

Improving Durability and Performance of Solid Oxide Electrolyzers by Controlling Surface Composition on Oxygen Electrodes

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Pacific Northwest National Laboratory

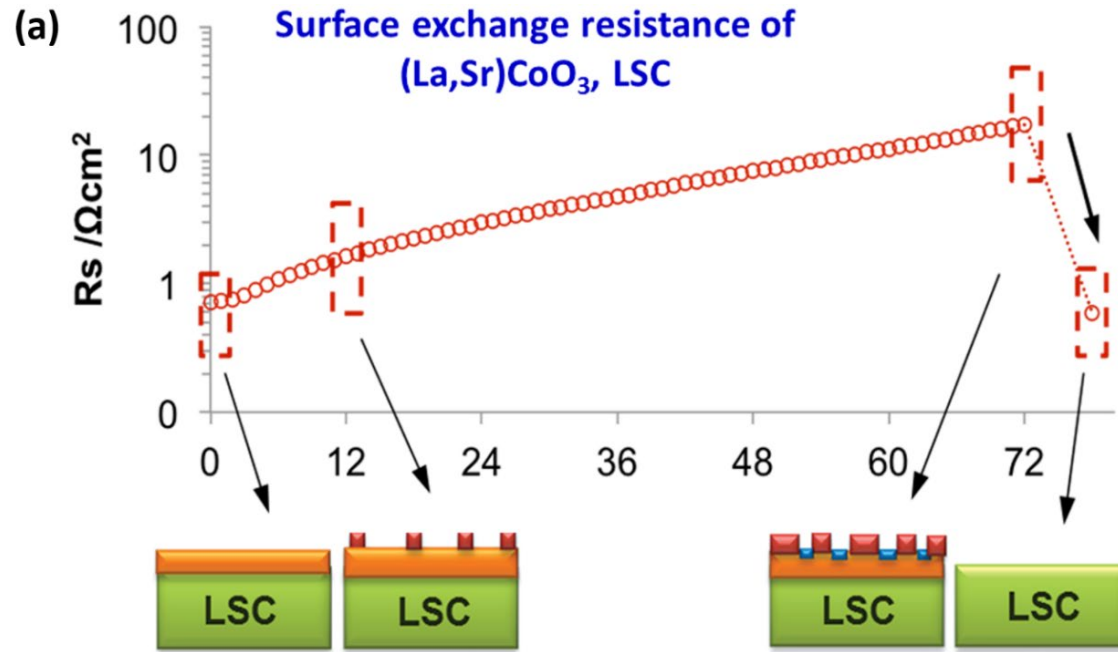


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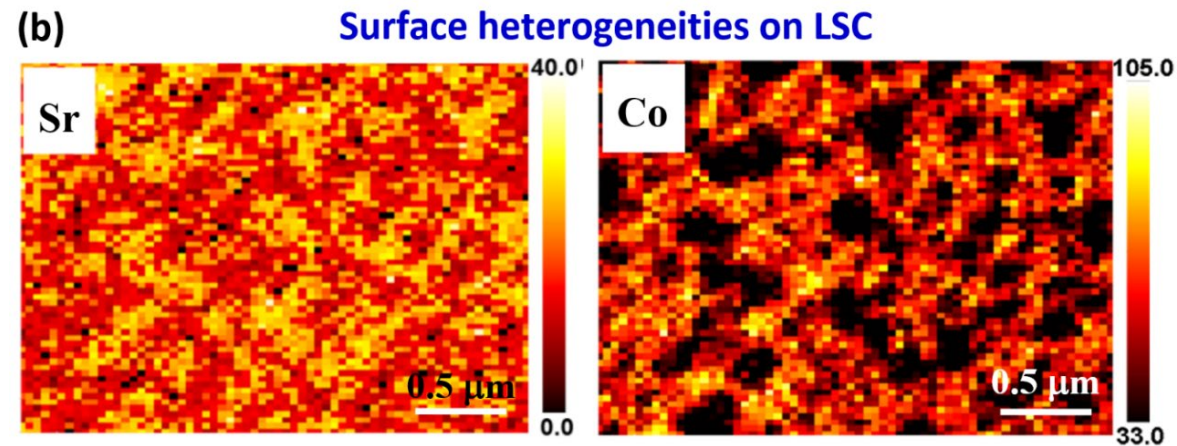
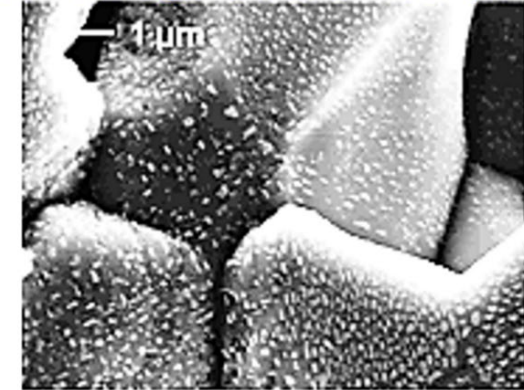
2022 Solid Oxide Fuel Cell Project Review Meeting
October 26, 2022



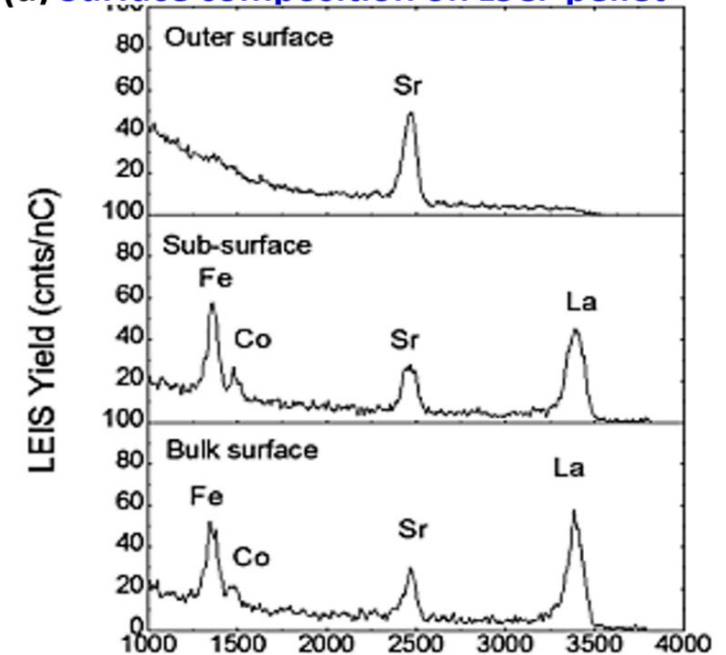
Detrimental Sr-segregation and precipitation at perovskite oxide surfaces



(c) Surface heterogeneities on LSCF pellet

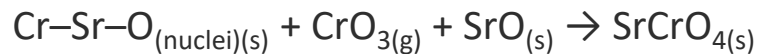
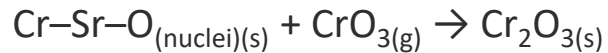


(d) Surface composition on LSCF pellet



Sr segregation and Cr & S poisoning of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$

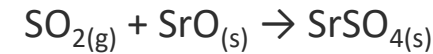
Cr Poisoning Nucleation Theory:



S.P. Jiang, X. Chen, *Int. J. of Hydrogen Energy*, 2014, 39.

K. Chen, S.P. Jiang, *Electrochemical Energy Reviews* 2020, 3.

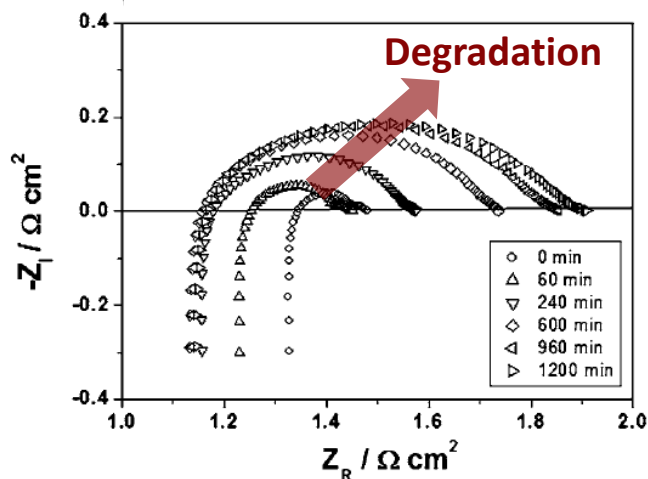
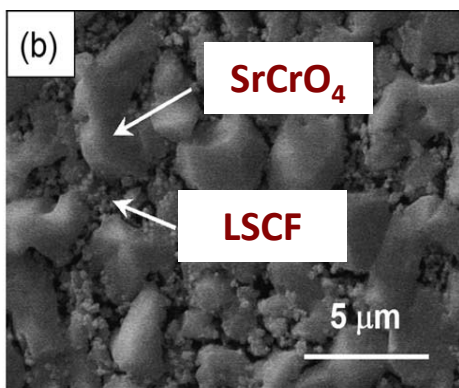
S Poisoning Nucleation Theory:



S.P. Jiang, X. Chen, *Int. J. of Hydrogen Energy*, 2014, 39.

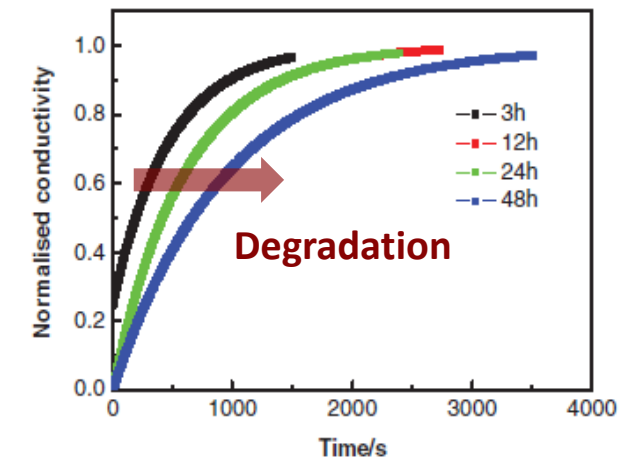
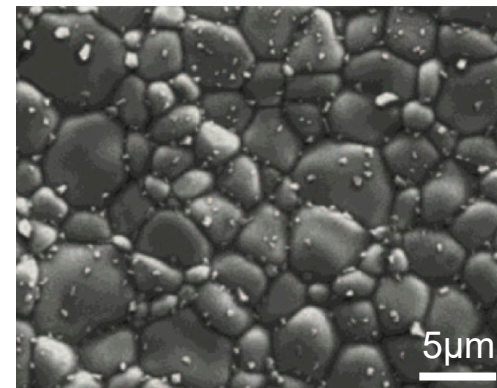
K. Chen, S.P. Jiang, *Electrochemical Energy Reviews* 2020, 3.

LSCF-GDC electrodes after operation at 200 mA/cm², 900°C:



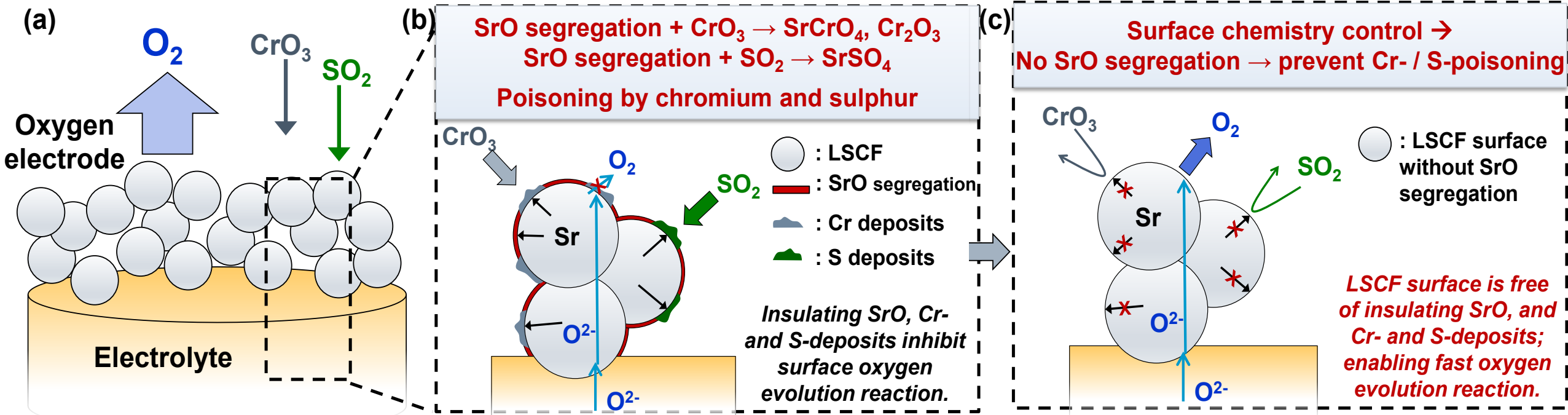
XRD, EDS, SEM → formation of SrCrO_4 and Cr_2O_3 on LSCF surface.

LSCF bar samples in the presence of 20 ppm SO_2 at 900°C:



XRD, EDS, Raman → formation of SrSO_4 on LSCF surface.

This project aims to attack the degradation pathway coupling surface chemistry to impurity poisoning on perovskite oxygen electrodes, taking LSCF as a state-of-the-art electrode.



1. **Improve the chemical and electrochemical stability** of the surface of LSCF, both the initial oxygen exchange kinetics and durability.
2. Develop **infiltration chemistries** to enable the surface modifications, to **suppress the Sr-segregation and the Cr- and S-poisoning processes**.
3. Advance our understanding of **the role of operational parameters on oxygen-electrode surface chemistry and performance**, combining experiments and computations.

Methods to achieve project objectives

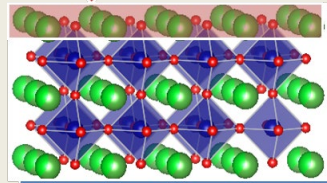
Collaboration with PNNL using well-established **button cell fabrication** process.



Pacific Northwest
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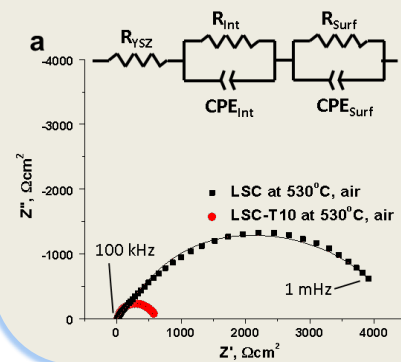
LSCF oxygen electrode **surface chemical modification** by solution infiltration.

Zr, Hf, Ti, Al, Nb

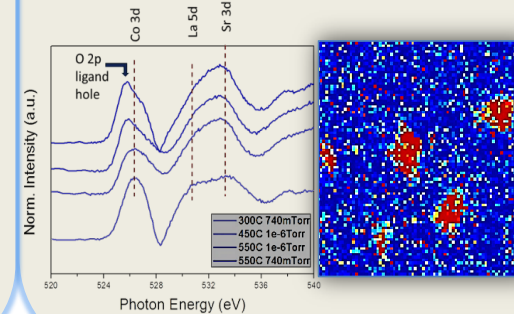


Bulk perovskite

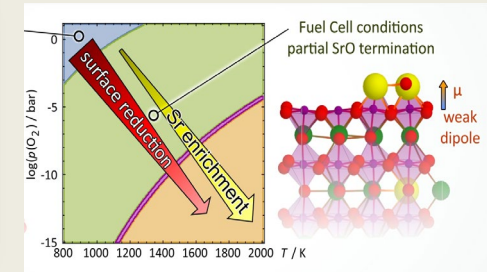
Electrochemical characterization of the electrode **performance and stability**.



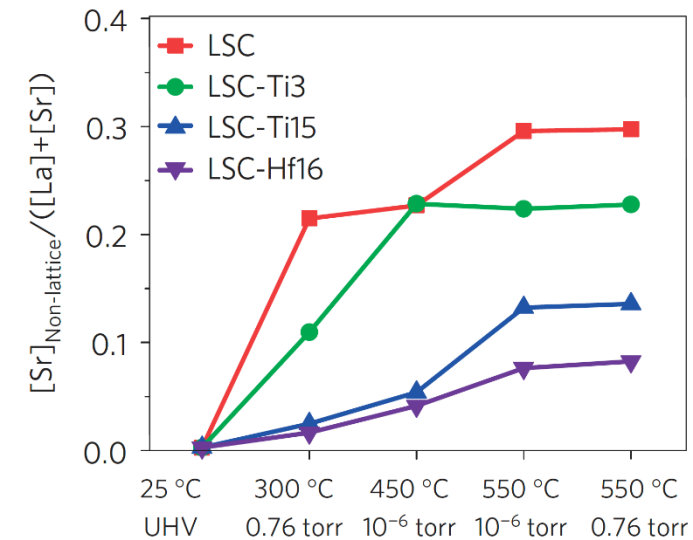
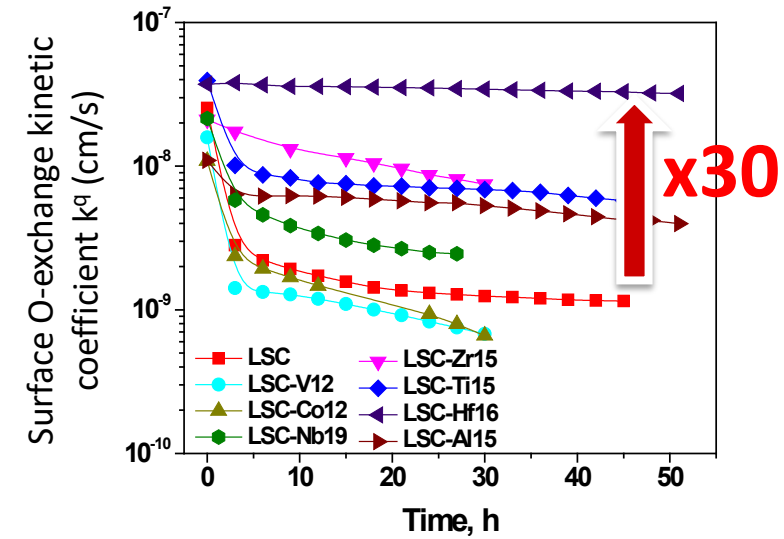
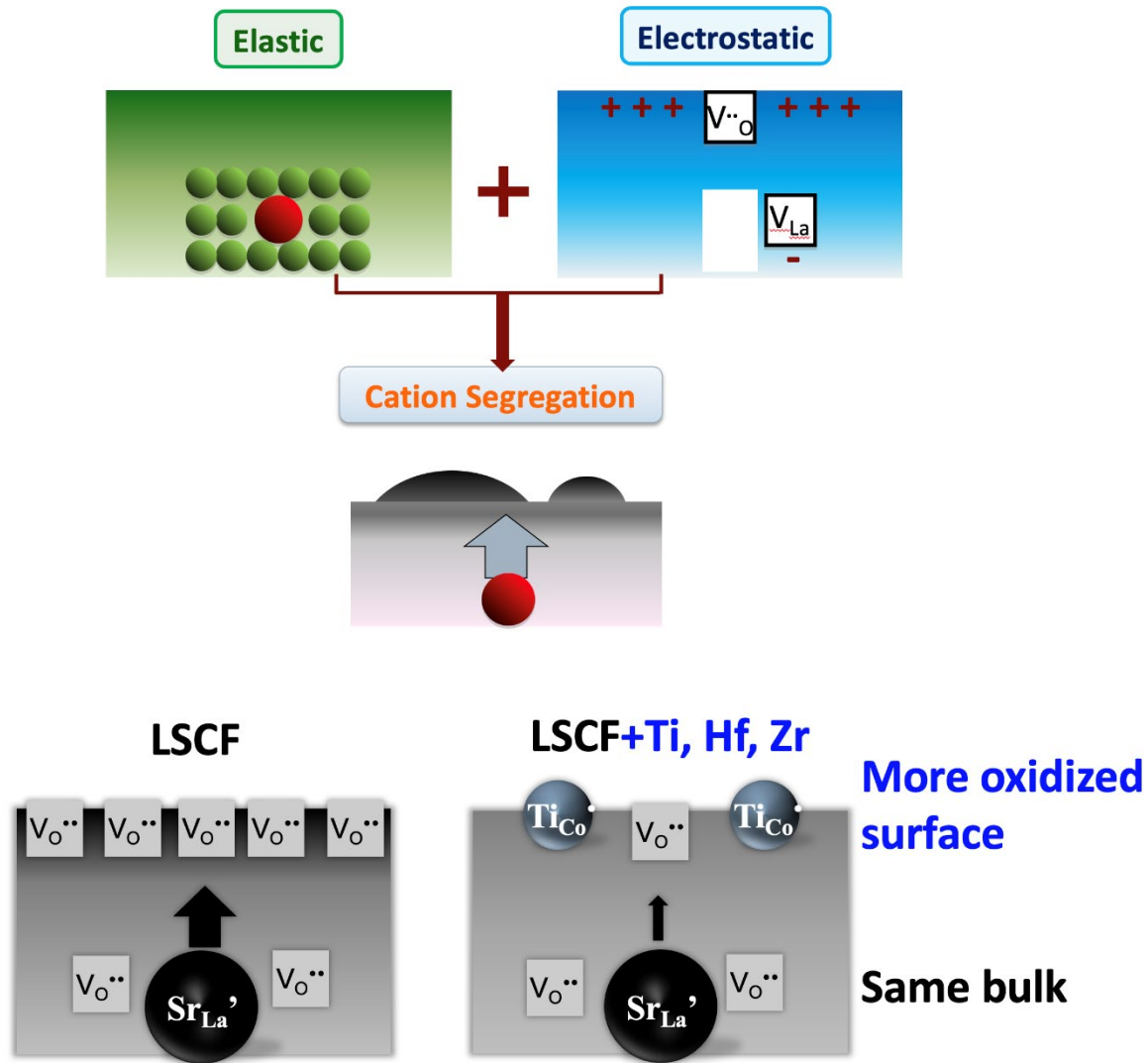
Characterization of **surface chemistry (Sr-segregation, Cr- / S-poisoning)** by XPS and AES, oxidation and bonding (XANES, EXAFS).



First-principles-based modeling of surface phase and reaction mechanisms. **Guide design of best surfaces.**



Perovskite oxide surface more stable and has faster oxygen exchange kinetics with oxidizable surface-cations.

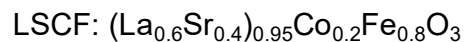
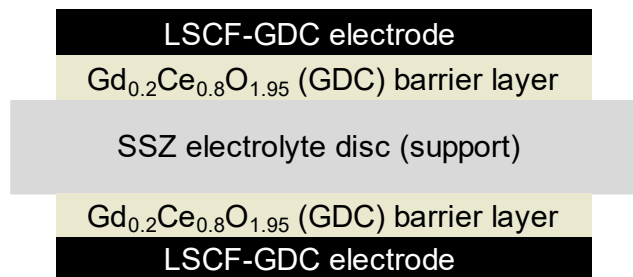


Lee et al. Yildiz, *J. Am. Chem. Soc.*, 2013, 135.
Kim, Bliem, Hess et al. Yildiz, *J. Am. Chem. Soc.*, 2020

LSC: Tsvetkov, Lu, Sun, Crumlin, Yildiz, *Nature Materials*, 2016, 15 (9).
LSM: Bliem, Kim, Yildiz, *J. Mat. Chem. A*. 2021

Surface modification of LSCF to suppress Sr (and ultimately Cr, S)

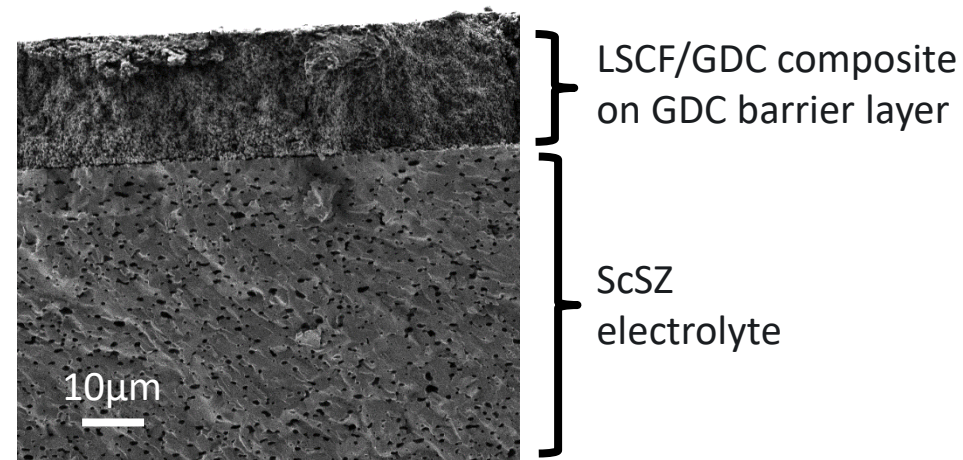
Our current system:



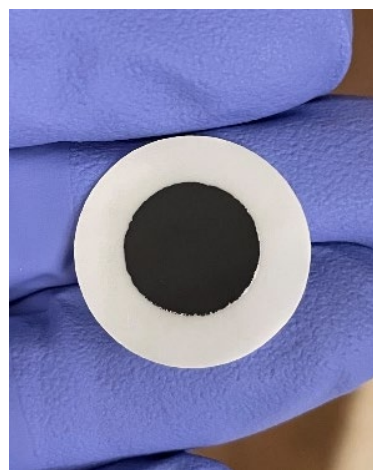
Cells fabricated at PNNL

Well-established button cell production process:

- Screen printing
- Sintering



Our approach controls surface chemistry through a physically-based and practical single-step infiltration:



As-prepared LSCF

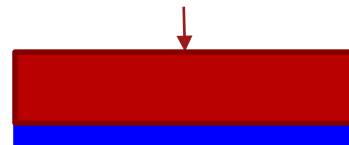


Aqueous solutions of metal nitrates, acetates and chlorides.



Metals: Zr, Hf, Ce, Pr, Nd
Infiltration parameters:
Reagent concentration, metal loading, surfactants.

Metal solution



Infiltrated LSCF

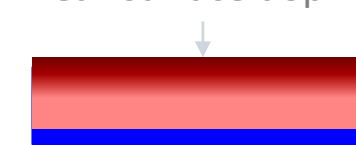


Anchoring of metal oxides on/into the LSCF surface



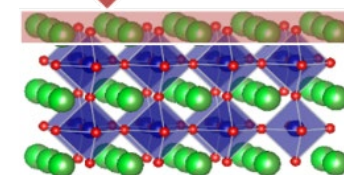
Annealing conditions:
Temperature, potential, gas.

Near-surface doping



Surface-modified LSCF

Hf, Zr, Ce, Nd, Pr

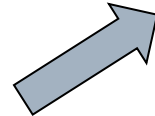
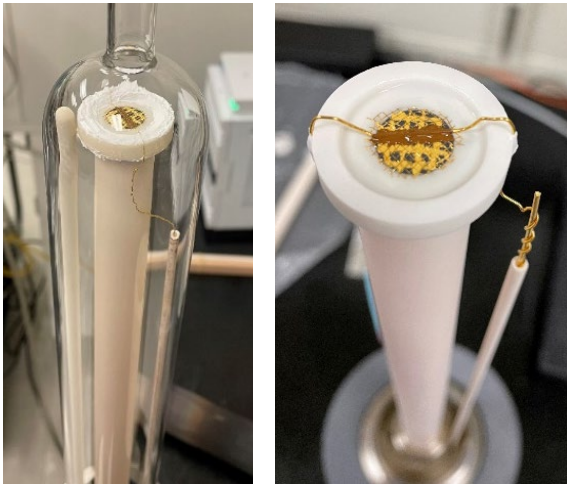


Bulk perovskite

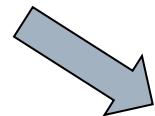
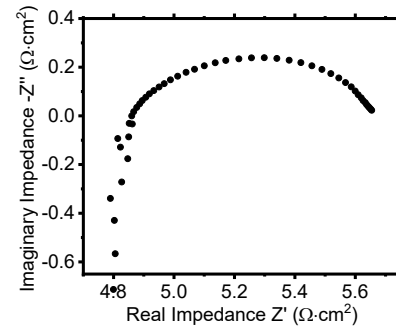
Electrochemical Characterization of Oxygen Electrodes at MIT

Double Chamber Electrochemical Setup

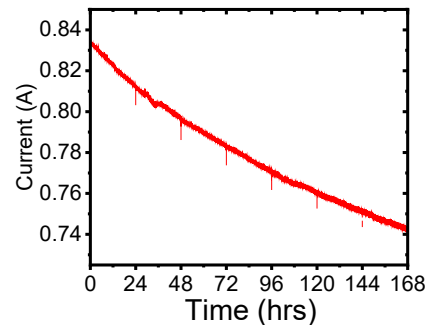
- I-V measurements
- Electrochemical impedance spectroscopy (EIS)



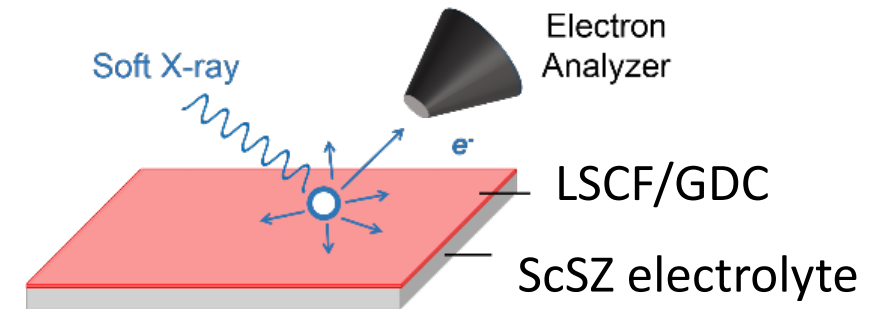
Charge transfer impedance



Temporal stability of current

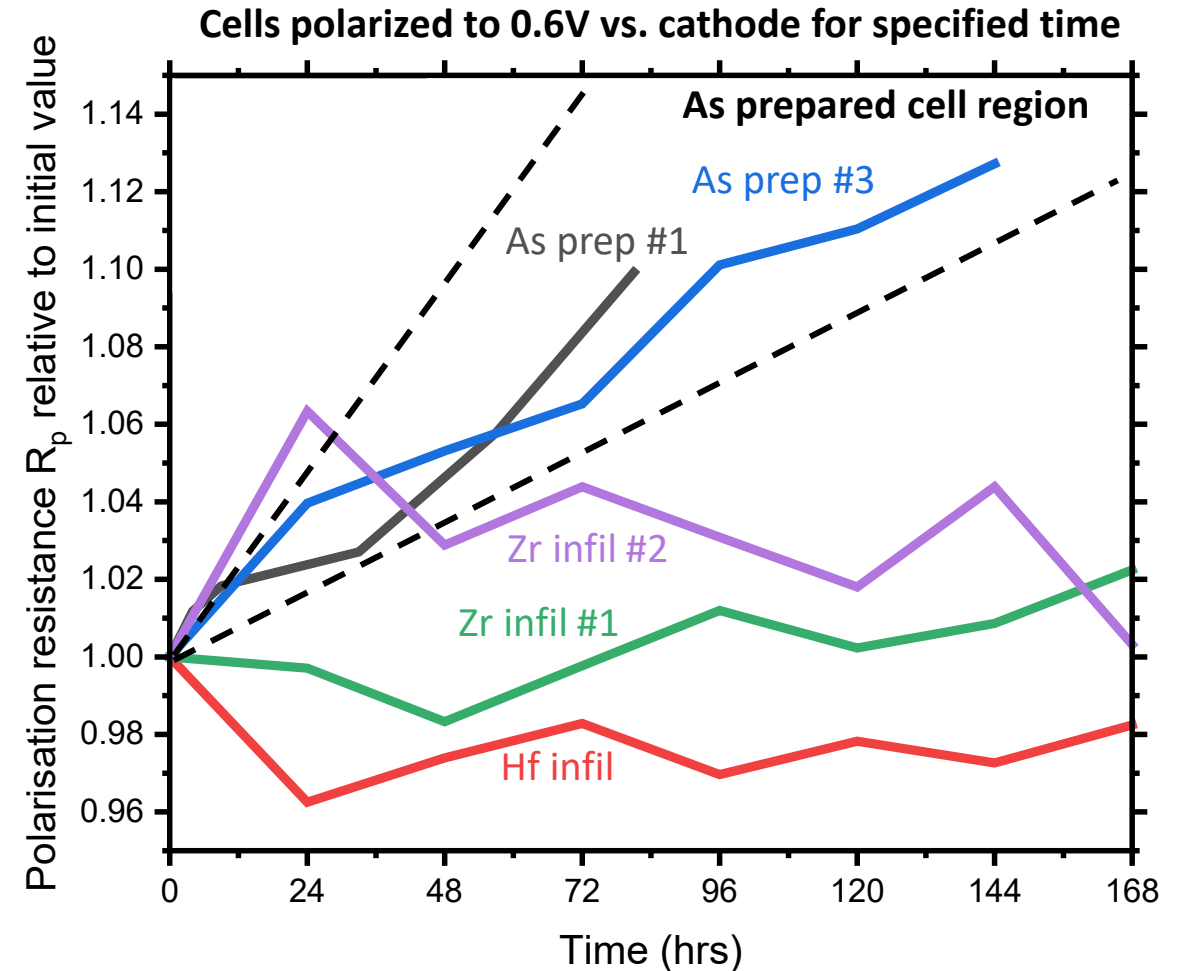
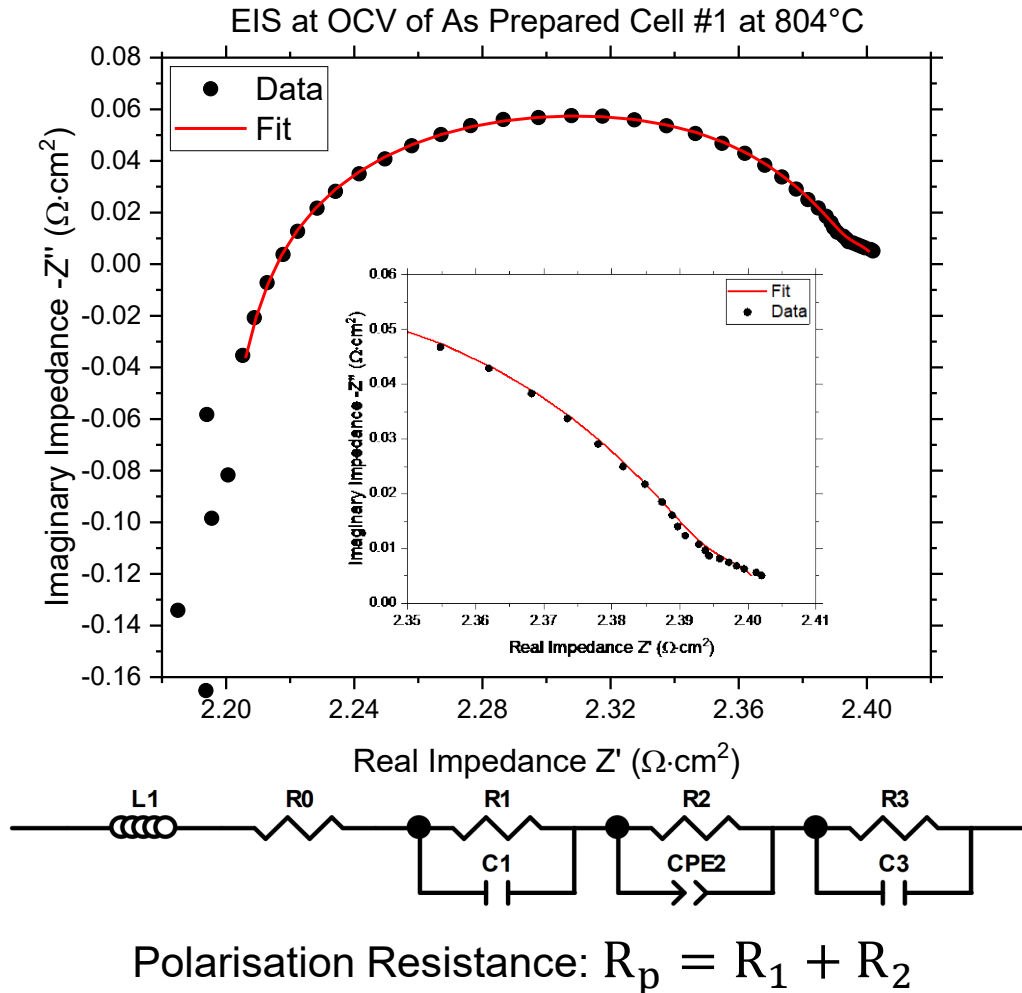


Surface chemical characterization: XPS, AES, EDX



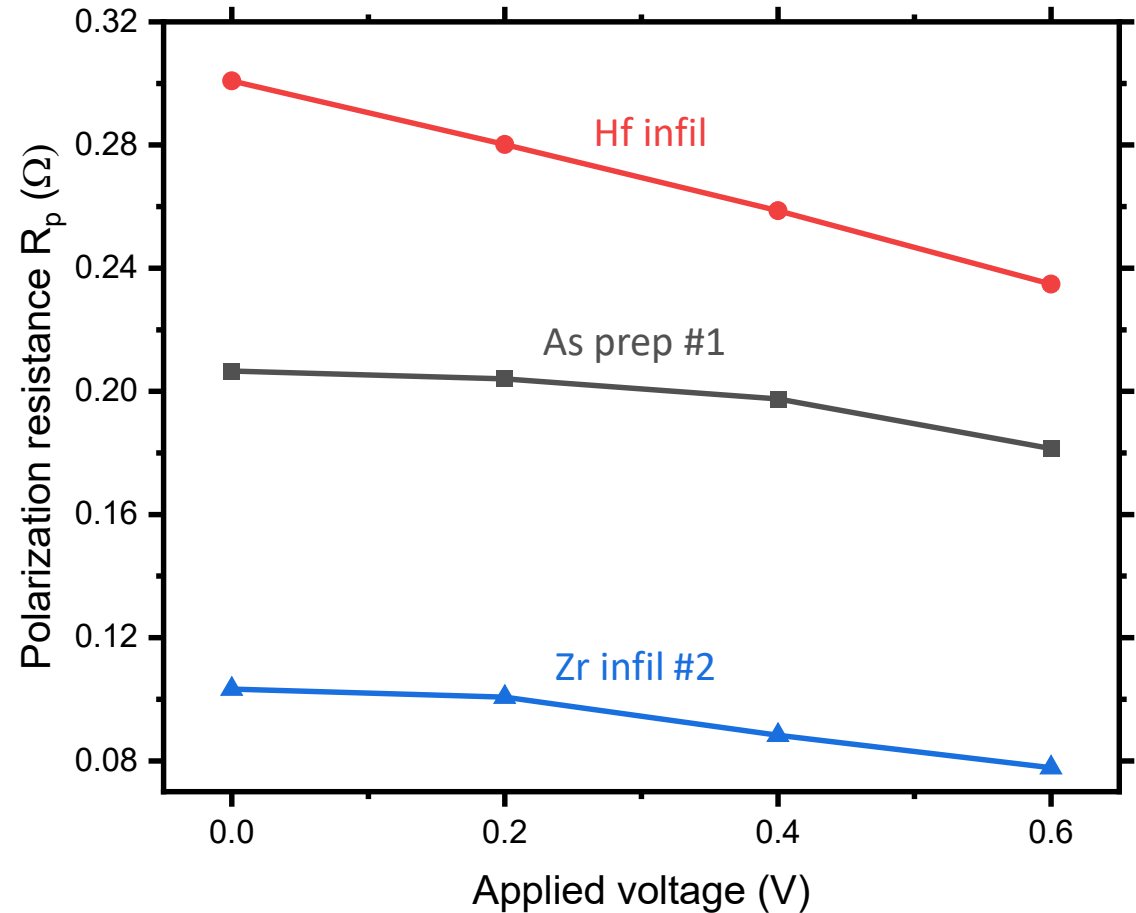
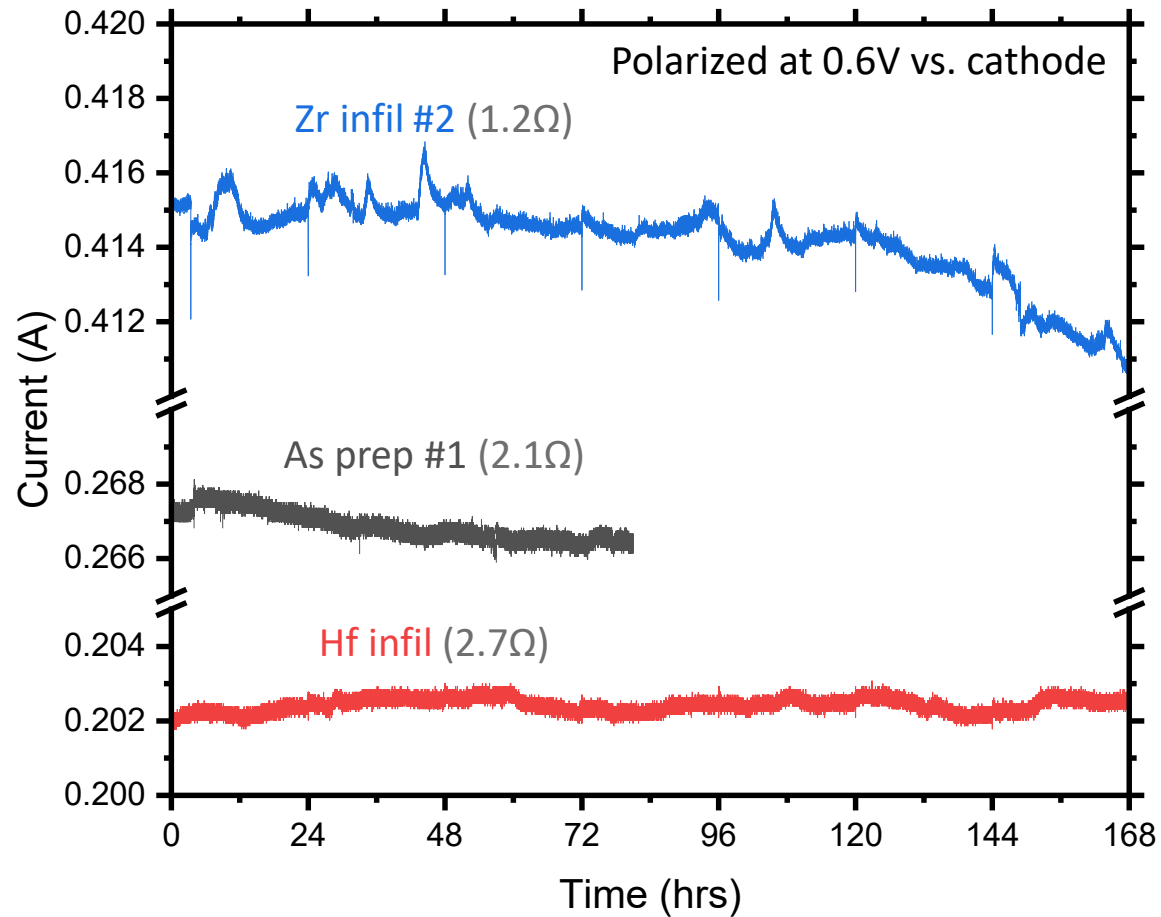
Structural characterization: XRD, SEM, TEM

EIS analysis at OCV – Hf, Zr infiltration stabilizes LSCF cells



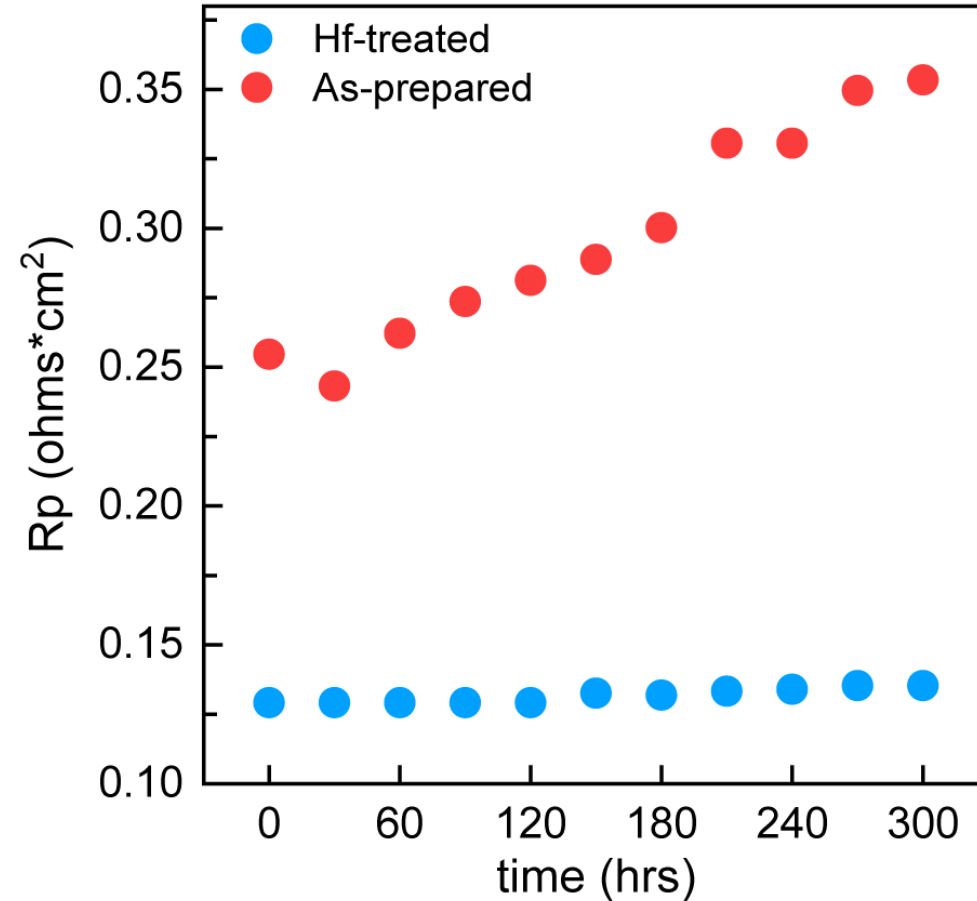
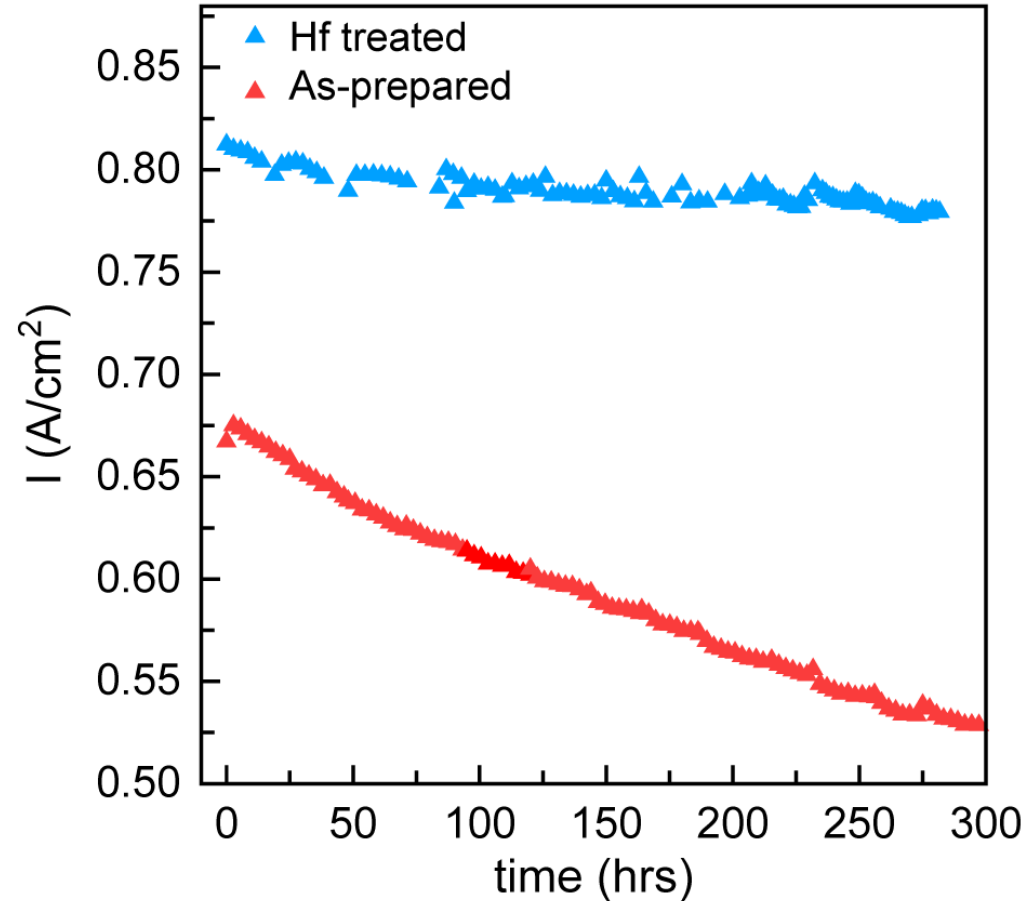
- For relative R_p changes, as prepared cells fall into a wide, monotonically increasing region (dashed black lines)
- Infiltrated cells show significantly suppressed R_p increase – LSCF stabilized by infiltration

Chronoamperometry analysis – Hf infiltration stabilizes current profile



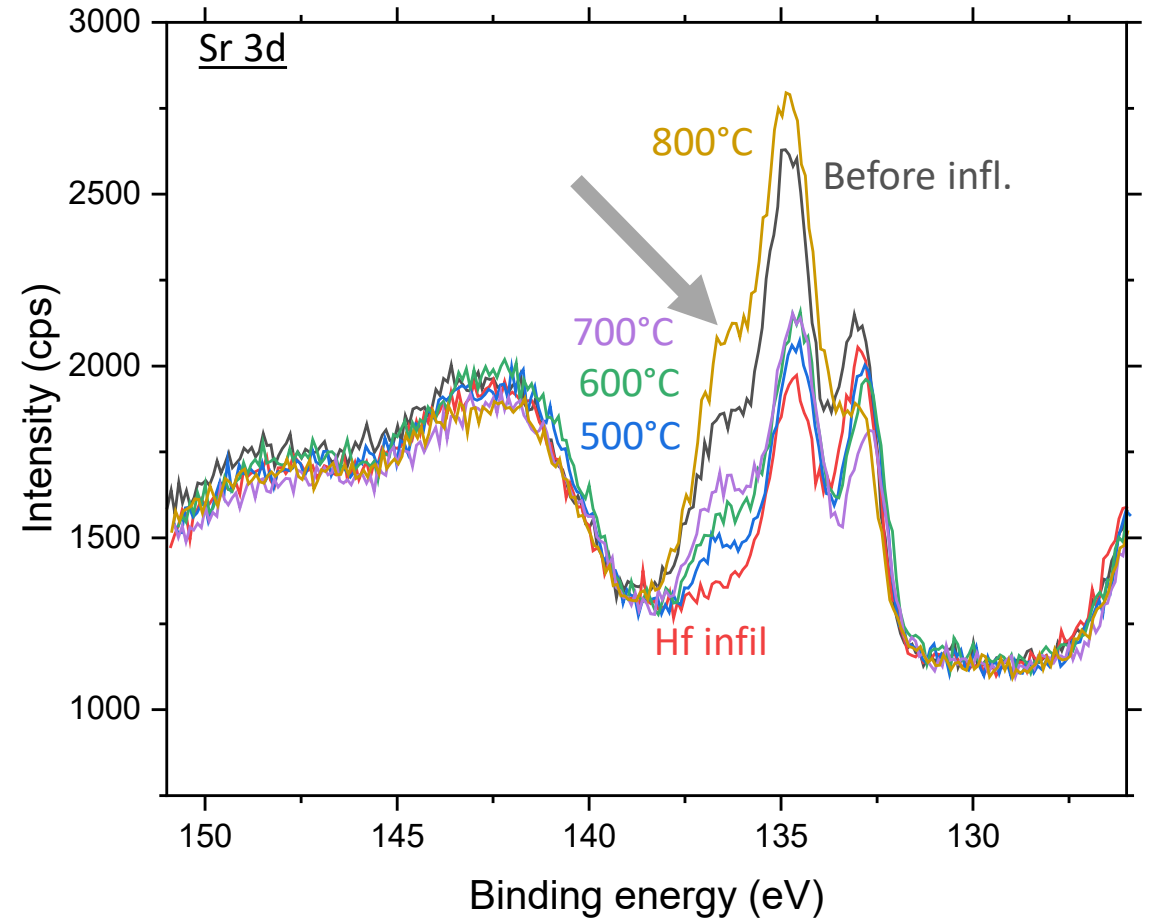
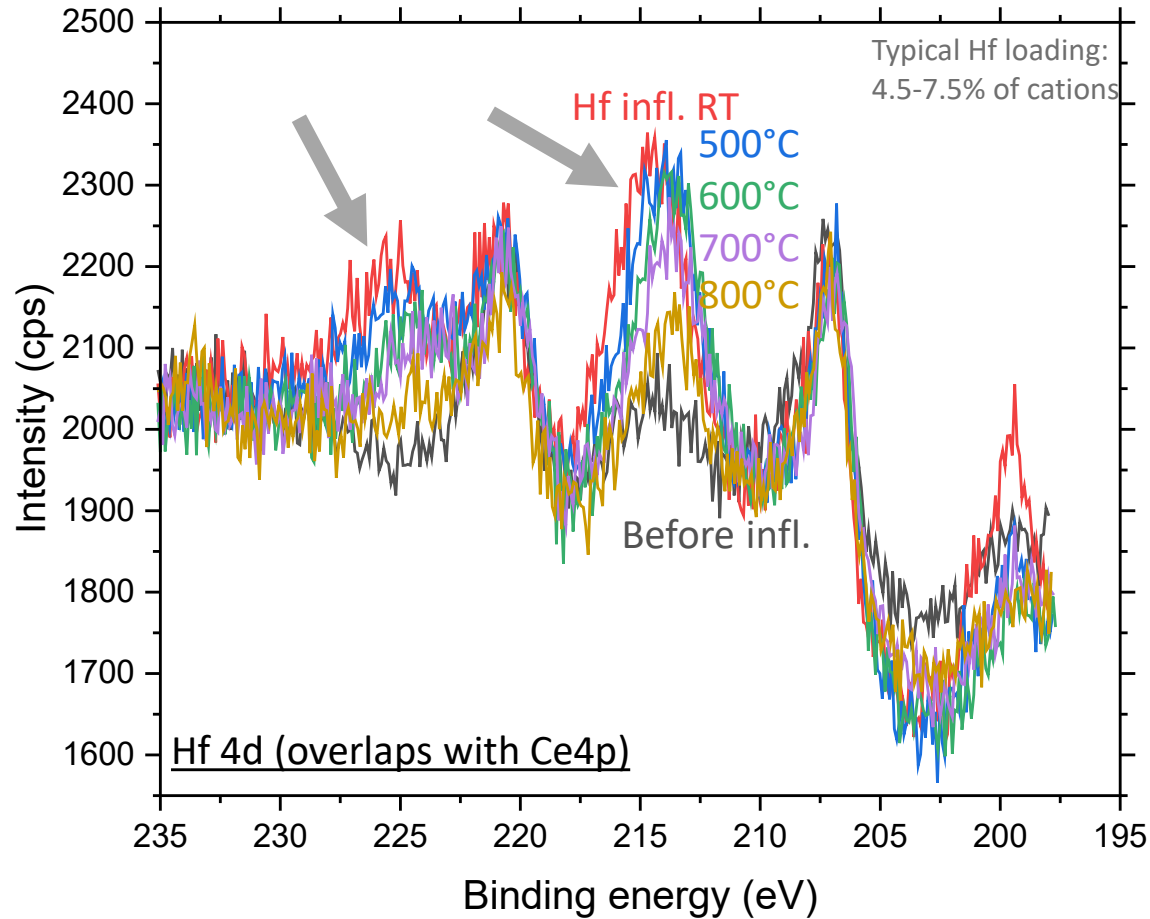
- As prepared cells: steady decrease in current vs. time
- Hf infiltrated cell: stable over 7 days – fluctuations due to furnace
- Zr infiltrated cell: initial stabilization but then sharp degradation

Improvement in electrochemical stability and activity with Hf infiltration in LSCF porous electrode (of OxEon)



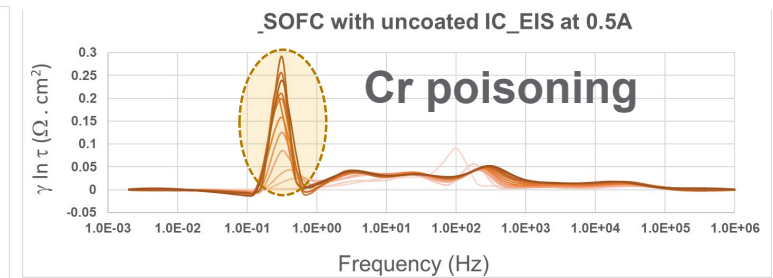
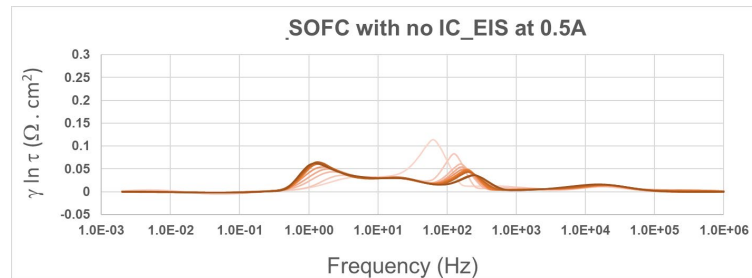
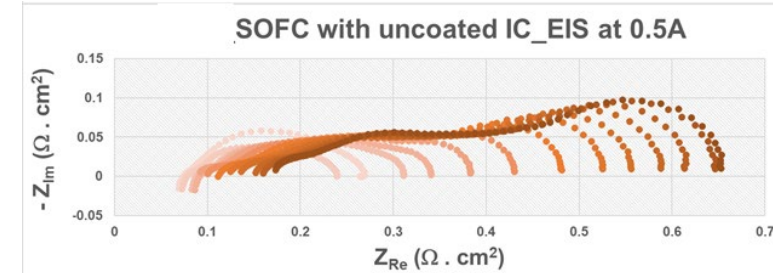
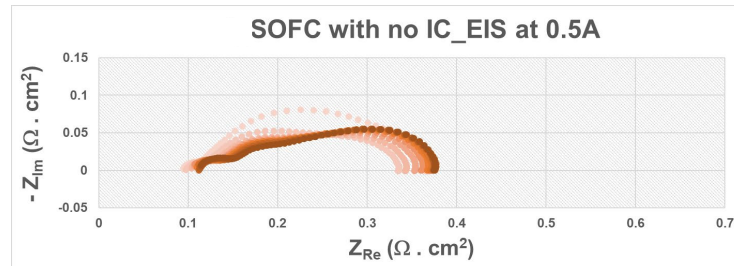
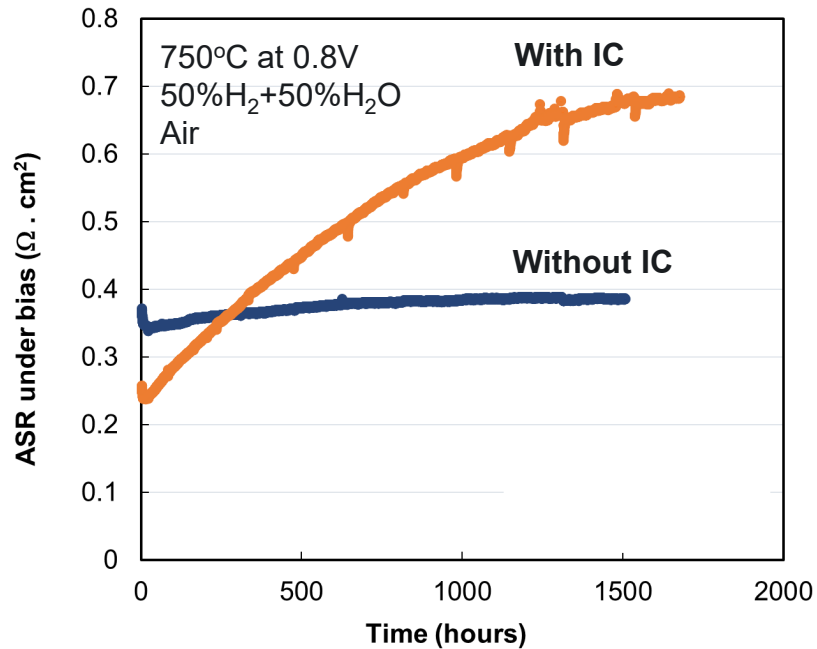
Samples made by OxEon (Tyler Hafen and Elango Elangovan)

XPS post-mortem analysis – dissolution of dopants at $T > 600^\circ\text{C}$



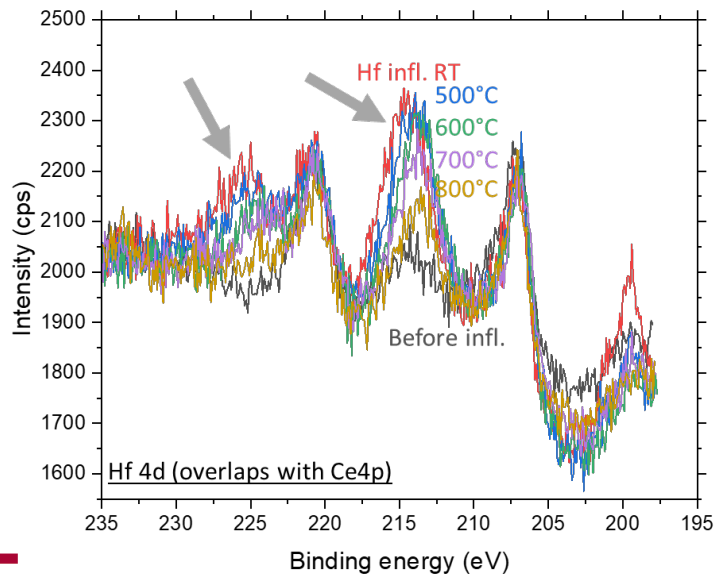
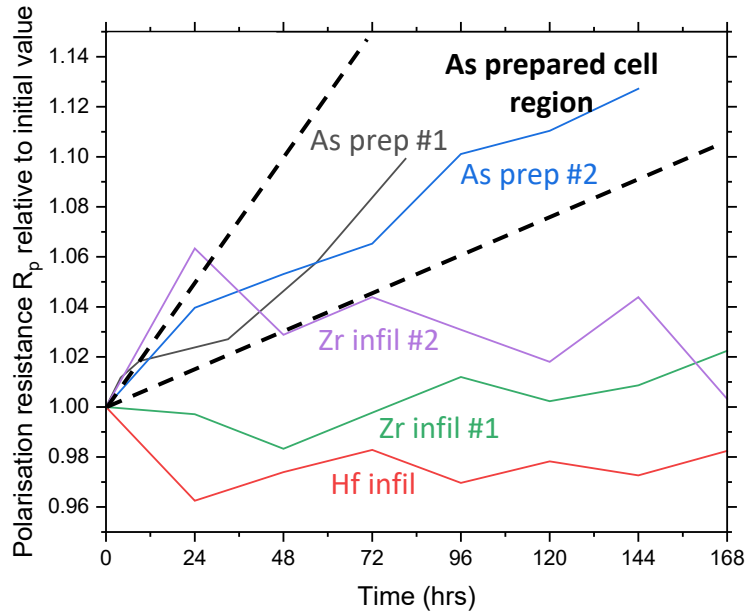
- Infiltrated Hf/Zr species exhibit dissolution away from surface at $T > 700^\circ\text{C}$
- Surface Sr 3d component constant to 500/600/700°C, much larger increase at 800°C (upon near complete dissolution of Hf).

SOFC Testing with and without Uncoated Metal Interconnect



- Cr contamination from uncoated IC limits oxygen adsorption or oxygen exchange process as indicated by DRT peak at 0.1 – 1 Hz
- Ohmic resistance significantly increased compared to test without IC.

Experimental summary – Hf/Zr infiltration stabilizes LSCF surfaces



□ Preliminary findings thus far:

1. Hf and Zr may increase LSCF cathode stability, by suppressing increase in polarization resistance.
2. Hf/Zr are diffuse away from surface at $T > 600^\circ\text{C}$, but still improve cell stability:

□ Possible sub-surface influence?

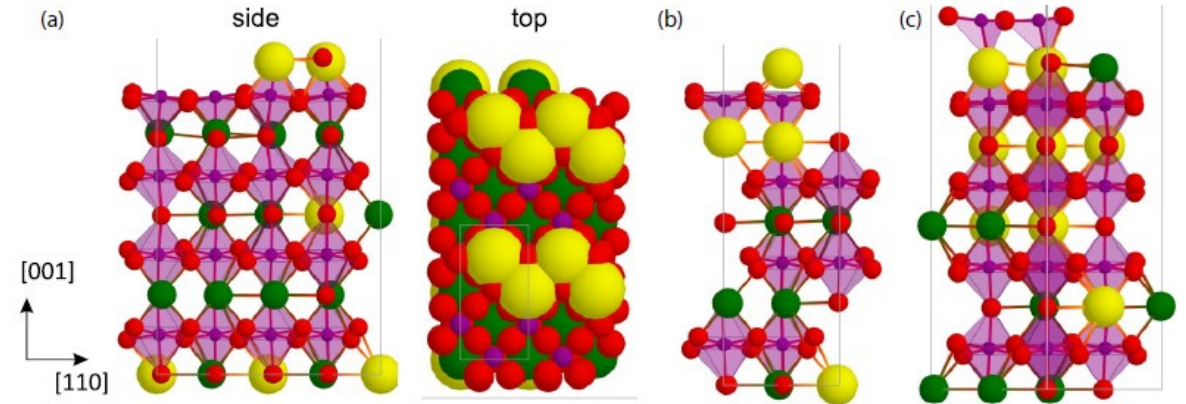
□ Future work:

1. Repeat experiments with new batch of samples from PNNL.
2. Investigate larger dopants: Nd, Ce, Pr which may not diffuse away due to their larger size.
3. Incorporate infiltration into sample preparation for Cr/S poisoning tests.

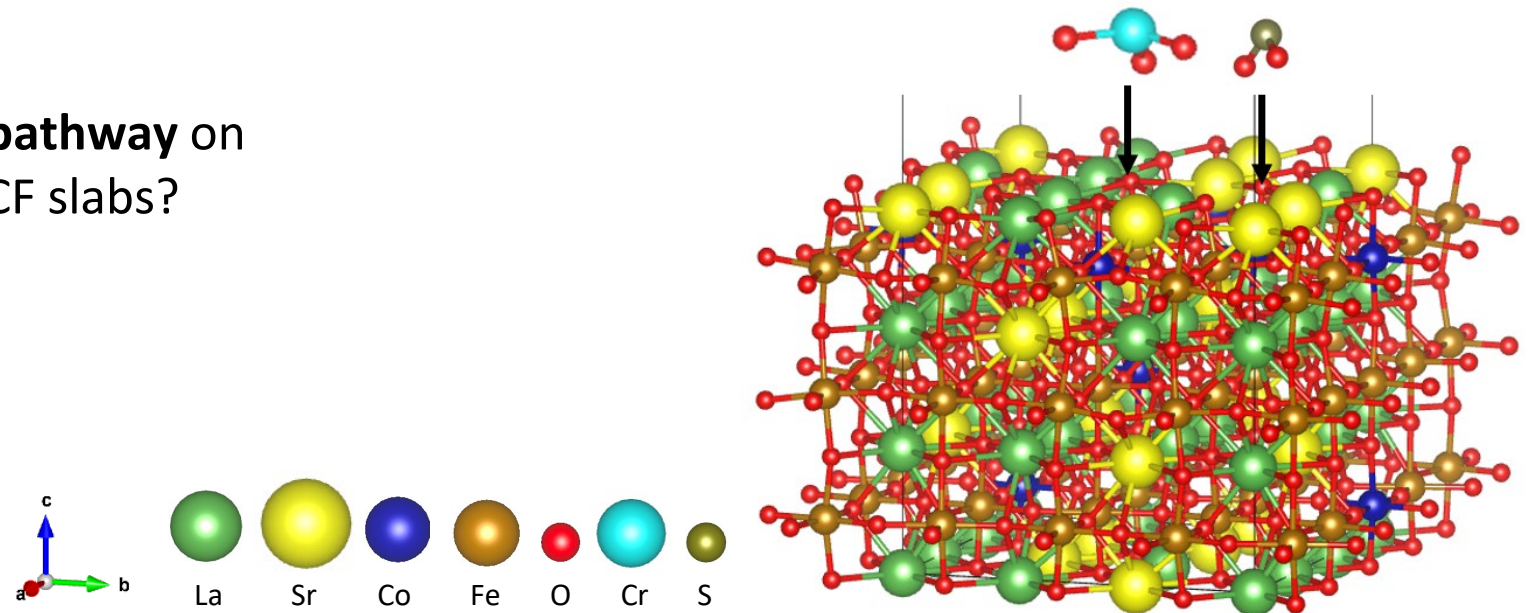
Computational investigation of Cr & S poisoning on realistic LSCF slabs

Aims to answer two questions:

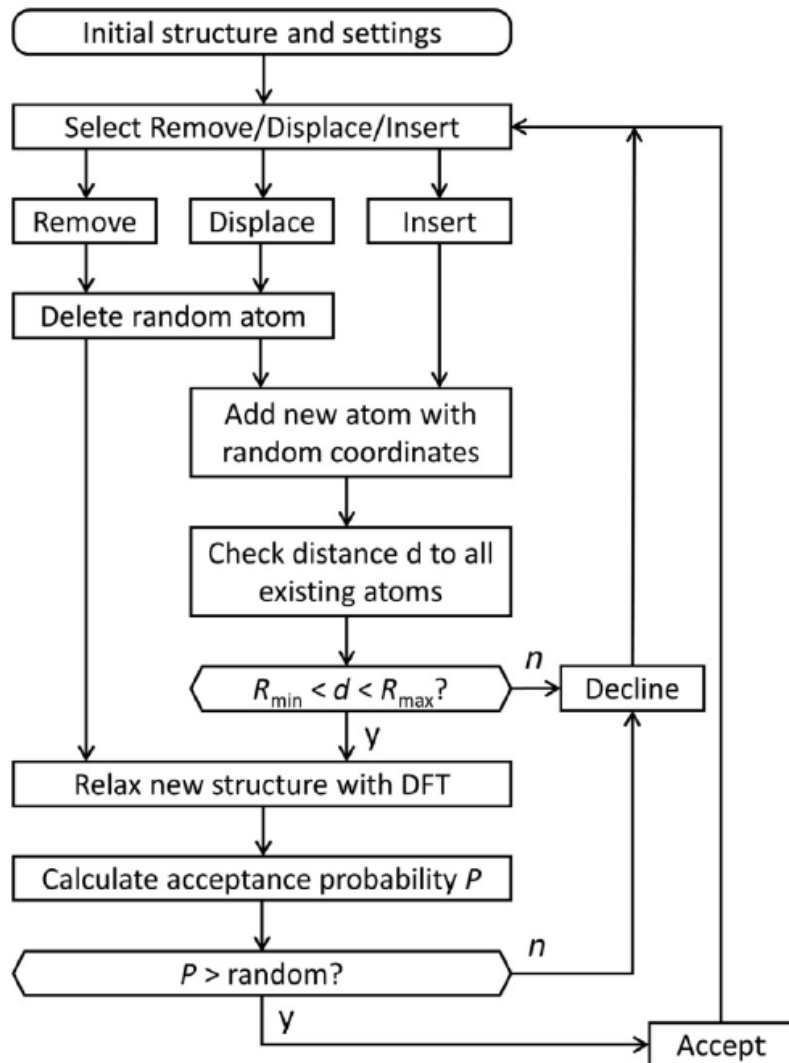
- What is the **realistic** surface reconstruction of the pristine and surface-modified LSCF at operational thermodynamic conditions?
- What is the **Cr and S deposition pathway** on pristine and surface-modified LSCF slabs?



Franziska Hess and Bilge Yildiz, Polar or not polar? The interplay between reconstruction, Sr enrichment, and reduction at the $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ (001) surface, *Phys. Rev. Materials*, 2020



Grand Canonical Monte Carlo with Density Functional Theory for resolving LSCF surface reconstructions



- Given the vast LSCF surface configuration space involved, we need an automated search for the minimum energy structure
- Grand canonical Monte Carlo (GCMC) is a physically motivated scheme to identify the most stable surface oxide configuration at a given chemical potential and temperature.

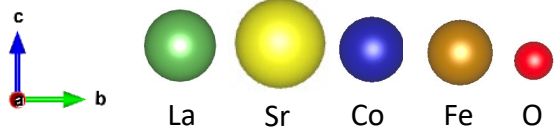
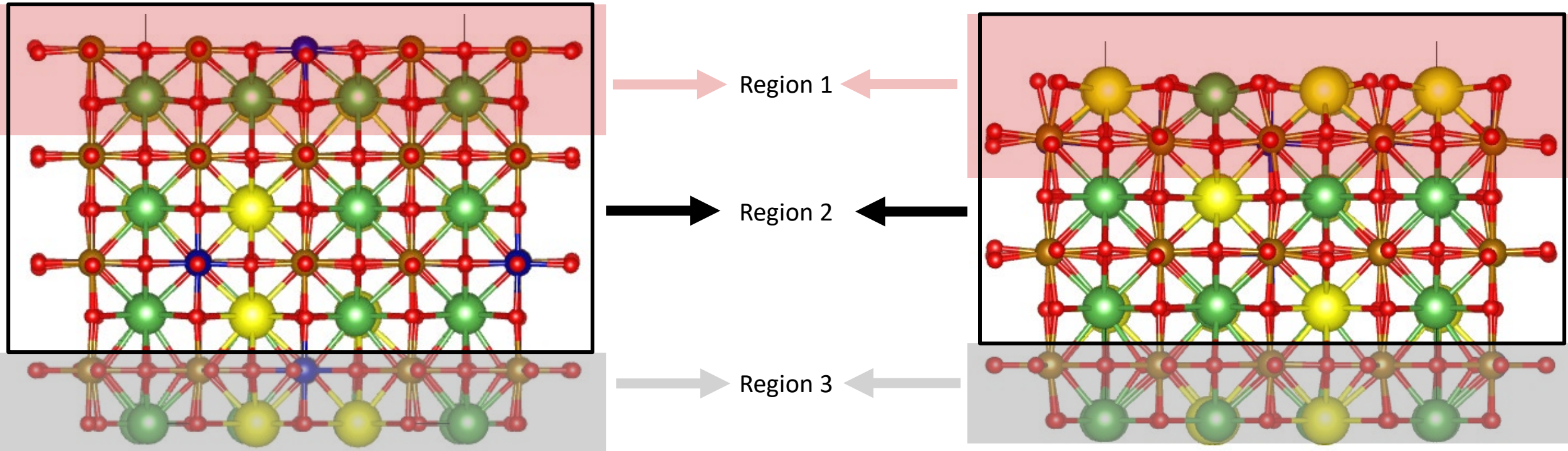
$$P_{\text{move}} = \min\{1, e^{-\Delta U/k_B T}\}$$

$$P_{\text{add}} = \min\left\{1, \frac{V}{(N+1)\Lambda^3} e^{-(\Delta U - \mu)/k_B T}\right\}$$

$$P_{\text{remove}} = \min\left\{1, \frac{N\Lambda^3}{V} e^{-(\Delta U + \mu)/k_B T}\right\}$$



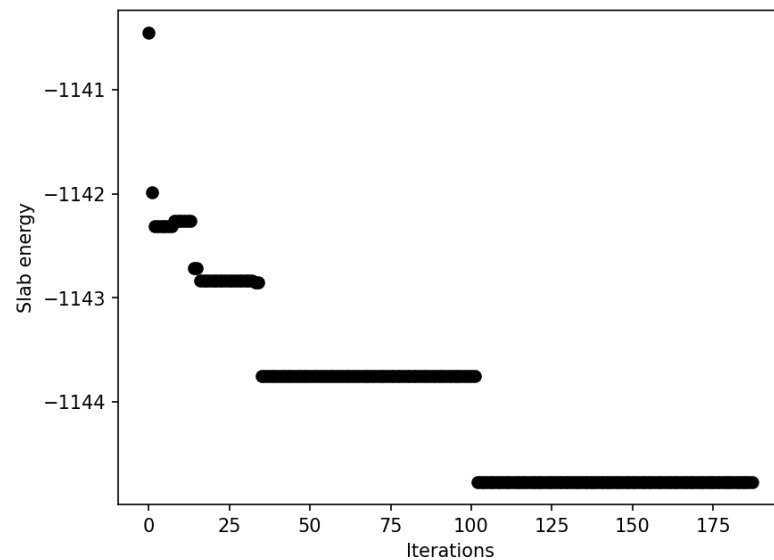
Initial structures and GCMC modifications



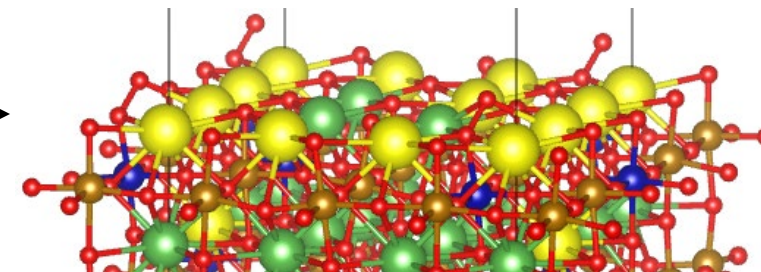
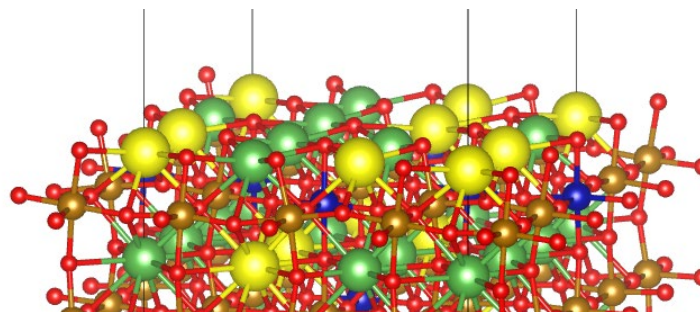
- Region 1: Full GCMC on both metal cations and oxygens
- Region 2: MC (exchange site position; exchange site cations positions; assume Sr and La still at A site, Co and Fe still at B site) on cations, GCMC on oxygens
- Region 3: Fix atoms in positions

Current most stable structures

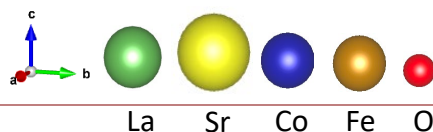
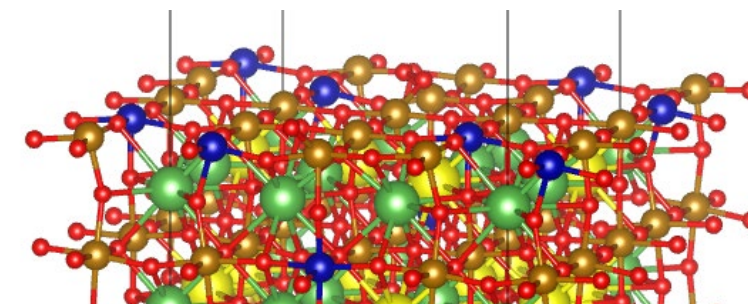
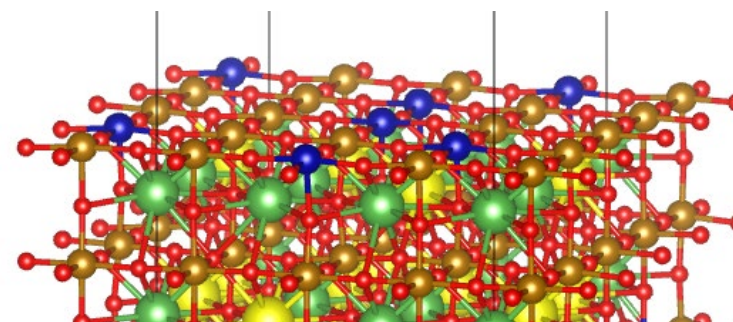
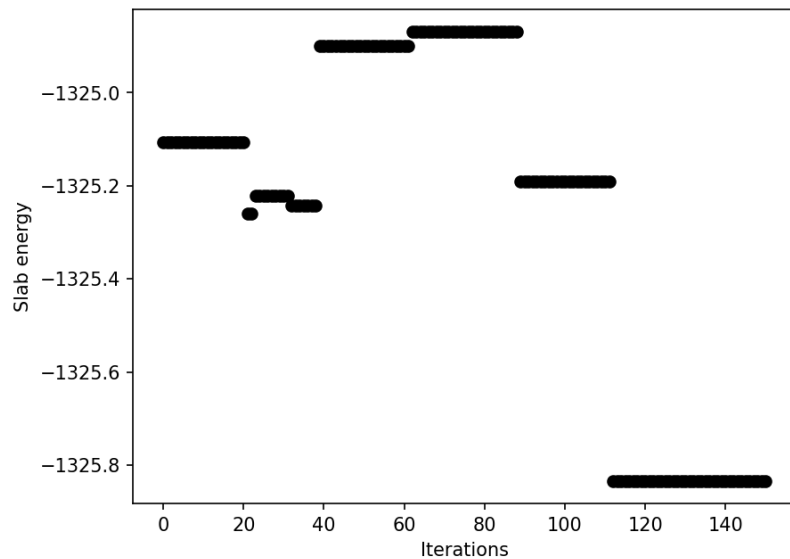
$T = 800 \text{ K}$, $P_{\text{O}_2} = 10^{-4} \text{ atm}$



Initial AO-terminated



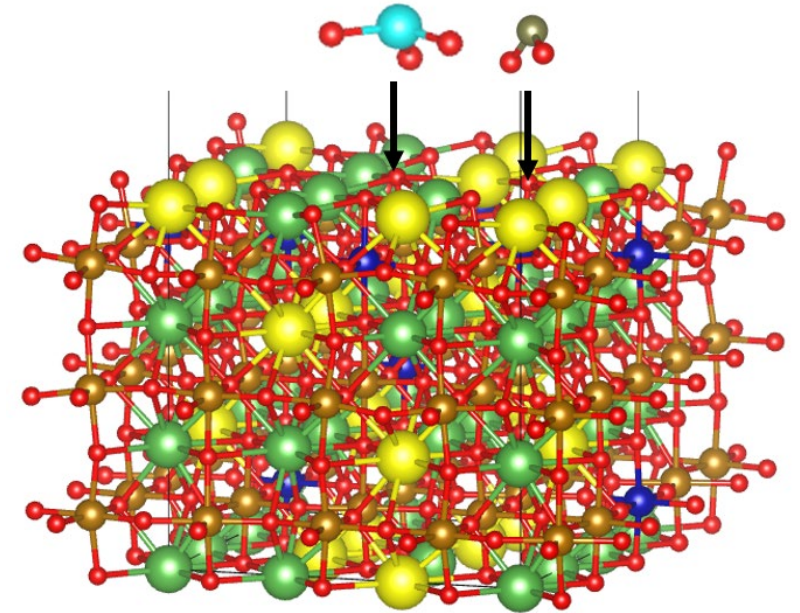
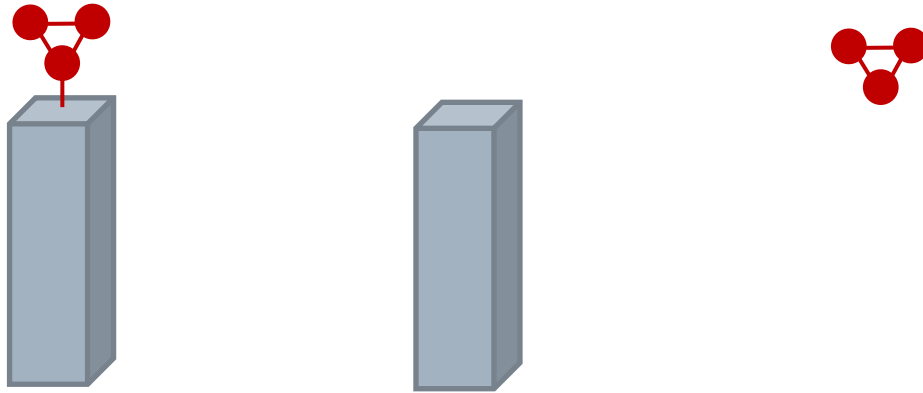
Initial BO₂-terminated



DFT calculation to find adsorption energies

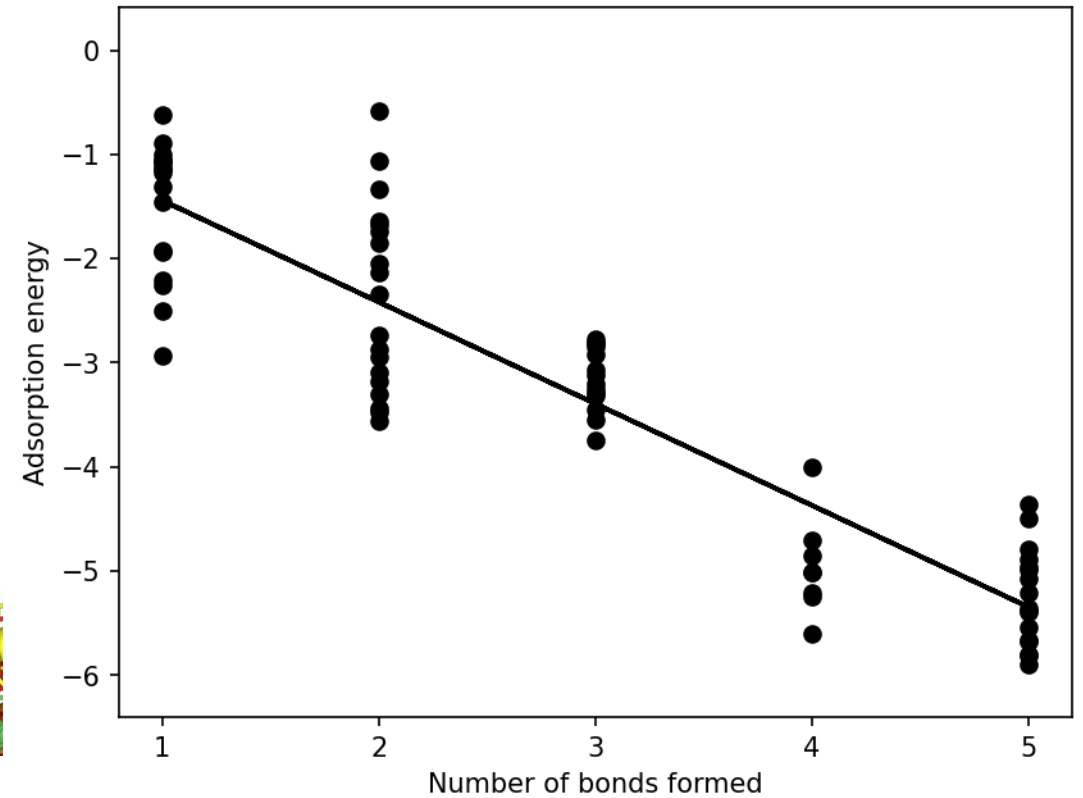
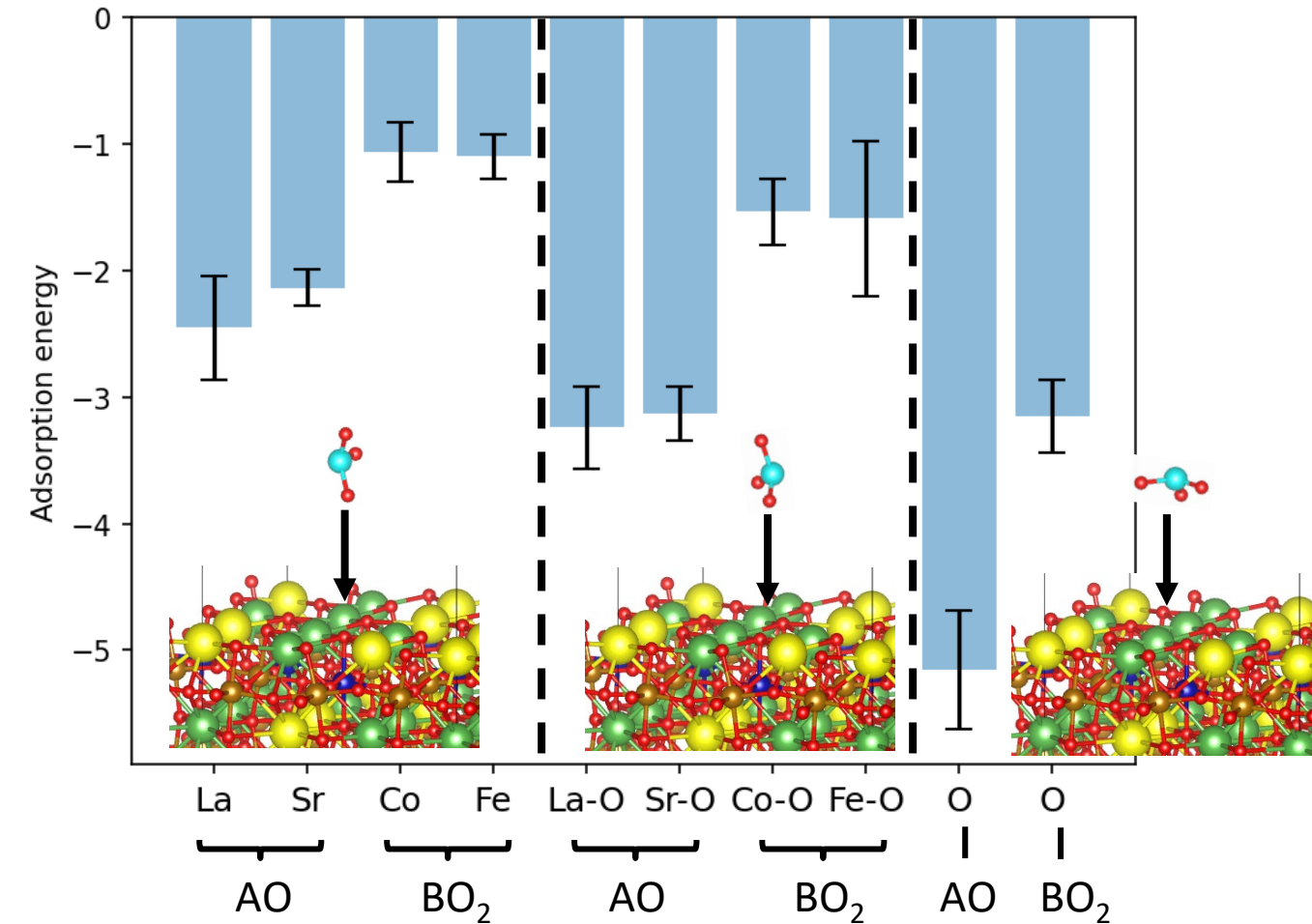
Adsorption energy:

$$E_{ads} = E_{adsorbed}^{DFT} - E_{unadsorbed}^{DFT} - E_{molecule}^{DFT}$$



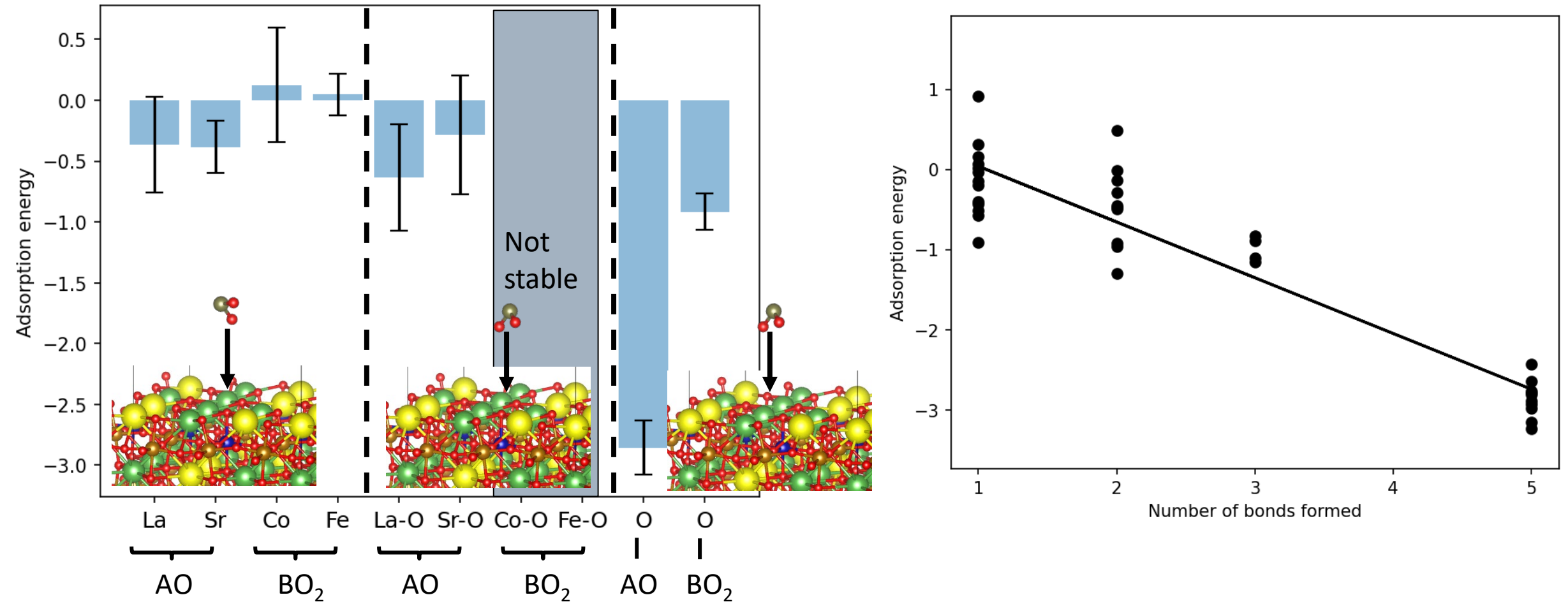
- First study the adsorption on pristine, non-polarized LSCF slabs
- Multiple adsorption configurations need to be studied

CrO₃ adsorption energies vs configurations



- CrO₃ adsorption energies are all negative for pristine LSCF slabs, whereas SO₂ is slightly more positive
- Adsorption energies decrease as the number of bonds formed from the adsorption increase
- BO₂-terminated slabs have higher (yet still negative) adsorption energies

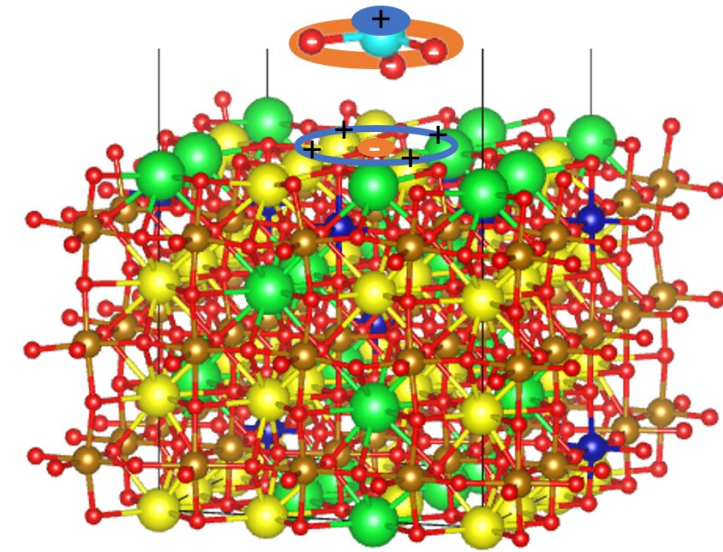
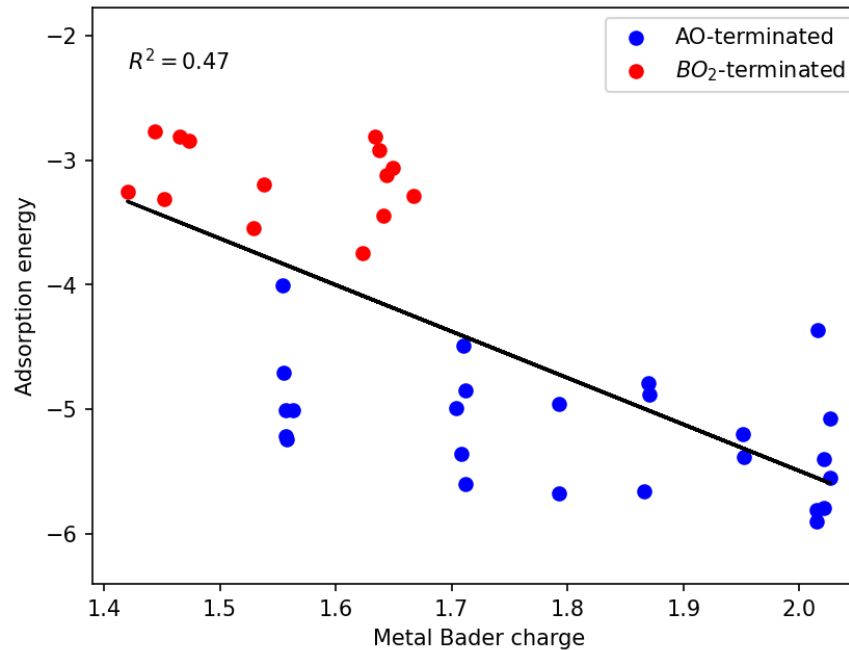
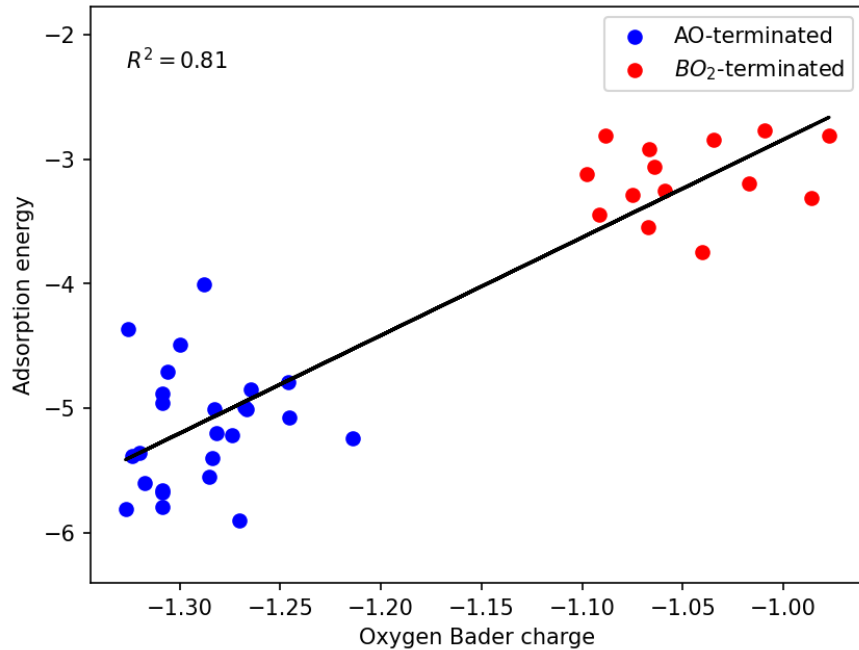
SO₂ adsorption energies vs configurations



- CrO₃ adsorption energies are all negative for pristine LSCF slabs, whereas SO₂ is slightly more positive
- Adsorption energies decrease as the number of bonds formed from the adsorption increase
- BO₂-terminated slabs have higher (yet still negative) adsorption energies

O-Bader charge as an electrostatic correlator for CrO_3 adsorption

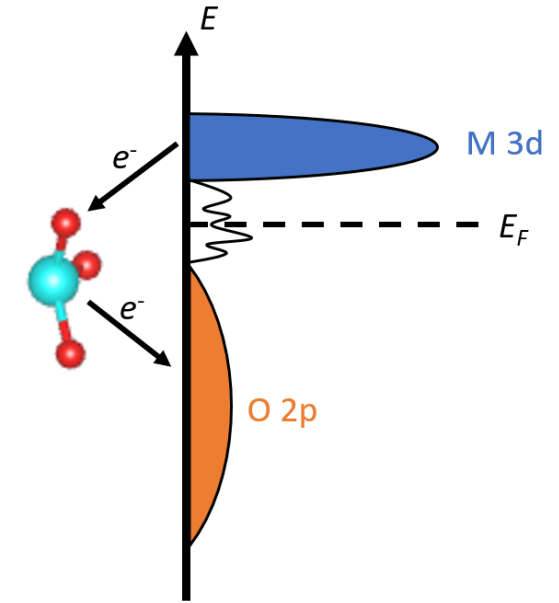
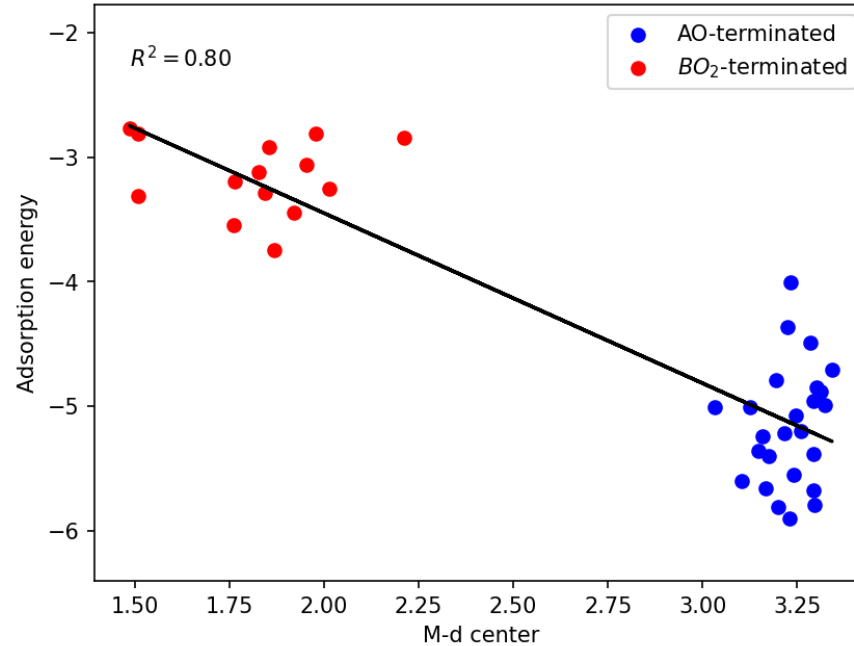
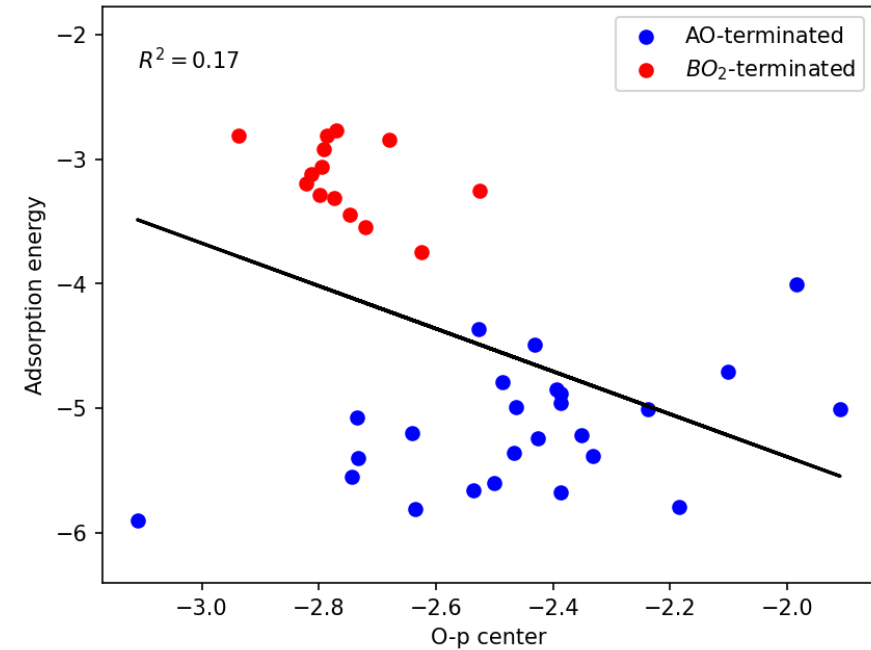
- Why adsorption energies differ at different surface oxygen adsorption site?
- What characteristics of the surface oxygen correlate with the adsorption energies?



- O-Bader charge as the dominant electrostatic correlator. The adsorption energy increases as O-Bader charge increases.
- M-Bader charge correlates less with the adsorption energies.
- Surface O – Cr electrostatic interaction is an important correlator with CrO_3 adsorption energies.

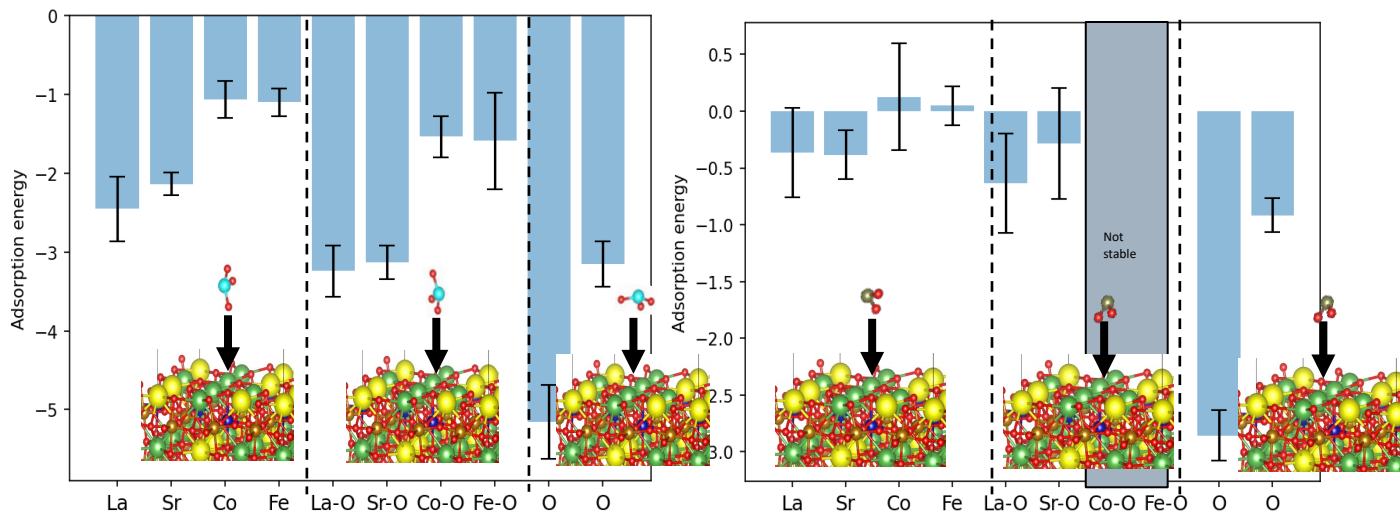
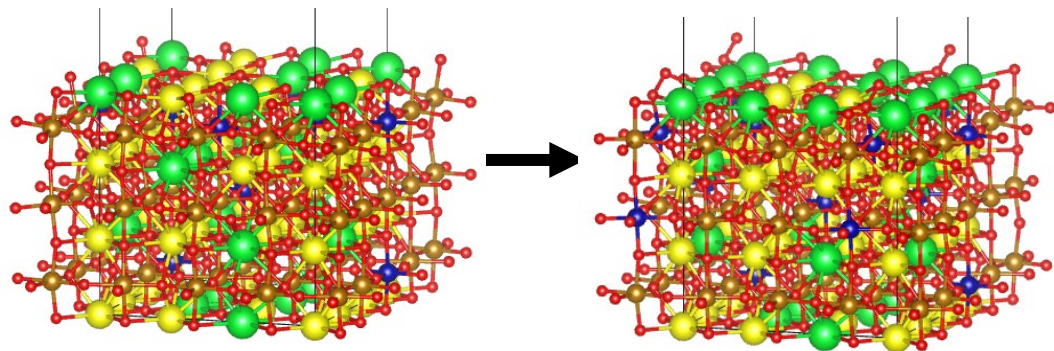
M d-center as an charge transfer correlator for CrO_3 adsorption

- Why adsorption energies differ at different surface oxygen adsorption site?
- What characteristics of the surface oxygen correlate with the adsorption energies?



- O-p center correlates less with the adsorption energies.
- M-d center as the dominant electrostatic correlator. The adsorption energy increases as M-d center decreases.
- O (of CrO_3) to M (of surface LSCF) charge transfer is an important correlator with CrO_3 adsorption energies.

Computational summary – modeling on realistic LSCF surfaces to investigate Cr & S poisoning pathways



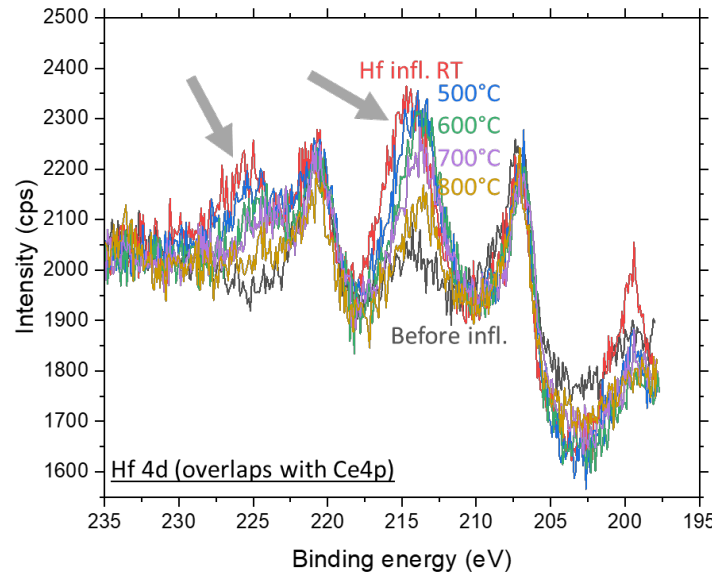
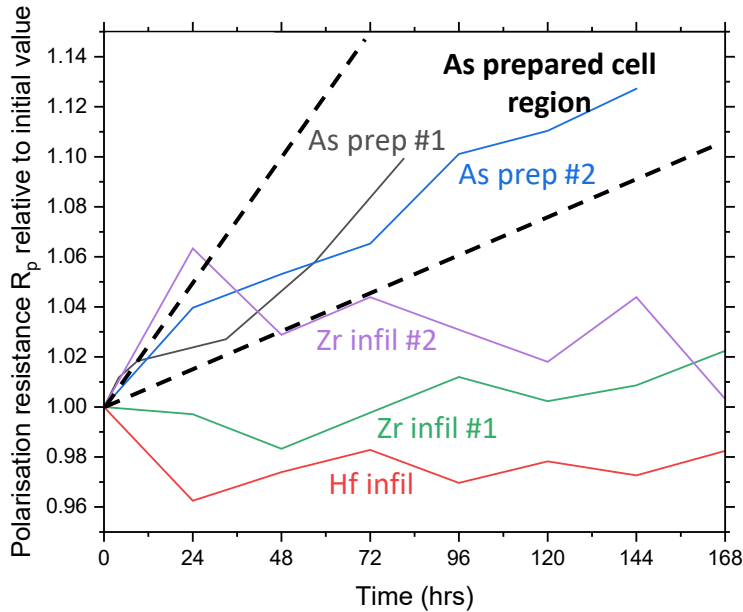
Key takeaways:

1. Established modified GCMC to identify the most stable surface oxide configuration
2. CrO_3 and SO_2 adsorption energies are mostly **negative** on LSCF.
3. **Electrostatic interaction** and **charge transfer** are two dominant factors for CrO_3 and SO_2 adsorption.

Future work:

1. Reaction path beyond adsorption in CrO_3 and SO_2 deposition using dynamic simulations.
2. Investigate the surface infiltrants stability and how they modify the surface structure and resistance against poisoning.

Summary and future work

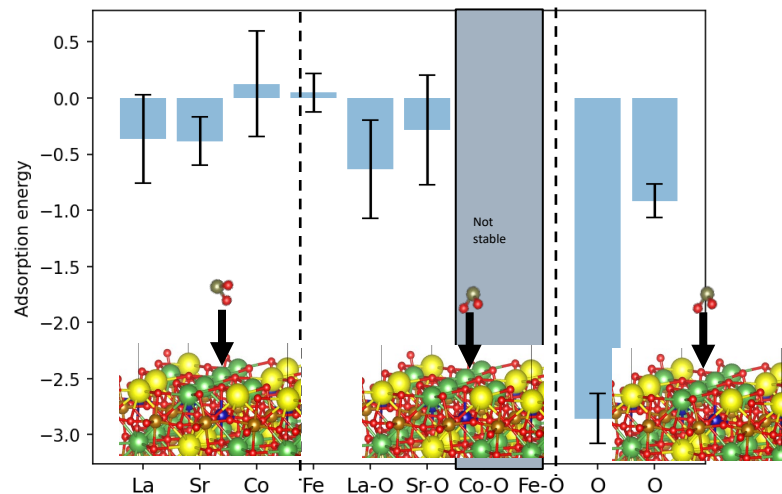
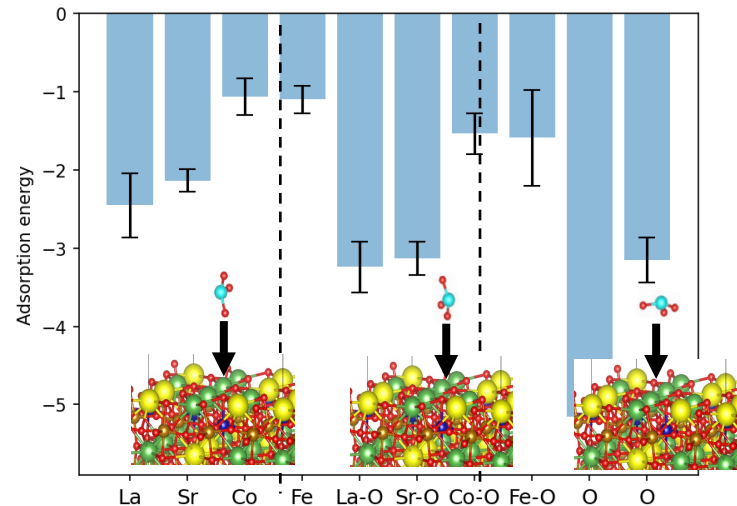


Till now:

- LSCF surface gets more stable with Hf/Zr, but how? Subsurface effects?
- AO-terminated surfaces more susceptible to CrO_3 and SO_2 adsorption.

Next Steps:

- Infiltrant stability and surface modification impacts with more samples/experiments, including in Cr and S environment.
- Cr and S poisoning mechanism at different surfaces, beyond adsorption.

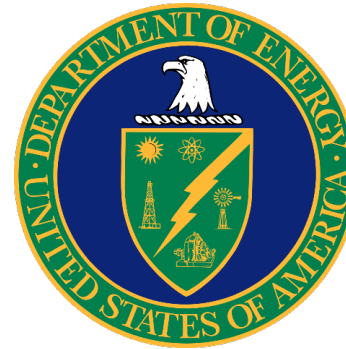


Acknowledgements

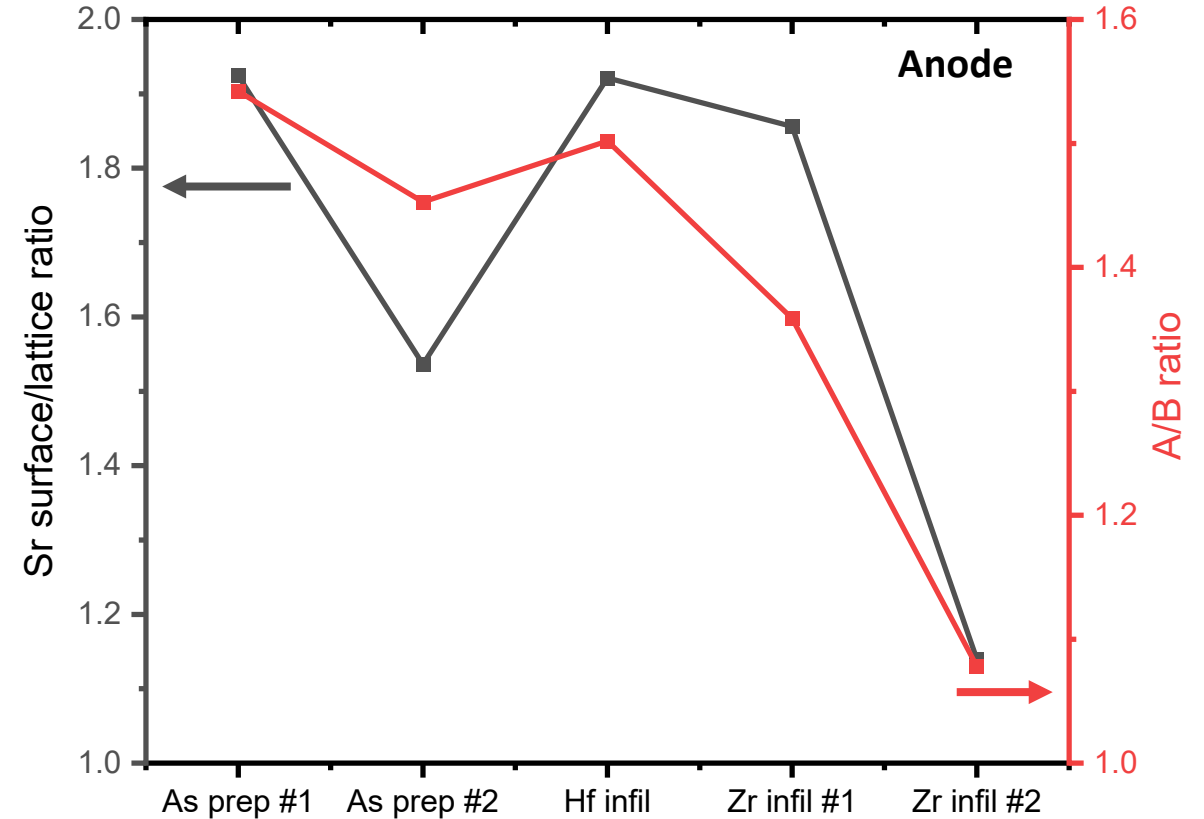
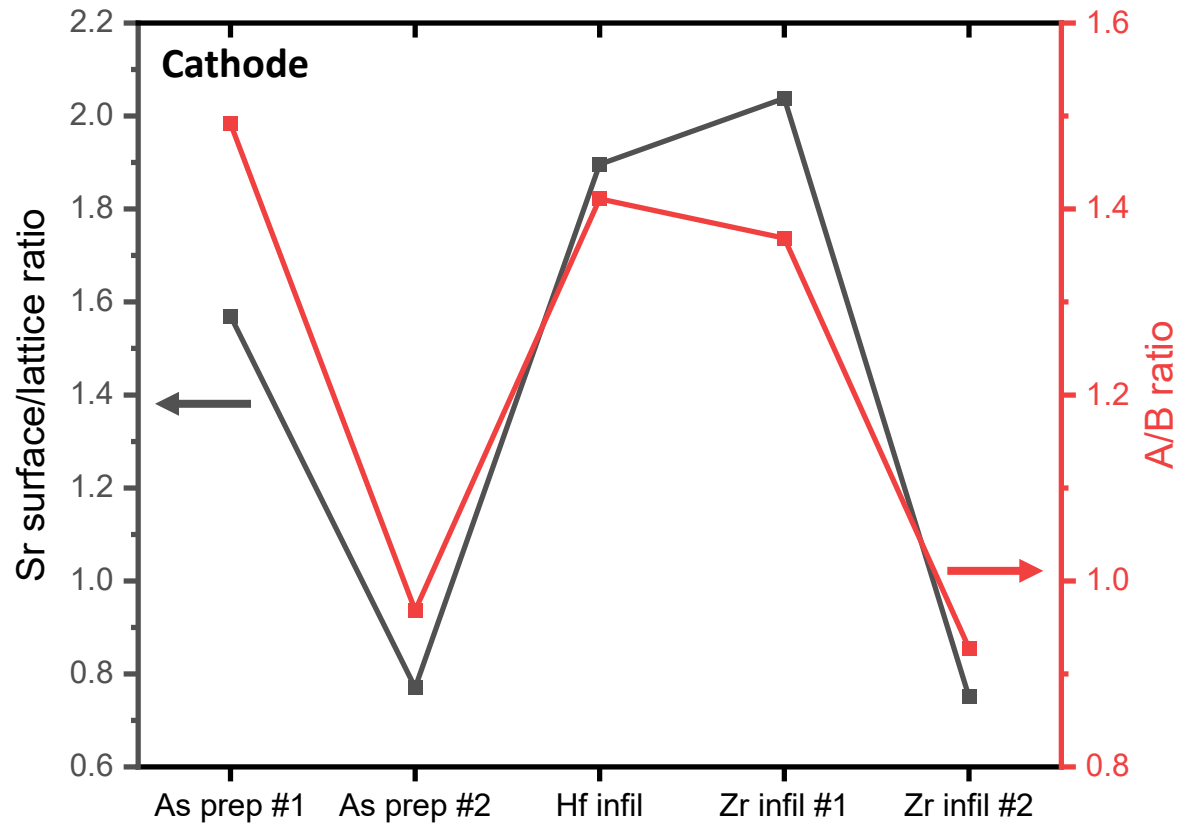
- This material is based upon work performed by the Massachusetts Institute of Technology and the Pacific Northwest National Laboratory, award DE FE0032102 supported by the Department of Energy's Solid Oxide Fuel Cells program.
- We thank Dr. Debalina Dasgupta for supporting this project.
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Backup slides

Acknowledgements

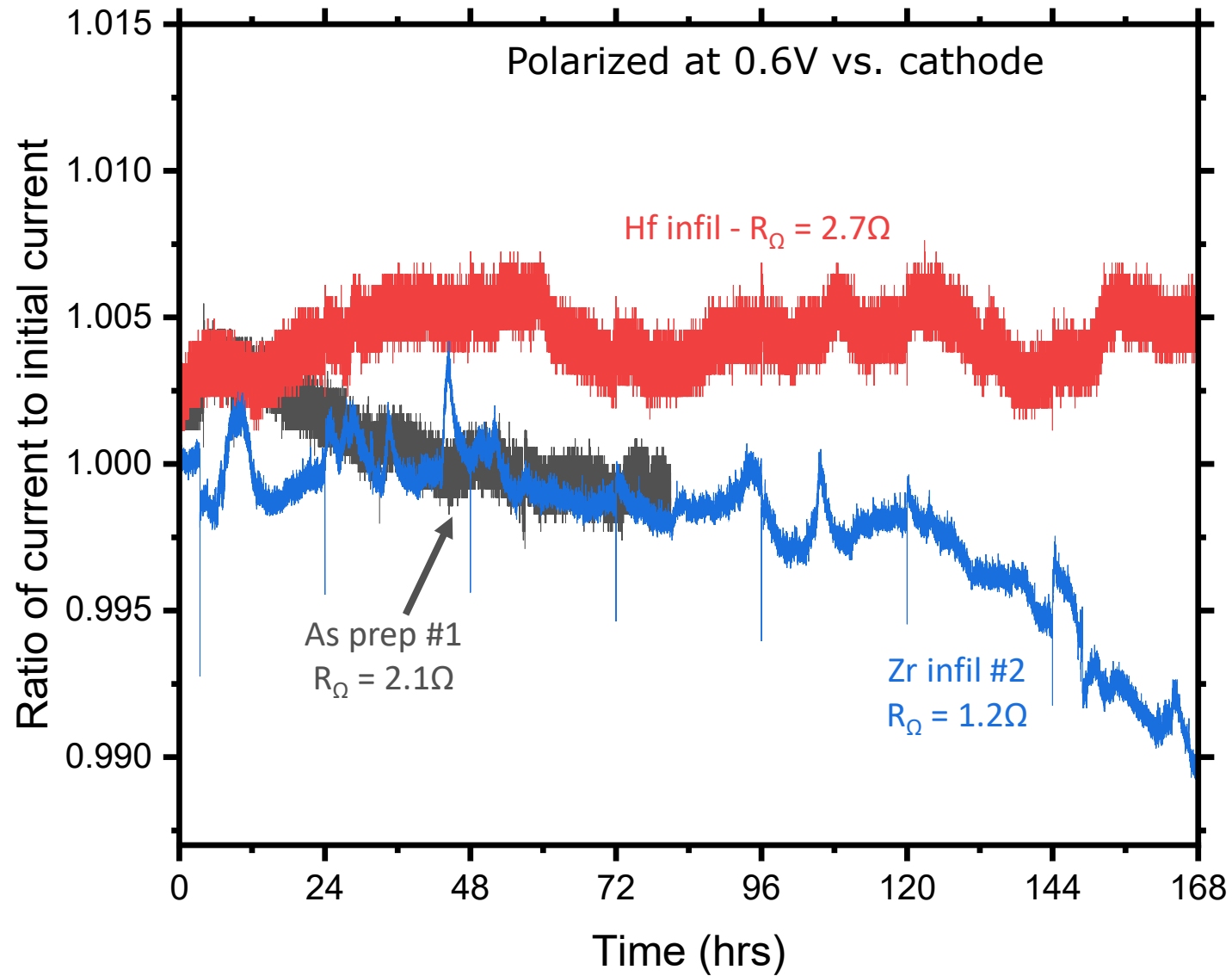


XPS post-mortem analysis – infiltration increases cathode side Sr content

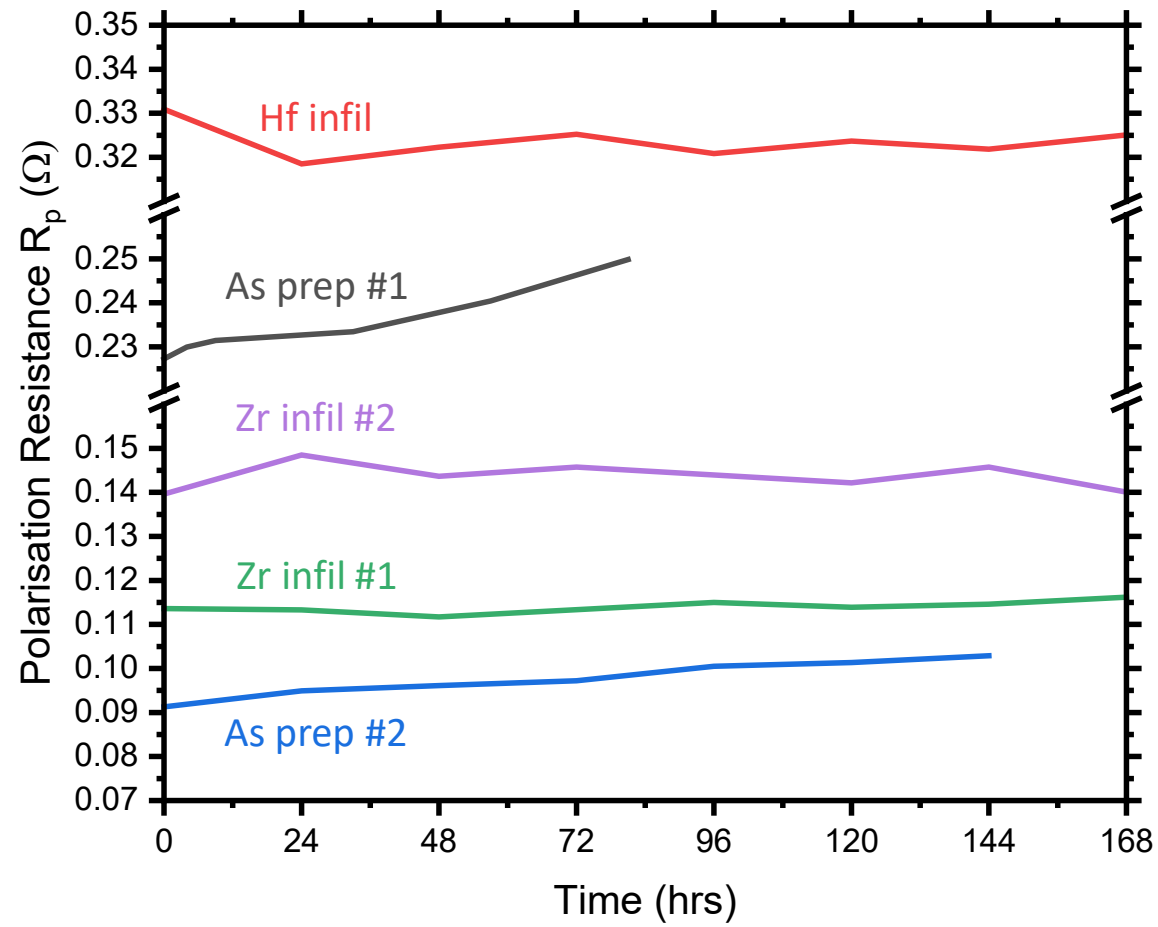


- Unclear what the relationship is here
- No clear trend in terms of the surface/lattice ratio or the A/B ratio
- Checked that the analyses are correct and not artefacts

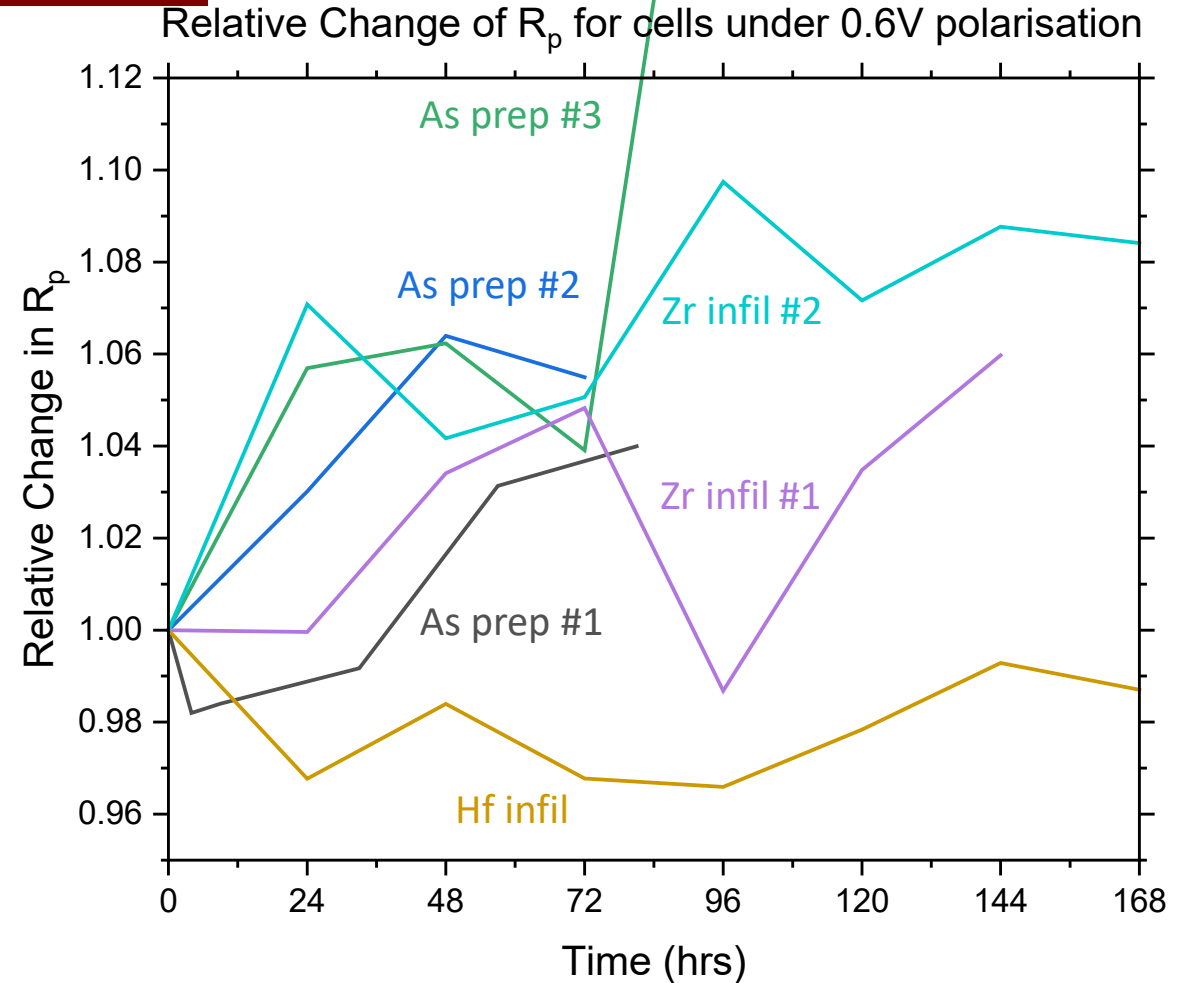
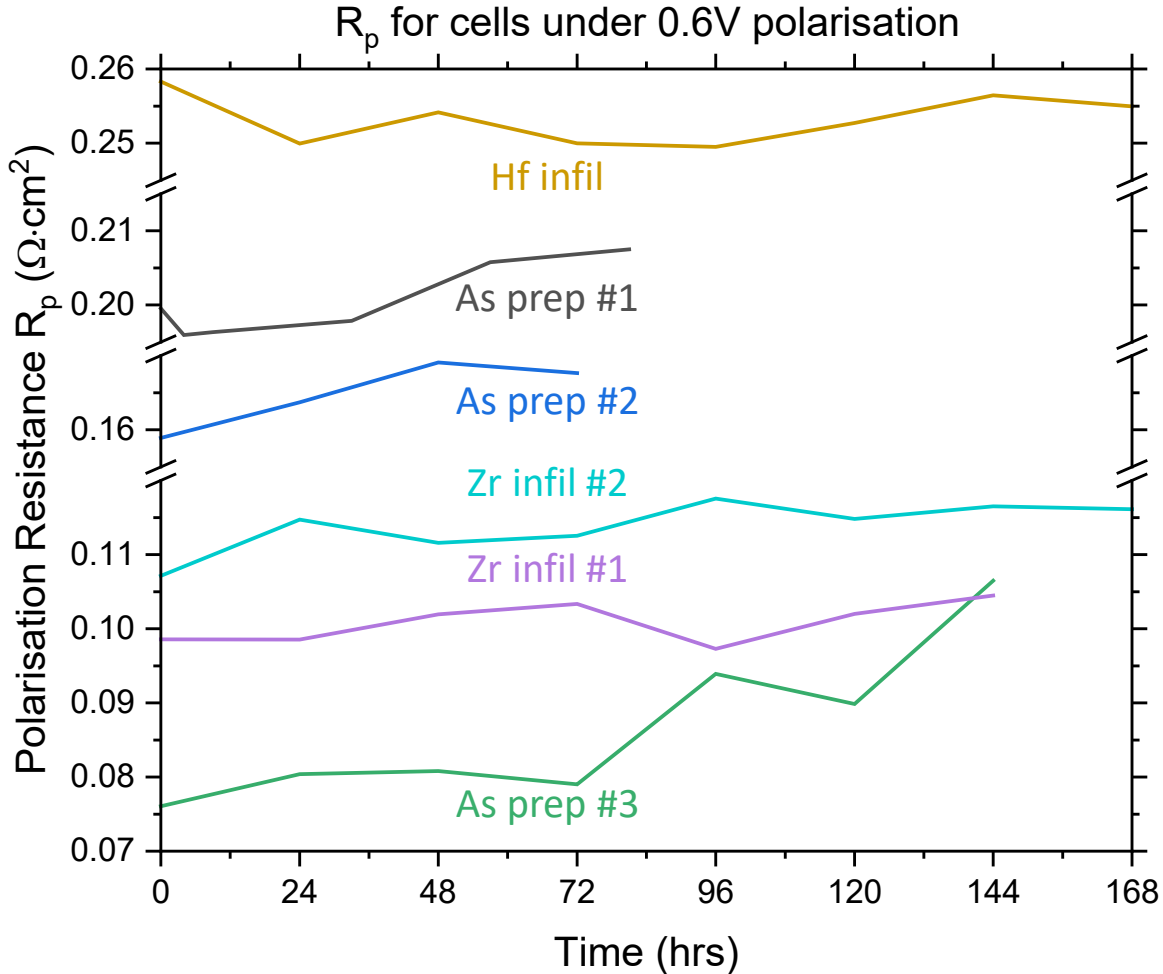
Chronoamperometry analysis – Hf infiltration stabilizes current profile



EIS analysis – R_p vs time analysis at OCV

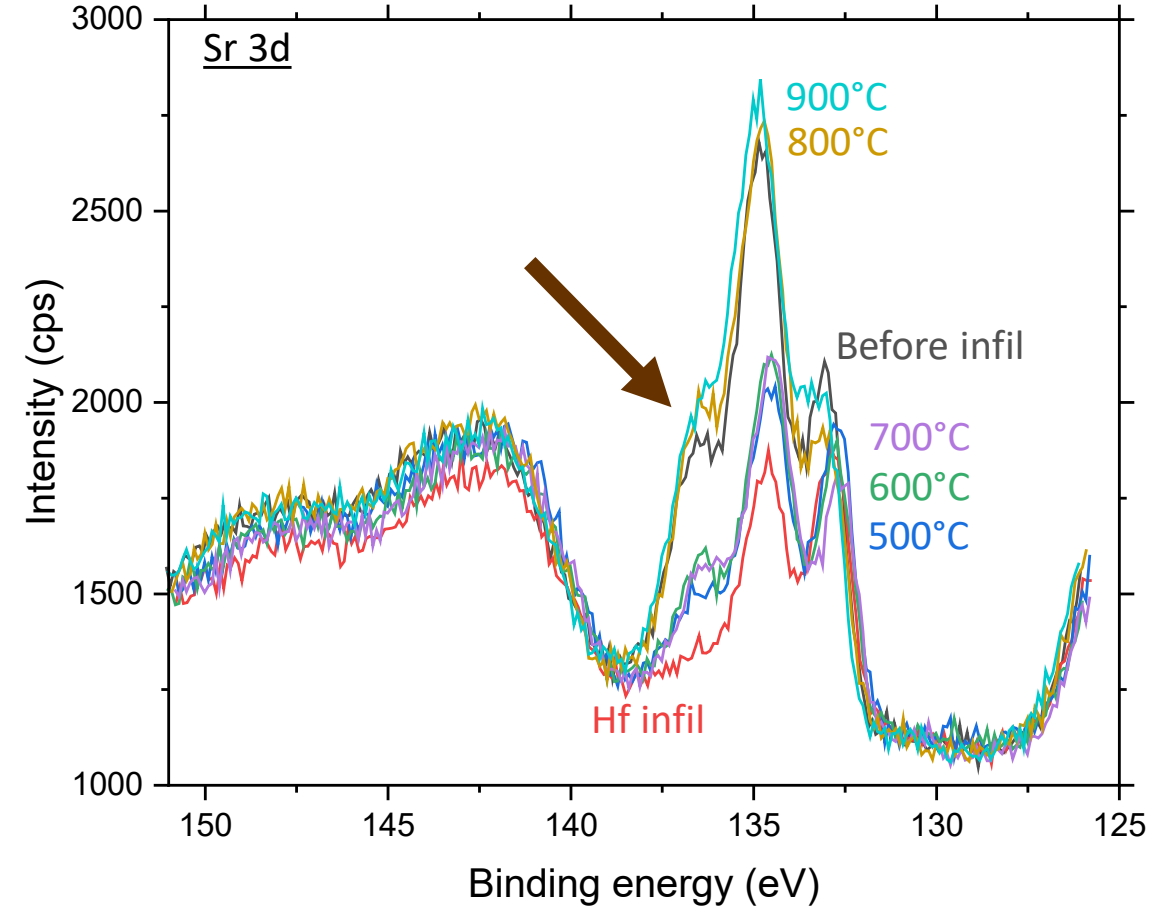
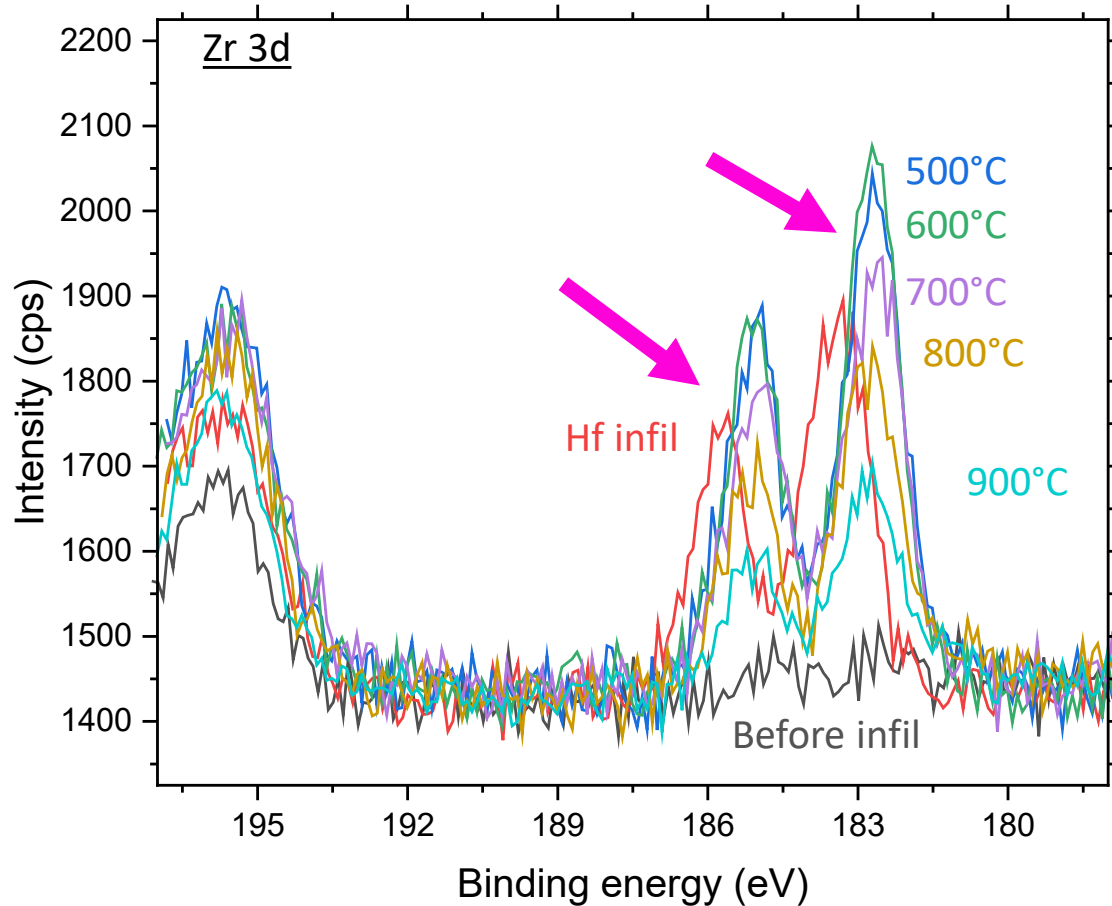


EIS analysis under polarization – infiltration stabilizes LSCF cells



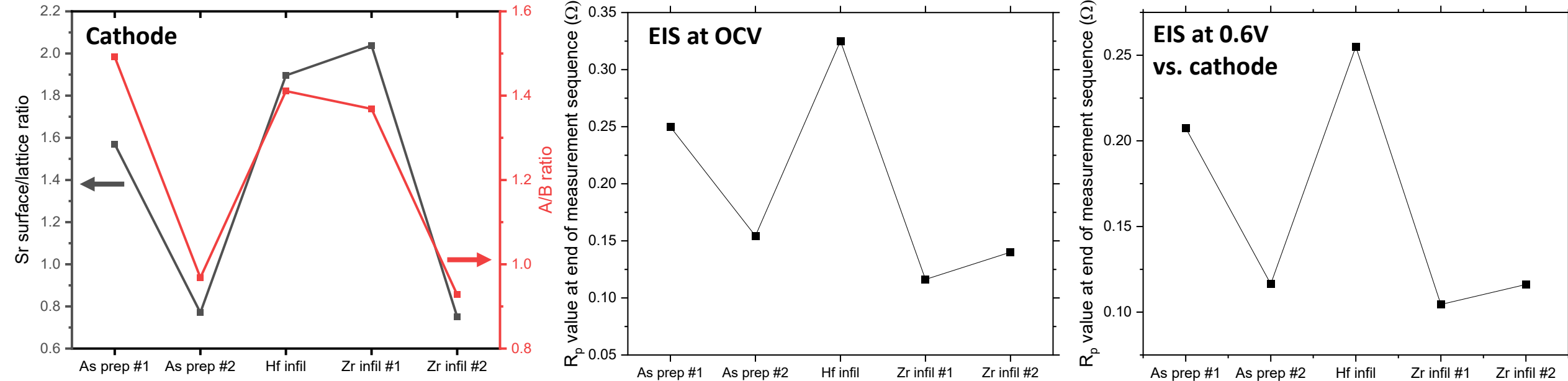
- EIS under polarization shows similar trend as at OCV – Hf infiltrated cell shows stable R_p
- However Zr infiltrated cells show a sizeable increase in R_p , indicating accelerated degradation

XPS analysis – Zr infiltration seems more stable



- ❑ Interestingly, Sr 3d surface component (brown arrow) returns to same intensity as before infiltration, but Zr 3d (pink arrows) is still detectable even after cycling at 900°C.
- ❑ Inconsistency?

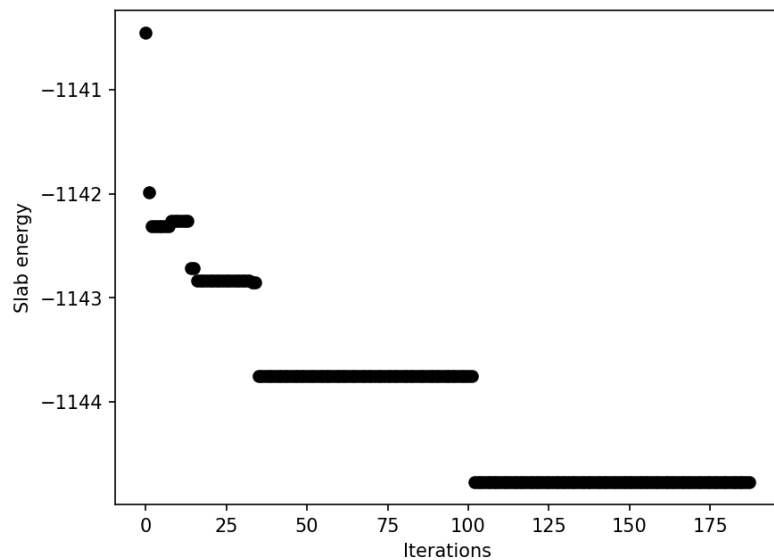
Cathode surface chemistry vs. cell polarization resistance



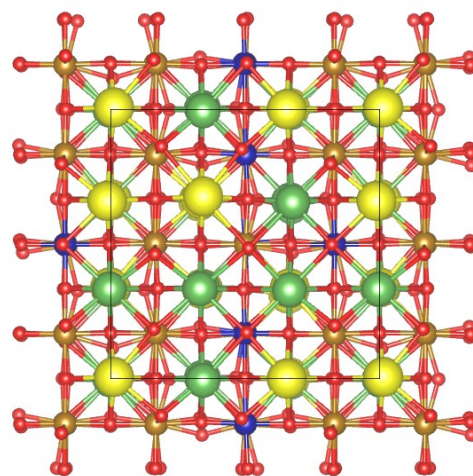
? Less surface Sr results in lower R_p ?

Current most stable structures

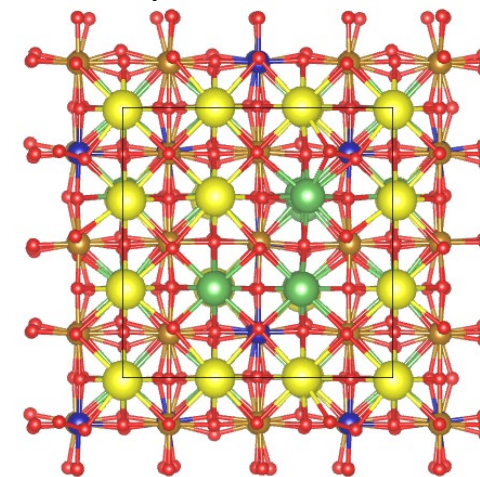
$T = 800 \text{ K}$, $P_{\text{O}_2} = 10^{-4} \text{ atm}$



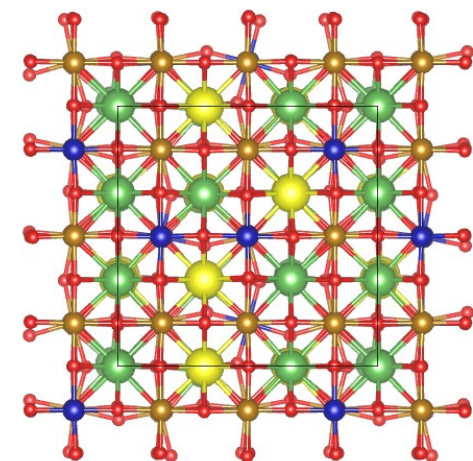
Initial AO-terminated



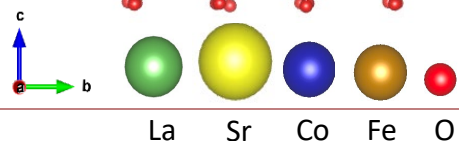
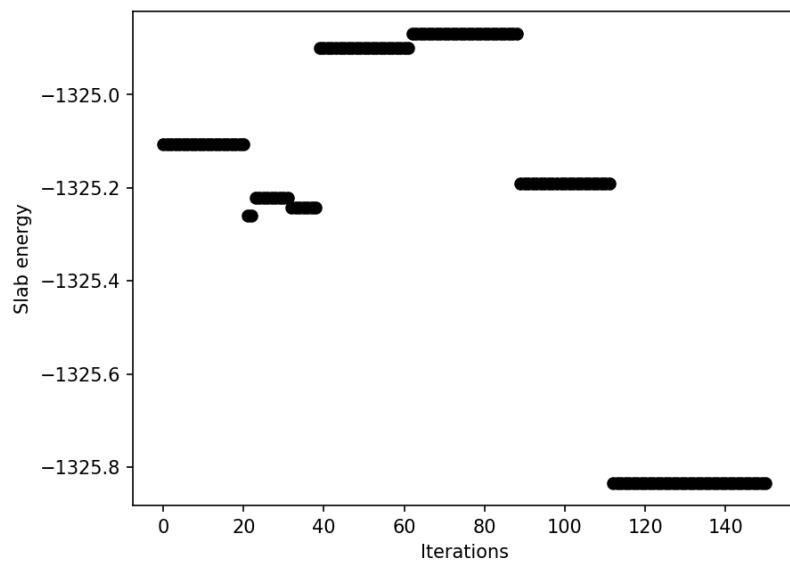
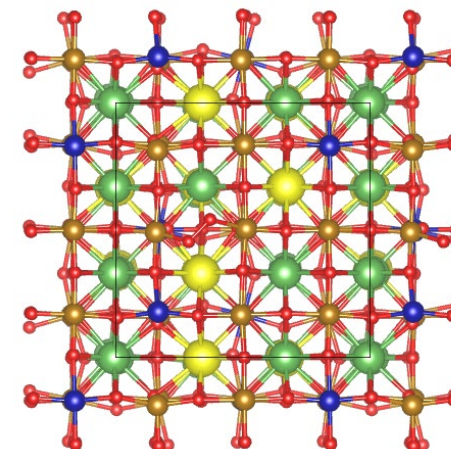
one extra oxygen vacancy on the surface,
one oxygen vacancy on the 3rd subsurface



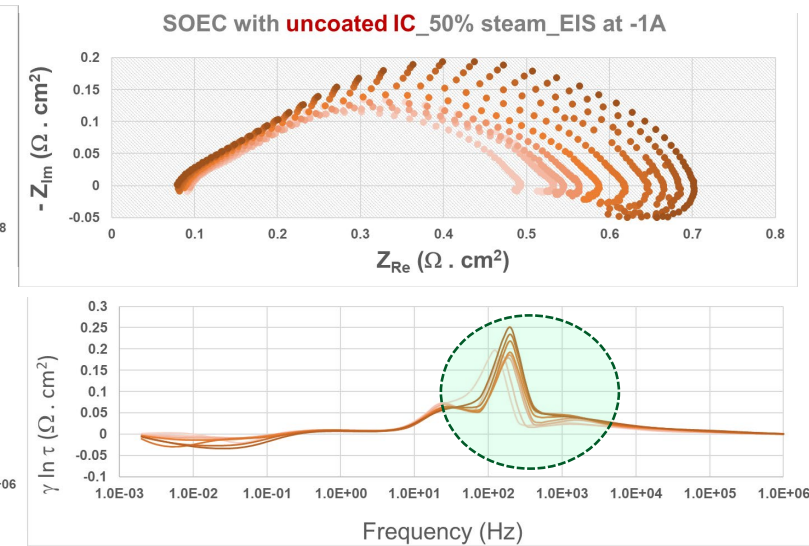
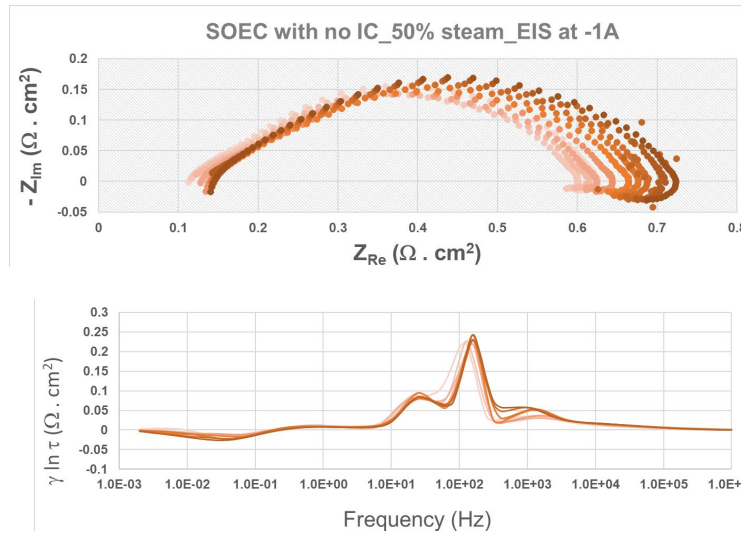
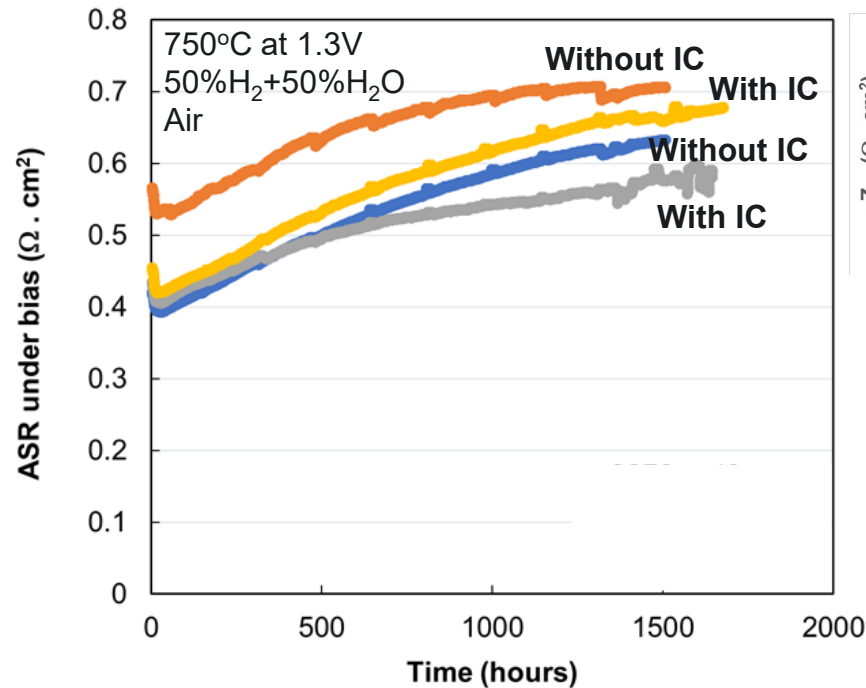
Initial BO₂-terminated



three extra oxygen on the surface
three oxygen vacancies on the surface

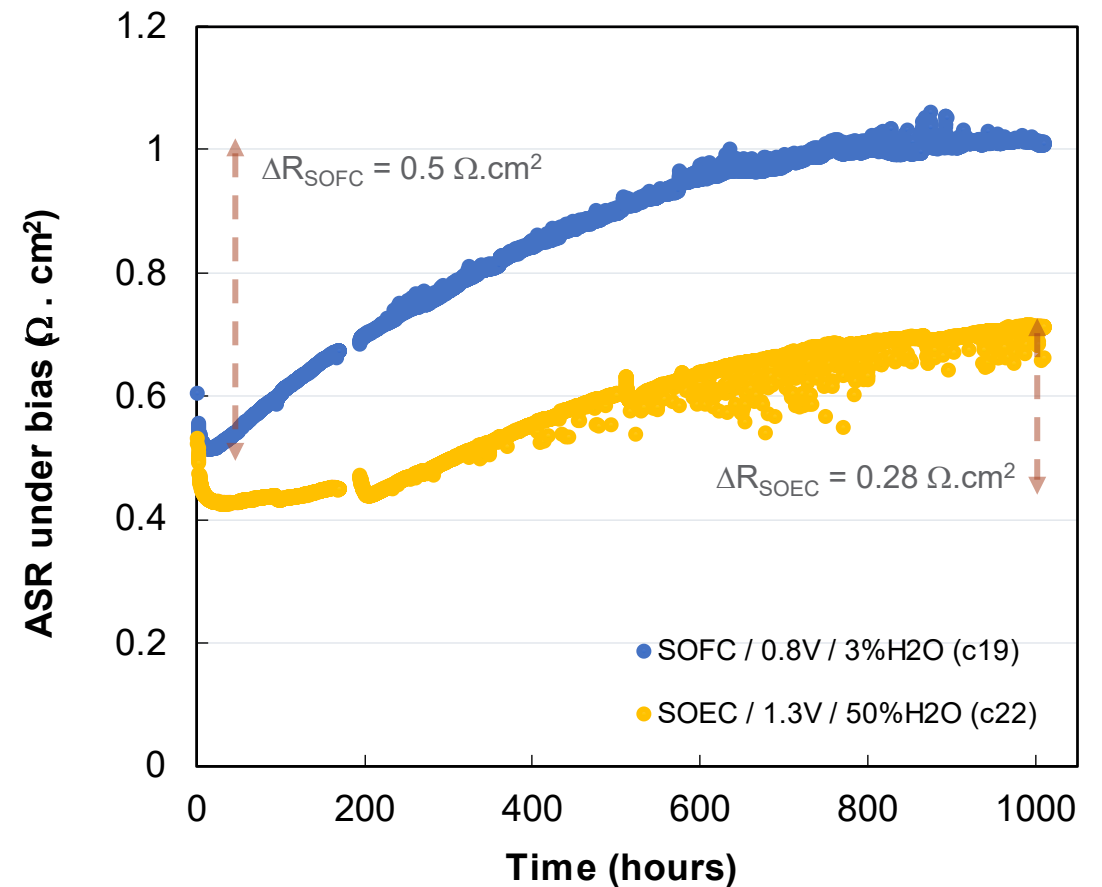
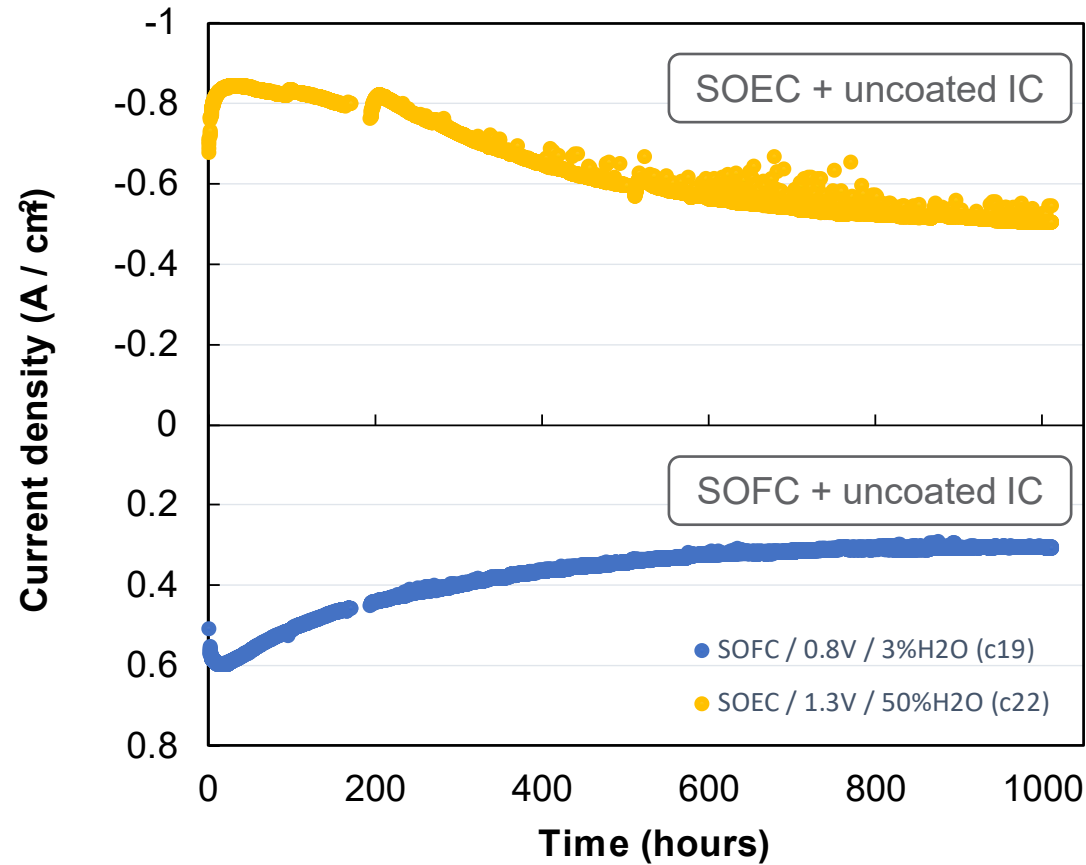


SOEC Testing with and without Uncoated Metal Interconnect



- In the absence of interconnect, SOECs have higher degradation than SOFCs.
- Unlike in SOFC, the main degradation peak for SOEC appears at 10^{+2} – 10^{+3} Hz, possibly (surface diffusion)
- Ohmic R does not increase; the change is in polarization R only

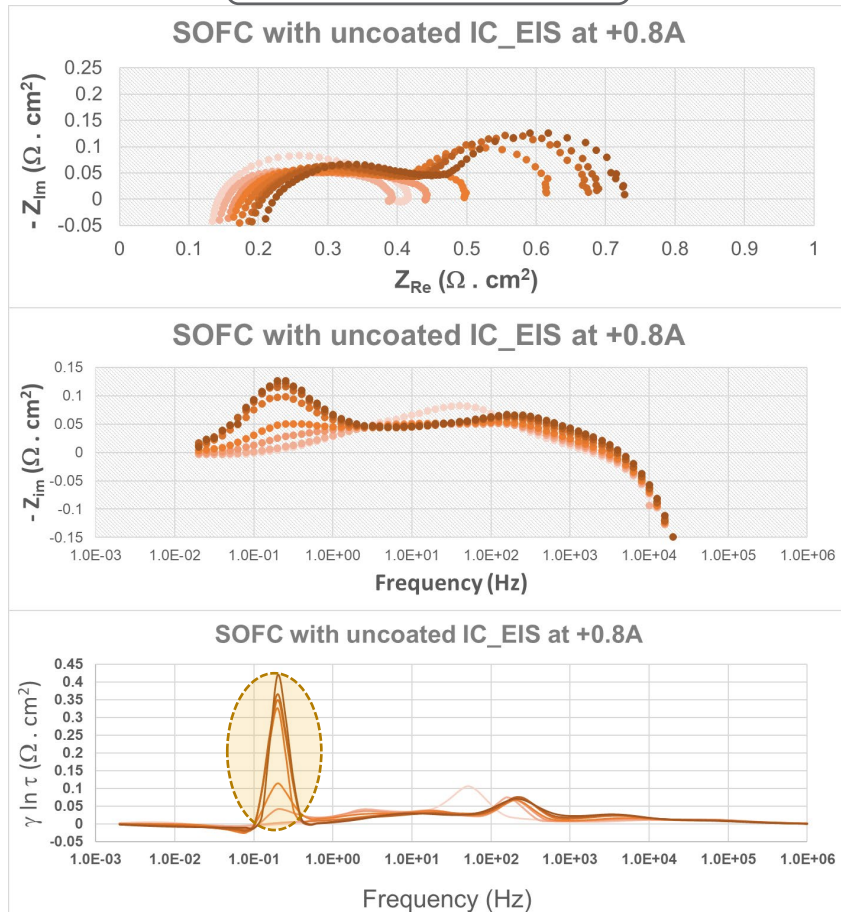
Observations of SOFC vs SOEC in the presence of uncoated interconnect are confirmed in another set of experiment



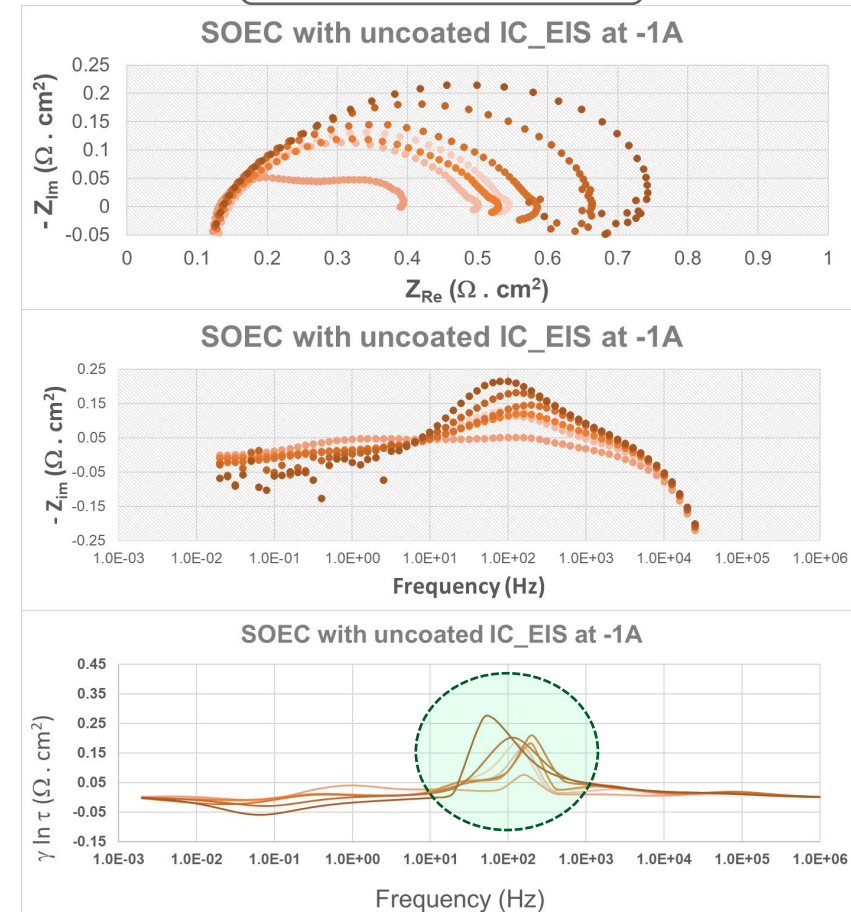
- In this case a 3%H₂O was used during SOFC operation
- Similar degradation rates are observed

Observations of SOFC vs SOEC in the presence of uncoated interconnect are confirmed in another set of experiment

SOFC + uncoated IC



SOEC + uncoated IC



- Again, SOFC has higher increase in ohmic R and in a low-frequency process
- Ohmic does not change in SOEC. Main degradation is at $10^{+2} - 10^{+3}$ Hz