Project Review for DE-FE32116

Heterostructured Cr Resistant Oxygen Electrode for SOECs

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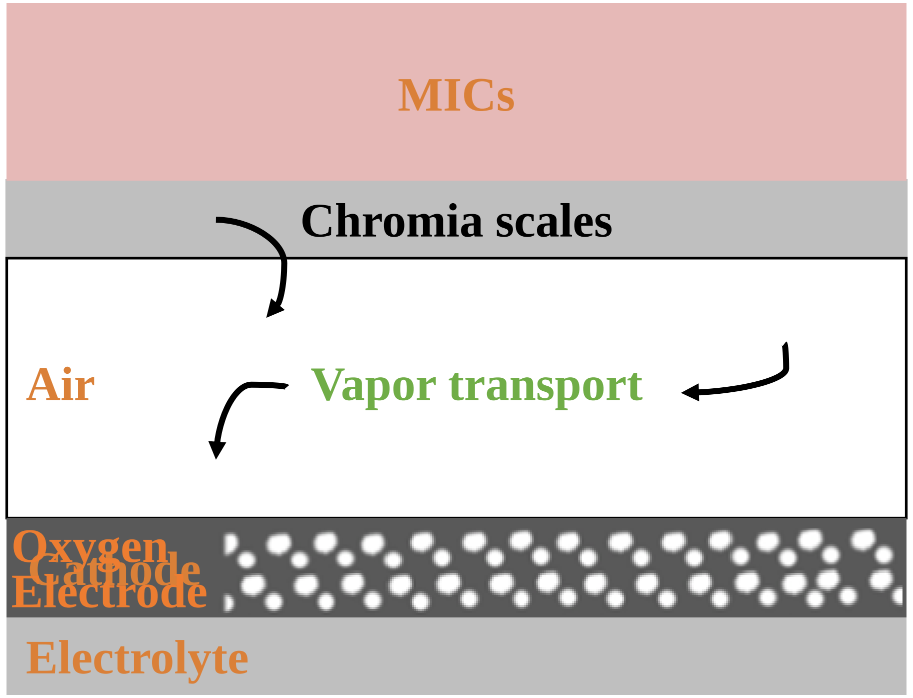
Outline

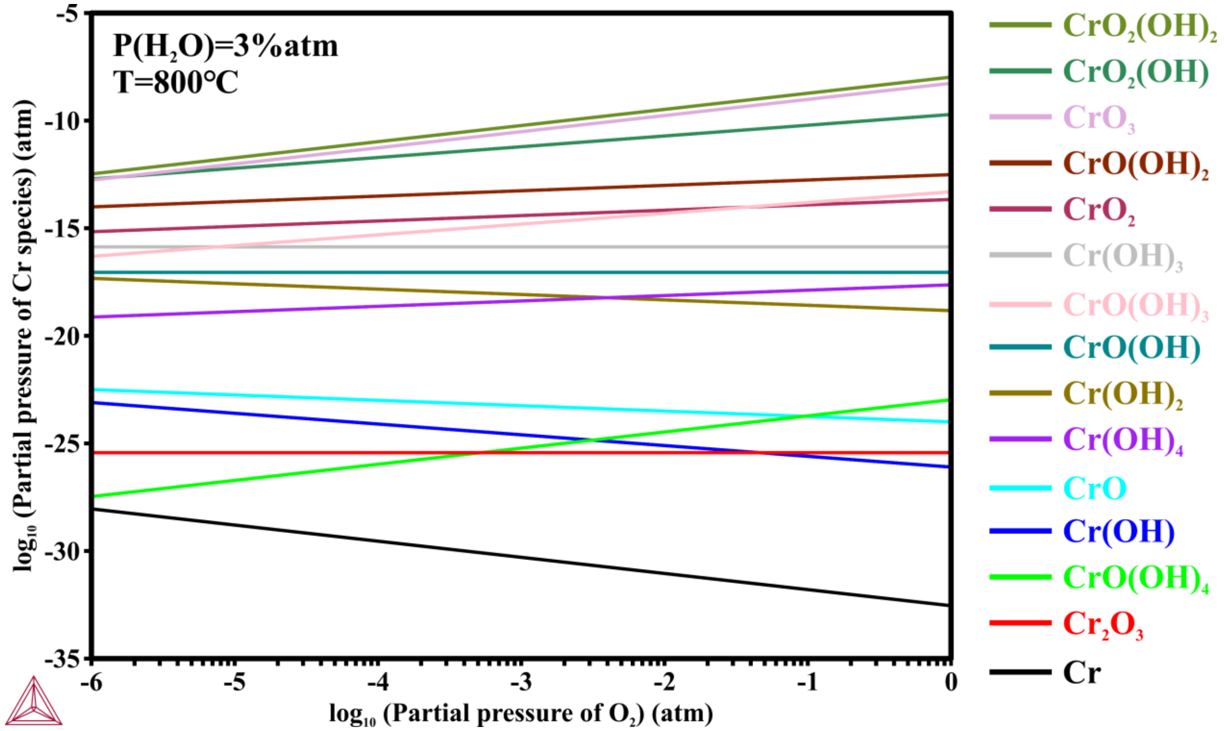
- Background
- Proposed novel La_2NiO_4-$LaCoO_3$ heterostructure
- Critical Factors to consider
- Overall Approach & Objectives
- Tasks

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



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

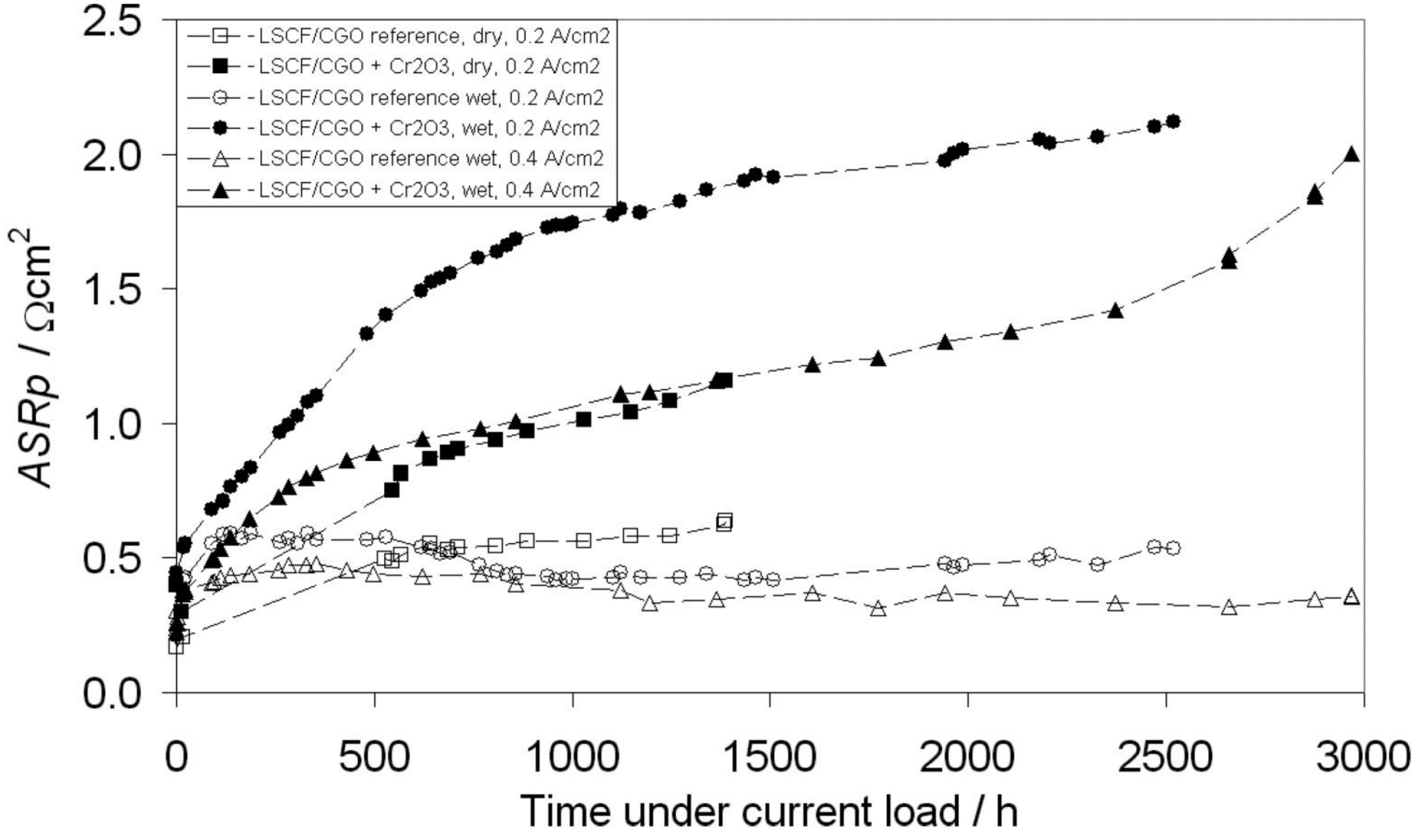
$$Cr - Sr - O(nuclei) + CrO_3(g) \rightarrow Cr_2O_3(s)$$

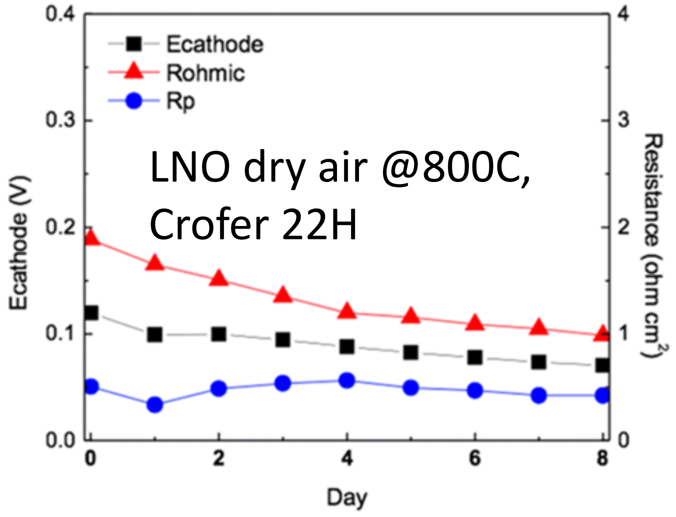
$$Cr - Sr - O(nuclei) + SrO + CrO_3(g) \rightarrow SrCrO_4(s)$$

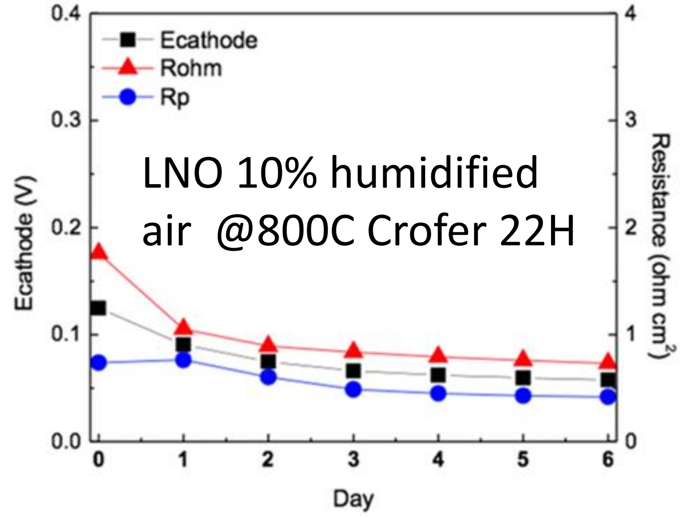
Alkaline-earth element - Sr is the triggering factor

Background: Cr to Poison Benchmark LSCF

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



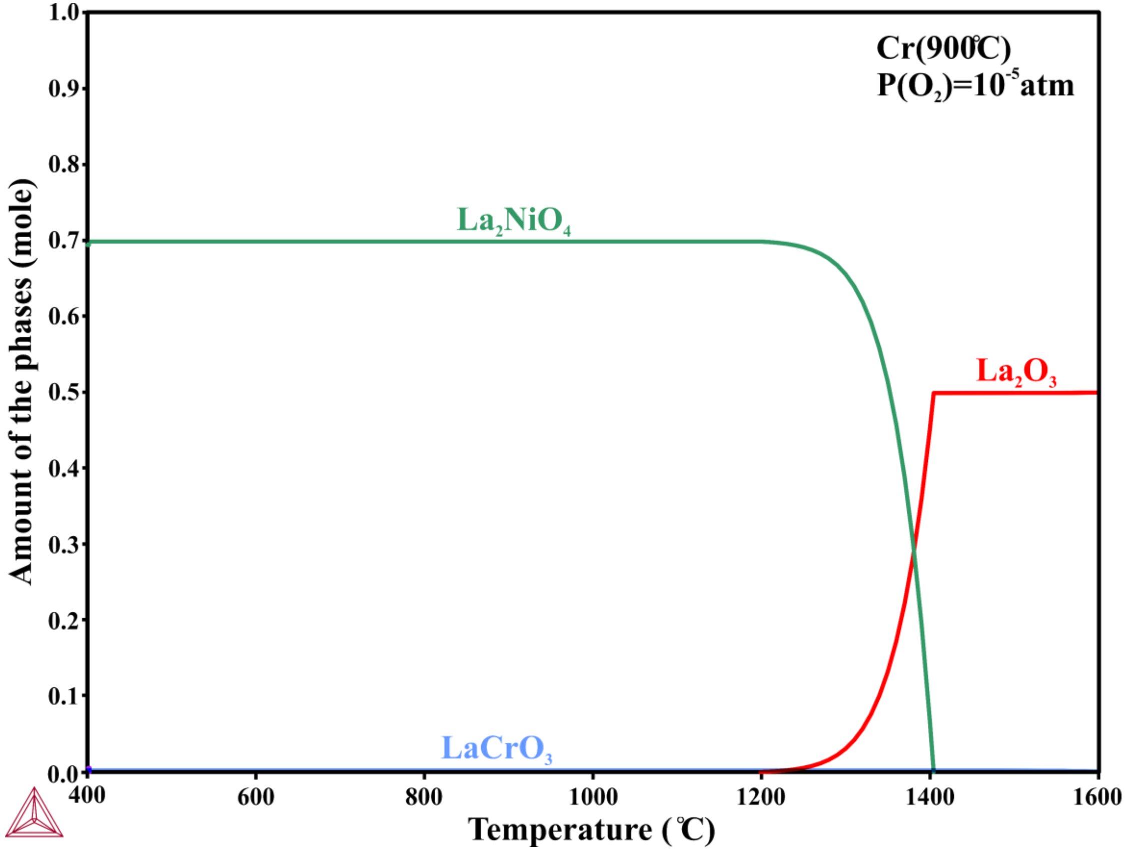




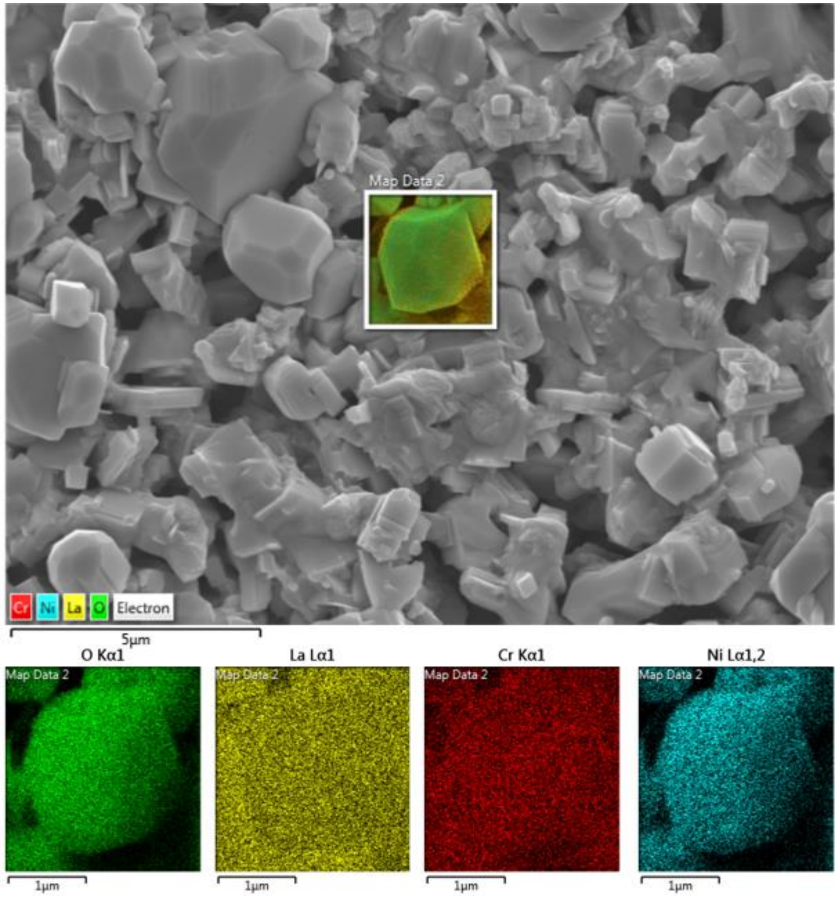
Promising short-term LNO tolerance to Cr

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

Previous Results From WPI on La_2NiO_4

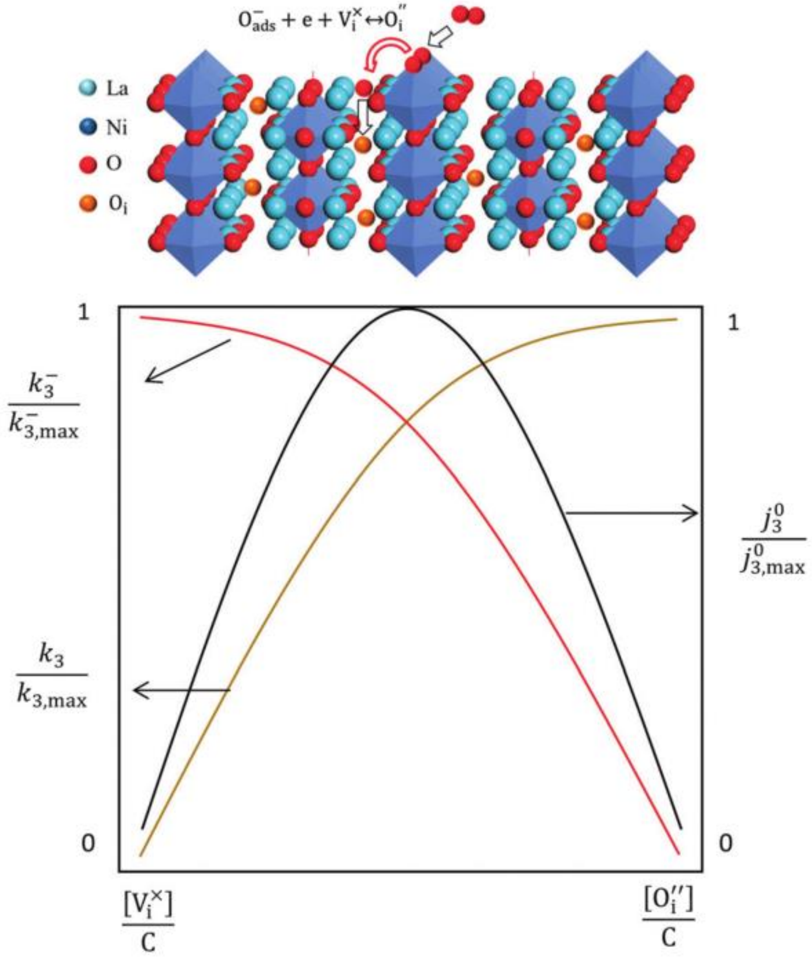


LNO is stable with the exposure to Cr



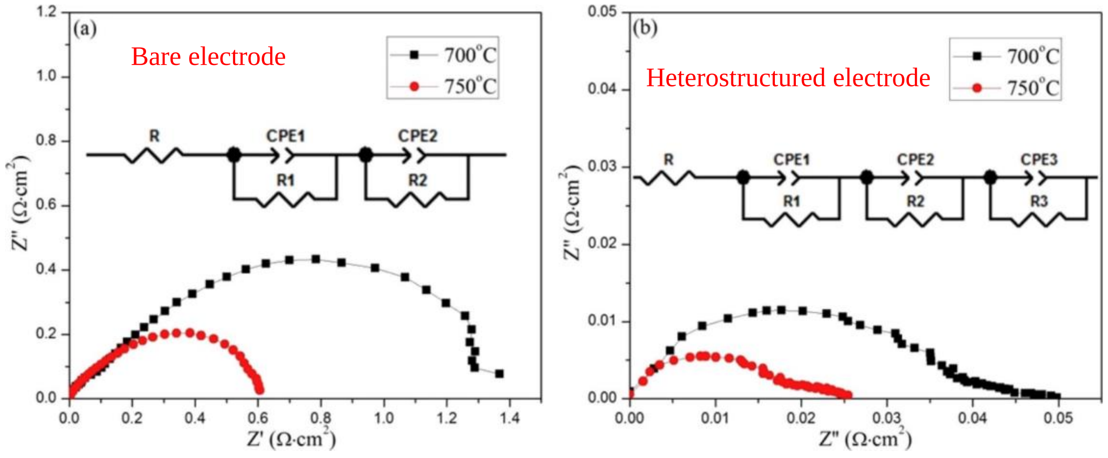
No apparent secondary phase formation

Previous Results From WVU: La_2NiO_4-$LaCoO_3$ Heterostructure



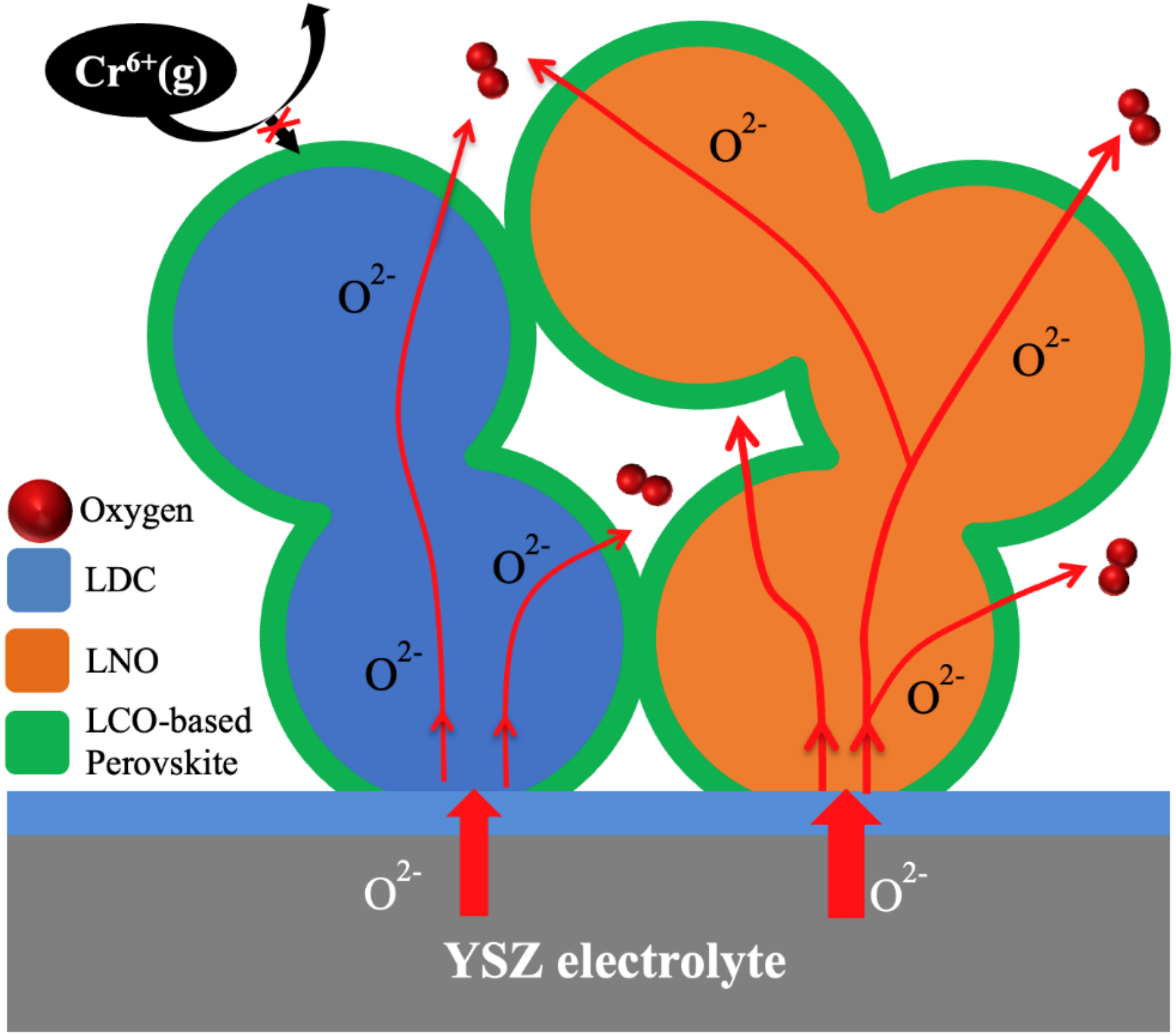
Previous WVU results

Interstitial oxygen defects in LNO to provide high ion conductivity in high P_{O2}



Infiltration to abruptly improve the performance

Proposed Novel La_2NiO_4-$LaCoO_3$ Heterostructure

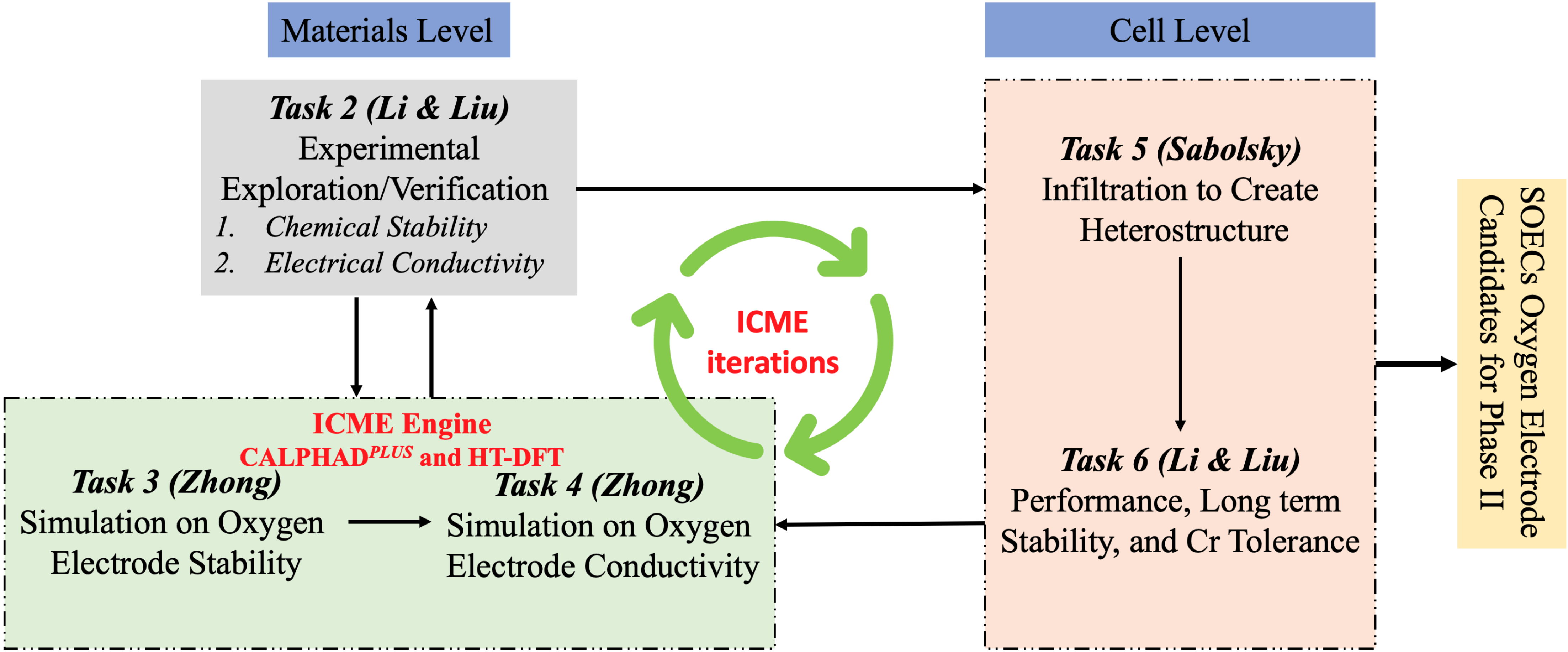


Sr-free, fast O-conducting LNO backbone plus active OER LCO surface coating as Cr-resistant, high performing oxygen electrode

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



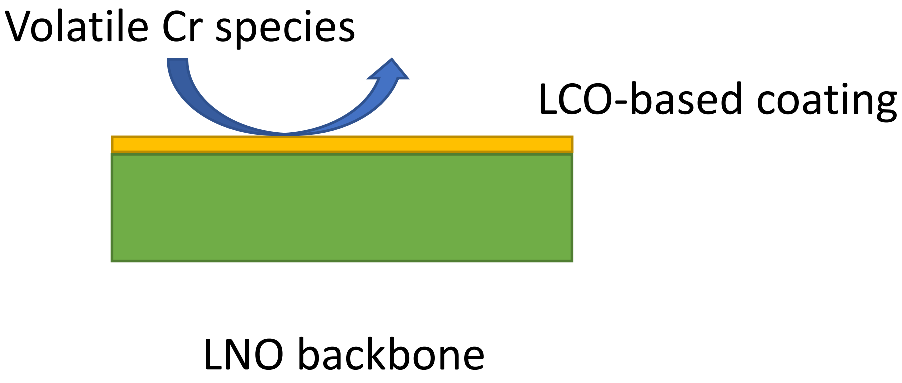
When fully optimized, this oxygen electrode material will target to an INTRINSIC long-term degradation rate of less than 0.3%/1000 hrs at 700^{o}C. By the end of the first year, it is expected to reach the 0.8A/cm^2 current density at 1.4V applied potential. By the end of the project, we will reach 1A/cm^2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

Task 2: Experimental exploration and verification

(1) LCO-based Materials

Various B site doped LCO materials (e.g. Ni, Cu, Mn) as surface coating candidates

(2) Chemical Stabilities Under Cr-Containing Gas Impurity Conditions



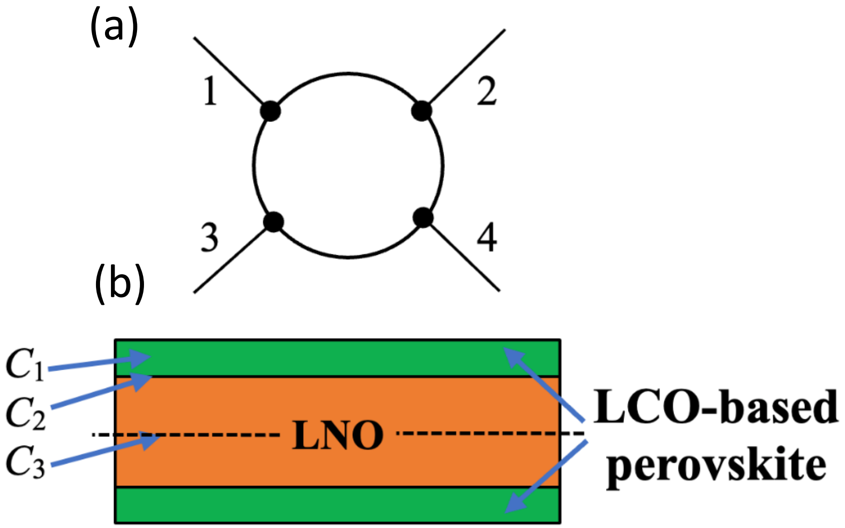
(a) Cr interaction with coating layer, (b) interaction between coating layer and substrate

Conducting phase/morphology stability experiments on the pellets at the typical operating temperatures 700°C. Cr species will be introduced by Cr_2O_3. The composition and amount of impurities from reaction between Cr and the pellets will be evaluated and iteration will be made with Task 3 for verification.

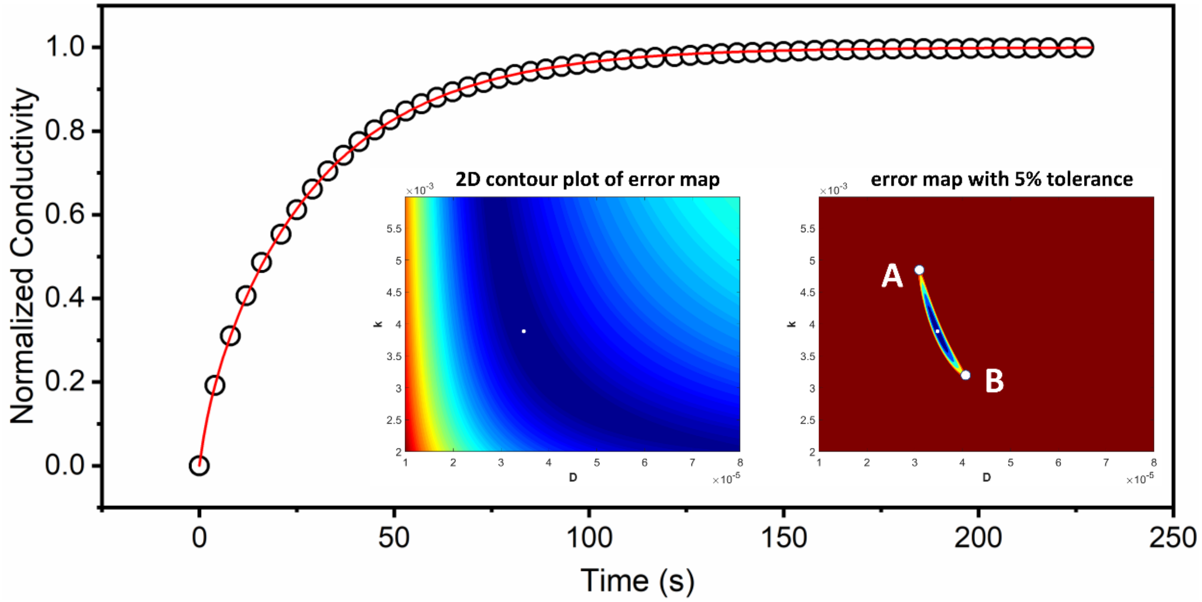
After verification of simulation in Task 3 based on these experimental data. Accelerated stress testing will be designed based on the reaction nature predicted by simulation in Task 3. Higher concentrations of Cr species in the flow air and/or higher operating temperatures will be used.

Task 2: Experimental exploration and verification

<u>(3) Electrical Conductivity and Conductivity Relaxation Experiments</u>



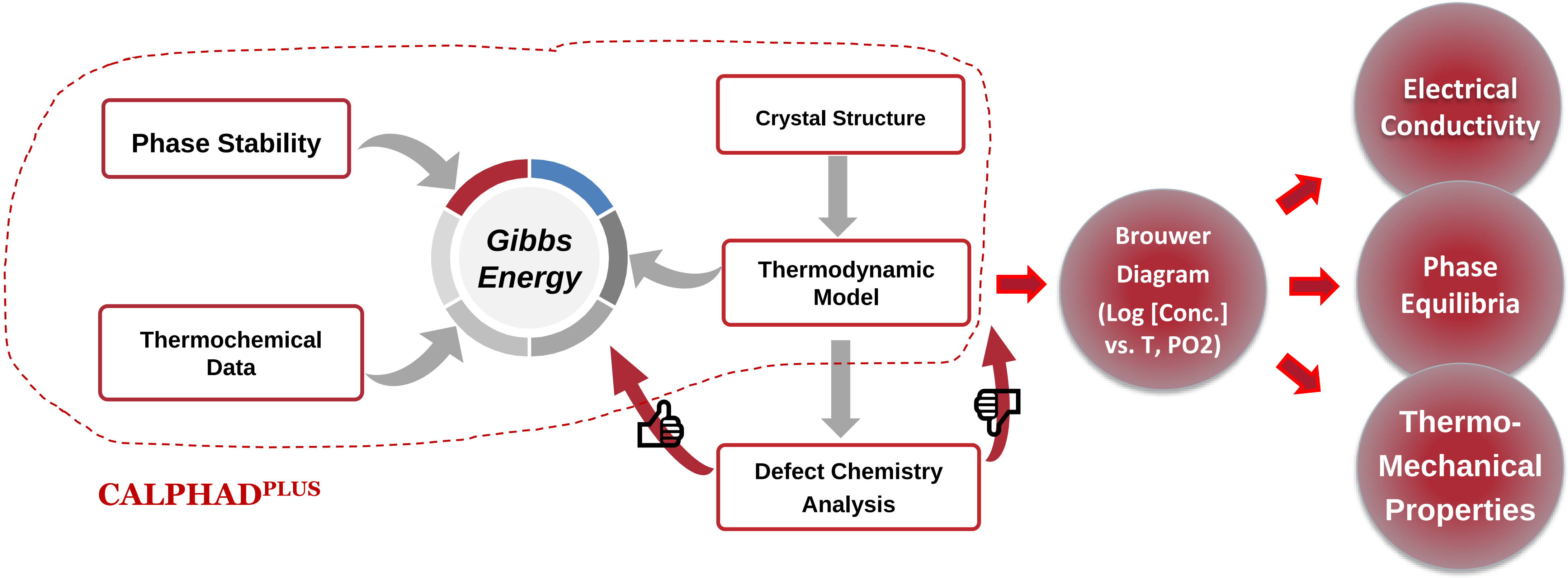
ECR sample configuration for OER kinetics on the heterostructured interface. (a) sample top view, (b) sample cross section



Conduct Electrical conductivity relaxation (ECR) measurements in the temperature range of 600~800° C with an oxygen partial pressure of 0.21~0.4. Pellets will be connected to a 4-probe Van der Pauw test stand with gold wires where the electrical conductivity change (upon partial pressure change of oxygen) will be recorded. Duplicate testing at two locations will be carried out to validate reproducibility. ECR measurements will be used to derive oxygen exchange coefficients. ECR with and without Cr impurities will be used to evaluate the performance of candidates on oxygen exchange coefficients and the impact of Cr poisoning on them.

Task 3. Simulation on Oxygen Electrode Stabilities

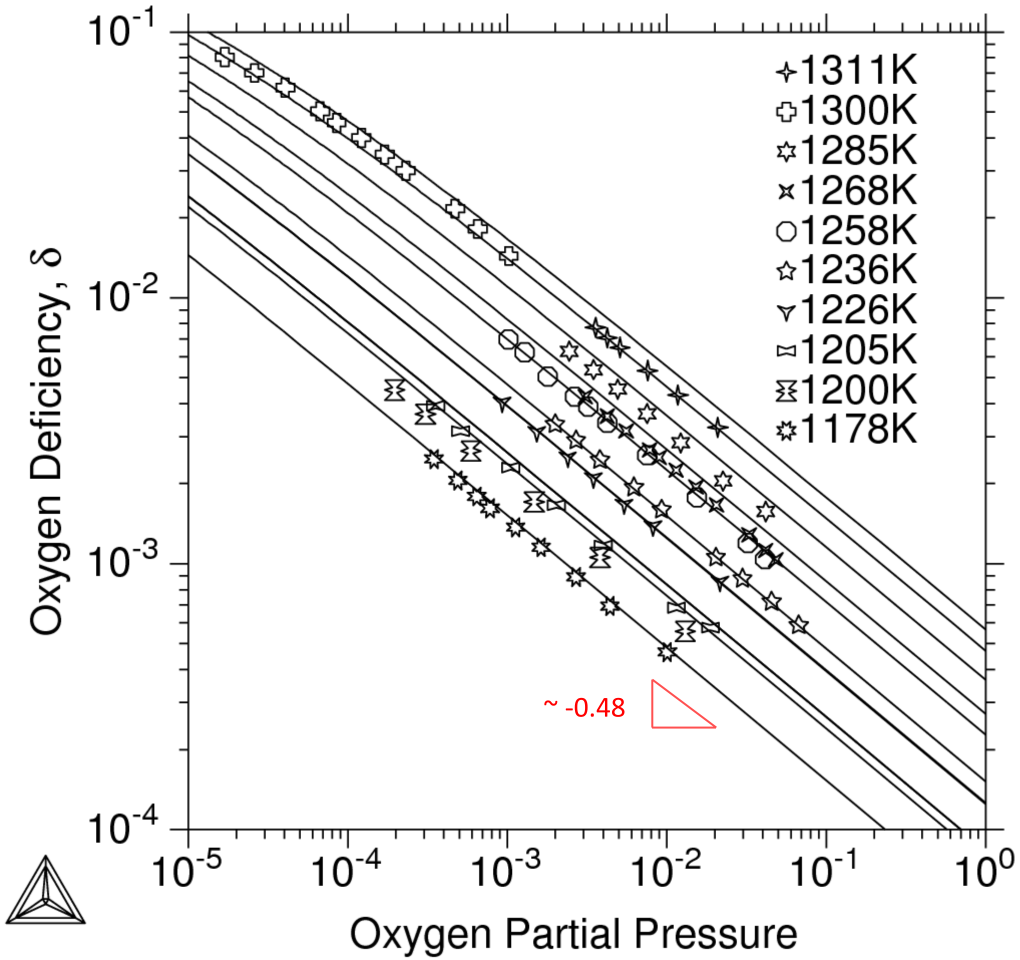
CALPHAD^{PLUS} Approach



Subtasks:

1. *Simulation of LCO-Based Perovskite Stability*
2. *Simulations of Oxygen Electrode Chemical Compatibilities*
3. *Simulations of Oxygen Electrode Surface Stability with Cr-Containing Gas Impurities*

Previous success: Thermodynamic Database Development

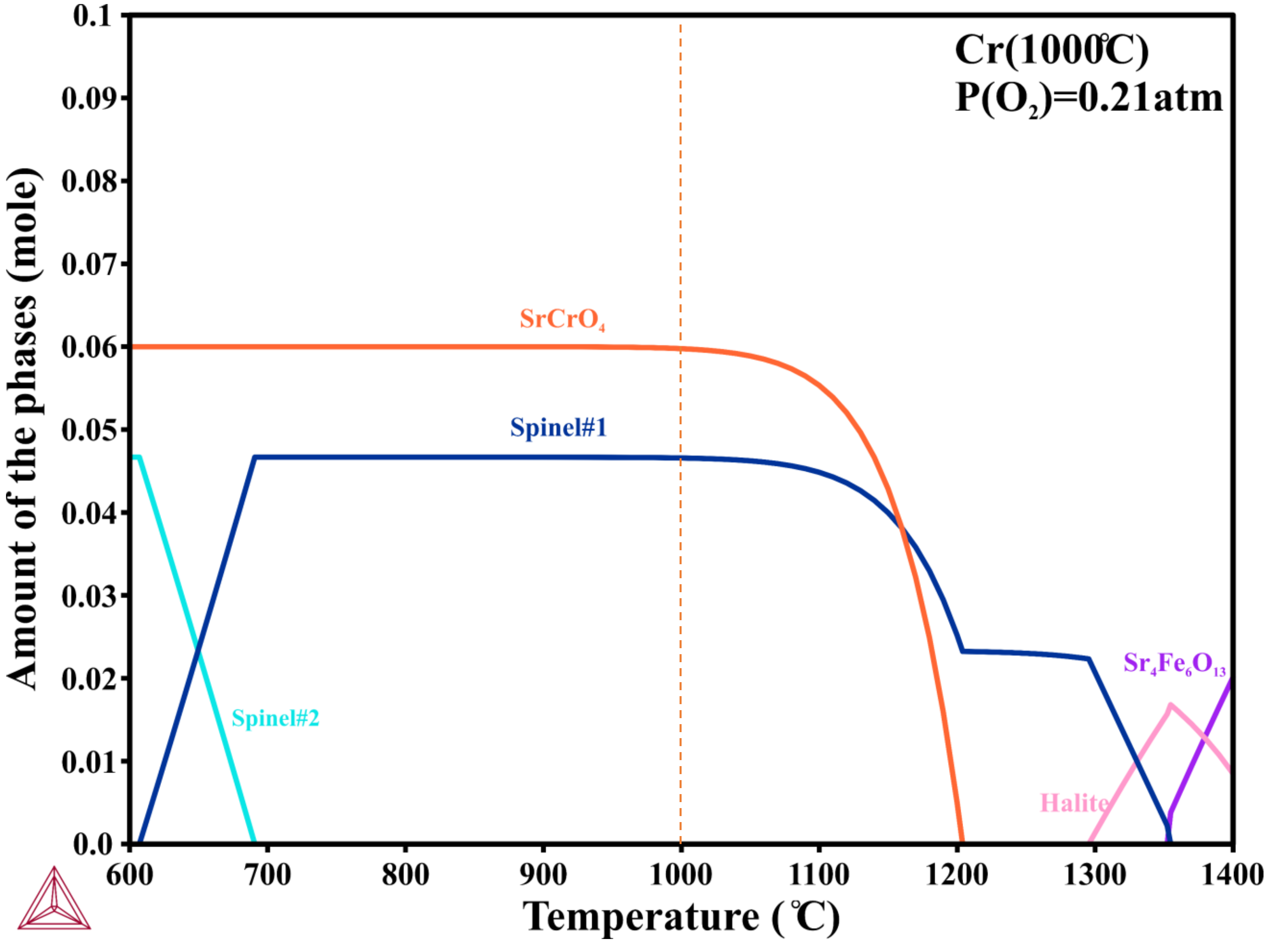


Thermodynamic Database for LCO

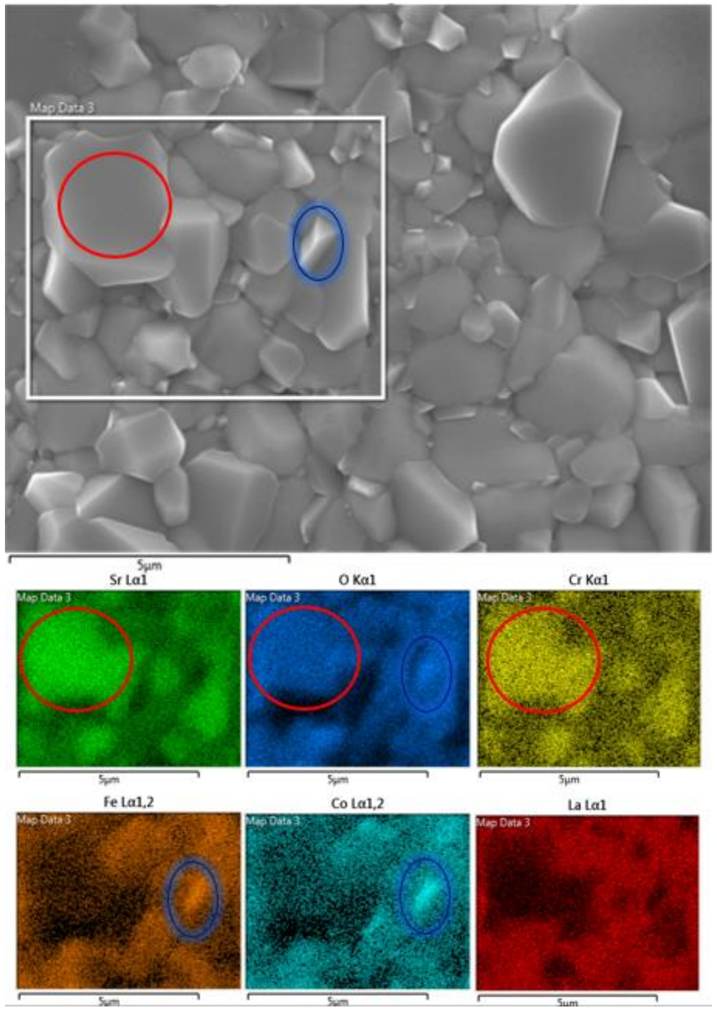
Seppanen *et al.*, *SCAND. J. METALL.*, 9, (1980) 3-11.

Previous Success: Phase equilibria prediction in comparison with thermodynamic experiments

The role of multiple gas impurities (Cr, SO_2, H_2O, CO_2)



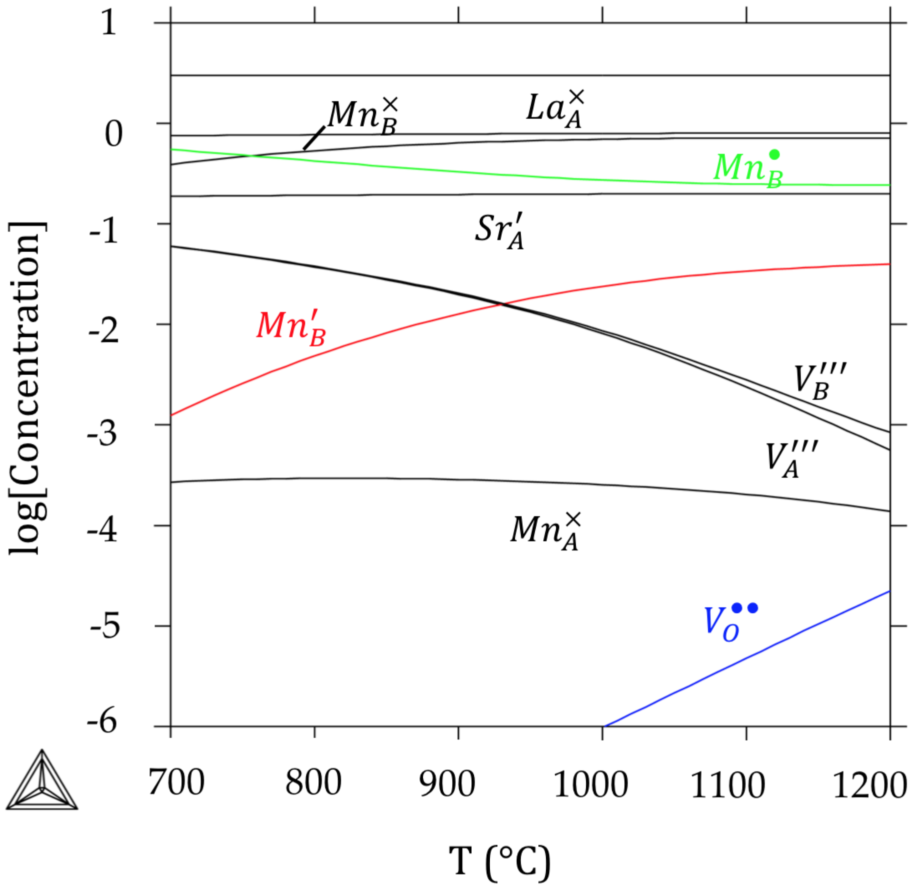
LSCF at 1000°C for 2 days with Cr_2O_3+Dry air

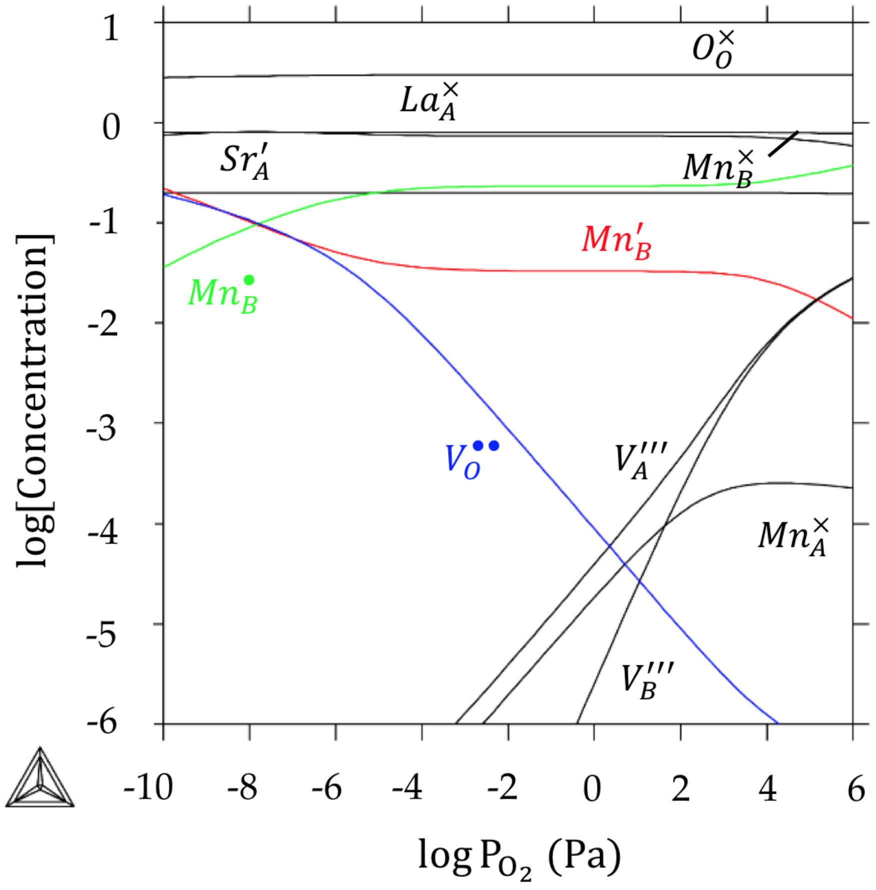


Task 4 Simulations on the Oxygen Electrode Electrical Conductivity

- *Simulation of LCO-Based Perovskite Point Defect Chemistry and Electrical Transport Properties (Ionic and Electronic Conductivities)*
- *Simulation of The Oxygen Ionic Conductivity For LNO/LCO-Based Perovskite Interface*

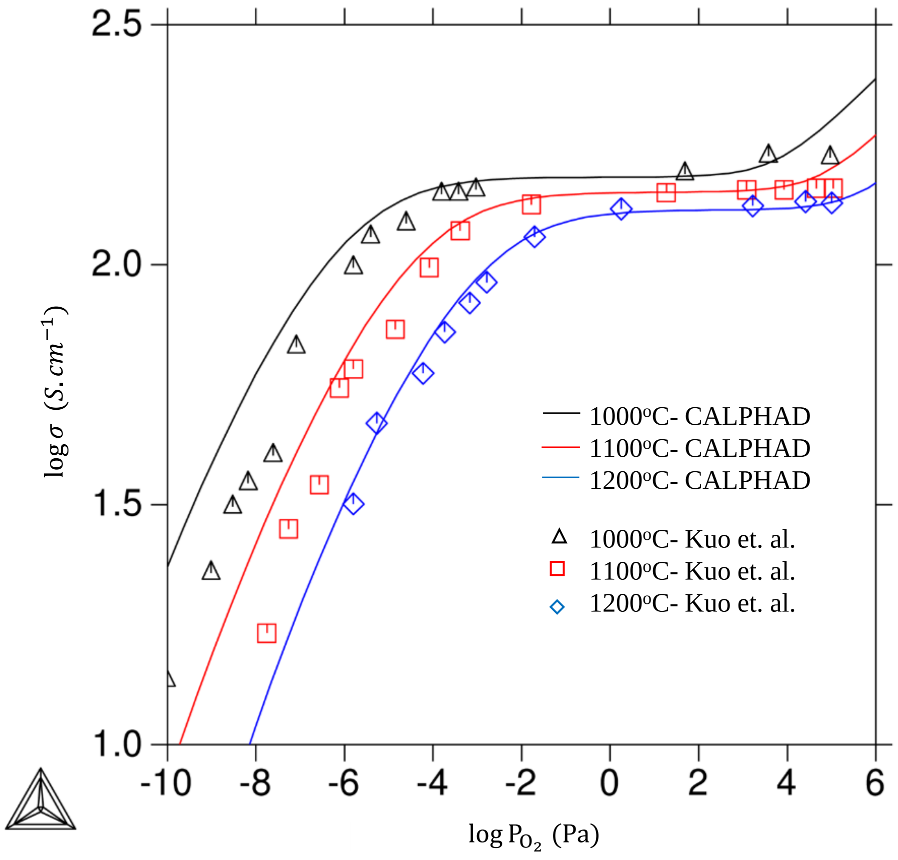
Previous Success: Defect Chemistry Prediction

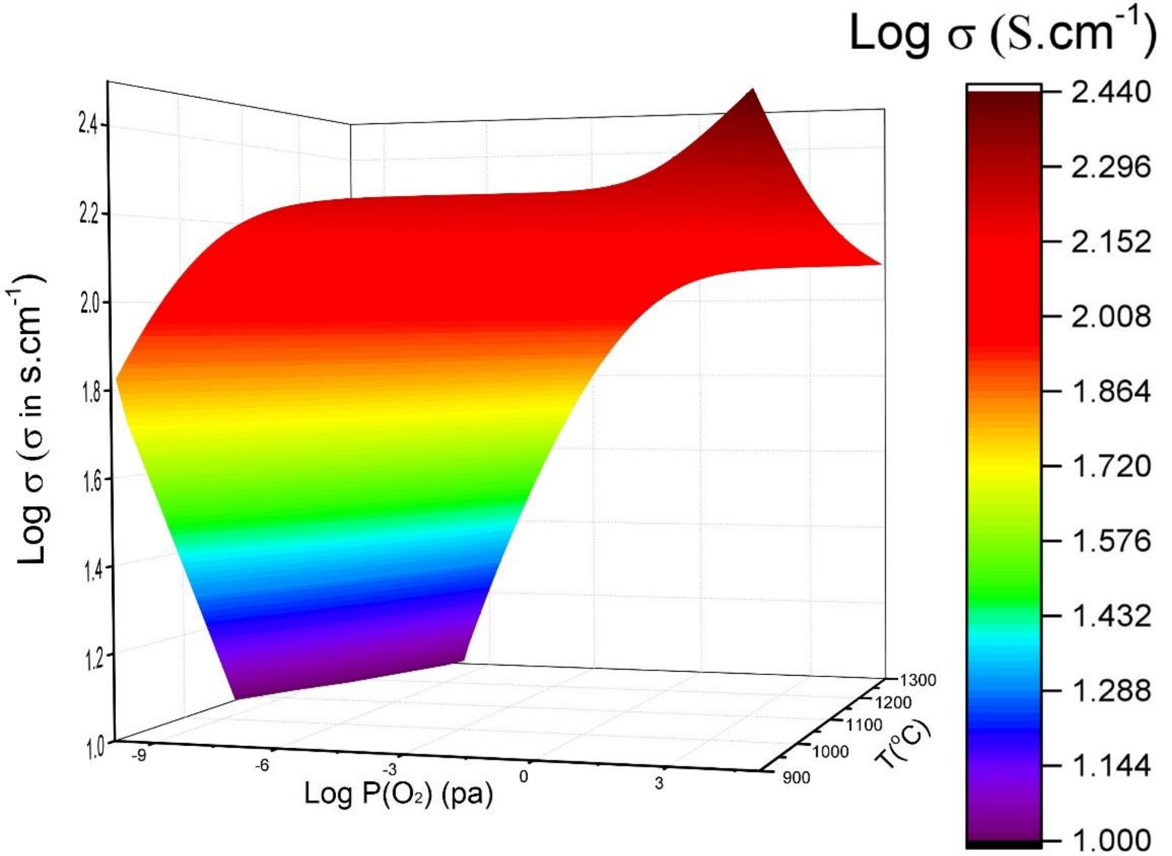




Quantitative Brouwer Diagrams for LSM with the changes of temperature and PO2

Previous Success on Conductivity Prediction

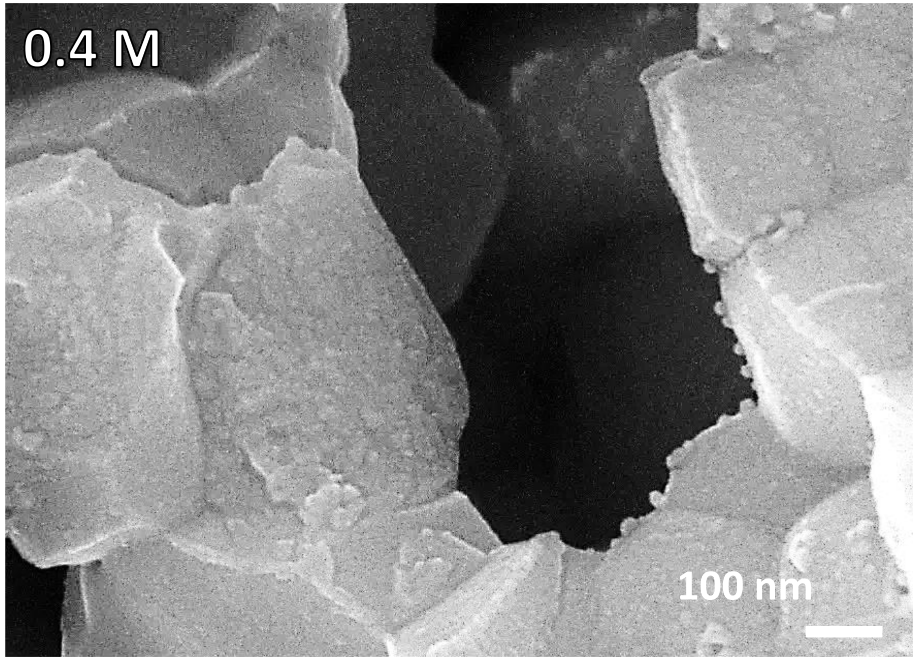


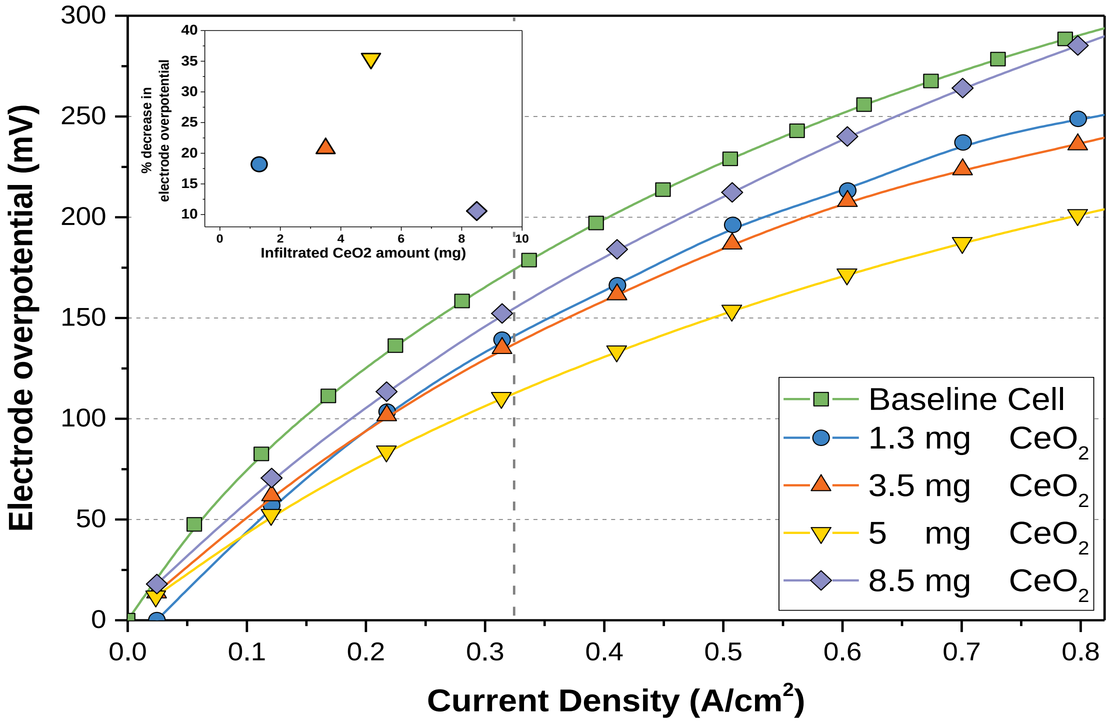


Electronic Conductivity

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

(1) Fabrication Development of Heterostructured Oxygen Electrode With Infiltration Method

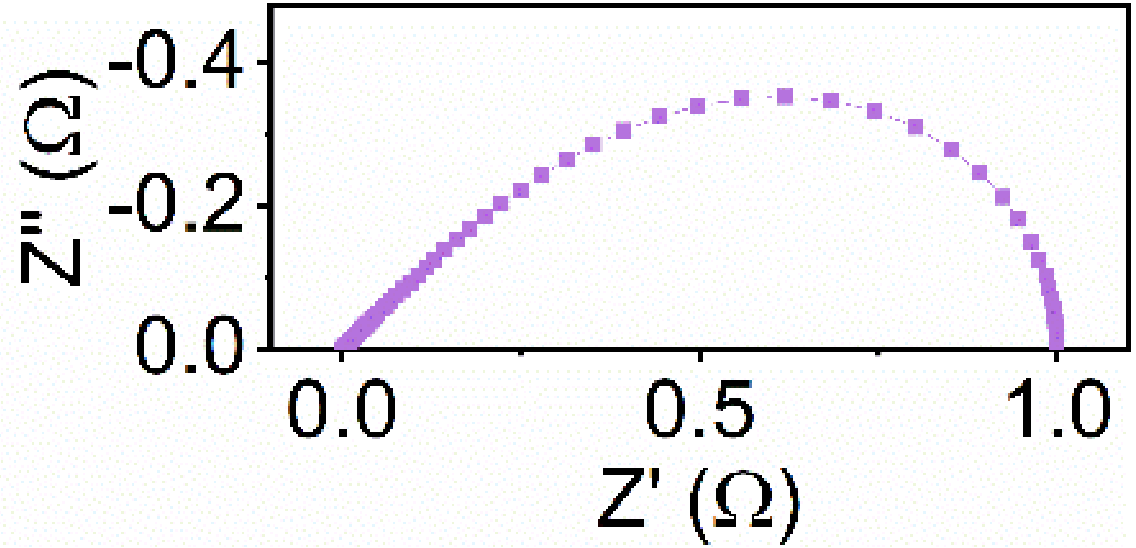


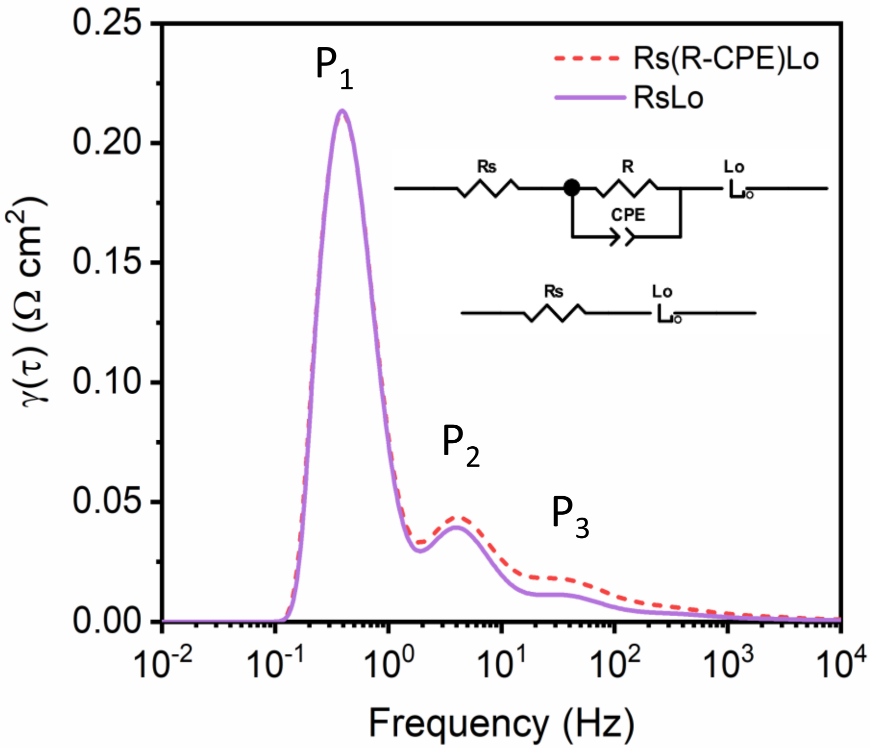


Prepare the heterostructured oxygen electrode (symmetrical cell) using the US patented two-step catechol deposition process for controlled nano-catalyst coating.

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

(2) Characterization of The Oxygen Electrode

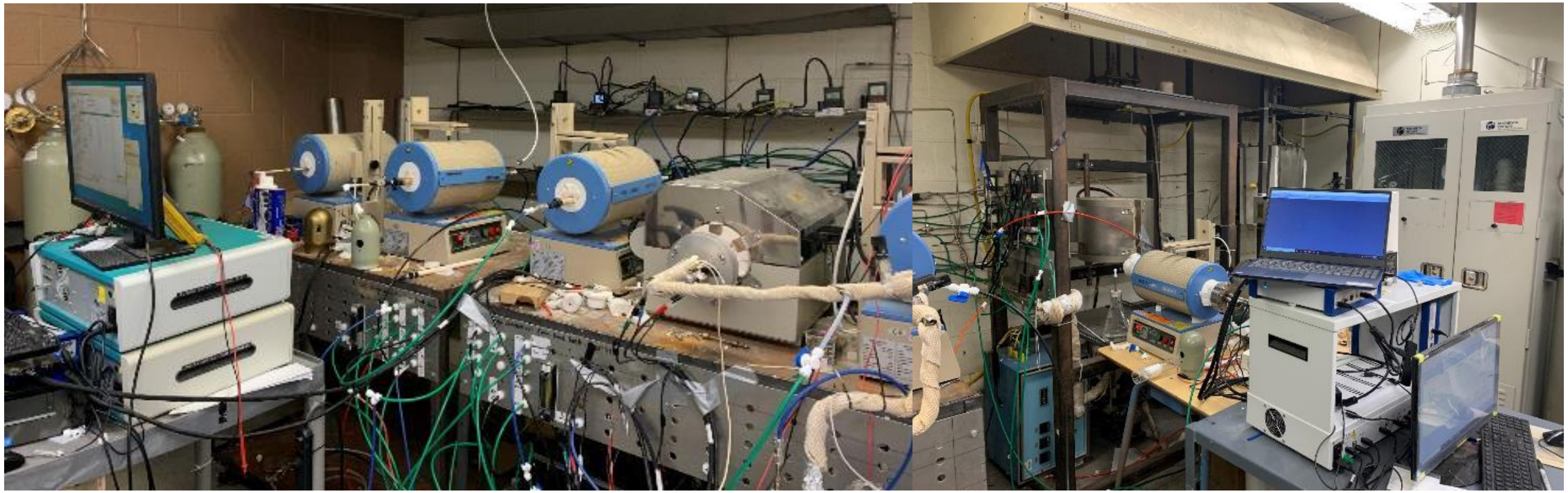




Symmetrical cell evaluation will be completed by EIS with varied N_2/O_2 at temperatures from 600-800ºC. In parallel, symmetrical cell microstructural and chemical analysis be carried out to define the optimal proposed microstructures.

Task 6: Performance, long-term stability of Cr tolerance investigation of button cells

Baseline cell (1) *Ni-YSZ//YSZ/LDC//LSCF-LDC-LSCF*
Baseline cell (2) *Ni-YSZ//YSZ/LDC//LNO-LDC-LNO*
Target cell (3) *Ni-YSZ//YSZ/LDC//Experimental oxygen electrode active layer (LNO-LDC-LCO-based perovskite)-Experimental current collector (LNO-LCO-based perovskite)*



Task 6: Performance, long-term stability of Cr tolerance investigation of button cells

(1) Operation of button cells

Operate button cells at a temperature of between 600^{o}C and 800^{o}C with a 50/50 ratio of H_2/H_2O at the hydrogen electrode and flowing air at the oxygen electrode.

At a given current density the electrolyzing voltage vs. time and EIS at a certain time intervals (e.g., every 200 hours) will be measured to monitor the ohmic/polarization resistance variations.

One of each cell type will undergo operation without Cr, while another identical cell undergoes operation with a sample of Cr_2O_3 providing a Cr source.

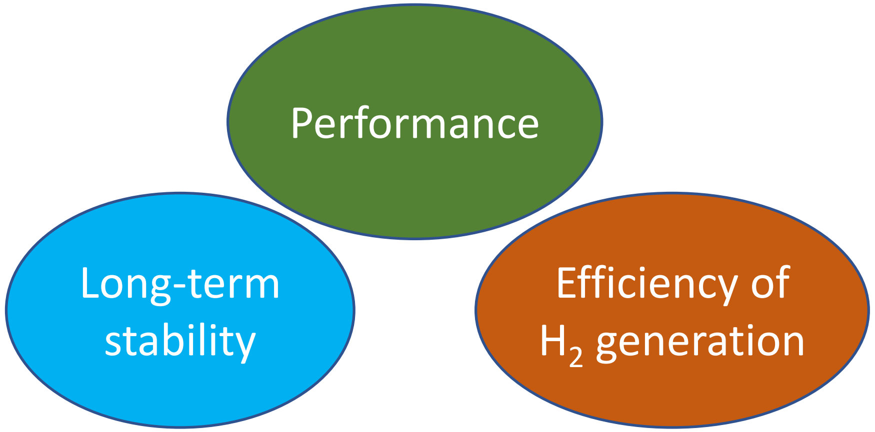
The exact operation temperature and Cr gas concentration for the accelerated stress tests (AST) will be determined by the verification from *Subtask 2.2*.

Task 6: Performance, long-term stability of Cr tolerance investigation of button cells

(2) Characterization of the button cells

The Recipient will analyze EIS data using the distribution relaxation times (DRT) method to understand the Cr's poisoning effect on the stability of the oxygen electrode.

The practical H_2 generation rate will be referenced to the calculated values to evaluate the Faradaic efficiency. Post-operational cells will be examined by SEM/TEM for microstructure/phase changes to determine stability.



Thank You!

Questions?