# IMPROVING DURABILITY AND PERFORMANCE OF SOLID OXIDE ELECTROLYZERS BY CONTROLLING SURFACE COMPOSTION ON OXYGEN ELECTRODES

**PI: Bilge Yildiz** 

Laboratory for Electrochemical Interfaces Departments of Nuclear Science and Engineering, and Materials Science and Engineering Massachusetts Institute of Technology

Co-PI: Olga Marina

Energy and Environment Directorate, Pacific Northwest National Laboratory



November 18, 2021 2021 SOFC Project Review Meeting

# Motivation for Solid Oxide Electrolysis Cells (SOECs) Fuels, chemicals industry, district heating



# Sr migration and redistribution correlated to degradation of SOECs





Extensive Sr migration, penetrating to the pores of the ceria barrier, and deeper into the YSZ electrolyte.

Commercial (Nexeris, US), and PNNL-made electrodesupported SOECs with the  $(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-d}$  (LSCF) oxygen electrode, tested at PNNL, at 750°C, 1.3 V. This project aims to attack the degradation pathway that couples surface chemistry to impurity poisoning on perovskite oxygen electrodes, taking LSCF as a state-of-the-art oxygen electrode.



SrO segregation is common on perovskite oxides, serves as nucleation sites to poisoning by Cr and S species

Goal: Avoid/minimize Sr segregation to the surface in the form of SrO on LSCF, thereby improve initial performance as well as cut the key poisoning pathways by avoiding Cr- and Sprecipitate formation.

(c) Surface chemistry control  $\rightarrow$ No SrO segregation  $\rightarrow$  prevent Cr- / S-poisoning



# Detrimental Sr-segregation and precipitation at perovskite oxide surfaces



(b)

Surface heterogeneities on LSC



Z. Cai et al., Chem. Mater. 2011, 24

#### (c) Surface heterogeneities on LSCF pellet



#### (d) Surface composition on LSCF pellet



D. Oh et al., J Mater Res. 2012, 27 J. Druce et al. Energ. Environ. Sci., 2014, 7

## Sr segregation and Cr poisoning of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub>

```
Nucleation theory (chemical process)

CrO_{3(g)} + SrO_{(s)} \rightarrow Cr-Sr-O_{(nuclei)(s)}

Cr-Sr-O_{(nuclei)(s)} + CrO_{3(g)} \rightarrow Cr_2O_{3(s)}

Cr-Sr-O_{(nuclei)(s)} + CrO_{3(g)} + SrO_{(s)} \rightarrow SrCrO_{4(s)}
```

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

**SOEC:** LSCF-GDC electrodes after operation at 200 mA/cm<sup>2</sup>, 900°C.



- XRD, Raman and XPS  $\rightarrow$  formation of SrCrO<sub>4</sub>, CrO<sub>2.5</sub>, and Cr<sub>2</sub>O<sub>3</sub> on the LSCF

B. Wei et al. Phys. Chem. Chem. Phys., 2015,17.

Cr deposition on the LSCF in the form of SrCrO<sub>4</sub>, under both SOEC and SOFC conditions, degrades the cell.

- Sr segregation on LSCF under both cathodic and anodic polarization.
- Initiated by the nucleation between the segregated SrO and gaseous Cr species.

**SOFC:** LSCF-GDC electrodes after operation at 200 mA/cm<sup>2</sup>, 900°C.







- XRD, EDS, SEM  $\rightarrow$ formation of SrCrO<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> on the LSCF surface.

S.P. Jiang et al. J. Electrochem. Soc., 2006,153, A127

## Sr segregation and S poisoning of La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub>

Nucleation theory (chemical process)

 $SO_{2(g)} + SrO_{(s)} \rightarrow SrSO_{4(s)}$ 

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 absence and presence of 20 ppm SO<sub>2</sub> at 900°C



# S deposition on the LSCF electrodes occurs in the form of SrSO<sub>4</sub>, and degrades the cell.

• Sr segregation in LSCF is usually more severe under SOEC than SOFC mode

\* LSCF in SOFC (-0.2 V vs. RE) at 800°C in 1 ppm SO2



 Cross-section EDS analysis identified the formation of SrSO<sub>4</sub> on the LSCF surface and at the LSCF/GDC interface.

F. Wang et al. J. Electrochem. Soc., 2017, 163

 XRD, EDS, and Raman analyses identified the formation of SrSO<sub>4</sub> on the LSCF surface.

C. C. Wang et al. J. Electrochem. Soc., 2014, 161

#### - Electrical conductivity relaxation

### **Objectives of this research:**

- 1. Improve the chemical and electrochemical stability of the surface of LSCF as a state-of-the-art oxygen-electrode, against Sr-segregation and the consequent poisoning by chromium and sulfur. Our approach will infiltrate the surface of LSCF with more oxidizable elements to suppress Sr-segregation and improve both the initial oxygen exchange kinetics and durability. This approach cuts a key pathway for poisoning of the LSCF electrode by deposition of SrCrO<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub> and SrSO<sub>4</sub> species.
- 2. Develop physically based and practical **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 oxygenelectrode surface chemistry and performance. This includes mapping out the chemistry and performance of the LSCF electrode as a function of voltage, cycling between anodic and cathodic conditions, temperature and pressure, and in the presence of volatile Cr and S species, combining experiments and computations.



## **Approach of this research:**

Surface modification introduced by oxidizable cations (e.g. Zr, Hf, Ti) onto the LSCF surface

Decrease the oxygen vacancy concentration and positive charge at the LSCF surface Eliminate the segregation and phase separation of Sr dopant at the LSCF surface

Improve performance, suppress degradation by Cr- and S-poisoning on LSCF oxygen electrode

- Modification (by surface doping or ultra-thin coating via infiltration) of the perovskite surface with more oxidizable transition metal cations (for example, Zr, Hf, Ti) reduces the concentration of oxygen vacancies and the net positive charge at the surface.
- This effect reduces the electrostatic driver to the segregation and eliminates the formation of insulating SrO layers and particles on LSCF.
- This improves the initial performance of LSCF by increasing the surface oxygen evolution rate, and also decreases the degradation rate by supressing poisoning by Cr- and S-species.

## Elastic and electrostatic drivers to dopant segregation



Lee, Han and Yildiz et al., J. Amer. Chem. Soc. 135 (2013) Kim, Bliem, Hess , Gallet and Yildiz, J. Amer. Chem. Soc. 142 (2020)

## Suppress electrostatic attraction to Sr segregation

Decrease the + charge, or the  $V_0^{\bullet \bullet}$  concentration, at the surface, by depositing cations that are more oxidizable than the host Bsite (i.e. than Co and Fe in  $(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-d}$  (LSCF) as a model system).



### LSC is more stable and has faster oxygen exchange kinetics with oxidizable surface-cations



Tsvetkov, Lu, Sun, Crumlin, Yildiz, Nature Materials, 2016, 15 (9)

# Methods to achieve project objectives





### 2.0 – Fabrication of SOEC Cells with LSCF Oxygen Electrodes and Surface Modifications

### **Electrode-Supported Cell Preparation Process**

#### **Cell Fabrication Steps**



- Well-established button cell production process
- Developed on FE-funded programs
- Currently developing strict QA/QC; collecting lessons learned; ongoing FOA-2400 project
- Making "a batch of cells" per request, instead of single cells on demand to reduce variability
- Perform microstructure characterization and quick validation test to approve the batch

Electrode–Supported Cells: Ni-YSZ |YSZ|GDC|LSCF-GDC







# Surface modification of LSCF to suppress Sr

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

Hf content: 12% by XPS





# **3.0 – Electrochemical Characterization of Oxygen Electrodes and SOEC Cells, at MIT and at PNNL.**

#### **Double Chamber Electrochemical Setup**

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







**High Throughput Button Cell Test Capability:** 6-8 cells/furnace, with individual gas flow controls, ~50 cells



Current Den dity (A/om?)



active area is 1-4 cm<sup>2</sup>

# 4.0 – Identification of the Oxygen Electrode Surface Chemistry and Stability

Reveal the LSCF surface chemistry, structure and oxygen exchange activity as a function of **temperature**, gas, voltage, modifiers, and impurities



Surface characterization, using in situ X-ray photo-electron and absorption spectroscopy at synchrotrons, and ex situ at MIT



### Surface chemistry depends on gas and temperature



# Prediction of surface structure and chemistry, and the oxygen evolution reaction mechanisms and kinetics with surface modifications, and impurities Using first principles based methods.



Surface phase diagram of the  $La_{0.75}Sr_{0.25}MnO_3(001)$  as a function of T and  $p(O_2)$ . Dominant configurations –

blue/oxidizing: Sr-depleted MnO<sub>2</sub> termination (left);

green/stoichiometric: partial SrO termination;

orange/reducing: Sr-enriched partial MnO<sub>2</sub> termination with additional oxygen vacancies (right).

Hess and Yildiz, Physical Review Materials 4 (2020)

Reaction pathways, energy barriers for oxygen incorporation/evolution (DFT, NEB, AIMD) This project aims to attack the degradation pathway that couples surface chemistry to impurity poisoning on perovskite oxygen electrodes, taking LSCF as a state-of-the-art oxygen electrode.



<u>Goal:</u> Avoid/minimize Sr segregation to the surface in the form of SrO on LSCF, thereby improve initial performance as well as cut the key poisoning pathways by avoiding Cr- and S-precipitate formation. <u>Impact:</u> Guide the design of better and more durable oxygen electrodes for SOECs.



We gratefully acknowledge DOE-NETL, Dr. Debalina Dasgupta for supporting and sponsoring this project.

# BACK UP SLIDES



## No Sr, no Cr poisoning and degradation of air electrode

Cr poisoning can be prevented by using oxides which don't have Sr or Mn as nucleation sites



M. Yang et al. J. Power Sources, 2011, 196

 $Nd_2NiO_4$  air electrode showed high Cr tolerance, thought to be because it does not have Sr. However,  $Nd_2NiO_4$  may have other issues such as compatibility issue with electrolyte

# **Candidate surface cations according to reducibility**



LSCF-Hf, LSCF-Al, LSCF-Mg

Tsvetkov, Lu, Sun, Crumlin, Yildiz, *Nature Materials*, 2016, 15 (9), <u>Tsvetkov, Lu, Yildiz</u>, *Faraday Discussions*, 2015. US Patent Pending, 2016

### 3.0 – Electrochemical Characterization of Oxygen Electrodes and SOEC Cells, at MIT and at PNNL.

#### In-house material/cell fabrication

- Material synthesis from raw precursors
- Powder conversion to inks
- Electrode screen-printing
- Symmetric and full cell
- Cell sintering
- Electrode modification
- Characterization (XRD, SEM, XPS, TEM, EDX)





#### **Double Chamber Electrochemical Setup**

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



#### Other equipment:

- High-temperature furnaces (x3)
- Brooks mass flow controllers (x4)
- PARSTAT 4000A Potentiostats (x2)
- Fideris bubble humidifier (x1)
- Agilent 990 Micro-GC (x1)







25

3.0 – Electrochemical Characterization of Oxygen Electrodes and SOEC Cells, at MIT and at PNNL Testing Multiple Cells for High Quality Data: Electrochemical Testing and Durability Studies Cr Poisoning – Quantification Test Stand

 $0.15 \Omega \text{ cm}^2$ 



### 3.0 – Electrochemical Characterization of Oxygen Electrodes and SOEC Cells

### **Cr Poisoning – Quantification Test Stand**









- Developed and validated in multiple tests for FE-funded project
- Small button cell is exposed to Cr vapor from a calibrated source (Cr pellet)
- Cr concentration controlled by adjusting Cr<sub>2</sub>O<sub>3</sub> temperature and moisture content of air
- Perform several repeats
- Na<sub>2</sub>CO<sub>3</sub> coated porous alumina foam collects Cr-species to form water soluble Na<sub>2</sub>CrO<sub>4</sub>
- ICP will be run on the dissolved material to determine Cr content

# Surface chemistry depends on and could be reversible with electrochemical potential



XPS intensity of surface (a) Ca, (b) Sr, and (c) Ba components, normalized by the total intensity of A-site cations of  $La_{0.8}Ca_{0.2}MnO_3$ ,  $La_{0.8}Sr_{0.2}MnO_3$ , and  $La_{0.8}Ba_{0.2}MnO_3$ , respectively, at 770 °C in 1 atm O<sub>2</sub> for 1 h. The arrows in the graphs indicate the regions where the electrostatic energy or elastic energy is the dominant reason for segregation of the dopant. Color lines serve only as a guide to the eye.

Kim, Bliem, Hess, Gallet and Yildiz, J. Amer. Chem. Soc. 142 (2020)

141

# Prediction of surface oxygen evolution reaction mechanisms and kinetics at the surface

Adsorption/desorption energies (DFT)

е  $\Theta_0 = 0.50$ а 1/20,: 0<sup>2</sup> -0.5 Adsorption energy / eV .5 00% Sr -2.5 50% Sr 25% S -3 0.2 0.4 0.6 0.8 0 Surface coverage

Reaction pathways, energy barriers for oxygen incorporation/evolution (DFT, NEB, AIMD)

