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

Bill Liu,¹ Filip Grajkowski,² Sophie Coppieters 't Wallant,¹ Lorraine Seymour³, Olga Marina³, and Bilge Yildiz^{1,4}

In collaboration with Elango Elangovan, Tyler Hafen and Jenna Pike, OxEon Energy

¹ Department of Materials Science and Engineering, ² Department of Chemistry,
 ⁴ Department of Nuclear Science and Engineering, Massachusetts Institute of Technology
 ³ Energy and Environment Directorate, Pacific Northwest National Laboratory

Electrochemical Interfaces

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Detrimental Sr-segregation and precipitation at perovskite oxide surfaces



(c) Surface heterogeneities on LSCF pellet



(d) Surface composition on LSCF pellet



Z. Cai et al., Chem. Mater. 2011, 24 D. Oh et al., J Mater Res. 2012, 27 J. Druce et al. Energ. Environ. Sci., 2014, 7

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Sr segregation and Cr & S poisoning of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃

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Cr Poisoning Nucleation Theory:

 $\begin{array}{l} \text{CrO}_{3(g)} + \textbf{SrO}_{(s)} \rightarrow \text{Cr}-\text{Sr}-\text{O}_{(\text{nuclei})(s)} \\ \text{Cr}-\text{Sr}-\text{O}_{(\text{nuclei})(s)} + \text{CrO}_{3(g)} \rightarrow \text{Cr}_{2}\text{O}_{3(s)} \\ \text{Cr}-\text{Sr}-\text{O}_{(\text{nuclei})(s)} + \text{CrO}_{3(g)} + \text{SrO}_{(s)} \rightarrow \text{SrCrO}_{4(s)} \end{array}$

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 \rightarrow formation of SrCrO₄ and Cr₂O₃ on LSCF surface.

S Poisoning Nucleation Theory: $SO_{2(g)} + SrO_{(s)} \rightarrow SrSO_{4(s)}$

S.P. Jiang, X. Chen, *Int. J. of Hydrogen Energy*, 2014, 39. K. Chen, S.P. Jiang, *Electrochemical Energy Reviews* 2020, 3.

LSCF bar samples in the presence of **20 ppm SO₂** at 900°C:



XRD, EDS, Raman → formation of SrSO₄ on LSCF surface.

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

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

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.
- 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.



Computational investigation of Cr & S poisoning on realistic LSCF surfaces



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Resolving surface structures on LSCF using Grand Canonical Monte Carlo with DFT and ML-IAP



- O Region 1: GCMC on both metal cations and oxygens
- O Region 2: MC exchange for cations, insert/deletion on the lattice sites for both metal cations and oxygens
- O Region 3: Fix atoms in positions

Current most stable structures





T = 1073 K, P₀₂ = 10¹⁰ atm (η = 0.5 V)





 $(La_{0.58}Sr_{0.42})_{0.77}(Co_{0.44}Fe_{0.56})O_{4.2}$

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(La_{0.44}Sr_{0.56})(Co_{0.22}Fe_{0.78})O₃



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CrO₃ and SO₂ behavior on pristine, non-polarized LSCF slabs



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

CrO₃ adsorption energies vs configurations



O CrO₃ adsorption energies are all negative for pristine LSCF slabs, whereas SO₂ is slightly more positive

- O Adsorption energies decrease as the number of bonds formed from the adsorption increase
- O BO₂-terminated slabs have higher (yet still negative) adsorption energies

SO₂ adsorption energies vs configurations



 \circ CrO₃ adsorption energies are all negative for pristine LSCF slabs, whereas SO₂ is slightly more positive

- O Adsorption energies decrease as the number of bonds formed from the adsorption increase
- O BO₂-terminated slabs have higher (yet still negative) adsorption energies

CrO₃ more strongly bound in dynamic simulations, too.



- AO-terminated surface: molecules are anchored on the adsorption site with a rotational degree of freedom
- O BO₂-terminated surface: molecules are more likely to diffuse on the surface

Oxygen site charge, and charge transfer as physical descriptors

- 1. Use as a **design principle** for future surface modifications
- 2. Gain **physical insights** behind adsorption on different surfaces



Surface modification of LSCF to suppress Sr

Our current system:

LSCF-GDC electrode

 $Gd_{0.2}Ce_{0.8}O_{1.95}$ (GDC) barrier layer

SSZ electrolyte disc (support)

Gd_{0.2}Ce_{0.8}O_{1.95} (GDC) barrier layer LSCF-GDC electrode

LSCF: $(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_3$

Cells fabricated at PNNL Electrolytes from OxEon

Well-established button cell production process:

- Screen printing
- Sintering



LSCF/GDC composite on GDC barrier layer

ScSZ electrolyte

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



As-prepared LSCF



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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

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



Samples made by OxEon (Tyler Hafen and Elango Elangovan)

Despite stabilization of ASR, Hf and Zr dissolution at T > 700°C



□ Considerable Hf cation diffusion away from the surface is noticeable > 700 °C.

□ As Hf diffuses away from the electrode surface, Sr segregates more strongly to the surface

Larger lanthanide dopants also suppress Sr, but diffuse, too.



- Lanthanide cations (Pr, Nd) are of interest as hard-to-reduce cations of a considerably larger size than transition metal cations.
- Pr- and Nd- infiltrated LSCF/GDC electrodes demonstrate substantial diffusion of Nd and Pr into the electrode bulk (away from surface) above 800°C.
- Sr segregates more strongly with increasing temperature for both Pr- and Nd- infiltration.

Dopant dissolution not dominated by GDC lattice diffusion.



- □ In both the pure LSCF and LSCF/GDC electrode samples, the Nd 3d XPS signal appears largely depleted above 800 ℃
- Suggests that surface Nd cation diffusion is not likely dominated by diffusion through GDC particles in the electrode

Surface infiltrated cation diffusion – lattice vs. grain boundary



Surface chemistry on epitaxial vs. polycrystal LSCF with Hf



Very similar results on epitaxial and polycrystal LSCF films, indicating the surface Hf can diffuse into the lattice, and upper limit of stability is 700 °C.



PNNL team established controlled Cr poisoning testing capabilities







Cell: Ni/YSZ | YSZ | GDC – LSCF/GDC T=750°C $H_2/H_2O=50/50$



during exposure to Cr in SOFC and SOEC

SOFC Testing With and Without Uncoated Interconnect

Northwest

Pacific

0





Frequency (Hz)

- Low frequency process is related to oxygen adsorption or oxygen exchange
- Ohmic resistance significantly increased compared to test without interconnect



Co-presence of Sr and Cr indicates SrCrO₄ precipitates.

Summary and future work



- LSCF surface chemistry gets more stable with Hf/Zr/Pr/Nd infiltration.
- 700 °C infiltrate stability limit.
- AO-terminated surfaces more susceptible to CrO₃ and SO₂ adsorption.
- Cr and S poisoning mechanism at different surfaces, beyond adsorption.
 - PNNL cells modified with surface infiltrates, to assess suppression of Cr and S poisoning.

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Backup slides

Acknowledgements

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Grand Canonical Monte Carlo with DFT + IAP for resolving LSCF surface reconstructions



Current most stable structures





T = 1073 K, P_{02} = 10¹⁰ atm (η = 0.5 V)

T = 1073 K, P_{02} = 0.2 atm (\eta = 0 \vee)



 $(La_{0.58}Sr_{0.42})_{0.77}(Co_{0.44}Fe_{0.56})O_{4.2}$



(La_{0.44}Sr_{0.56})(Co_{0.22}Fe_{0.78})O₃





(La_{0.44}Sr_{0.56})(Co_{0.33}Fe_{0.67})O_{2.89}

Computational summary – modeling for realistic LSCF slabs 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 pristine LSCF.
 - **3.** Surface oxygen Bader charge and sub-surface oxygen pband center can describe the electrostatic interaction between molecules and surface.
- □ Future work:
 - 1. Investigate the surface infiltrants stability and how they modify the surface structure
 - 2. Probe the Cr and S poisoning mechanisms on realistic LSCF surfaces with and without infiltrants

Identify thermodynamic condition for GCMC simulation

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$$P_{O_2} = P_{O_{2,gas}} exp\left(\eta \frac{4F}{RT}\right)$$

TABLE I. Thermodynamic conditions for GCMC simulations.							
Overpotential	Temperature	Effective partial pressure					
0.42V	1073 K	10 ⁷ atm					
0.25 V	1073 K	10 ⁴ atm					
0 V	1073 K	0.2 atm					
-0.18V	1073 K	10 ⁻⁴ atm					
-0.34 V	1073 K	10 ⁻⁷ atm					

Current most stable structures



AIMD to study the reaction steps beyond the initial adsorption

a) AO-termination



- AO-terminated surface: molecules are anchored on the adsorption site with a rotational degree of freedom
- □ BO₂-terminated surface: molecules are more likely to diffuse on the surface

IAP MD to study the reaction steps beyond the initial adsorption



- Given a larger distance between molecules, molecule surface diffusion is also possible for AO-terminated surfaces.
 However, the molecule diffusion always require a Sr atom to be present next to the site where diffusion is taking place.
- □ Given a distorted LSCF slab with one surface Sr atom coming out of the surface, this distorted surface Sr atom can interact with the adsorbed molecules. The structure can be mapped to a SrCrO₄ unit.

Chronoamperometry analysis – Hf infiltration stabilizes current profile



- □ As prepared cells show a steady decrease in current vs. time
- □ Hf infiltrated cell shows no current change over 7 days fluctuations due to furnace
- Zr infiltrated cell shows initial stabilization but then sharp degradation
- All cells show a linear dependence of R_p on applied voltage

Comparison – YSZ100 (Hf) vs. YSZ110 (no Hf)



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Comparison – YSZ100 (Hf) vs. YSZ110 (no Hf)



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Comparison – poly vs epi Hf infiltrated



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Electrochemical Characterization of Oxygen Electrodes at MIT



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





Surface chemical characterization: XPS, AES, EDX



Structural characterization: XRD, SEM, TEM

XPS post-mortem analysis – dissolution of dopants at T > 600°C



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

Surface infiltrant cation diffusion – lattice vs. grain boundary





Thin film characterisation - STO



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Comparison – poly vs epi Hf infiltrated







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

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Electrode Surface is Sr Enriched, Shows Cr Presence after 1000 hrs



At. %	0	Cr	Fe	Со	Sr
Spectrum 26	55.79	3.75	13.94		15.59
Spectrum 27	56.49		4.47	35.42	
Spectrum 28	60.16	1.28	14.01		18.56
Spectrum 29	59.26		14.42		19.59
Spectrum 30	58.42		11.20	4.29	19.44

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SOFC Testing With and Without Uncoated Interconnect





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Low frequency process is related to oxygen adsorption or oxygen exchange Ohmic resistance significantly increased

compared to test without interconnect