Stanford University

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Surface-Modified Electrodes: Enhancing Performance Guided by *In-Situ* Spectroscopy and Microscopy

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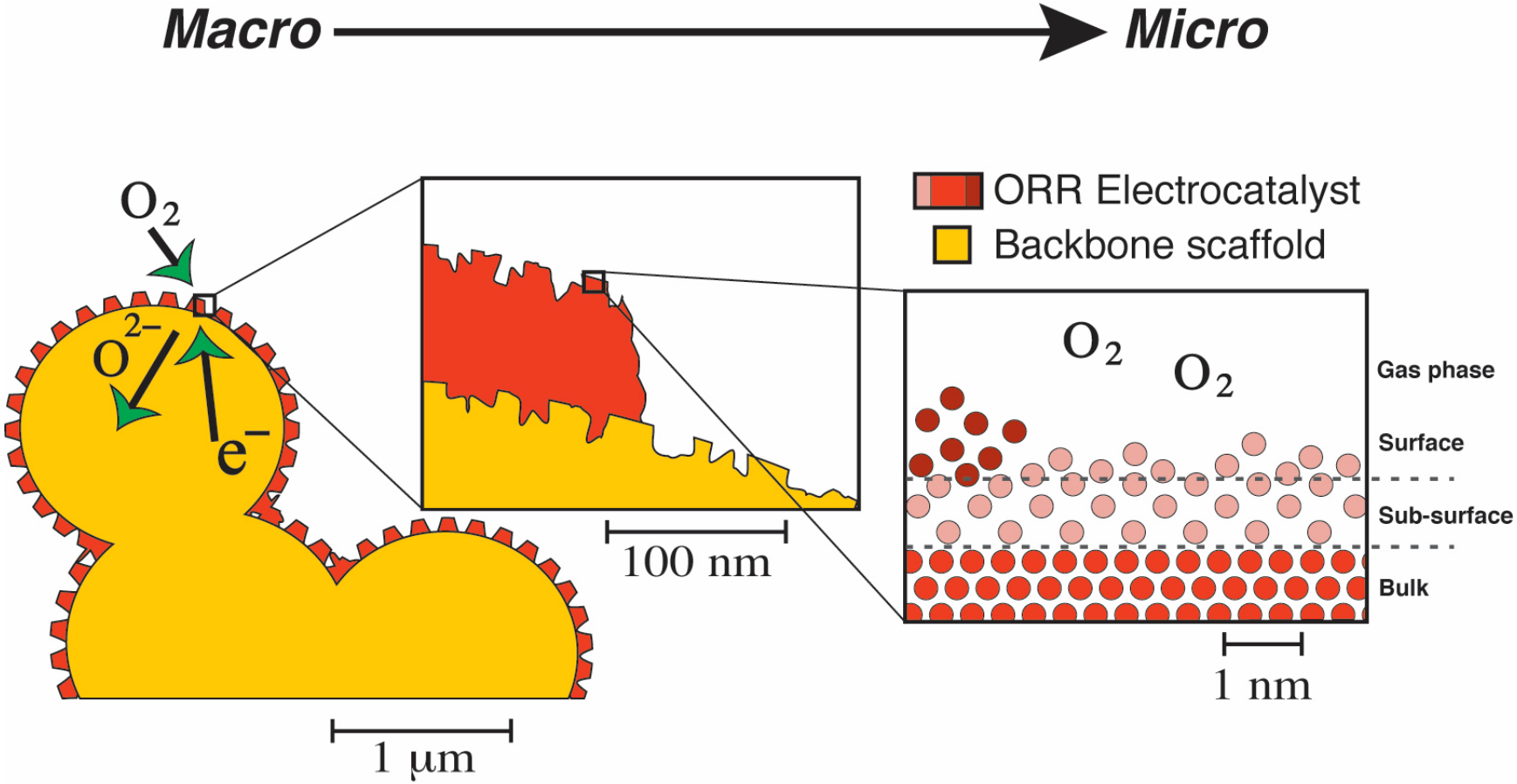
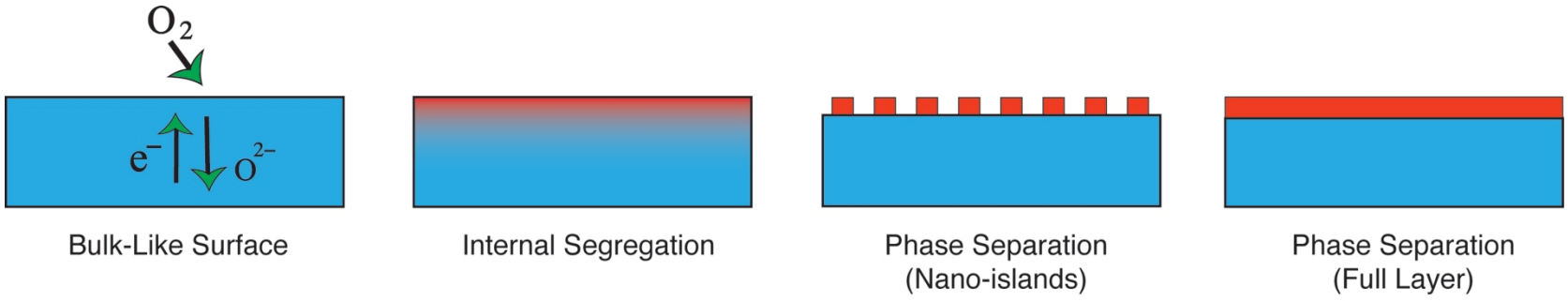
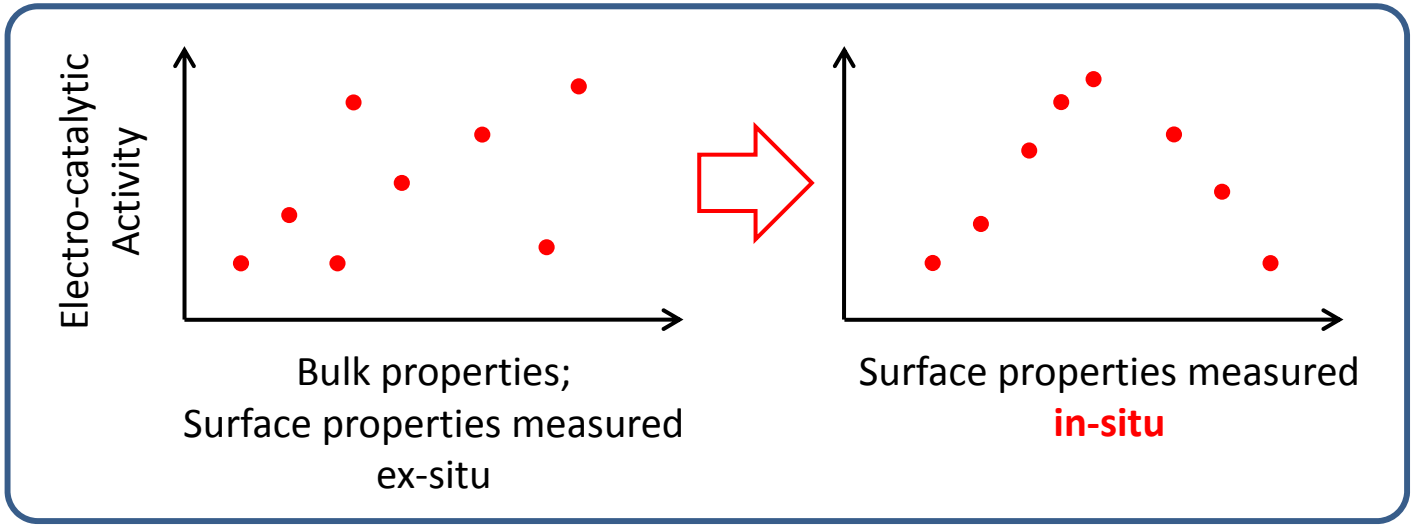


What's the nature of the active site?

What controls ORR activity?





1. Identify the nanoscale active phase
2. Identify microscopic activity descriptors
3. Stabilize the active phase on (La,Sr)(Co,Fe)$O_{3-\delta}$

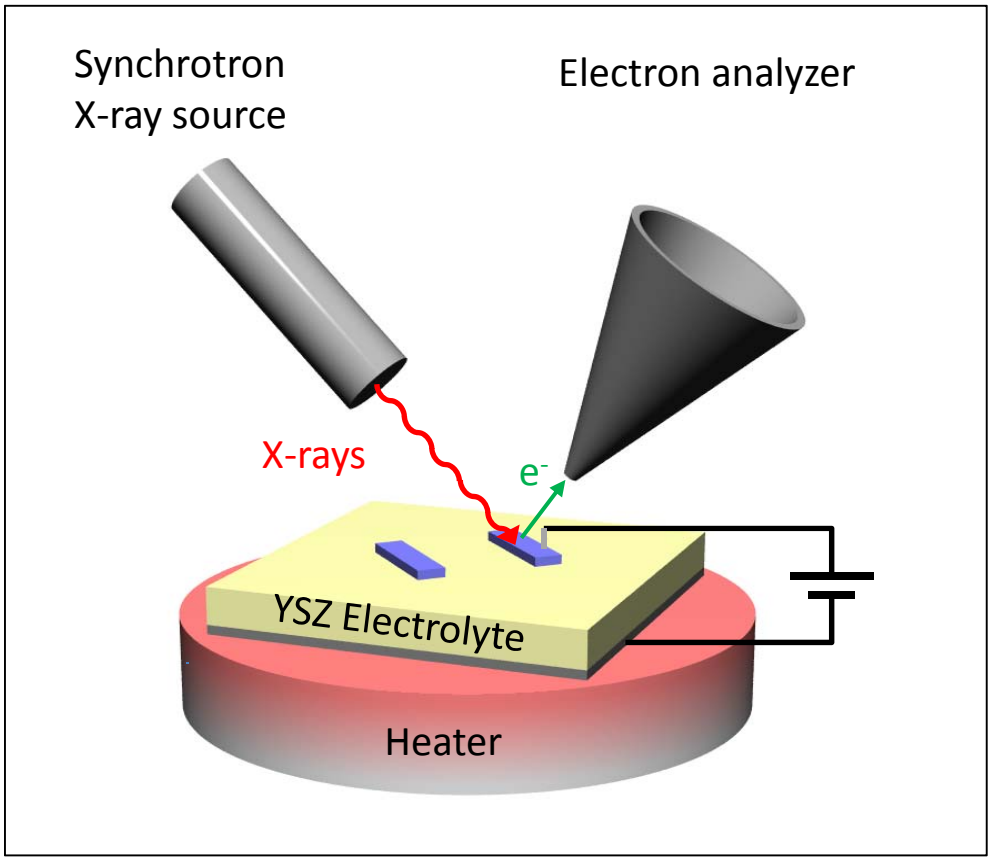
Probing surface of electrocatalysts

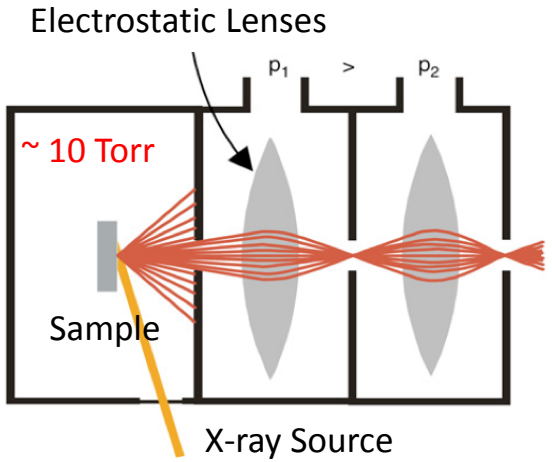
Model system

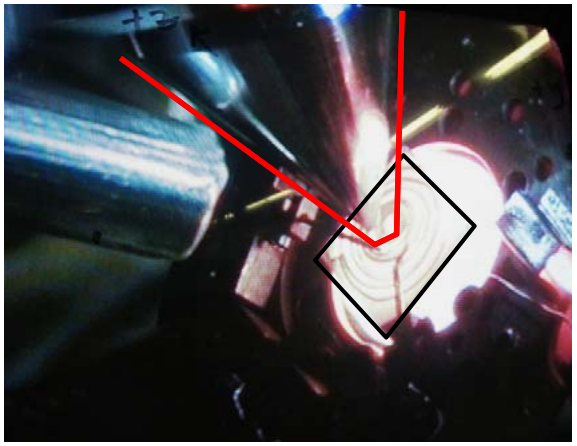
Surface sensitive

Element specific

Operating conditions (T, P)



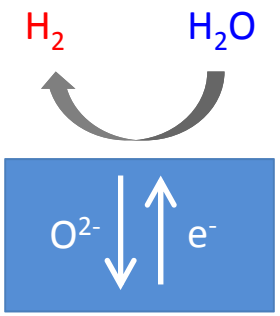


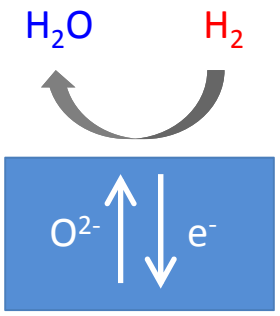


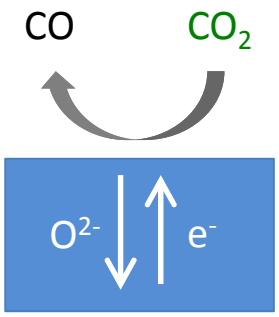
BL 11.0.2 at Advanced Light Source

M. Salmeron, R. Schlogl. *Surf. Sci. Rep*. **63**, 169 (2008)

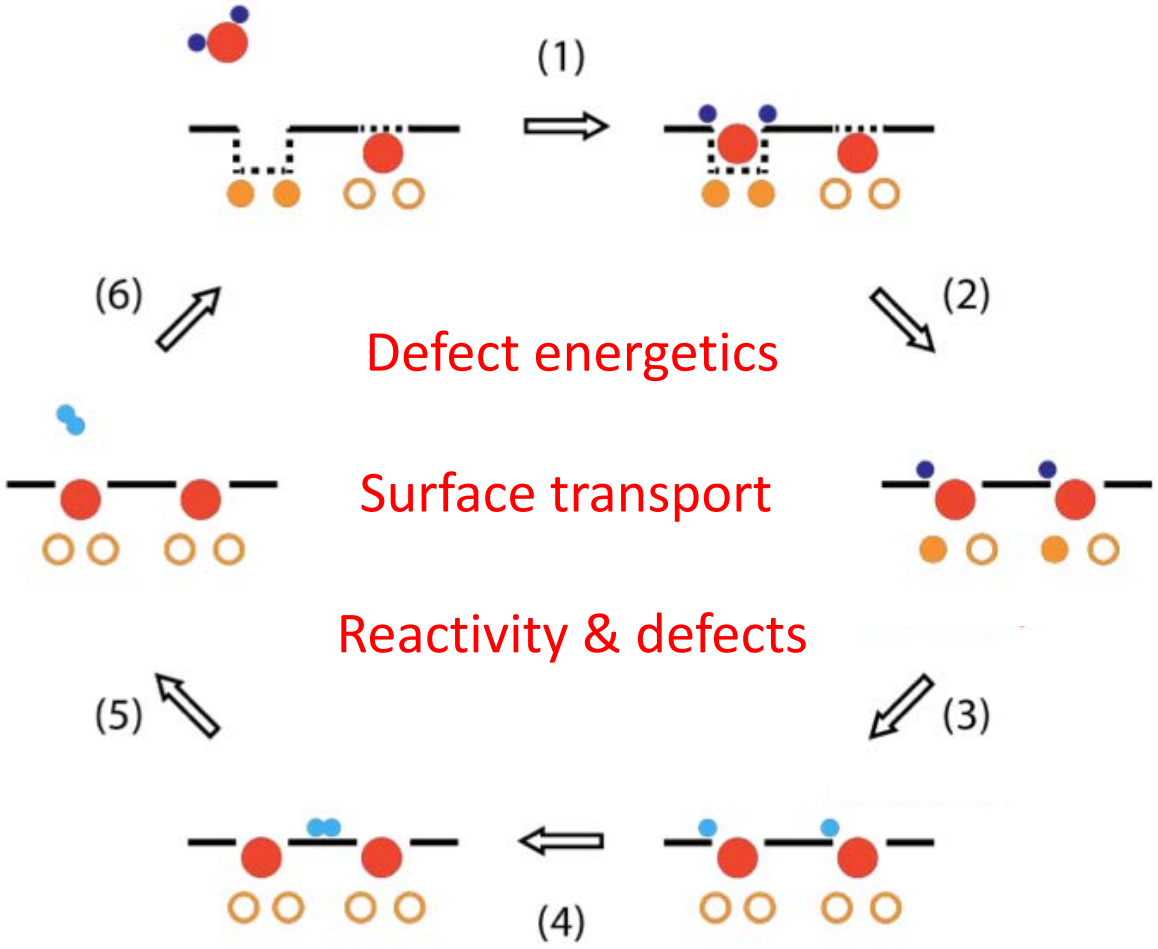
Anode reactions in ceria





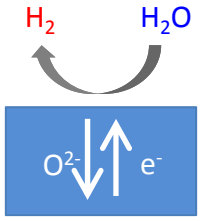


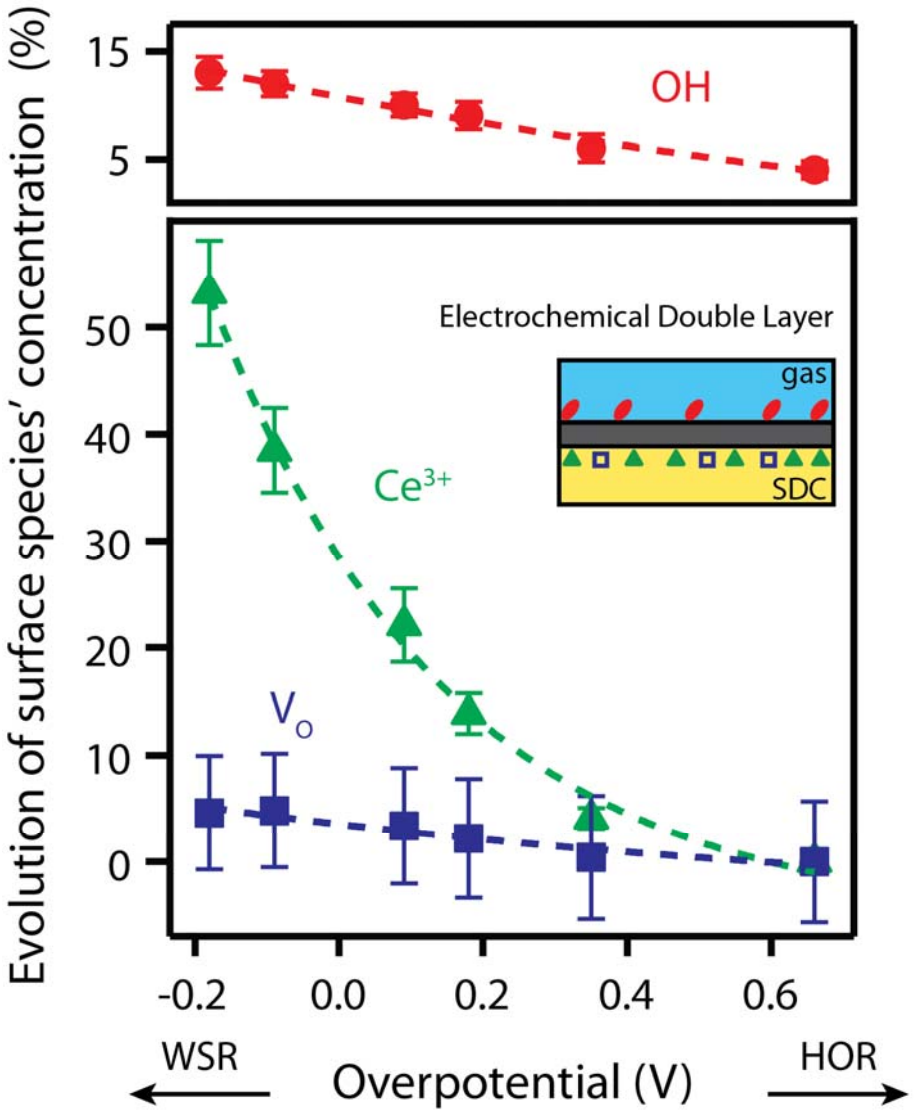
$$H_2O_{(g)} + V_O^{\bullet\bullet} + 2Ce'_{Ce} \rightleftharpoons H_{2(g)} + O_O^{\times}$$

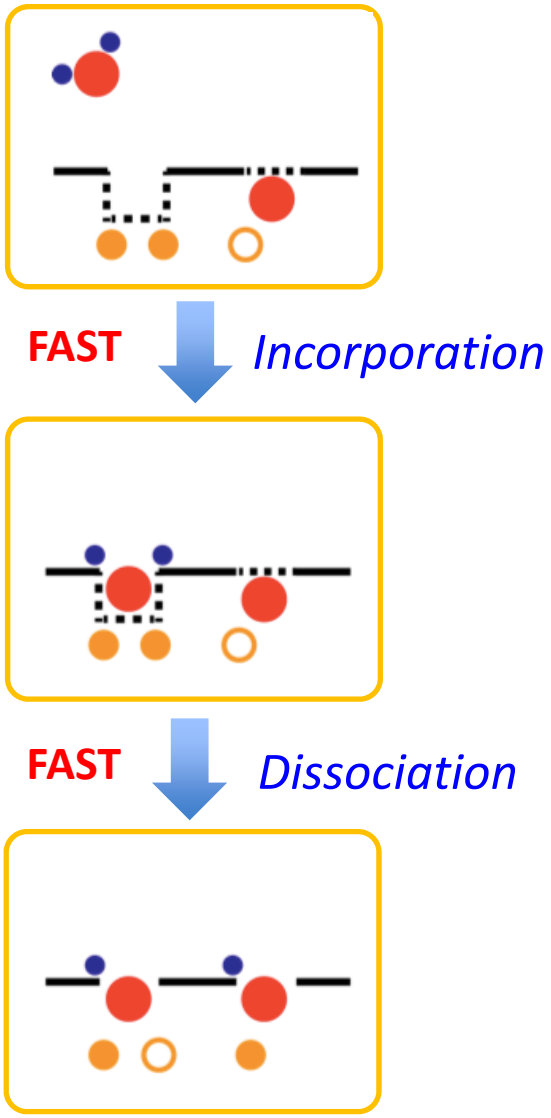


Feng, El Gabaly, Ye, Shen, Chueh. *Nature Comm* (2014).

Anode reactions in ceria







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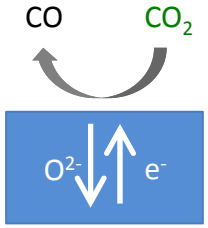
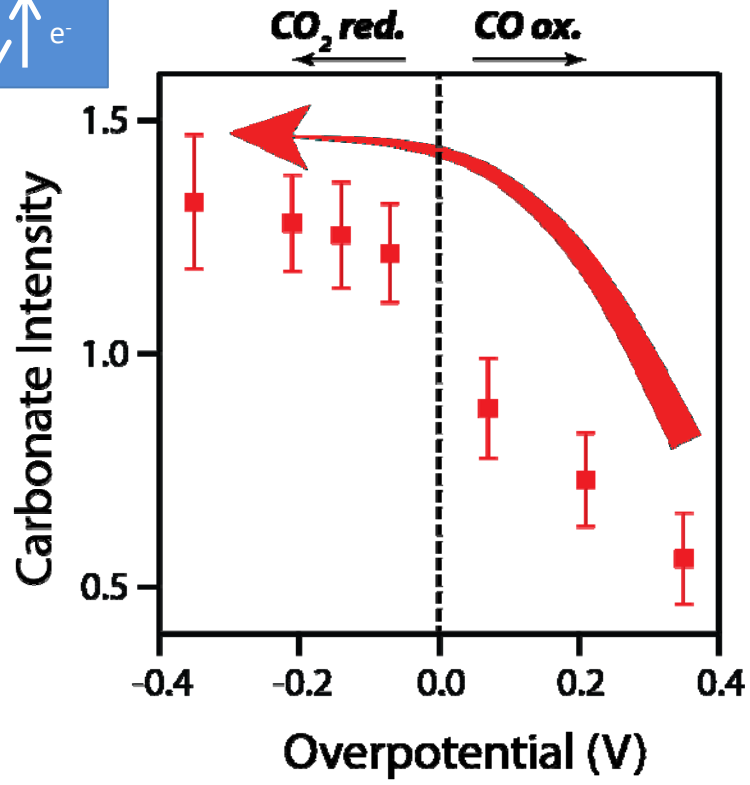
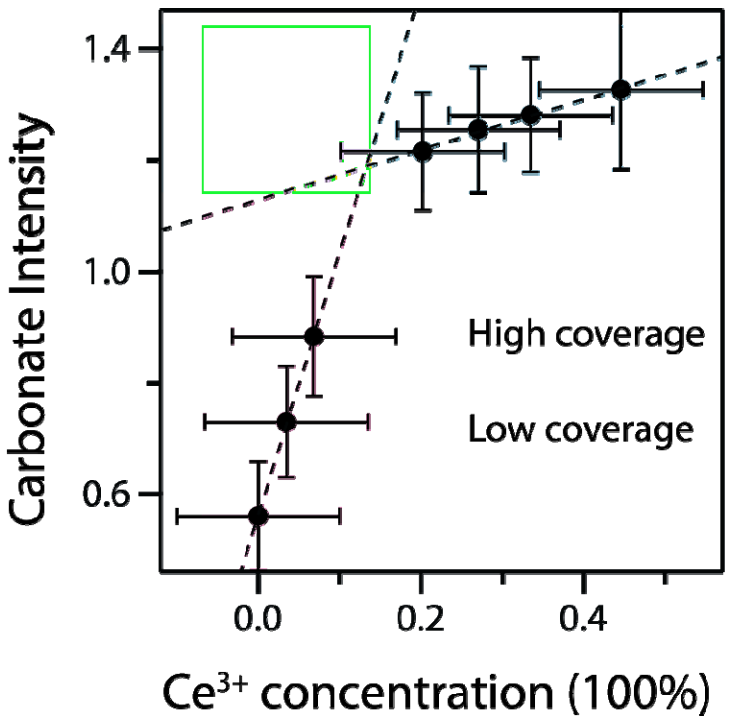
Anode reactions in ceria



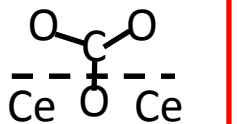




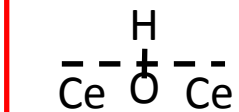
1st e- transfer $CO_{2(g)} + O_O^{\times} + Ce_{Ce}^{'} \rightarrow (CO_3)_O^{'}$

2nd e- transfer $(CO_3)_O^{'} + Ce_{Ce}^{'} + V_O^{\bullet\bullet} \rightarrow CO + 2O_O^{\times}$

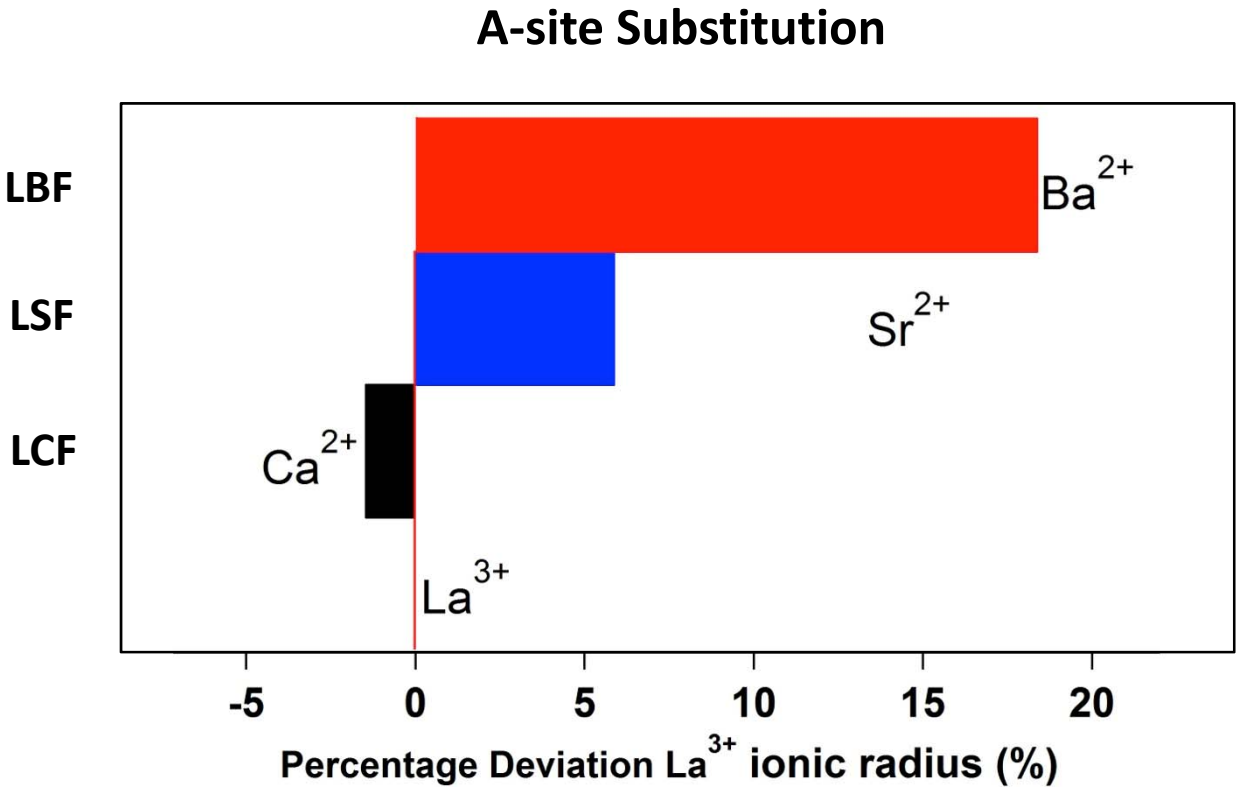
carbonate

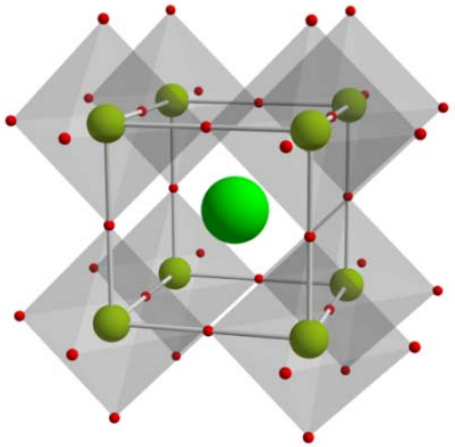


hydroxyl



Ferrate as a model system





(La,AE)FeO$_{3-\delta}$

Shannon, Acta Cryst. (1976). A32, 751

A thermodynamic framework for precipitation & segregation

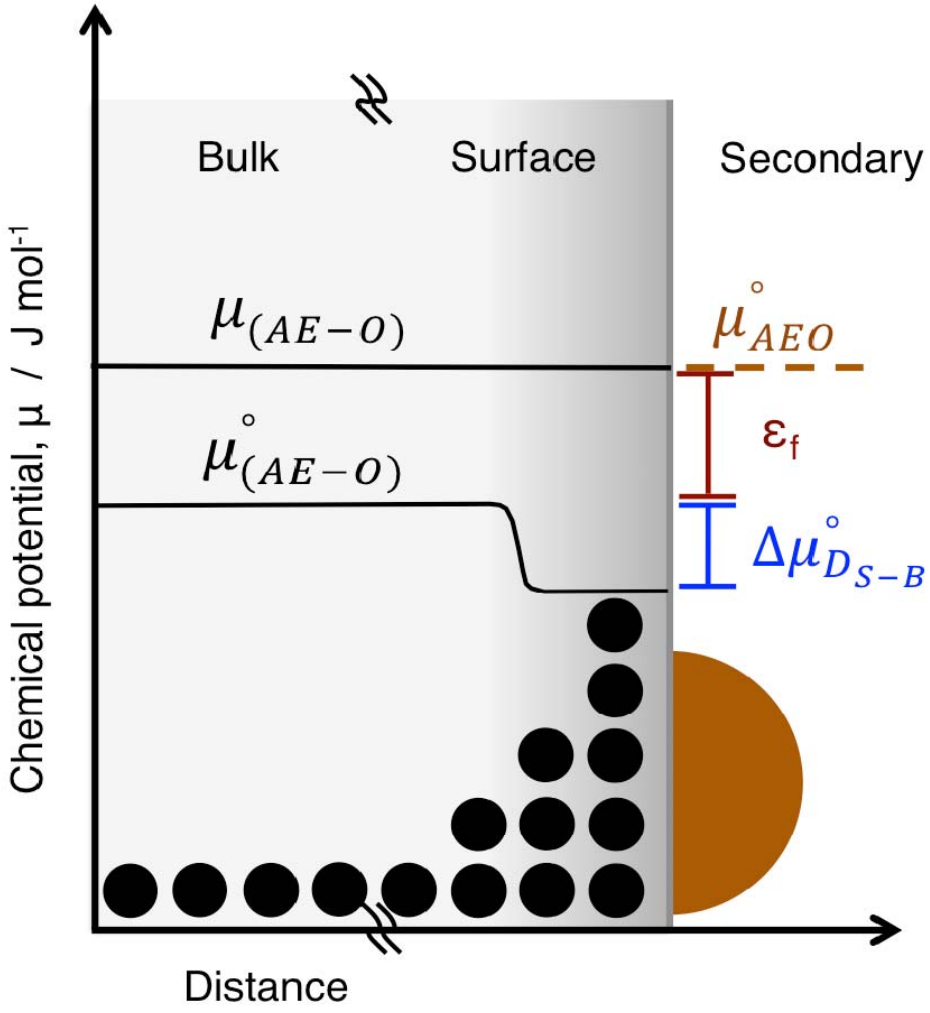
Equilibrium Segregation

$$A_{bulk} \rightleftharpoons A_{surf}$$

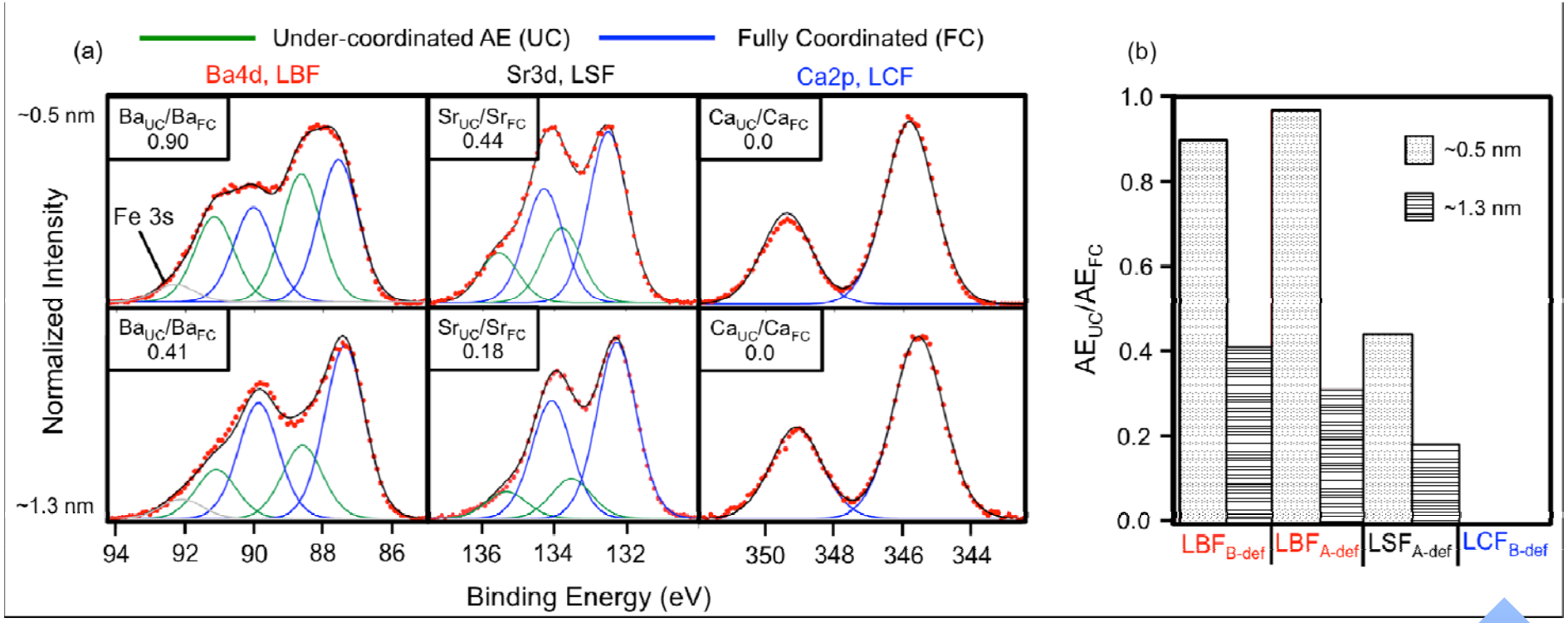
Equilibrium Precipitation

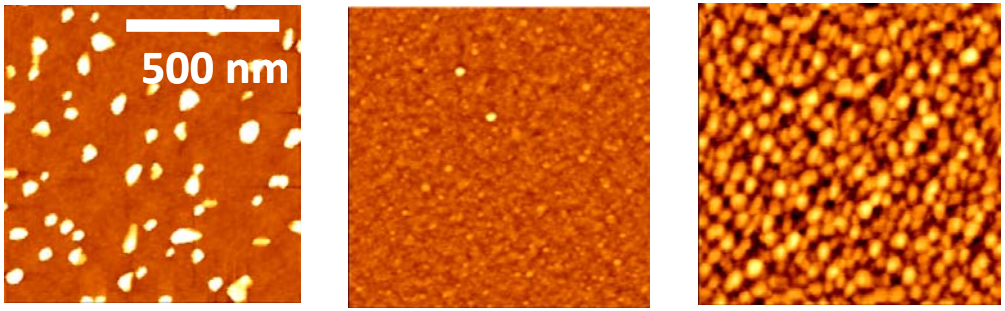
$$\boxed{{}^{1}/_{2}\, O_{2,g} + AE'_{La} \rightleftharpoons V'''_{La} + 2h^{\cdot}} + \text{AEO}$$

"AE-O"

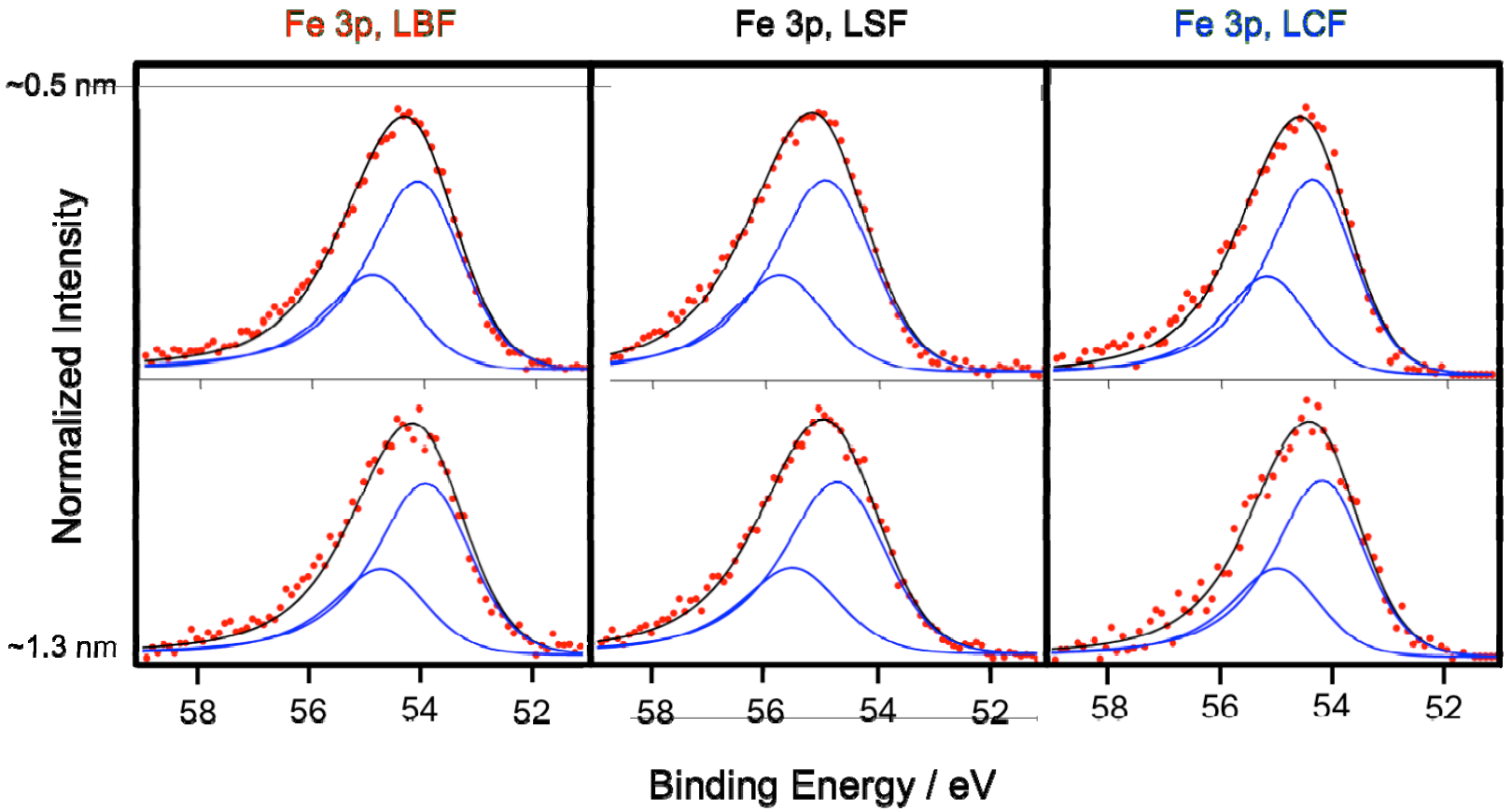


Precipitation



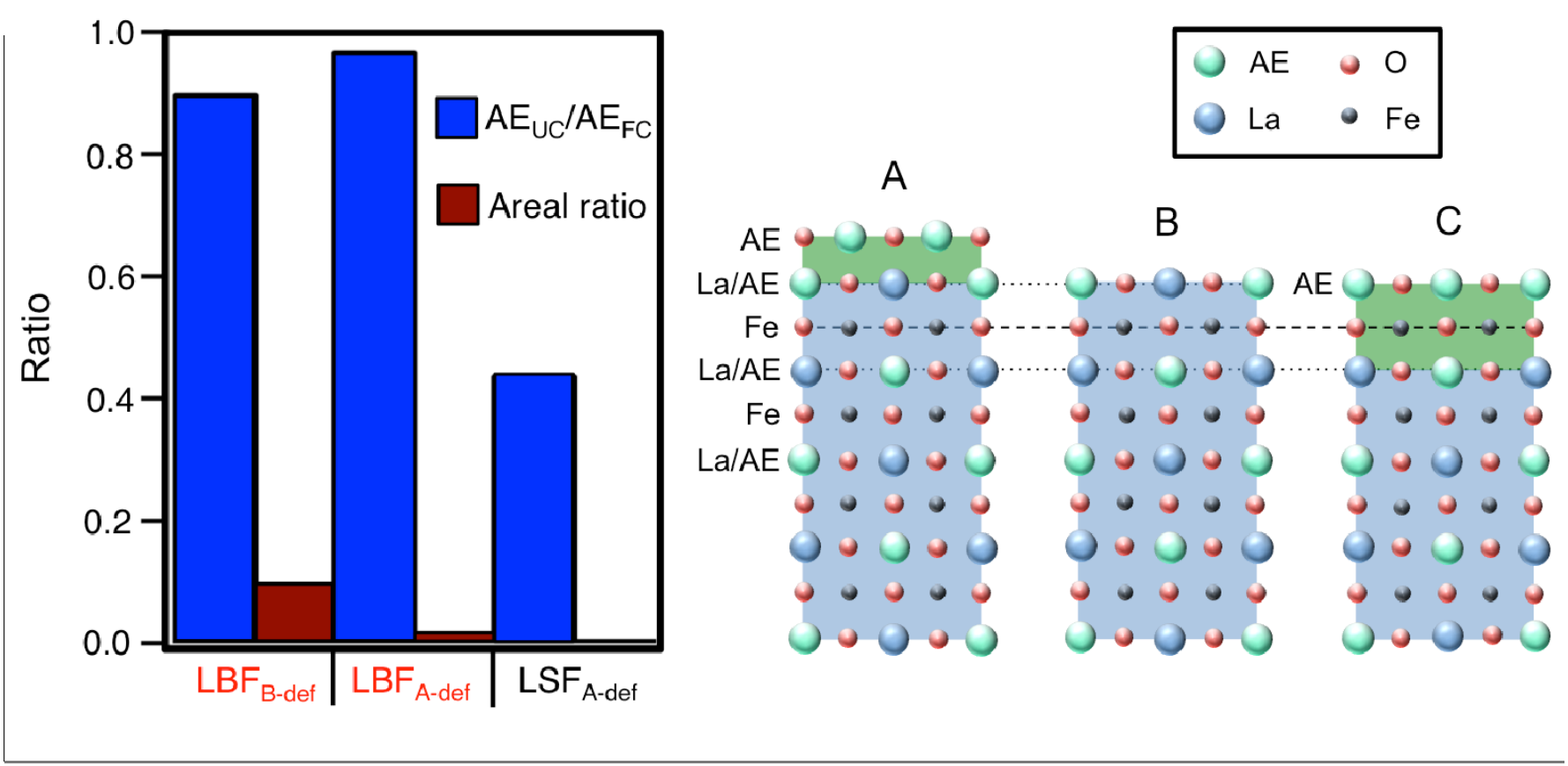


Precipitation



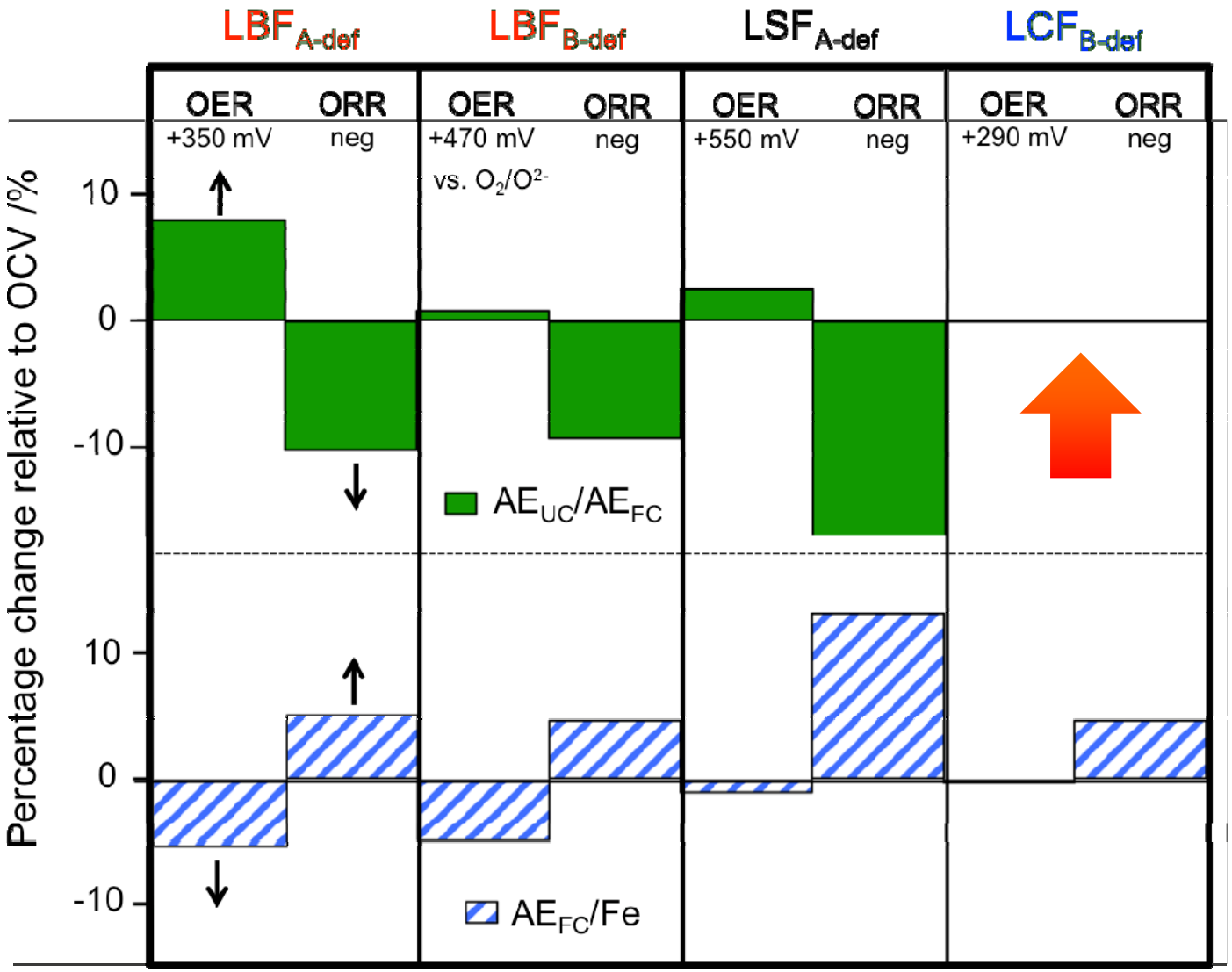
- Precipitate identified in LBF and LSF as BaO_x and SrO_x with no Fe content
- No precipitation identified in LCF

Precipitation vs. Ba/Sr termination

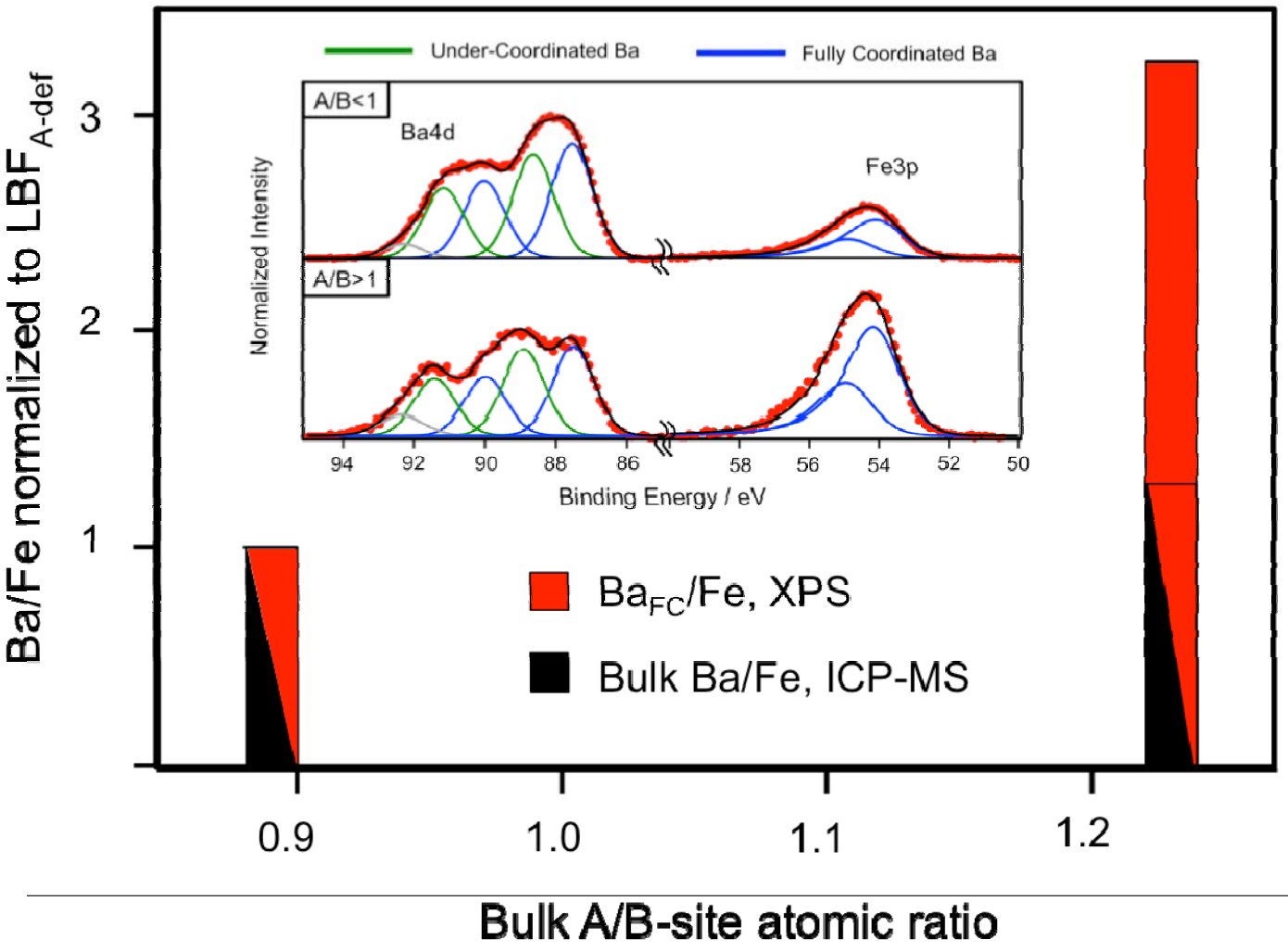


- LBF and LSF likely has Ba/Sr-O termination layer in addition to precipitates and/or < 10 nm precipitates
- LCF is <u>not</u> Ca-O terminated

Electrochemical-driven precipitation



Fe/AE Vacancy Segregation



Segregation takes place side by side with precipitation

Summary

- Thermodynamically consistent treatment of segregation of defects, and precipitation of secondary phases
- Experimentally differentiated precipitate and segregate
- Ba- and Sr-substitution produced secondary phases in ferrates that respond to electrochemical bias predicted by thermodynamics
- Ca-substitution produced no secondary phase

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Core Technology Program

Graduate Research Fellowship Program