

Introduction & Goals

Strontium Segregation in SOFC Cathodes:

- Study focuses on state-of-the-art SOEC cathode material (La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF)
- LSCF exhibits Sr segregation from cathode lattice to cathode surface
- Segregated SrO then reacts with Cr and S to form inactive surface phases



Predominant Sr Segregation Mechanism:

- Under cathodic polarization, an electrostatic attraction mechanism drives Sr segregation
- Electrostatic driver: attraction of negatively charged A-site dopant to surface enriched with positively charged oxygen vacancies



Surface Composition Control Methods:



Experimental Results





- segregation.

<u>Temperature dependence of surface infiltrated cations:</u>



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

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Electrochemical Characterization Suggests Stabilized Cells with Surface Infiltration:

• Infiltrated cells - significant stabilization of R_p. Monotonic increase for as-prepared cells. • As prepared cells - steady decrease in I vs. t. Infiltrated cells - stable current (Hf infil) or stable initial current that later degrades sharply (Zr infil).

<u>Comparison of surface chemistry and polarization resistance:</u>

• Sr surface/lattice and A/B ratios show no clear trend – results not consistent with infiltration reducing Sr

R_p values at end of experiment – again no clear trend.

• Surface Sr 3d – nearly constant up to 700°C, large increase after 800°C cycling.



Computational Results

Grand Canonical Monte Carlo (GCMC) + Density Functional Theory (DFT) to

Construct Realistic LSCF Surface Reconstruction





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

CrO₃ and SO₂ Adsorption Energies on Pristine LSCF slabs



- show the same trend with sublattices are the most
- the adsorption increase



-1.30 -1.25 -1.20 -1.15 -1.10 -1.05 -1.00 1.6 1.7 1.8 1.9 Metal Bader charge • O-Bader charge as the dominant electrostatic correlator. The adsorption energy increases as O-Bader charge increases. Surface O – Cr electrostatic interaction is an important correlator with CrO₃ adsorption energies.

1.5



• M-d center as the dominant electrostatic correlator. The adsorption energy increases as M-d center decreases. • M (of surface LSCF) to O (of CrO_3) charge transfer is an important correlator with CrO3 adsorption energies.

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Tsvetkov, Lu, Sun, Crumlin, Yildiz, Nature Materials, 2016, 15 (9). Lee, Han, Chen, Cai, Yildiz, J. Am. Chem. Soc., 2013, 135, 7909-7925.