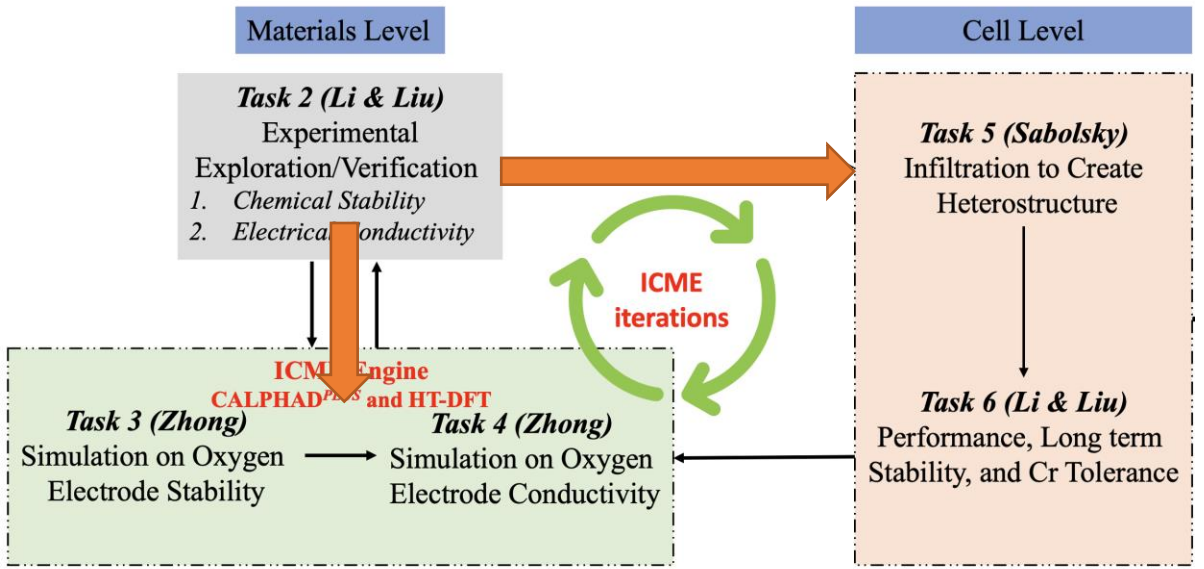
The experiments were carried out between LNO(r-p phase) and various HEP.

ECR tests were carried out in the following three conditions:

- After doping (coating as is)
- After heat treatment (aged at 700C for 200h)
- After exposure to Cr (exposed to Cr source at 700C for 200h)

The following candidates worth the Further Investigation

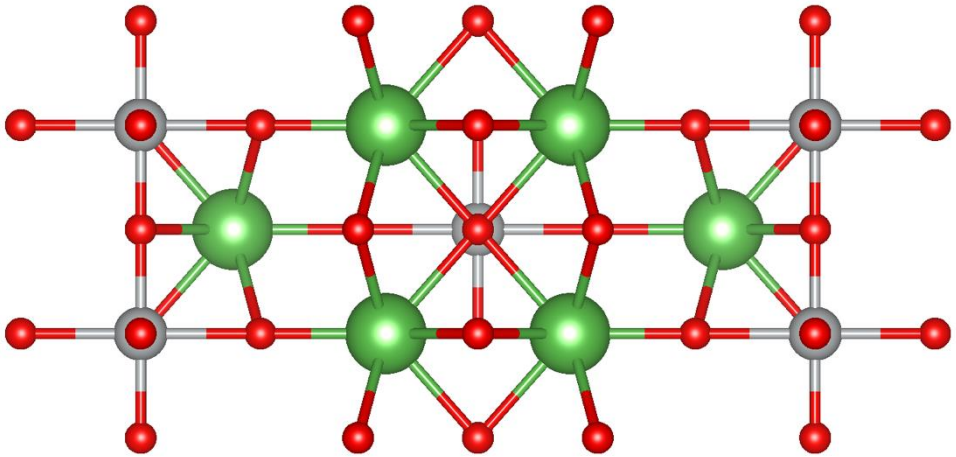
- LSPYB
- LSPGB



# Task 3. Simulation on Oxygen Electrode Stabilities

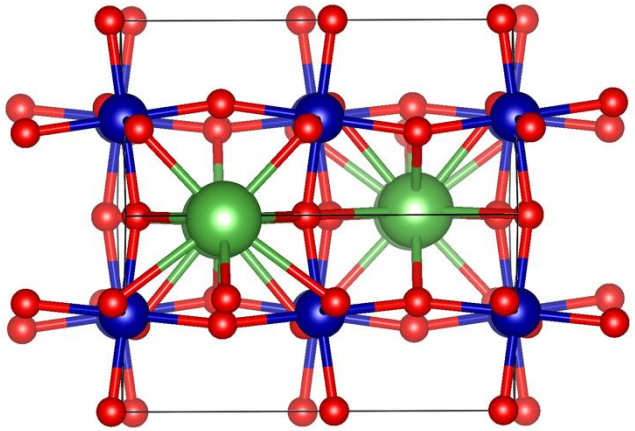
- Interfacial stability of LNO/LCO heterostructure interface

$La_2NiO_4$



R-p phase

$LaCoO_3$



Perovskite

Interfacial Energy

$$\gamma_{A/B} = (N_{\text{int}}E_{A/B} - (N_A E_A + N_B E_B))/2A$$

$N_{\text{int}}$: The number of atoms for the interfacial structure

$N_A$: The number of atoms for phase A in the interfacial structure

$N_B$: The number of atoms for phase B in the interfacial structure

$A$: The area of the interface

# Task 3. Simulation on Oxygen Electrode Stabilities

## *Interface Generation*

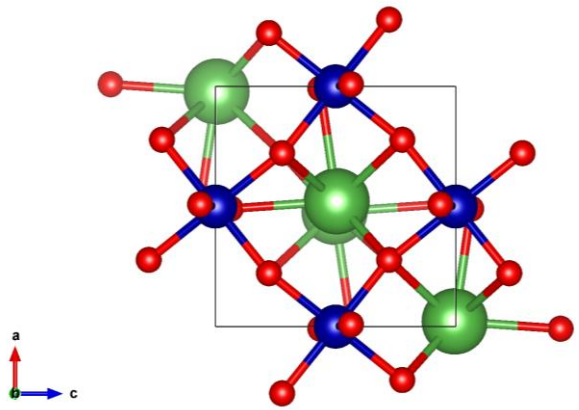
**Lattice Matching**

Vector mismatch (%) = 0.192574046

Angle mismatch (°) = 0.000000000

Area mismatch (%) = 1.002102329

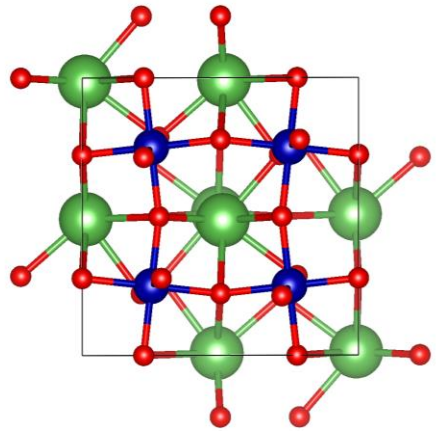
LCO



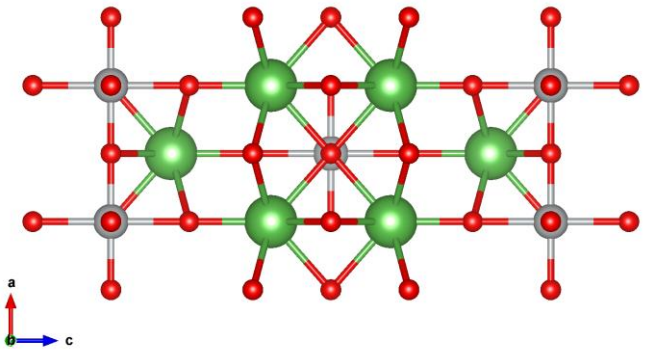
Transmat 1

| $a$ | $b$ | $c$ |
|---|---|---|
| $-1$ | 0 | 1 |
| 0 | 1 | 0 |
| 1 | 0 | 1 |

$LCO_{Trans}$



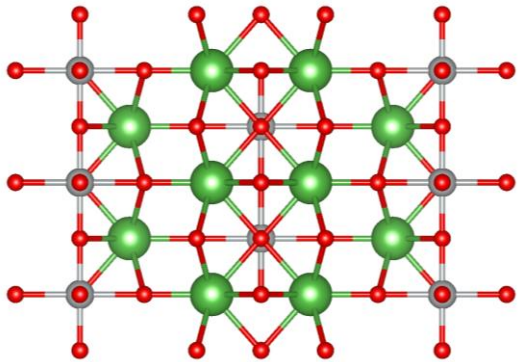
LNO



Transmat 2

| $a$ | $b$ | $c$ |
|---|---|---|
| 0 | 2 | 0 |
| 2 | 0 | 0 |
| 0 | 0 | 1 |

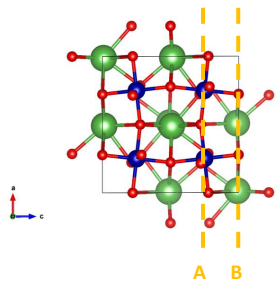
$LNO_{Trans}$



# Task 3. Simulation on Oxygen Electrode Stabilities

## *Interface Generation*

$LCO_{Trans}$



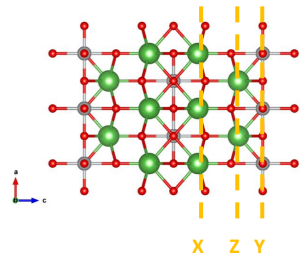

Surface Termination

$LCO_{(001)} = 2$

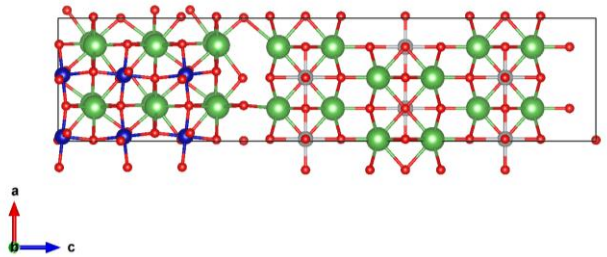
$LNO_{(001)} = 3$

Total = $LCO_{(001)} * LNO_{(001)} = 6$

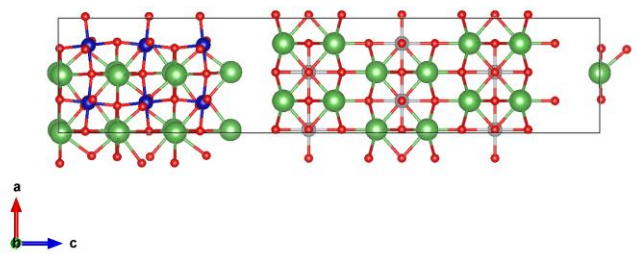
$LNO_{Trans}$



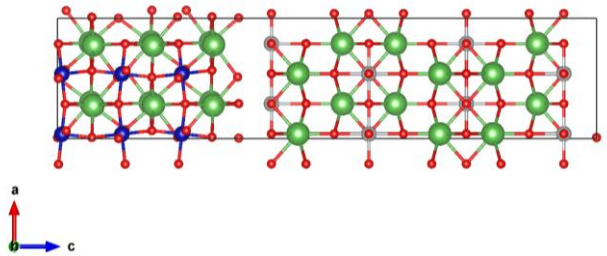

[A-X] Interface #1



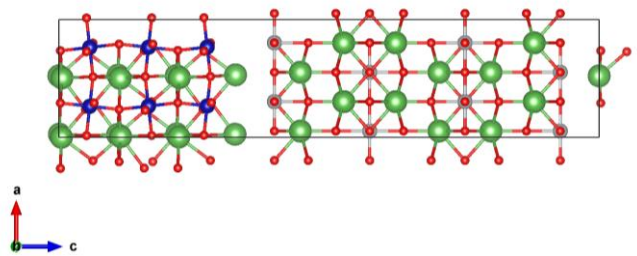
[B-X] Interface #4



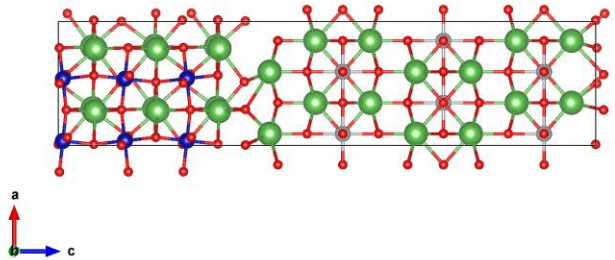
[A-Y] Interface #2



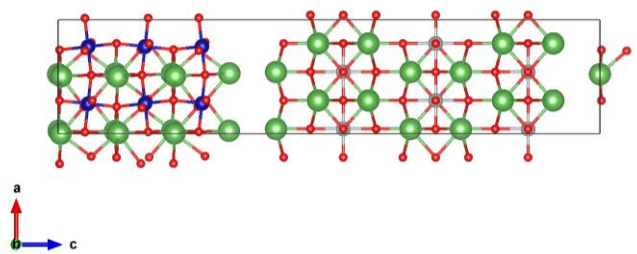
[B-Y] Interface #5



[A-Z] Interface #3



[B-Z] Interface #6



# Task 3. Simulation on Oxygen Electrode Stabilities

## *Interface Generation*

Interface Manipulation

Interface shift (a,b,c),(%,%,Å)

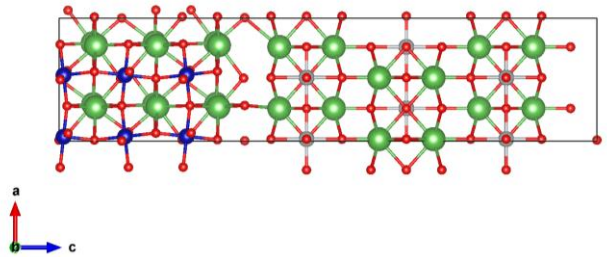
#1-1 (0.105263,0.039474,1.650000)

#1-2 (0.092105,0.039474,1.650000)

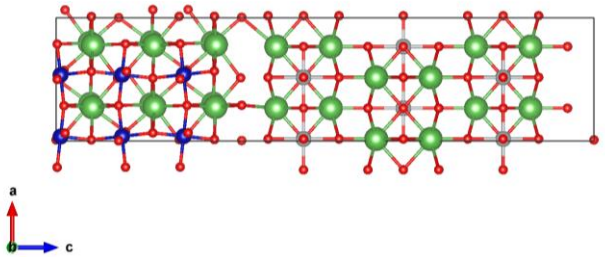
#1-3 (0.092105,0.039474,1.500000)

#1-4 (0.605263,0.039474,1.650000)

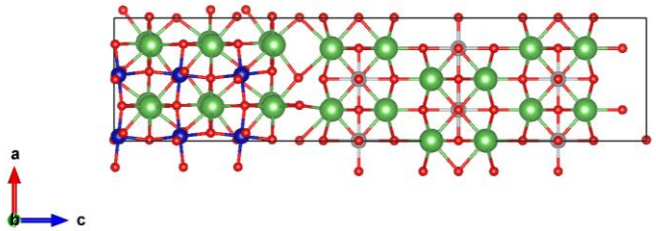
[A-X] Interface #1



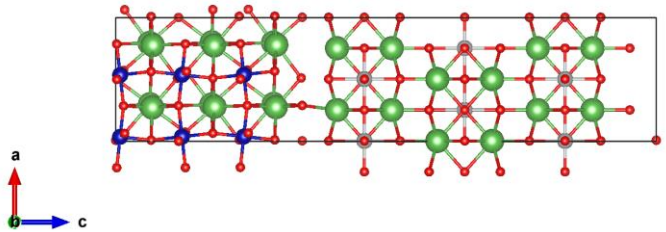

Interface #1-1



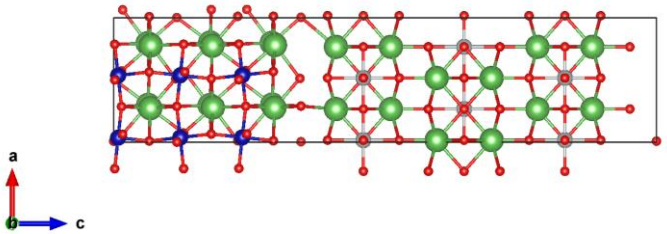

Interface #1-3




Interface #1-2

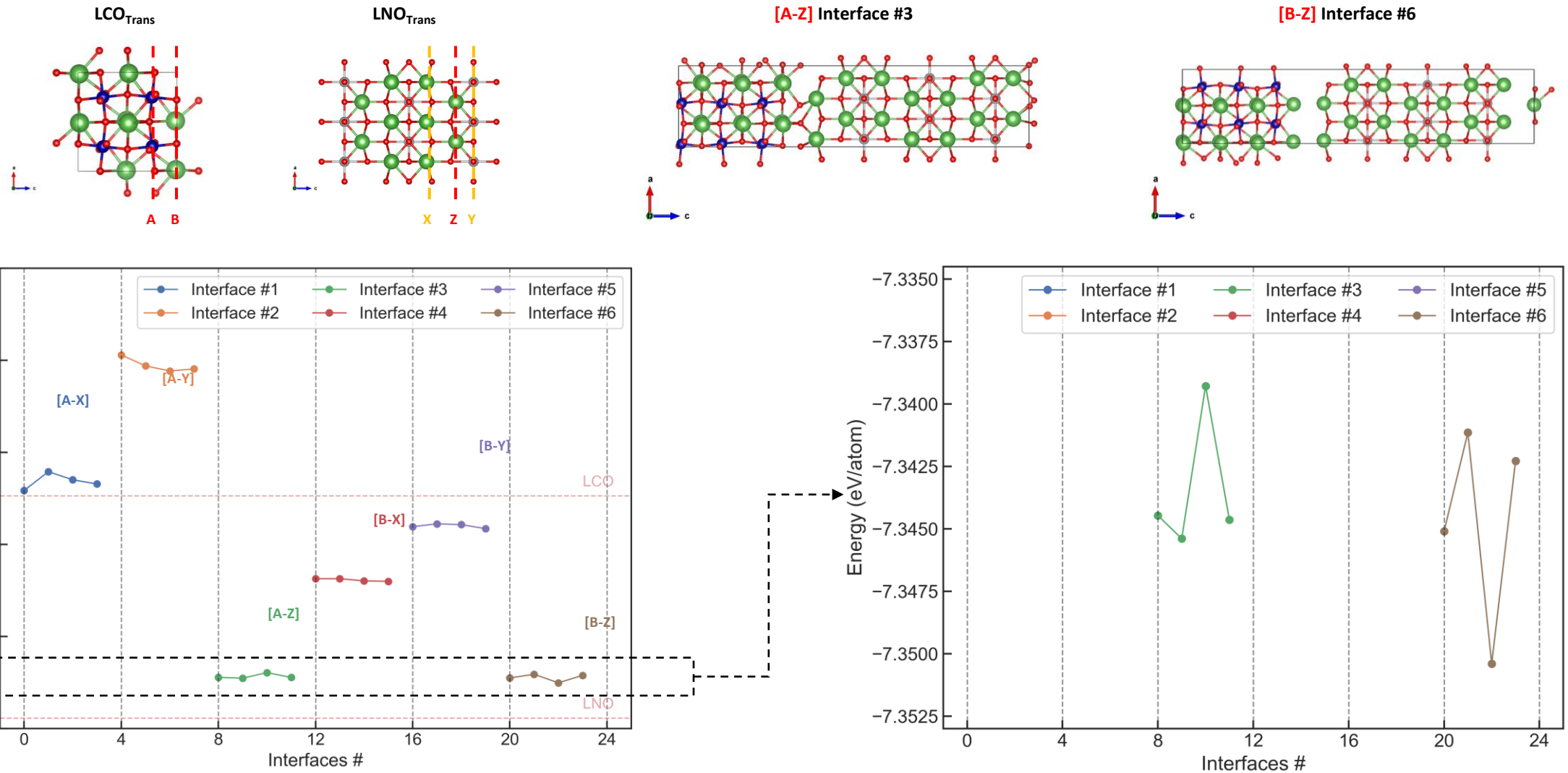



Interface #1-4



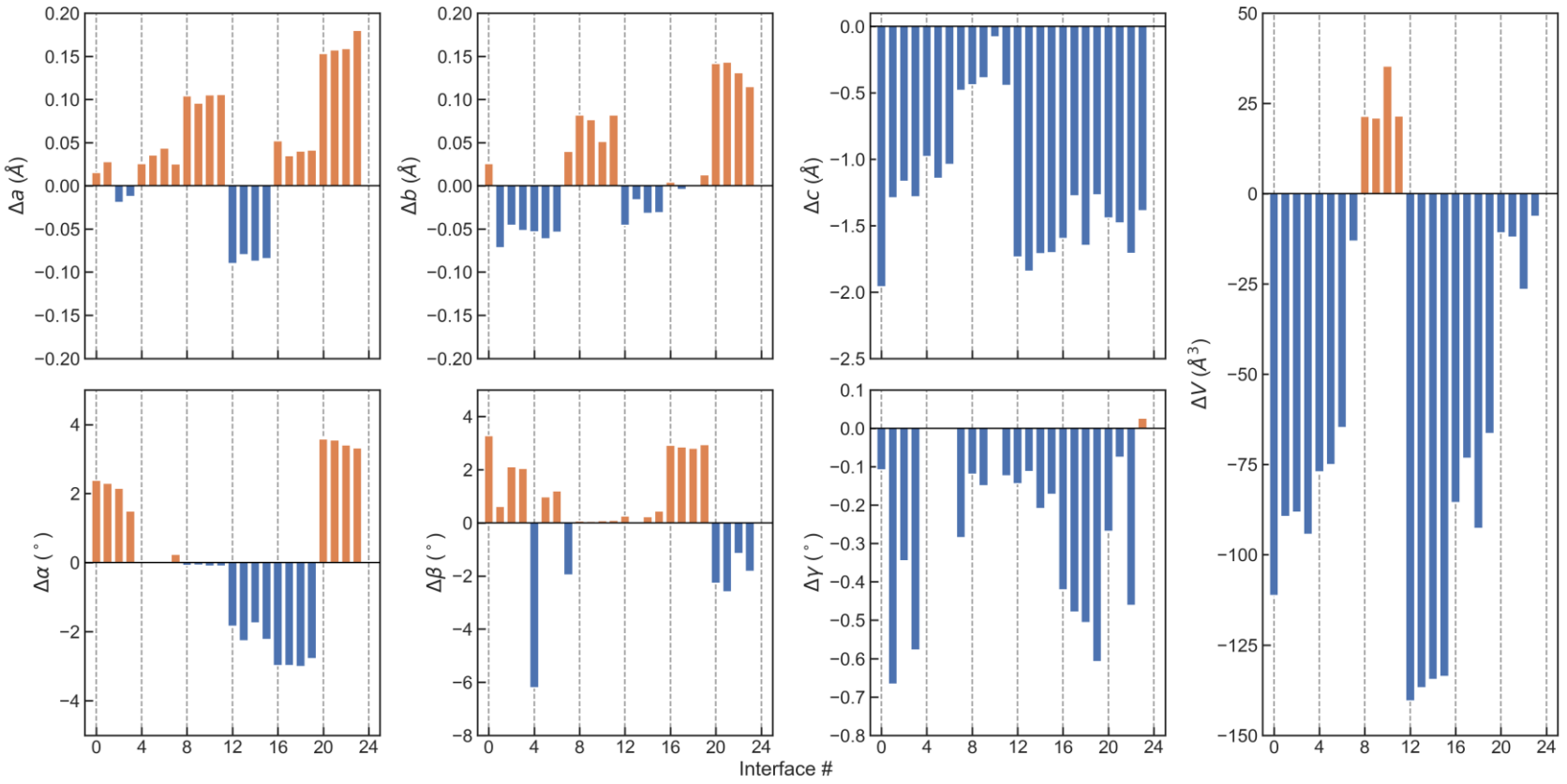
# Task 3. Simulation on Oxygen Electrode Stabilities

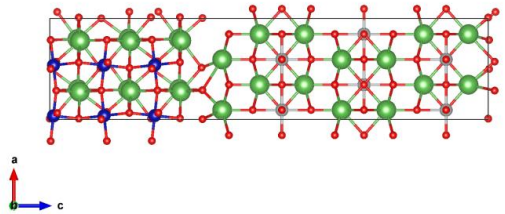
## *Interface Stability*



# Task 3. Simulation on Oxygen Electrode Stabilities

## *Interface Structure: Lattice Parameters & Volume*

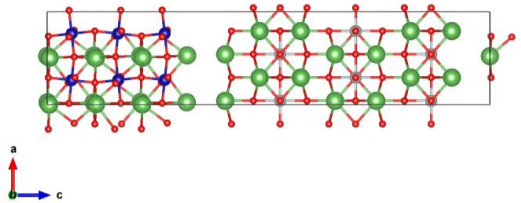


[A-Z] Interface #3

**Preferred lattice parameters**

a ↑ b ↑ c ↓
α - β - γ ↓
Final volume ↑

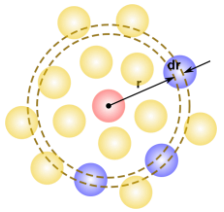


[B-Z] Interface #6

**Preferred lattice parameters**

a ↑ b ↑ c ↓
α ↑ β ↓ γ ↓
Final volume ↓

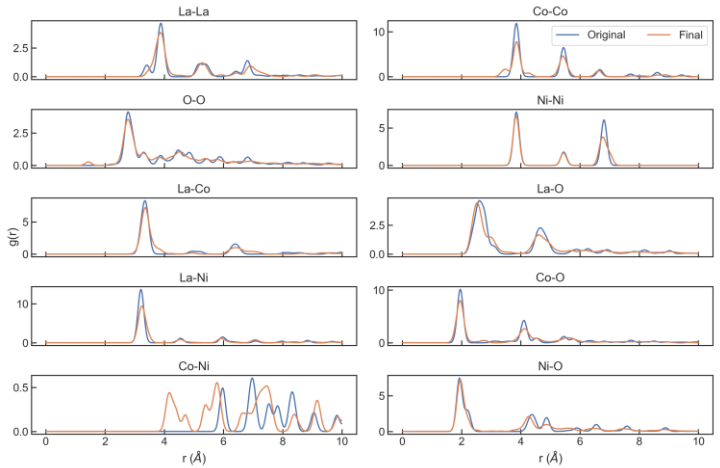
# Task 3. Simulation on Oxygen Electrode Stabilities



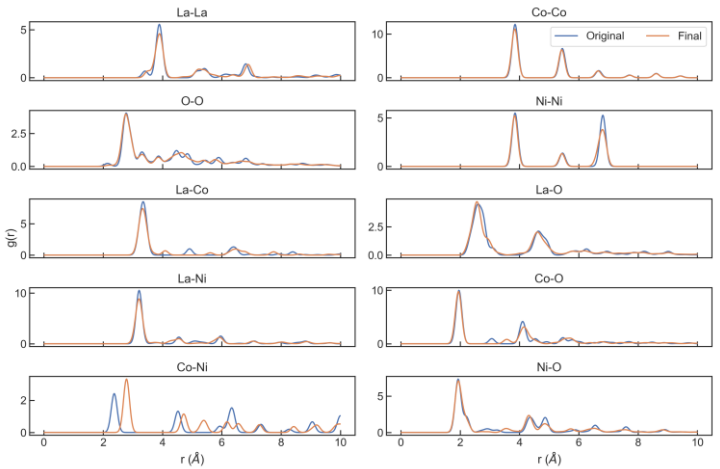

## *Interface Structure: Coordination Environment*

*Radial Distribution Function (RDF)*

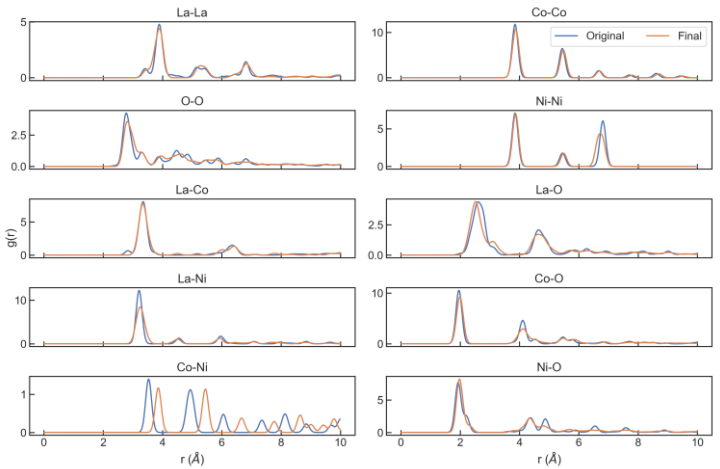
**[A-X] Interface #1**



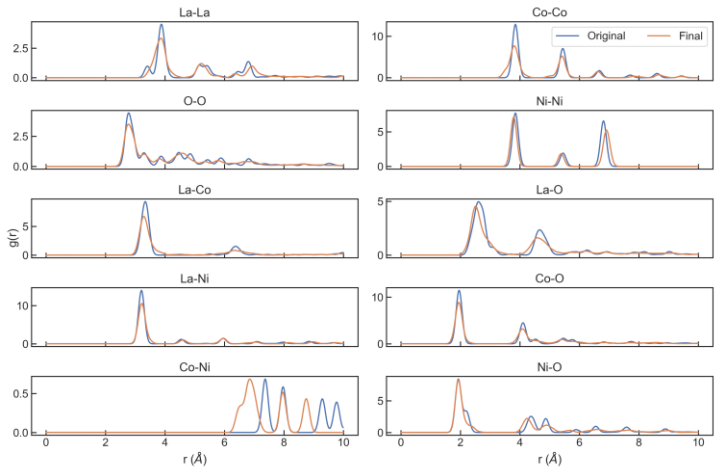

**[A-Y] Interface #2**



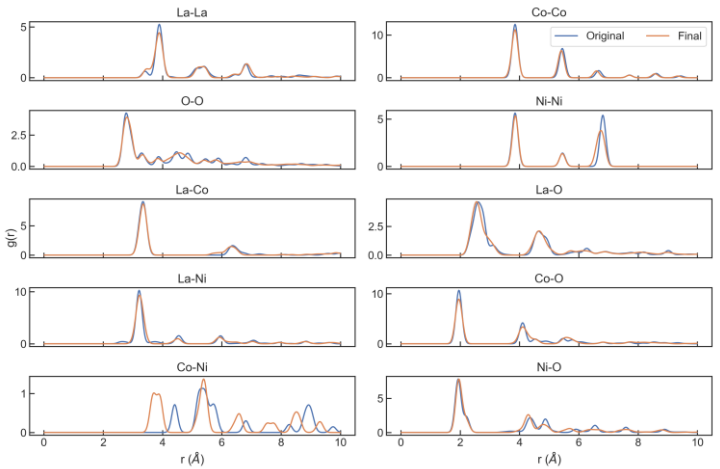

**[A-Z] Interface #3**



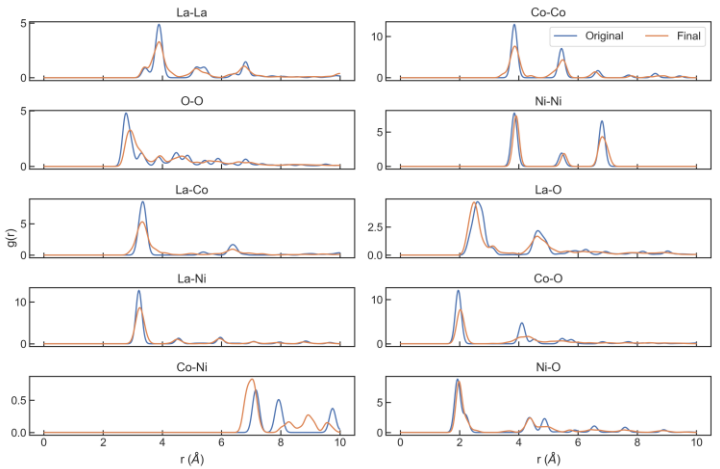

**[B-X] Interface #4**




**[B-Y] Interface #5**



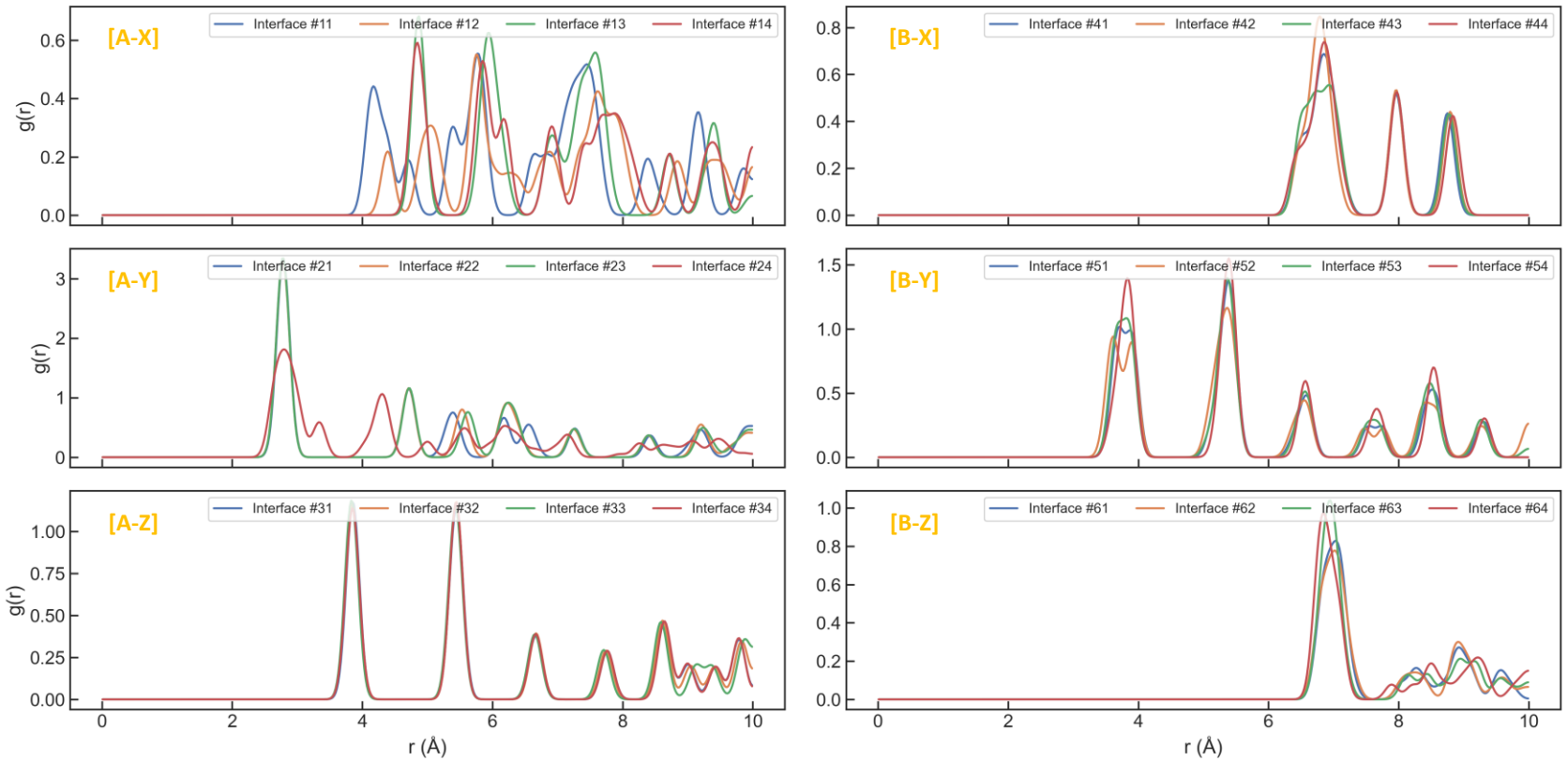

**[B-Z] Interface #6**



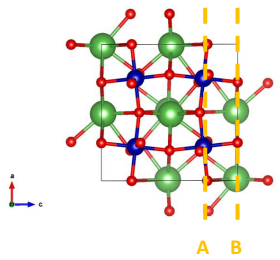
# Task 3. Simulation on Oxygen Electrode Stabilities

## *Interface Structure: Co-Ni Pairs*

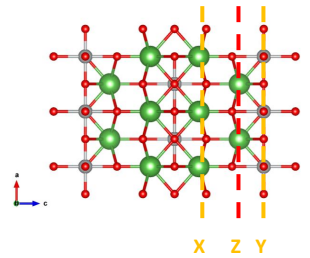
*Radial Distribution Function (RDF)*




$LCO_{Trans}$




$LNO_{Trans}$




Co-Ni Pairs Length ↑

↓

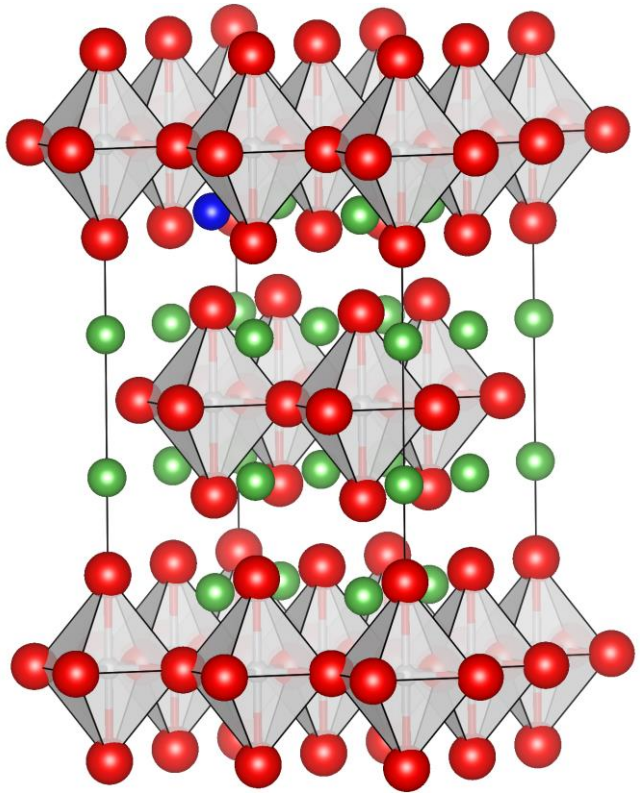
Interface Energy ↓

↓

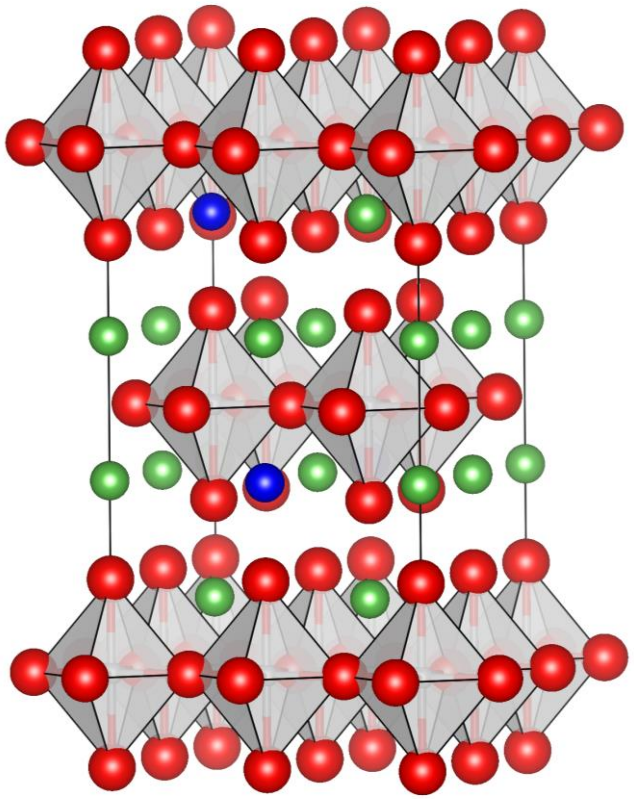
Interface Stability ↑

# Task 3. Simulation on Oxygen Electrode Stabilities

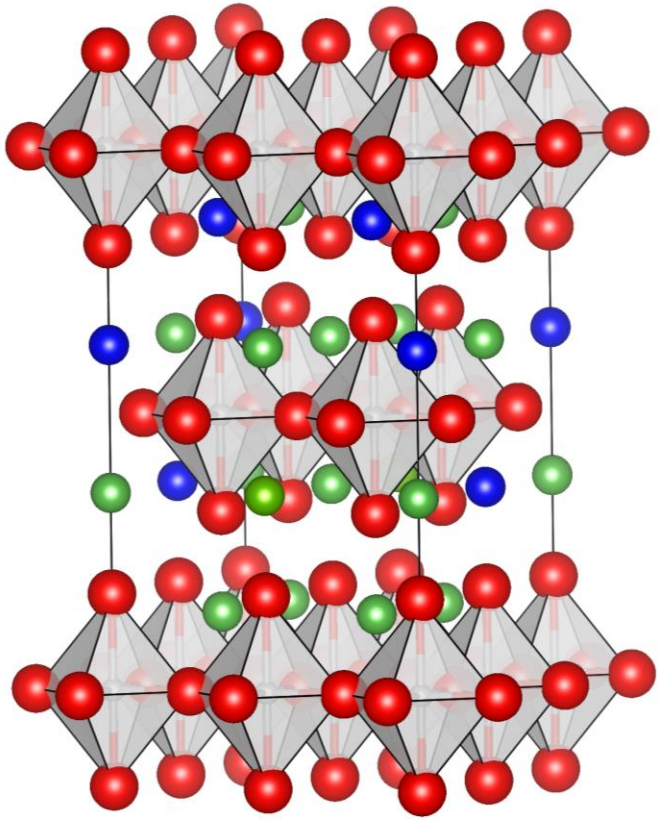
## Selected 56-atom supercells for the modeling (SQS)



6.25% Dopants A (Ca, Sr, Ba)

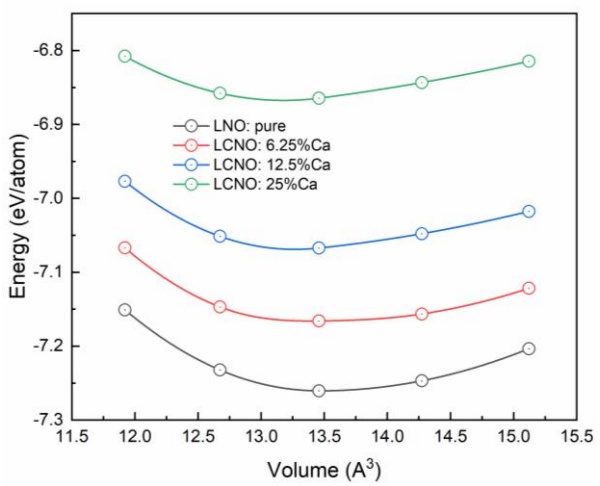


12.5% Dopants A (Ca, Sr, Ba)

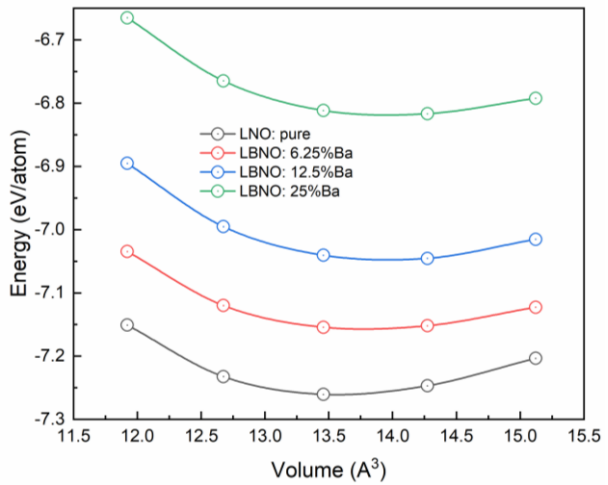


25% Dopants A (Ca, Sr, Ba)

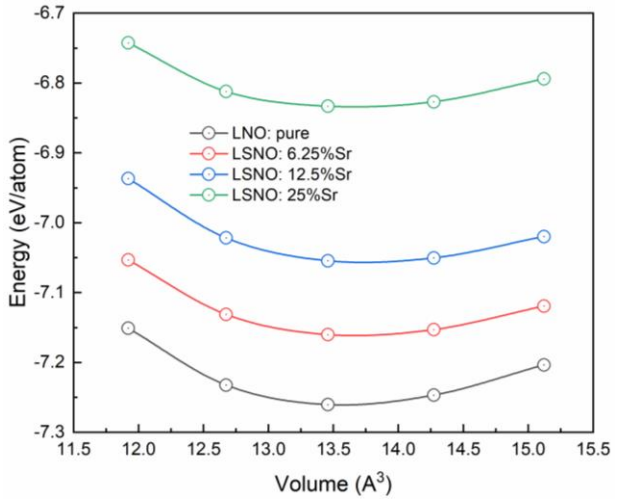
# Task 3. Simulation on Oxygen Electrode Stabilities



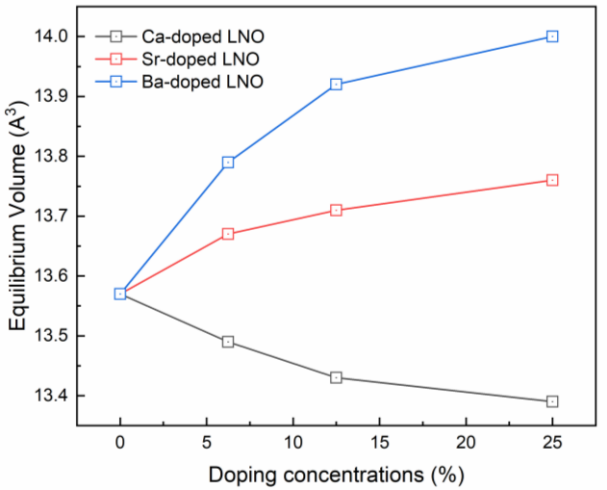

Ca-doped LNO




Ba-doped LNO



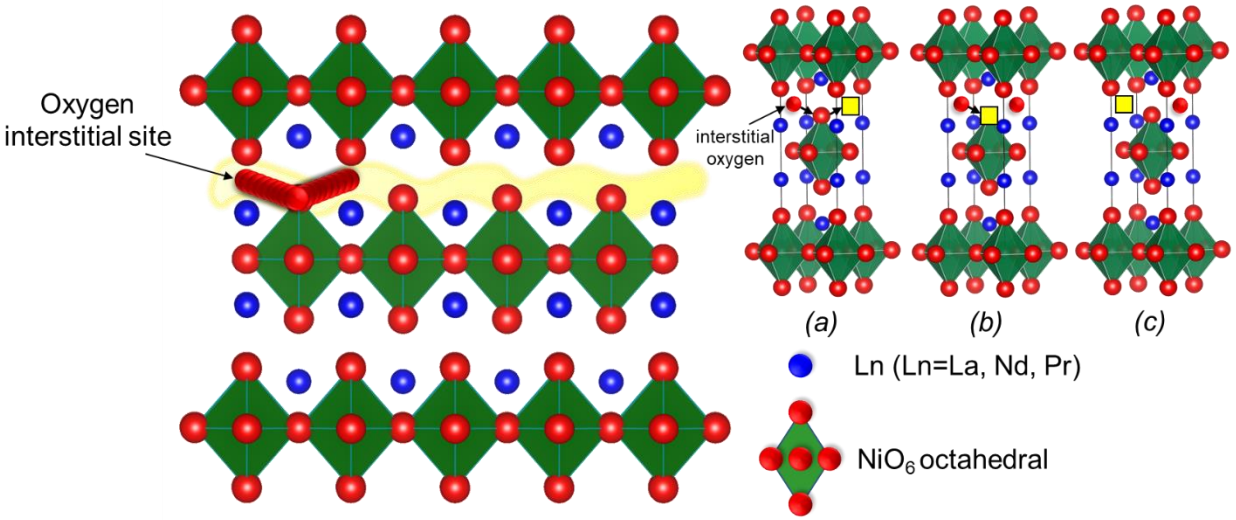

Sr-doped LNO

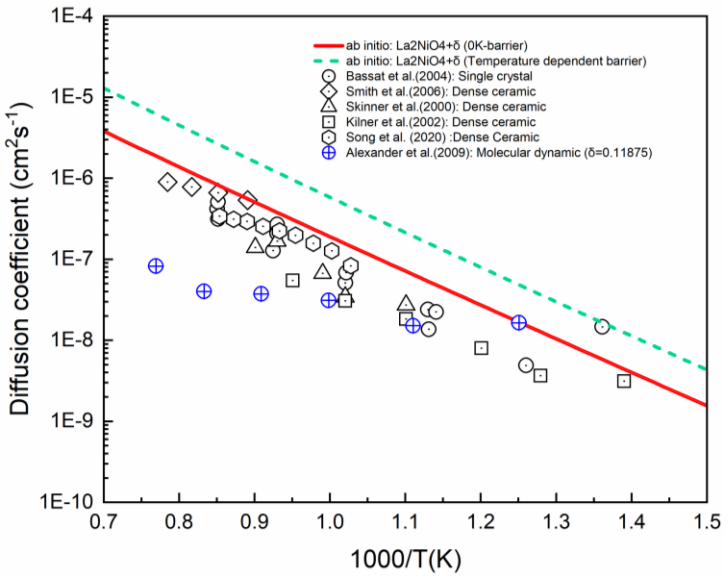


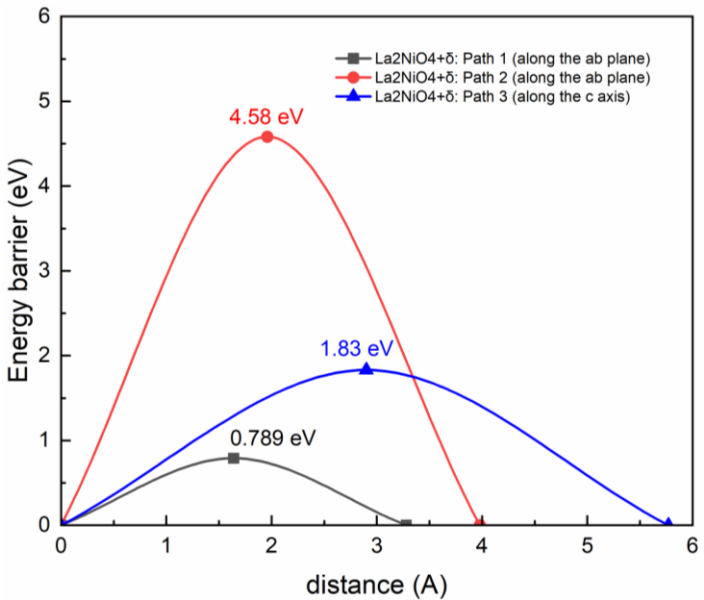

The volume of LNO decreases with an increase in Ca doping concentration, whereas it increases with the increasing concentration of Sr and Ba

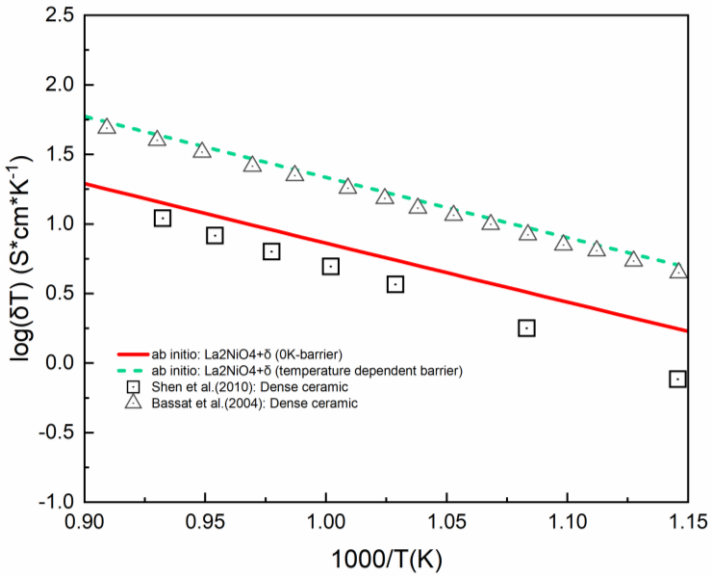
# Task 4 Simulations on the Oxygen Electrode Conductivity

## NEB approach



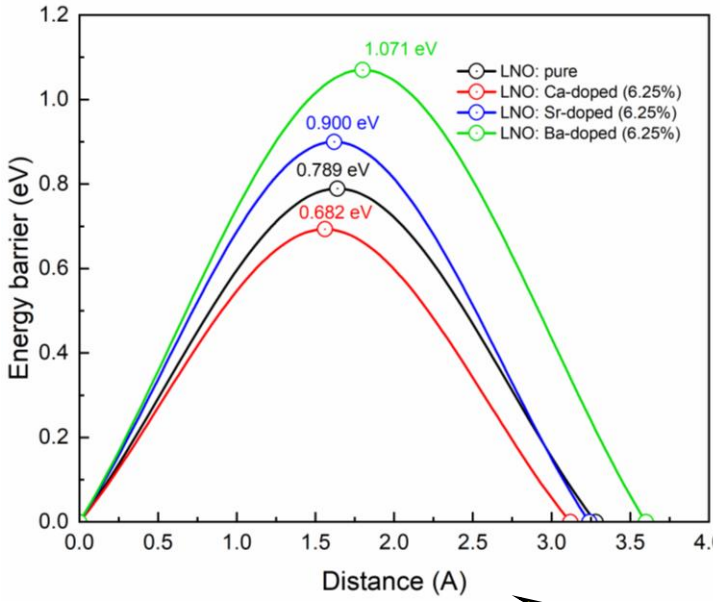



# Task 4 Simulations on the Oxygen Electrode Conductivity

## The diffusion and ionic conductivity of LNO with different dopants



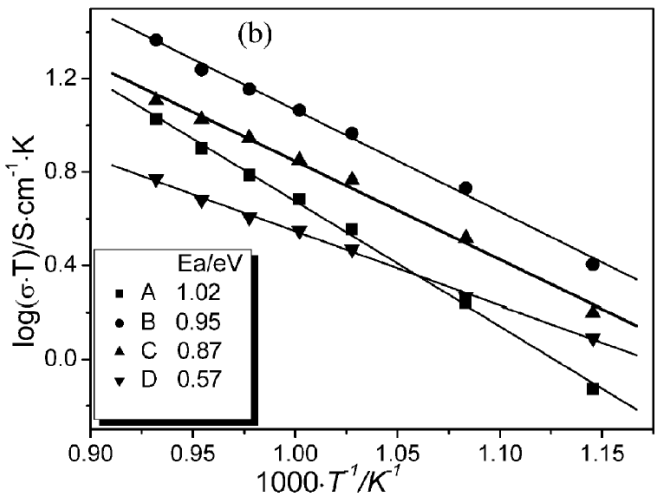




**Fig. 8** Ionic conductivity of $La_{2-x}Ca_xNiO_{4+\delta}$ ceramics as functions of temperature and Ca-doping level: (A) $x = 0.0$; (B) $x = 0.1$; (C) $x = 0.2$; (D) $x = 0.3$.

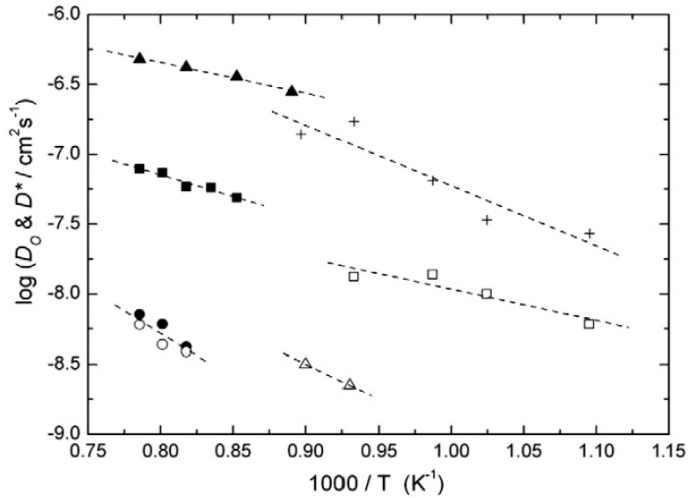


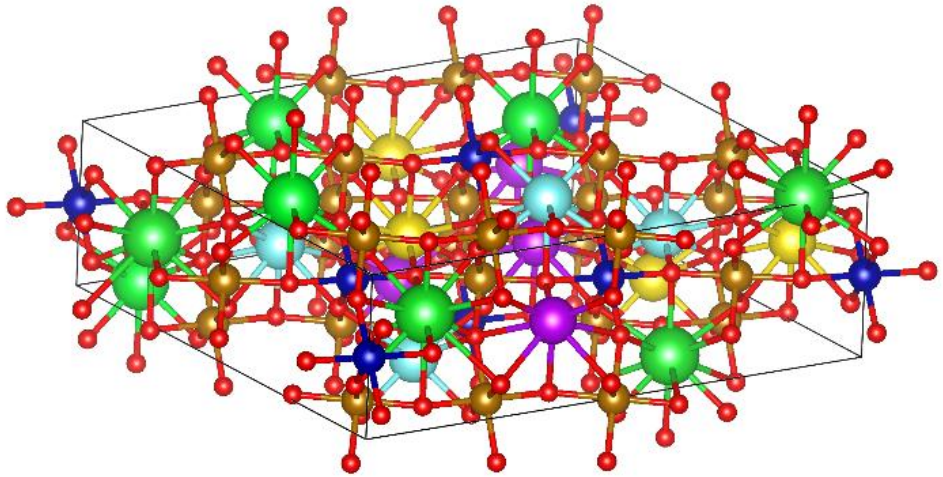

**Fig. 3.** Comparison of oxide ion self diffusion coefficient with tracer diffusion coefficient. $La_2NiO_{4+\delta}$ – [2] ($pO_2 = 1$ atm, ▲), $La_2NiO_{4+\delta}$ – [3] ($pO_2 = 1$ atm, +), $La_{1.9}Sr_{0.1}NiO_{4+\delta}$ – this work ($pO_2 = 0.21$ atm, ■), $La_{1.9}Sr_{0.1}NiO_{4+\delta}$ – [3] ($pO_2 = 1$ atm, □), $La_{1.8}Sr_{0.2}NiO_{4+\delta}$ – this work ($pO_2 = 0.21$ atm, ● and ○), and $La_{1.8}Sr_{0.2}NiO_{4+\delta}$ – [4] ($pO_2 = 1$ atm, Δ). The dashed lines are linear fitted curves based on the experimental data of each composition.

- The doping of Ca reduces the activation energy barrier, whereas the doping of Ba and Sr increases the barrier. This is because the Ca has a much smaller ionic radius.

- According to the experimental data, the doping of Ca will increase the ionic conductivity, whereas the doping of Sr will reduce the ionic conductivity.

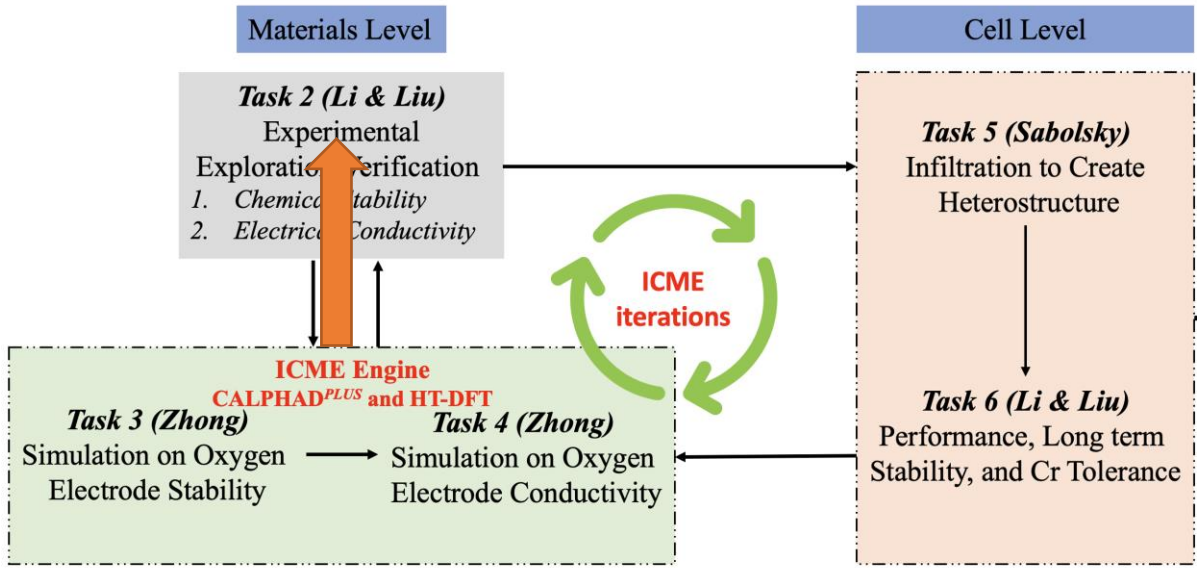
# Summaries of Task 3 and Task 4

- The LNO-LCO interface was constructed
- Ca is considered a good dopant for LNO due to its smaller ionic radius




**The following items will be explored**

- the ionic conductivity of doped LNO.
- Develop the doped LNO conductivity map
- Explore the HEP proposed by Task 2
  - LSPYB
  - LSPGB



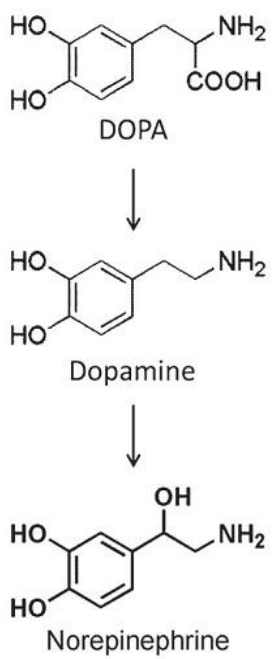
# Task 5: Fabrication and operational evaluation of electrode with heterostructured surface

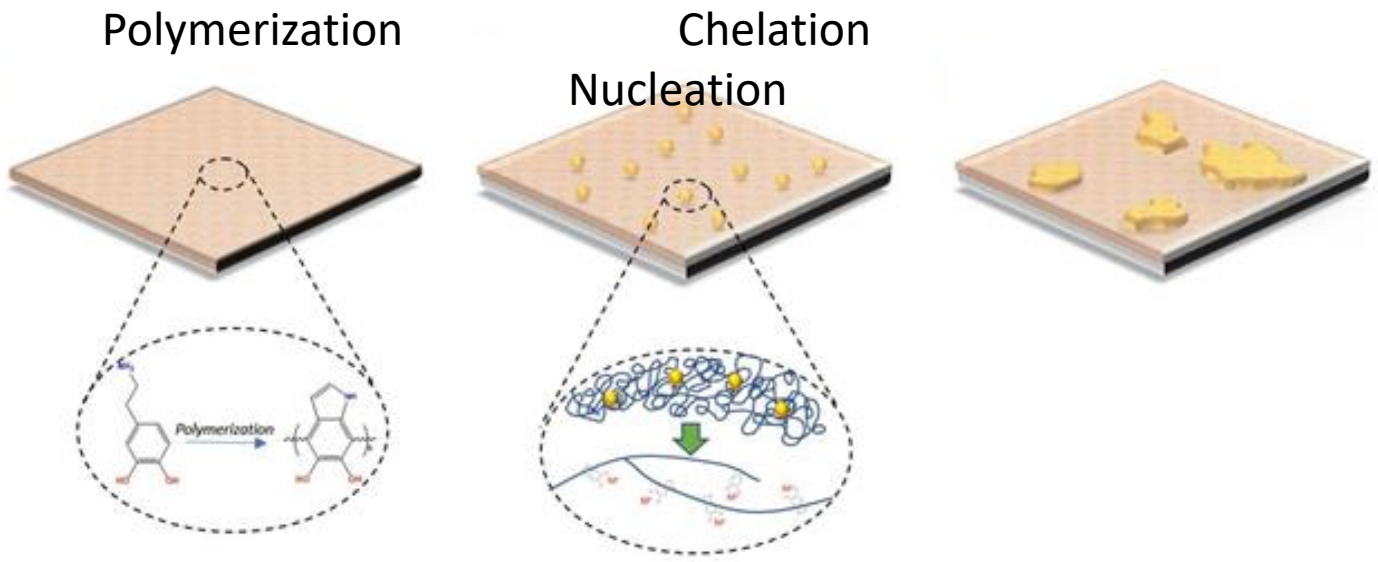
## ***Process Review:*** *Wet-Impregnation of Nano-Catalyst for SOFCs/SOECs*

**Objective:** to deposit full phase, $LaCoO_3$ (and similar) nano-catalyst via controlled deposition throughout a porous structure of the 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.*

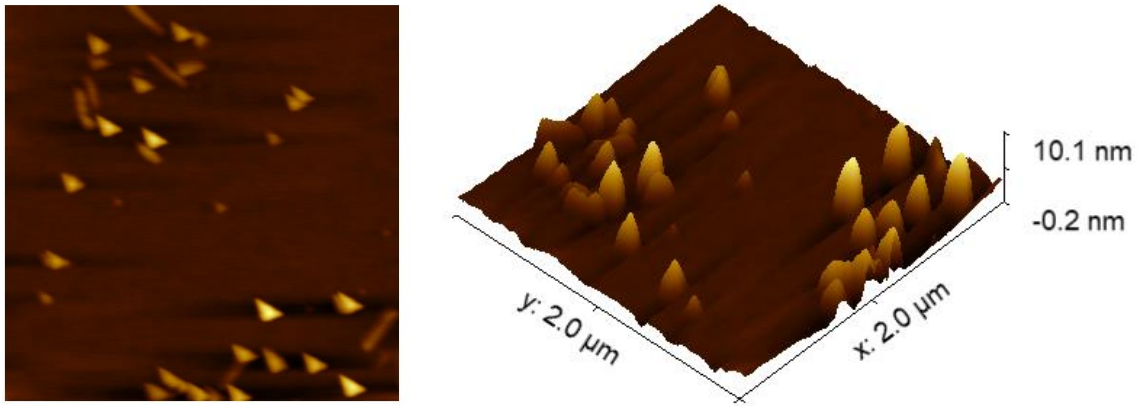


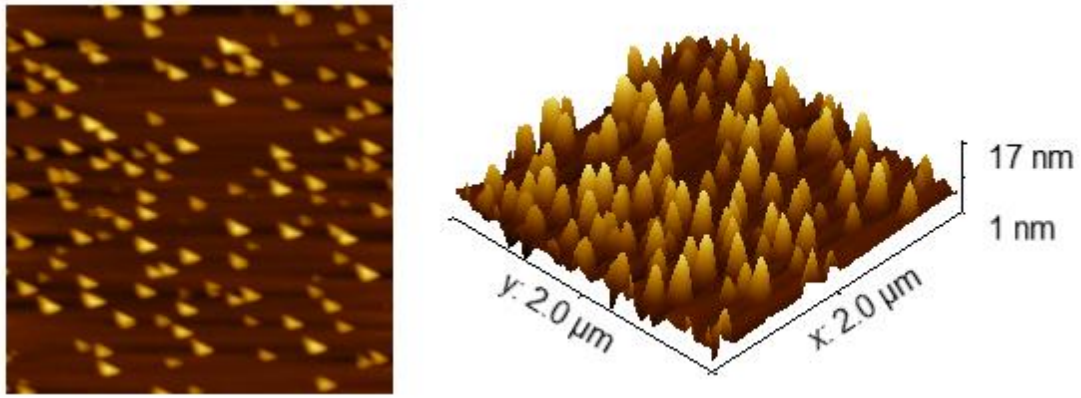

- *Catechol deposited in first-step within the porous electrode in aqueous solution.*
- *Salt solution is then impregnated in second-step to deposit and nucleate/grow onto surfactant coating.*

# ***Lanthanum Cobaltite Deposition Study:*** *Single Crystal YSZ Deposition*

To study the deposition of nano-$LaCoO_3$ onto single crystal YSZ. These substrates were chosen due to their polished flatness increasing ease of use for atomic force microscopy (AFM) to understand nucleation and growth kinetics.




$LaCoO_3$ on YSZ deposited using 0.5 M solution



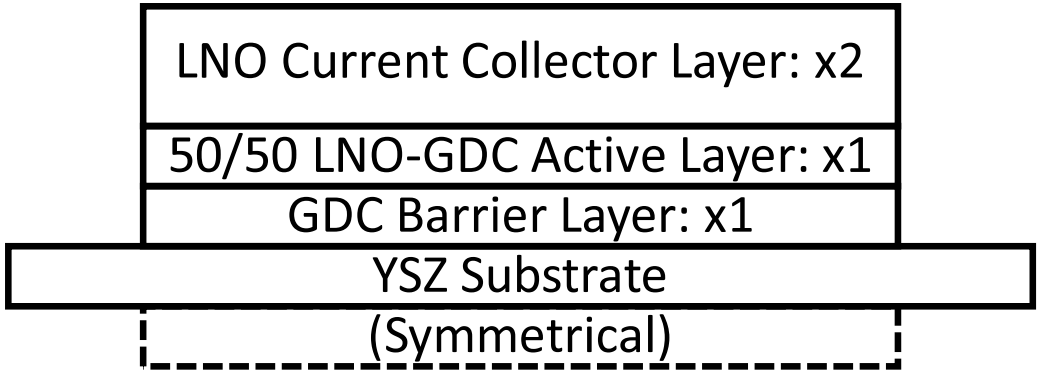

$LaCoO_3$ on YSZ deposited using 1.0M solution

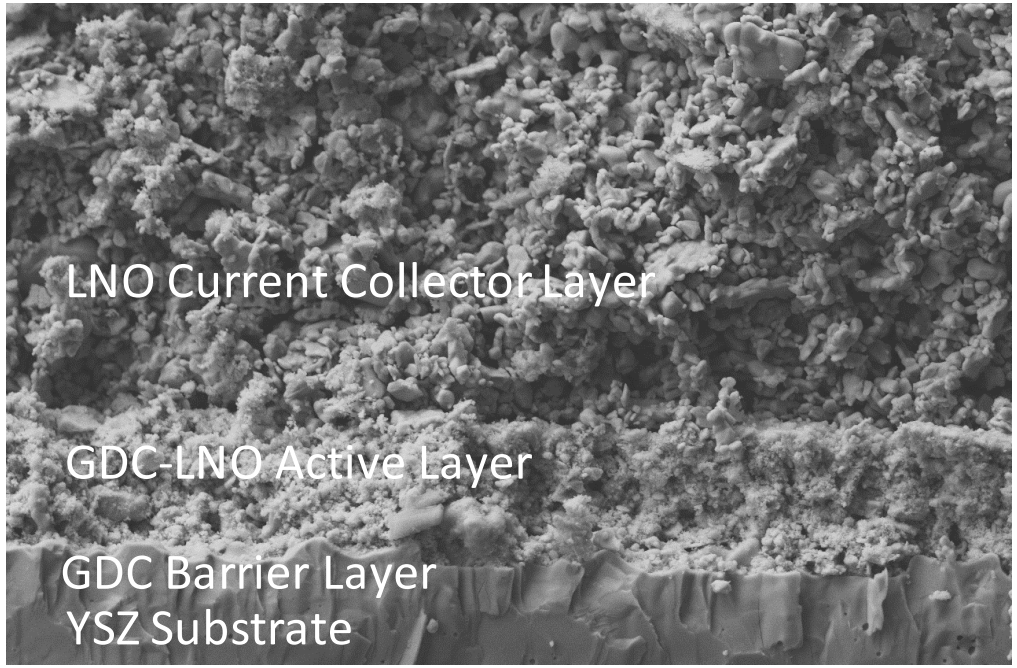
**Procedure:** pNE solution was made and started to polymerize, YSZ substrate was inserted and rocked.

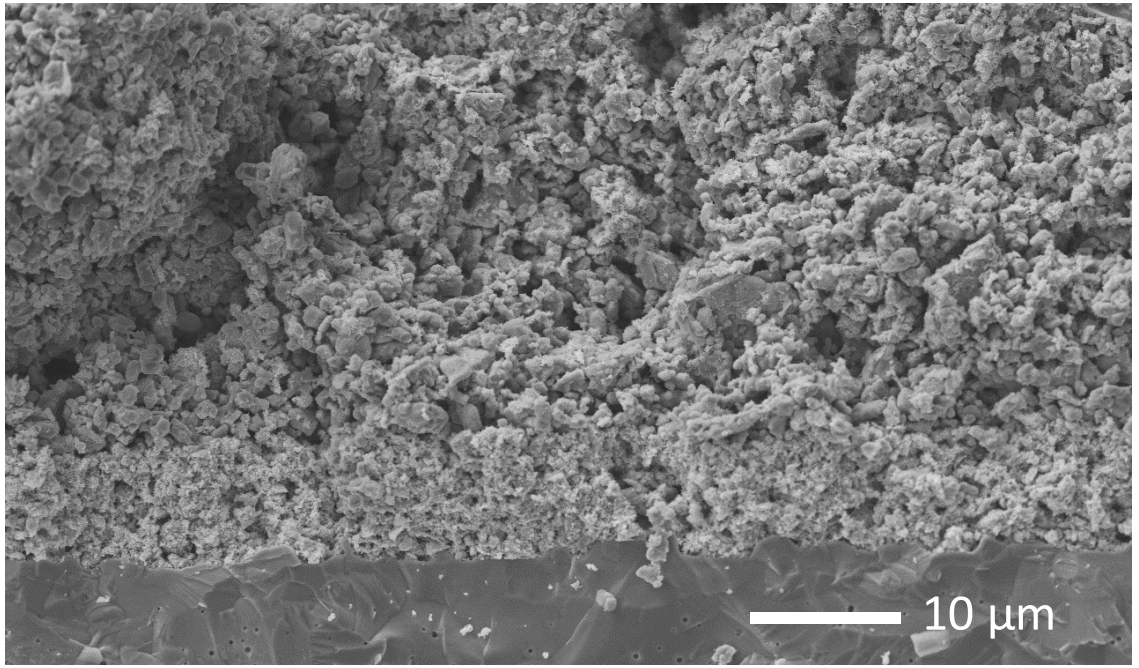
- Substrates taken out, rinsed gently, placed into a La Co nitrate mixed solution, and rocked at equal
- Substrates gently rinsed then fired to 800 °C.

# ***Lanthanum Nickelate Symmetrical Cells:*** *Synthesis and Infiltration Results*

- Symmetrical cells using LNO have been created and infiltrated with LNO created in house
- The layers for the symmetrical cell shown on right
- Comparison of the non-infiltrated cell to the infiltrated cell can be seen below, with layers labeled.



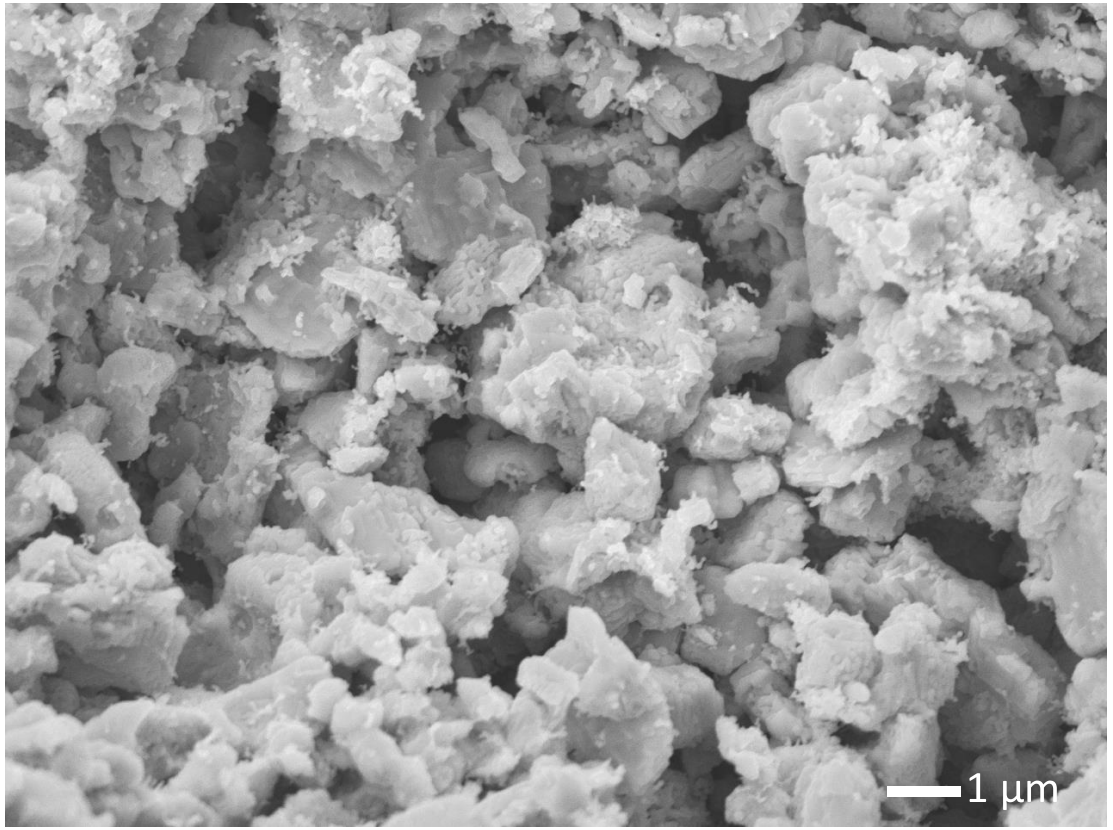



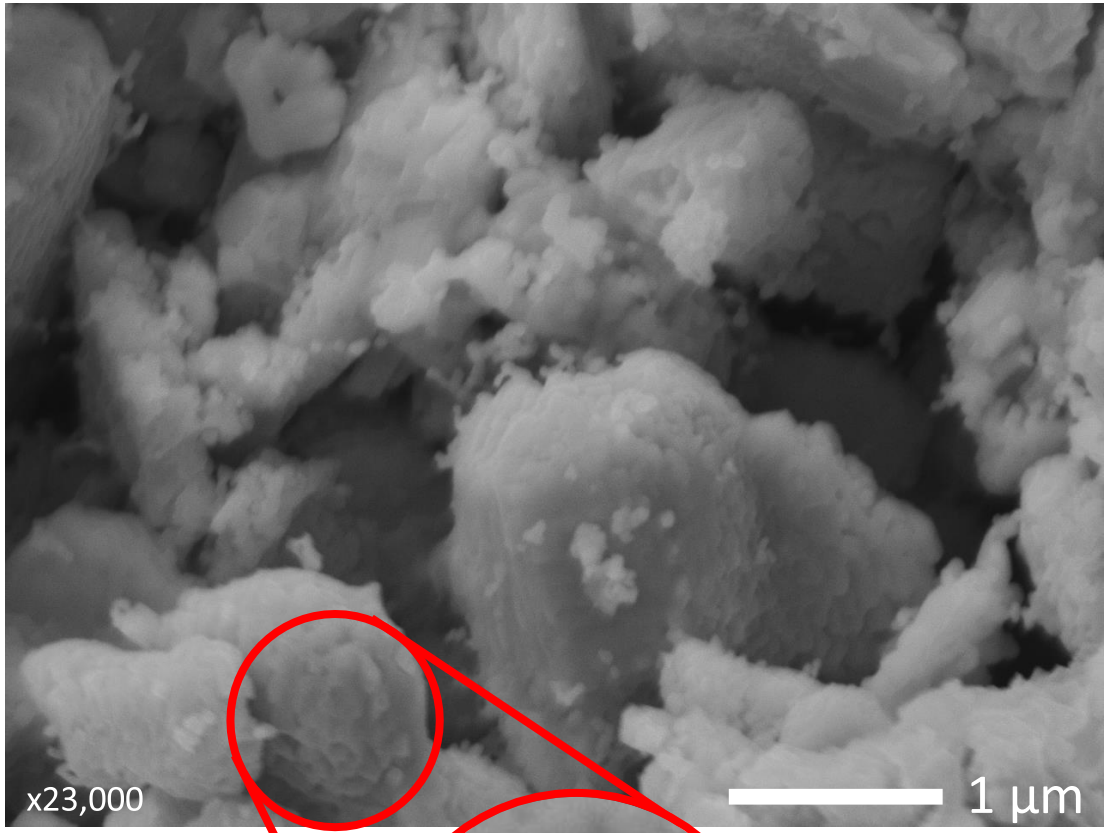

- Microstructure is unoptimized for performance, but will serve as a standard to compare impregnation process methods and coatings while optimization is investigated.

# ***Lanthanum Nickelate Symmetrical Cells:*** *Synthesis and Infiltration Results*

Infiltrated Cell Close-up, x8,000




Infiltrated Cell Close-up, x23,000




Coverage in the cell may be a little too high, as can be seen here:
A lower deposition time will be tested to assess cell coverage

# *EIS Testing of Infiltrated Cells:*

| Temperature: | Non-Infiltrated Cell Polarization Resistance ($\Omega \cdot cm^2$) | Infiltrated Cell Polarization Resistance ($\Omega \cdot cm^2$) |
|---|---|---|
| 600 °C | 174.21 | 267.35 |
| 650 °C | 44.15 | 89.16 |
| 700 °C | 11.83 | 11.71 |
| 750 °C | 4.27 | 2.36 |
| 800 °C | 1.66 | 0.53 |

Table 1: Polarization resistances over different temperatures of infiltrated and non-infiltrated symmetrical LNO cells in non-humidified air

| Temperature: | Non-Infiltrated Cell Electrolyte Resistance ($\Omega \cdot cm^2$) | Infiltrated Cell Electrolyte Resistance ($\Omega \cdot cm^2$) |
|---|---|---|
| 600 °C | 5.30 | 4.90 |
| 650 °C | 3.14 | 2.71 |
| 700 °C | 2.07 | 1.68 |
| 750 °C | 1.32 | 1.11 |
| 800 °C | 0.87 | 0.81 |

Table 2: Ohmic resistances over different temperatures of infiltrated and non-infiltrated symmetrical LNO cells in non-humidified air

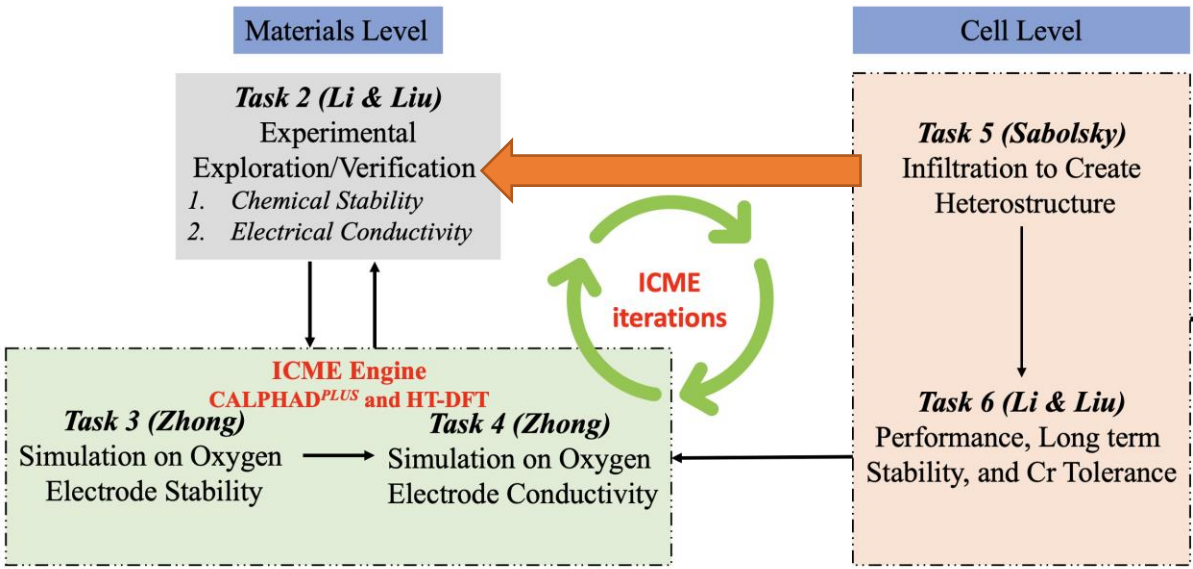
# Task 5: Fabrication and operational evaluation of electrode with heterostructured surface

**Summary:**

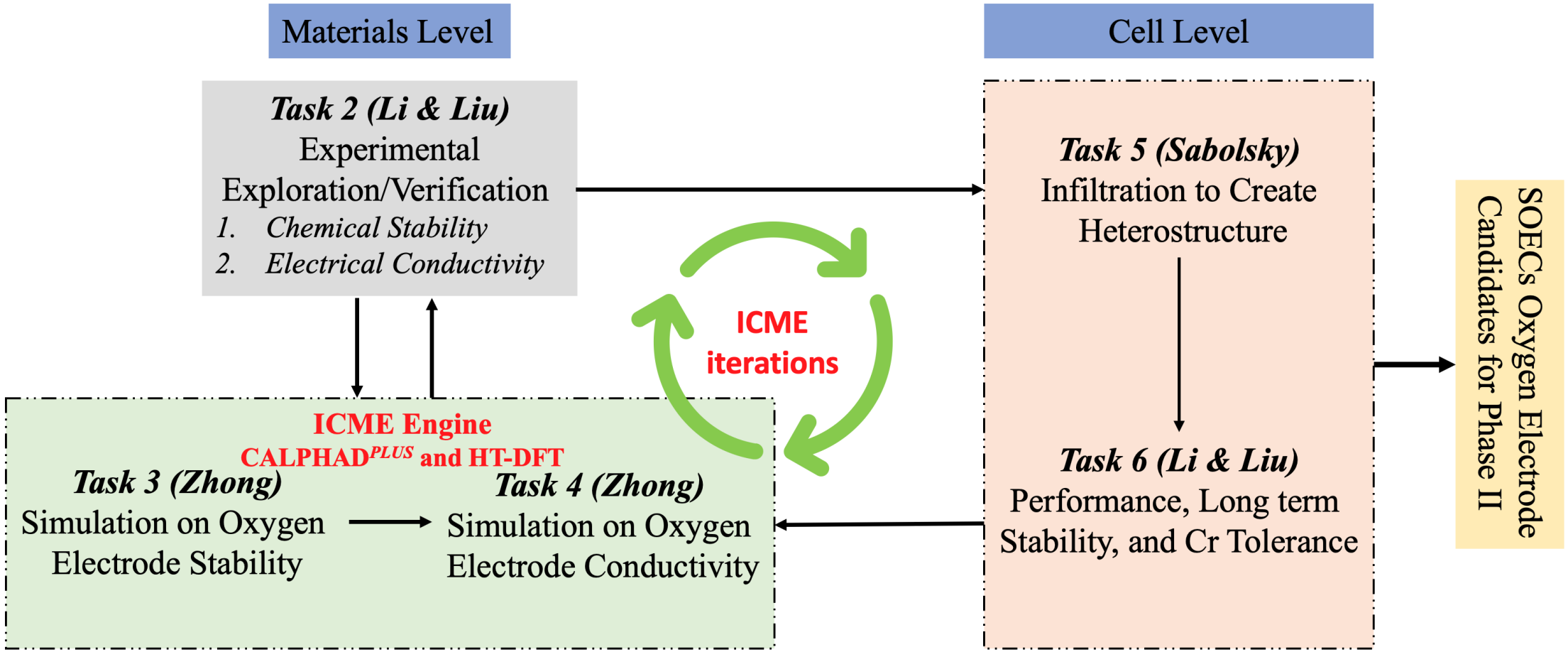
- Nano-LCO was successfully on YSZ
- EIS testing show promising resistances from the infiltrated cells

**Future work**

- Optimize the microstructure for performance
- Test the HEP coatings.



# ICME Approach to develop the oxygen electrode material



# Thank You!

Thanks to Program manager Andrew O’Connell

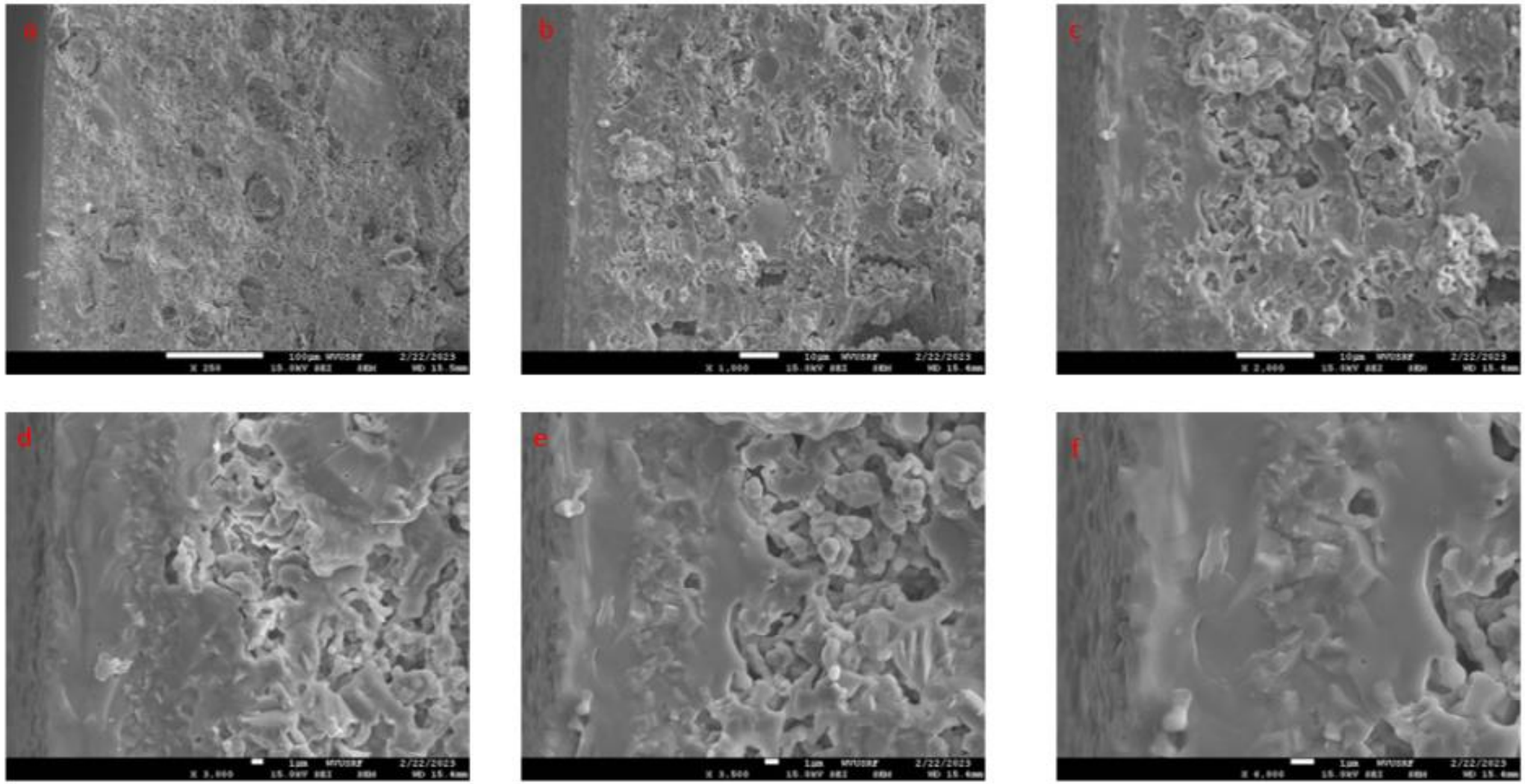



Fig.1. SEM Cross -section showing the substrate, AFL, and the electrolyte surface

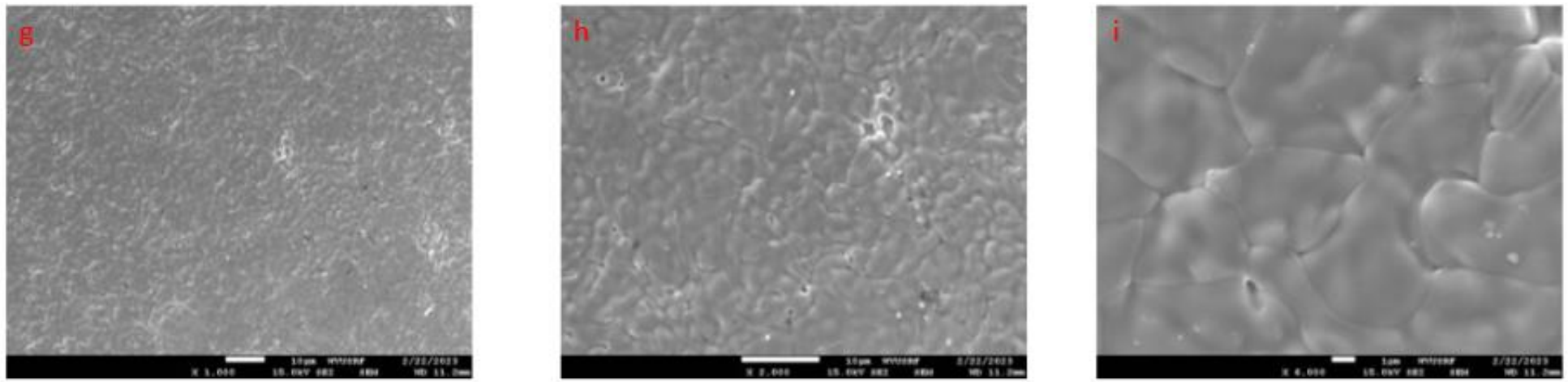



Fig.2. SEM images of electrolyte surface