Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Mixed Ionic Electronic Conducting Quaternary Perovskites: Materials by Design for STCH H_2

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Project Overview

Project Partners

PI, Arizona State University

Co-PI, Princeton University

Award #	EE0008090
Start/End Date	10/01/2018 – 09/30/2019
Phase 1 Funding*	$0.25M

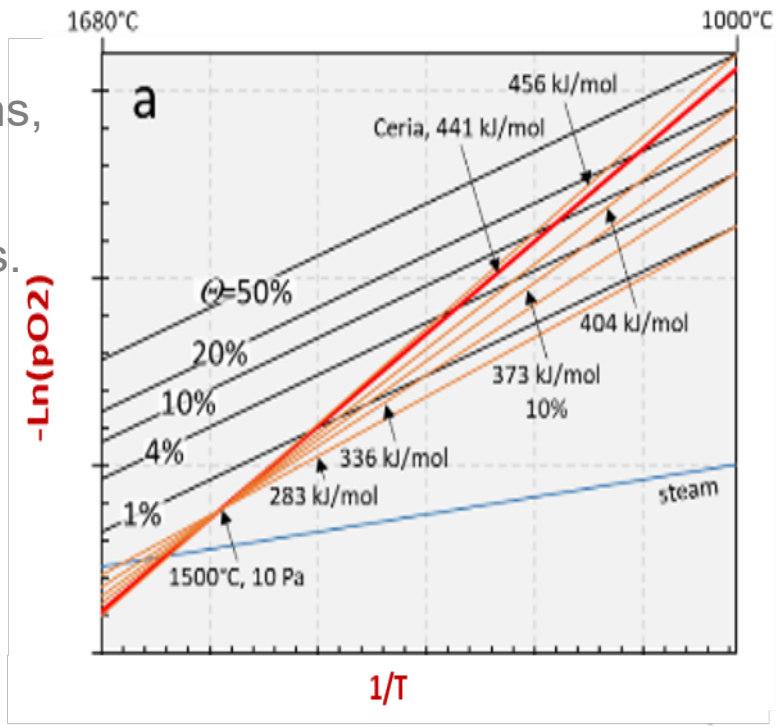
** this amount does not include cost share or support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Project Vision

We are solving the challenge of computing the solid state oxygen chemical potential for complex mixed ionic electronic (off-stoichiometric) perovskite solid solutions by using a sublattice model formalism and accurate zero temperature first principles calculations, from which we can extract off-stoichiometry as a function of gas phase conditions (temperature, pO_2, steam/H2 mix) and provide inverse design principles.

Project Impact

We expect to contribute to materials discovery for improved STCH materials. We expect to offer strategies that will boost solar to hydrogen thermal efficiency, as well as provide experimentalists with crucial input by determining best possible, thermodynamically consistent targets depending on operating conditions to guide systems design.



Approach- Summary

Project Motivation

In order to optimize the search for better materials for STCH, the field needs inverse design criteria, hence we see a need to determine the optimum reduction enthalpy (ΔH) that balances degree of reduction, hydrogen yield, and temperature swing and given that strategies to tune the ΔH.

Barriers

- Direct comparison theory & experiment is difficult
- Open shells and disorder, difficult to calculate.
- Calculating sublattice models without experimental input is very difficult.
- Calculating the "equation of state" **off-stoichiometry δ as a function of the oxygen chemical potentia**l from 1st principles has never been attempted.
- Inverse design problem poorly defined because of wide range of possible operating conditions.

Metric	State of the Art	Proposed
Reduction Temperature	> 1500°C	< 1450 °C
Reduction Capacity ($\Delta\delta$ per cation)	~ 0.03	> 0.15
Accuracy of modeled chemical potentials over relevant operating window	N/A	±20%

Partnerships

Dean Emily Carter and Dr. Sai Gopalakrishnan, Princeton University

Expertise: Developing new DFT capabilities, complex oxides, calculating chemical potentials in complex disordered materials

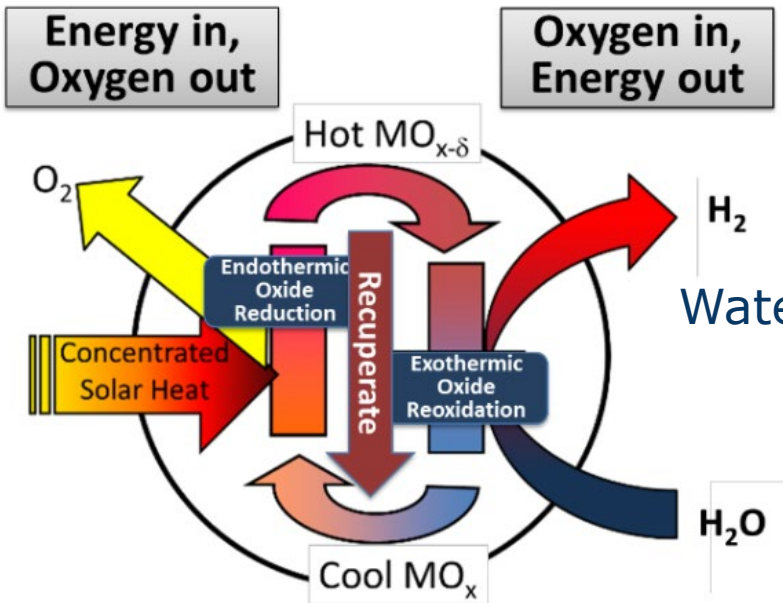
Specific capabilities: DFT functionals (SCAN+U), Computational Sublattice Model Formulation, detailed thermodynamic constraints.

Approach- Summary

Four interrelated pillars

1. Core of the project is methodology that can calculate the off-stoichiometry and the solid state oxygen chemical potential from first principles
   - Based on the sublattice model formulation (aka Calphad, compound energy formulation)
   - Zero temperature DFT (using SCAN + U energy functional)
   - Validated using Zinkevich and Grundy Calphad models for ceria (last year) and $La_{1-x}Sr_xMnO_3$
2. Using insights gained from the sublattice model formulation to suggest new candidates
   - Validate with experimental synthesis and characterization
3. Identify rigorous thermodynamic relationships to determine ideal enthalpy of reduction to optimize for efficiency and by extension cost
   - Given constraints on practicalities to define (1) minimum yield, (2) minimum oxidation temperature, (3) minimum partial pressure of O_2, and (4) maximum reduction temperature
4. Identify and quantify model uncertainty to answer a key question
   - How accurate is accurate enough?

Approach: Innovation
Background



Thermal reduction (TR): High T, low pO_2

$$\frac{1}{d\delta} MO_x \rightarrow \frac{1}{d\delta} MO_{x-d\delta} + \frac{1}{2} O_2$$

Endothermic

Water splitting (WS): "Low" T, high (pH_2O/pH_2)

$$\frac{1}{d\delta} MO_{x-d\delta} + H_2O \rightarrow \frac{1}{d\delta} MO_x + H_2$$

Exothermic

TR and WS reactions are thermodynamically feasible, if,

$$\Delta G_{TR} = \frac{1}{d\delta} G_{MO_{x-d\delta}} + ½\, G_{O_2} - \frac{1}{d\delta} G_{MO_x} \leq 0$$

$$\Delta G_{WS} = \frac{1}{d\delta} G_{MO_x} + G_{H_2} - \frac{1}{d\delta} G_{MO_{x-d\delta}} - G_{H_2O} \leq 0$$

Both expressions have solid and gas phase energetics.

We decouple the solid from the gas-phase thermodynamics

Approach: Innovation
Thermal reduction energetics

$$\frac{1}{d\delta} MO_{x-\square} \rightarrow \frac{1}{d\delta} MO_{x-\delta-d\delta} + ½ O_2$$

Target T: 1673.15 K maximum, pO_2: 10 Pa minimum

The reduction reaction is favorable if the Gibbs energy of the reaction is negative

$$\Delta G_{TR} = \frac{1}{d\delta} G_{MO_{x-\delta}} + ½\, G_{O_2} - \frac{1}{d\delta} G_{MO_x} \leq 0$$

Rearrangement of terms

$$½\, G_{O_2} \leq \frac{1}{d\delta} G_{MO_{x-\delta}} - \frac{1}{d\delta} G_{MO_{x-\delta-d\delta}}$$

Chemical potential of oxygen in gas stream

$$\mu_O^{O_2,gas} = ½\, G_{O_2} = \frac{1}{2}(H_{O_2} - TH_{O_2} + RT \ln pO_2)$$

H and *S* are *T* dependent and well known

Chemical potential of oxygen in solid

$$\mu_O^{MO_{x-\delta}} = \frac{1}{d\delta}\left(G_{MO_{x-\delta}} - G_{MO_{x-\delta-d\delta}}\right)$$

$$-\frac{dG_{MO_{x-\delta}}}{d\delta} = -\frac{dH_{MO_{x-\delta}}}{d\delta} + T\frac{dS_{MO_{x-\delta}}}{d\delta}$$

Main *T* dependence is from TS terms

Reduction is at equilibrium if

$$\mu_O^{MO_{x-\delta}} = \mu_O^{O_2,gas}$$

Approach: Innovation
Calculate oxygen chemical potential (μ_O)

- μ_O of gas phase components (H_2O, H_2, and O_2) is well known and available $\mu_O^{H_2O/H_2,gas} = \mu_{H_2O} - \mu_{H_2}$
  - e.g., from National Institute of Standards and Technology (NIST) or HSC
- μ_O of the solid phase requires calculating the Gibbs energy as a function of temperature and δ and differentiating wrt δ
  - Density functional theory (DFT) based approaches can yield good estimates for enthalpy, but estimating entropy is non-trivial
  - We aim to construct "simple" thermodynamic models based on the sublattice model formulation to get an "accurate enough" estimate of Gibbs energies and the solid state oxygen chemical potential
- Validate models with available data
  - For CeO_2, $(Ce,Zr)O_2$ (last year) and $La_{1-x}Sr_xMnO_3$ (since last year)
- Then devise a thermodynamic criteria for screening promising candidates

Approach Innovation:
Comprehensive uncertainty management

- Overall goal is to predict thermodynamic efficiency given the thermodynamics of a material and a fixed operating cycle subject to thermodynamic constraints and specify uncertainty.
- SNL UQ (Uncertainty Quantification) node determines confidence needed in the components that feed into the efficiency evaluation, whether it comes from experiment or computation or a combination.
  - Bayesian model inference for thermodynamic behavior (oxygen chemical potential) of the redox active materials
  - Bayesian model comparison for thermodynamics
  - Propagation of parametric uncertainty into thermodynamic properties is ongoing

Relevance & Impact

- **Efficiency** of the hydrogen production pathway is of critical importance to achieving **< $2/kg**.
  - This project makes a direct connection between computational thermodynamics, the potential efficiency, and management of the uncertainties.
- "**Good fit**" with the HydroGEN Consortium R&D model
  - **Uncertainty Quantification** in Computational Models of Phys. Sys.
    - ✓ Facilitate answering the question how accurate in measurements or computation is accurate enough to meaningfully inform materials discovery
  - Controlled **Materials Synthesis** and Defect Engineering
    - ✓ Facilitate validation of DFT predictions and further testing of candidates
  - **HT-XRD** and Complementary **Thermal Analysis**
    - ✓ Facilitate experimental determination of the oxygen chemical potential, μ_O
  - Laser Heated **Stagnation Flow Reactor**
    - ✓ Facilitate a potentially faster but less accurate determination of μ_O
- Enhances the broader consortium by providing a missing link between computation, experiment, efficiency, and cost of H_2

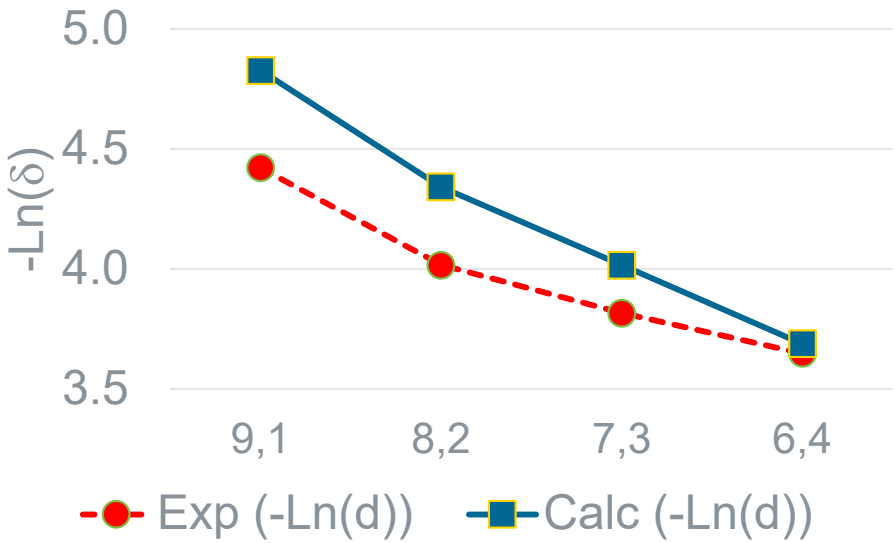
Accomplishments & Progress

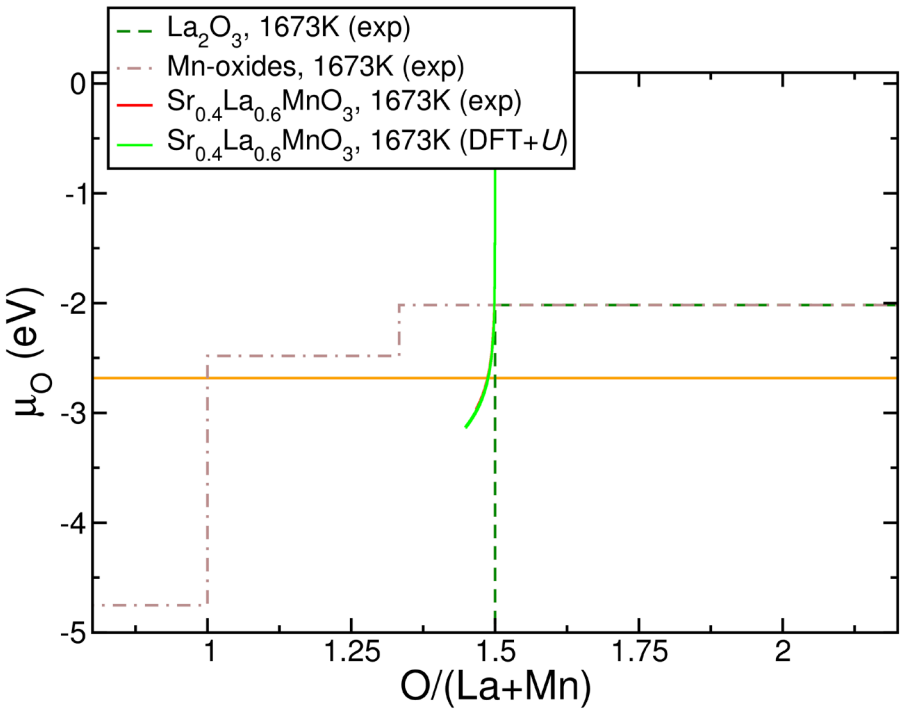
- Go/No-Go due 6/30/2019
  - **Goal: Identify candidate material with promise to perform better at lower temperature and/or higher partial pressure when compared to ceria.**
  - Synthesize, in collaboration with NREL STCH Node, two candidates with calculated thermodynamic response maps completed to be synthesized
  - Measure X-ray diffraction (SNL) to determine structure, phase purity, and lattice constants
  - Calculate μ_O and compare with experiment (two SNL Nodes)
    - ✓ **Goal: 20% agreement between derived thermodynamics and inferred from the measurements (have demonstrated this for ceria)**
    - ✓ **Enthalpy & entropy of reaction rigorously from derivatives of μ_O**
- Significance: Direct comparison between theory and experiment through one function (the chemical potential), which can be directly inferred from and calculated with zero temperature DFT.
  - Using a realistic operating cycle **connects materials discovery to technology**.
  - Uncertainty Quantification answers the question how good do measurements or computation have to be to differentiate between materials.

Accomplishments & Progress

$La_{1-x}Sr_xMnO_{3-\delta}$: Computation vs. Experiment

Equilibrium oxygen concentrations



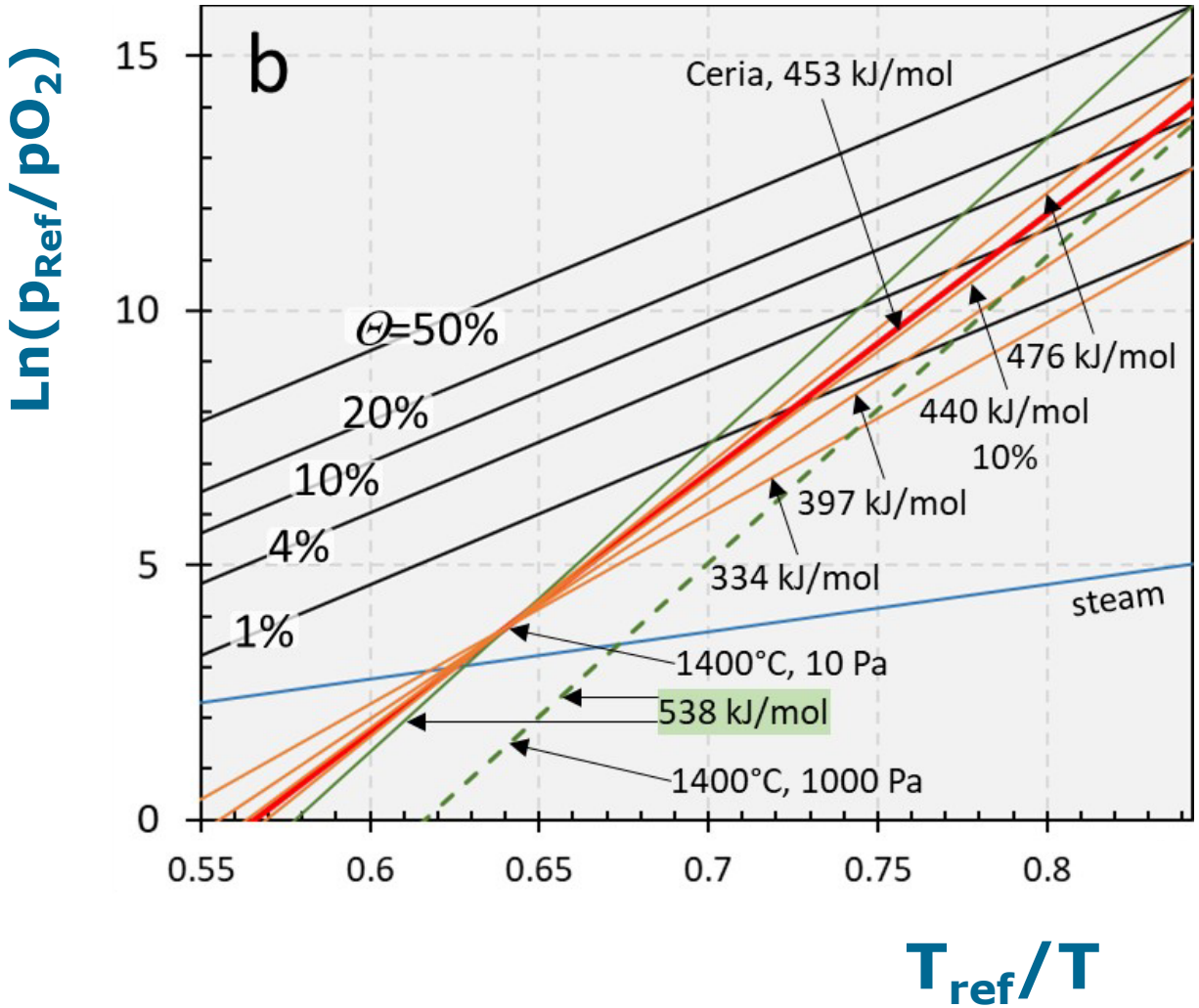


9,1 refers to $La_{0.9}Sr_{0.1}MnO_{3-\delta}$
8,2 refers to $La_{0.8}Sr_{0.2}MnO_{3-\delta}$
Etc.

Error: 5.9% ± 3.6%
All errors < 10%

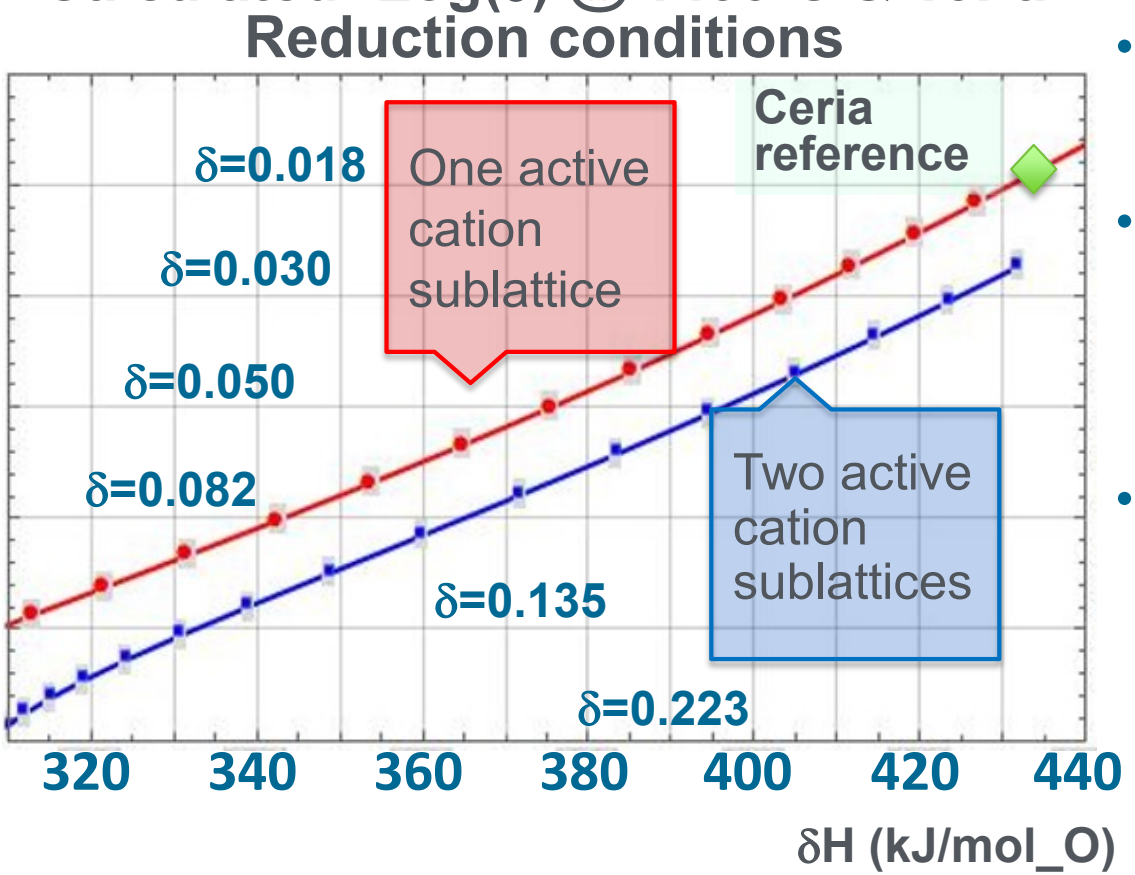
Experimental data from Grundy *et al.*, **CALPHAD 2004**, 28, 191

Accomplishments & Progress



- Utility of these coordinates
- Lines of constant yield and of constant δ are linear
- Choosing reduction conditions and yield tells us optimum enthalpy of reduction
- Not so good news at 1400C & 10Pa, optimum is not much lower than ceria
- δ = 0.015 for ceria at these conditions

Accomplishments & Progress



- δ has a strong dependence of δH as expected
- More entropy, such as from a second active redox sublattice – increases δ for the same δH
- Strategy: tune δH to optimal operating conditions
  - i.e., Reduction conditions; yield, ΔT
- Increase entropy with a second redox active sub-lattice

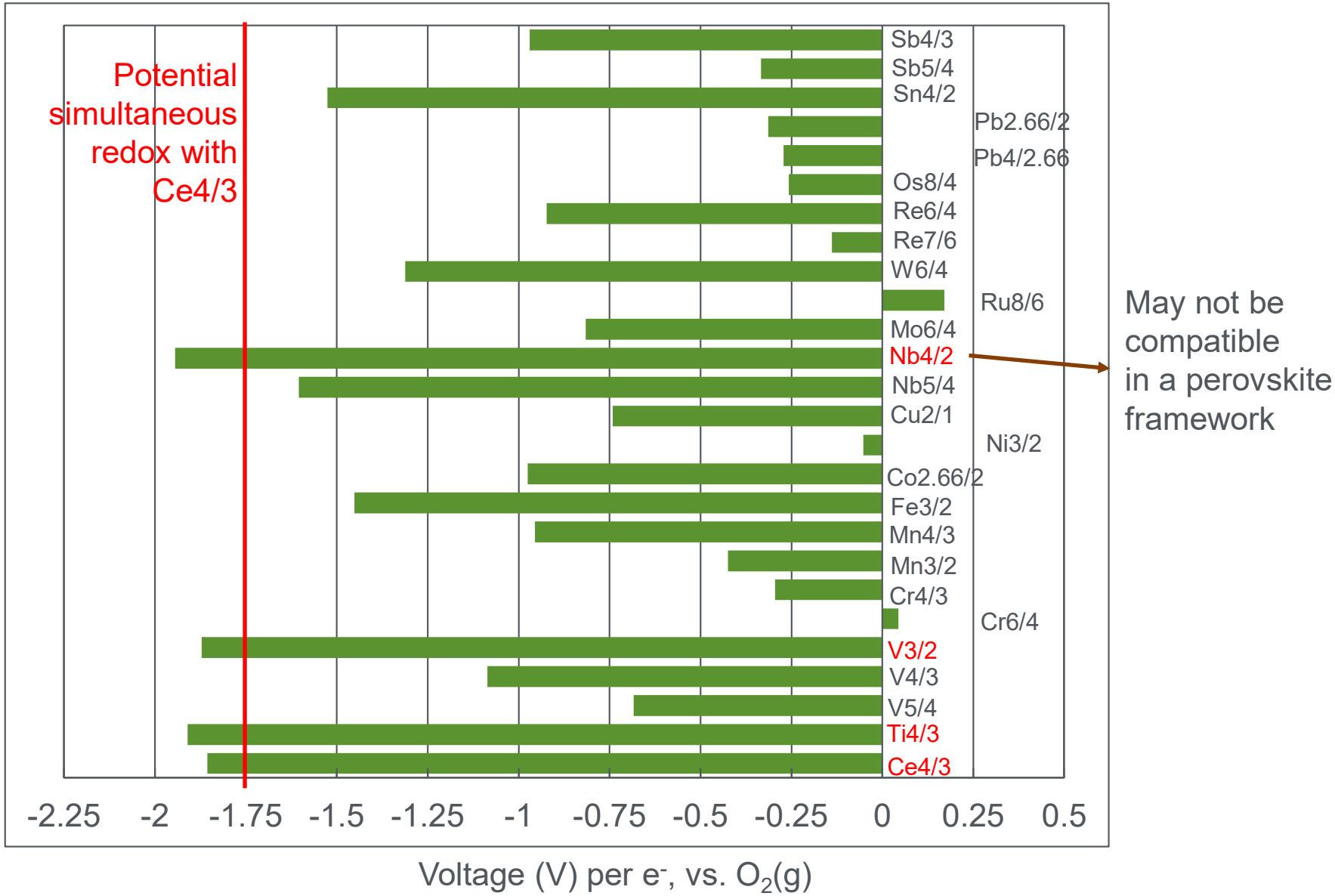
Zinkevich model for $Ce_2O_{4-2\delta}$

<u>Artificially</u> changing energy difference between $^{F}Ce_2O_3$ and Ce_2O_4

Allowing for configurational entropy on two sublattices

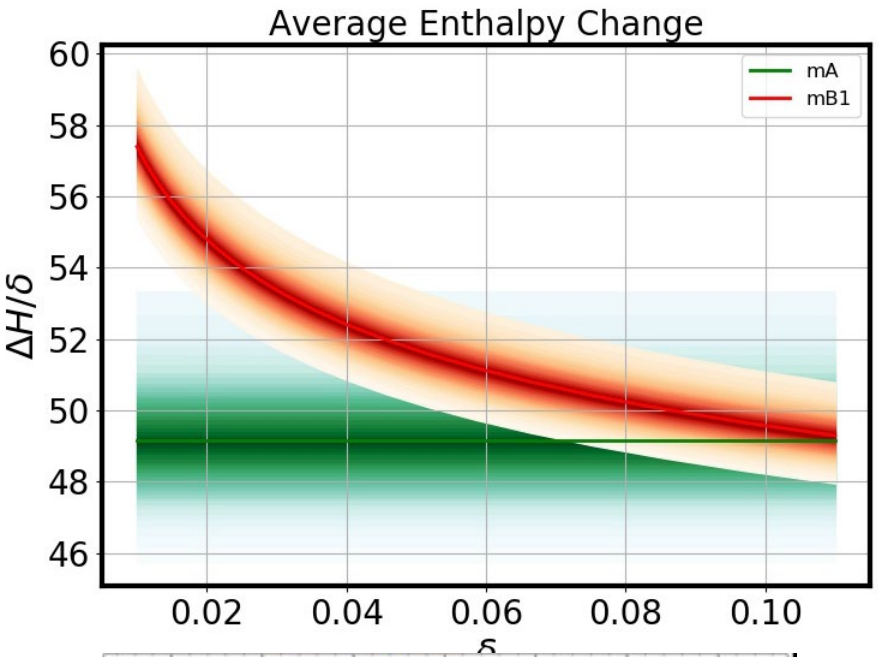
Accomplishments & Progress

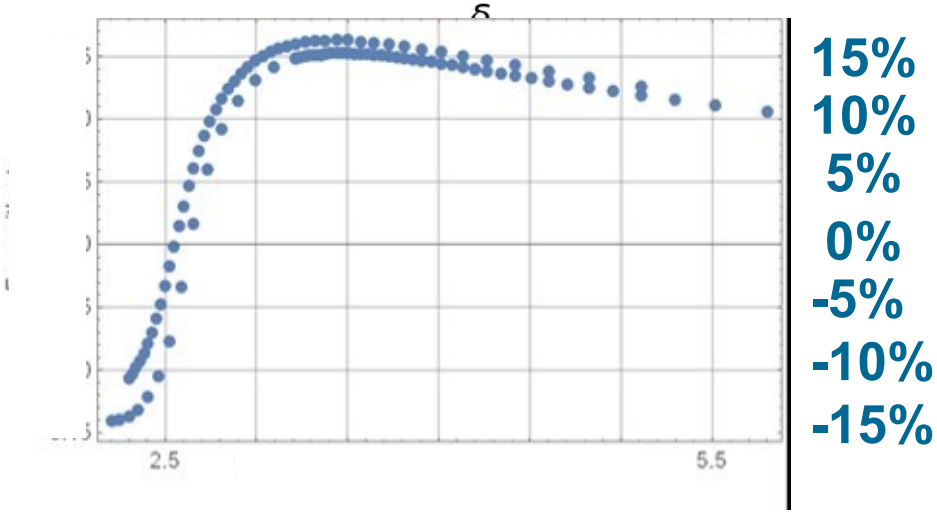
Potential cations redox-active simultaneously



Data from Kubaschewski *et al.*, **Metallurgical Thermochemistry 1967**

Accomplishments:
Quantifying Uncertainty





Propagation of Model Error into Enthalpy Change

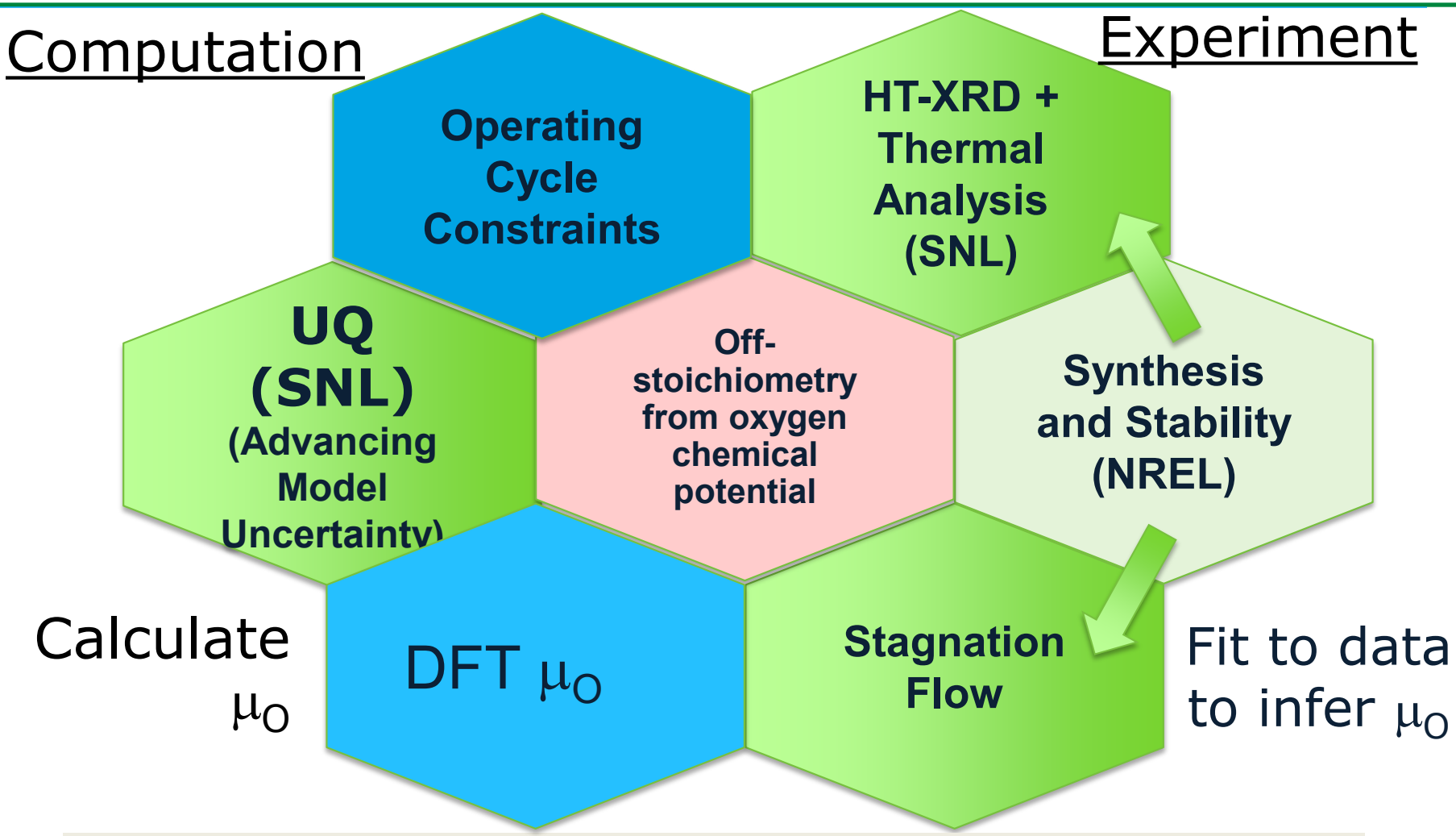
- Model B1 has more complexity and lower model error
- Model error leads to larger uncertainty in the enthalpy change predicted by minimal Model A than by Model B1

Assessing Model Error from dropping temperature terms

- Assessing the impact of tossing most of the temperature dependence terms
- Keeping only the ideal configurational entropy
- Confirms results are dominated by the enthalpy of formation and configurational entropy

Collaboration: Effectiveness

It takes a "village"



All the important thermodynamics is encompassed in the oxygen chemical potential: gas phase known – solid phase modeled with sub-lattice formalism (either from experiment, computation, or combination)

Collaboration: Effectiveness

- Specific interactions
  - Have been working very closely with the SNL Uncertainty Quantification Node (Dr. Bert Debusschere and a student)
  - Have been working closely with the NREL Synthesis and Characterization Node (Drs. Dave Ginley, Robert Bell, and Phil Parilla) on synthesizing candidate materials
  - Have been gearing up to work closely with SNL Thermal Analysis Nodes (Dr. Eric Coker) to measure equilibrium off-stoichiometry as function of temperature and pO2
  - Regular conversations with SNL STCH lead and Node Owner for Stagnation Flow (Dr. Tony McDaniel)
  - Phase 1 was primarily computational and developing capabilities – just now starting to need experimental results
- This project has a close association with the 2B team as PI (Prof. Stechel) here is co-PI on the 2B project
- Expected benefits will derive from a closer relationship between what experimentalists measure and theorists calculation with defined protocols
  - Standardization and defined protocols will lower the barrier to entry
  - First calculating off-stoichiometry and quantifying uncertainty will guide experiments and limit what needs to be synthesized and characterized

Proposed Future Work
Remaining Challenges and Barriers

- Build sub-lattice models for (A,A')(B,B')O_3 quinary perovskites, with both A' and B simultaneously redox active
  - Predict oxygen off-stoichiometries and validate with experimental data
- Identify key performance limiting factors and formulate design rules
- Nodes: NREL developing synthesis routes and synthesizing newly proposed candidates
  - Two SNL nodes will measure off-stoichiometry and we will infer enthalpy and entropy
- Uncertainty Quantification
  - Characterization of model error– tradeoff between accuracy and simplicity
  - Refine propagation of model error into thermodynamic properties
  - Propagate uncertainties into full cycle efficiency model
  - Quantify DFT uncertainty (calculation of formation energies and eliminating temperature dependence)
- Port computational sublattice formalism up through quinary perovskites to prime (ASU) and develop protocol with the 2B team and NREL computational node for DFT sublattice model formulation for estimating the off-stoichiometry.
  - Compute solid state oxygen chemical potential as function of δ and T for a range of water splitting materials – identify best trade-offs between yield, ΔT, reduction temperature/pO2, and enthalpy of reduction
  - Methodology for in silico materials discovery verified and validated and improved materials identified.

Project Summary

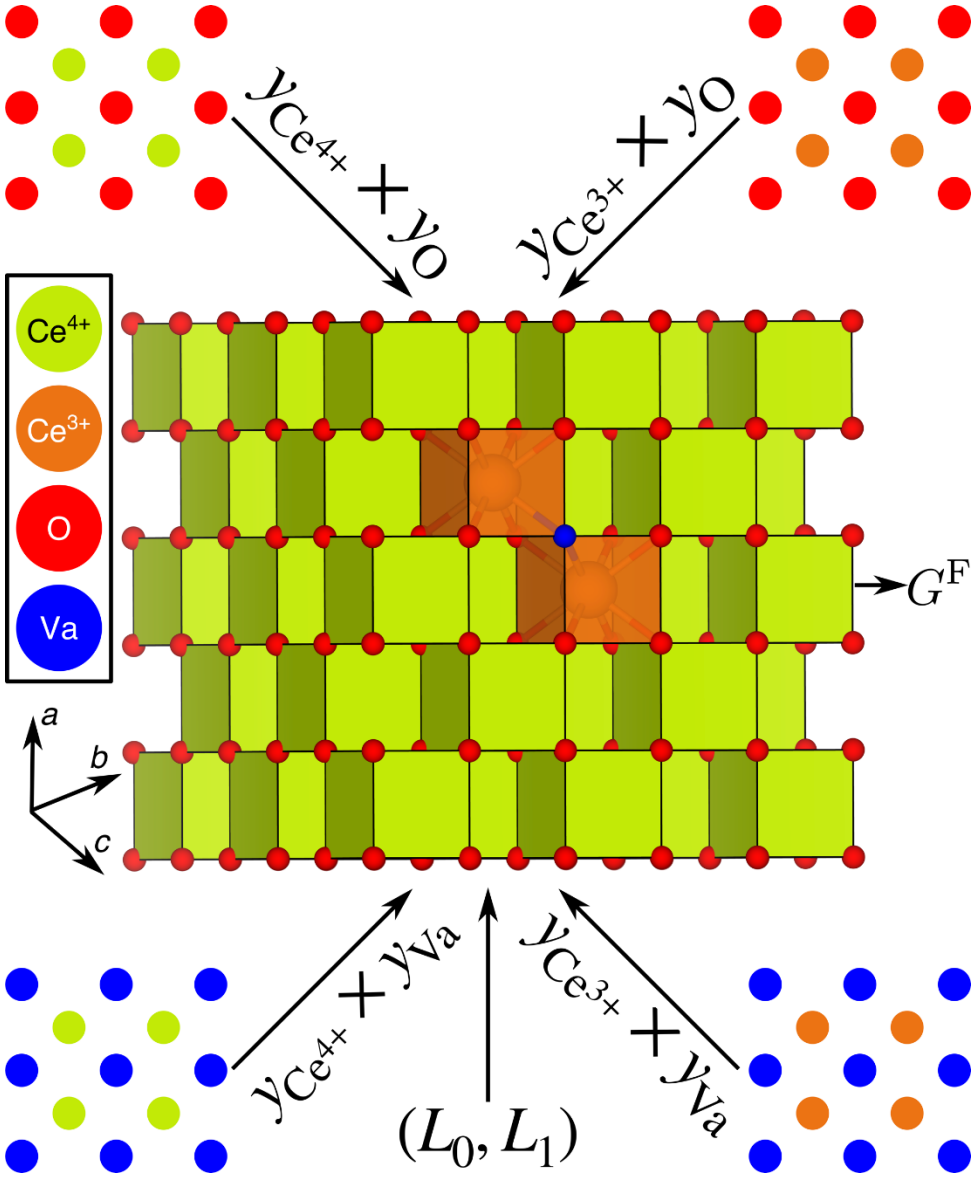
- Construction of chemical potential maps is useful to decouple the energetic contributions of the gas and solid phases in a thermochemical cycle –
  - equilibrium δ comes from equating solid state and gas phase chemical potentials
- Prediction of chemical potentials in solid phases is not trivial
  - Construction of sub-lattice models, with energy values from DFT, is proving to be a promising approach – not high-throughput but reasonable number of zero-temperature DFT (SCAN+U is proving good accuracy) calculations
- We have identified a promising pathway to improve capacities (modest increase in entropy, without compromising kinetics from phase transitions)
  - Redox (cation) couples for (A,A')(B,B')O3 quinary perovskites with A' and B simultaneously redox active.
- We have developed a way to extract the chemical potential from experimental measurements of off-stoichiometry (δ), which can be used to validate computation
- We are developing a methodology for model uncertainty quantification to determine how accurate is accurate enough (either experiment or computation) and provide uncertainty bands to differentiate between materials.

Thank you for your attention

Technical Back-Up Slides

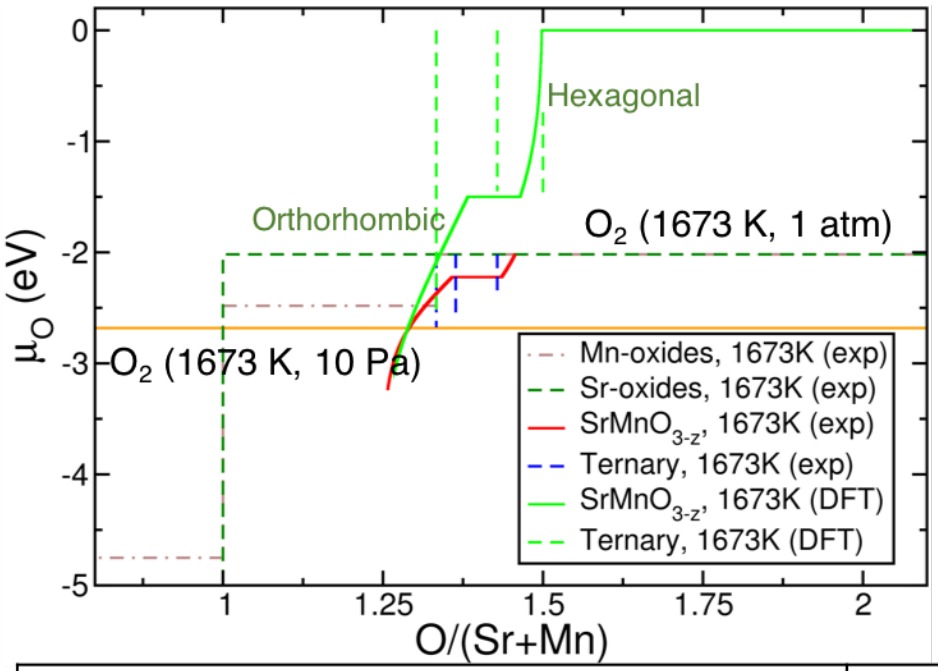
Approach: Innovation

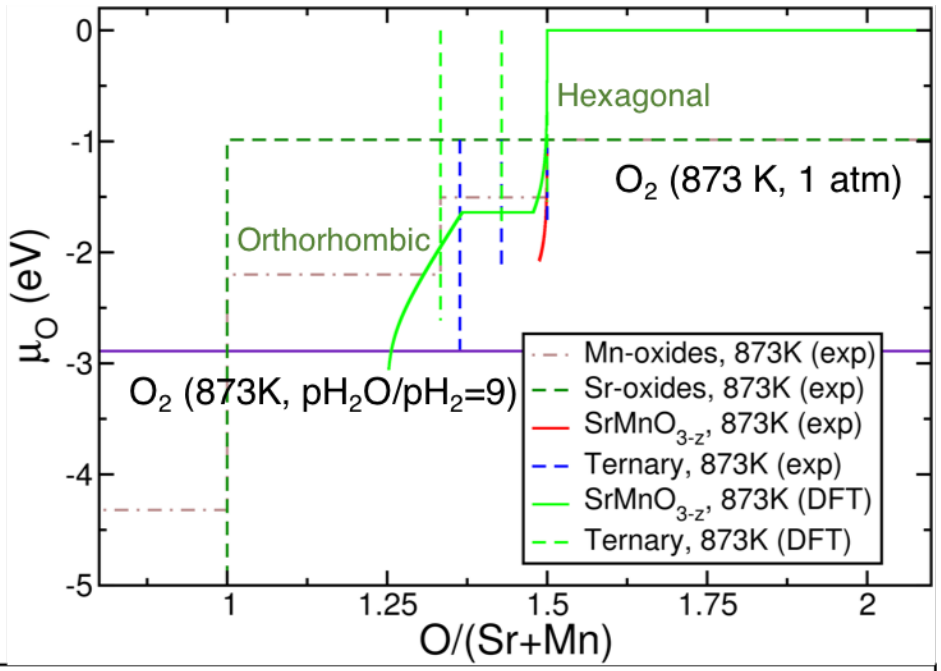
"Sub-lattice" formalism in $CeO_{2-\delta}$



Accomplishments & Progress

$SrMnO_3$: Theory vs. Experiment



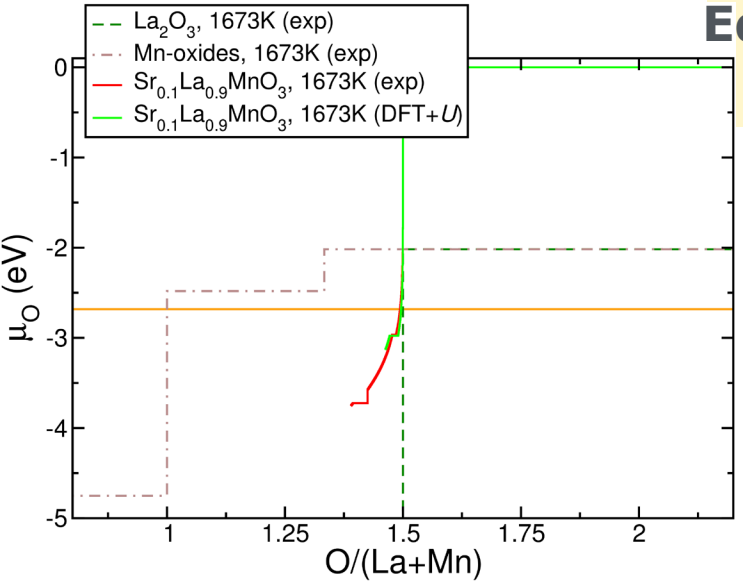


Source	Redox capacity (mol O_2/mol oxide)
Experimental- hexagonal	0
DFT (SCAN+*U*+ sub-lattice)-hexagonal	0
Experimental- orthorhombic	0.419 ($SrMnO_3$-$SrMnO_{2.581}$), irreversible
DFT (SCAN+*U*+sub-lattice)- orthorhombic	0.065 ($SrMnO_{2.578}$-$SrMnO_{2.513}$), reversible

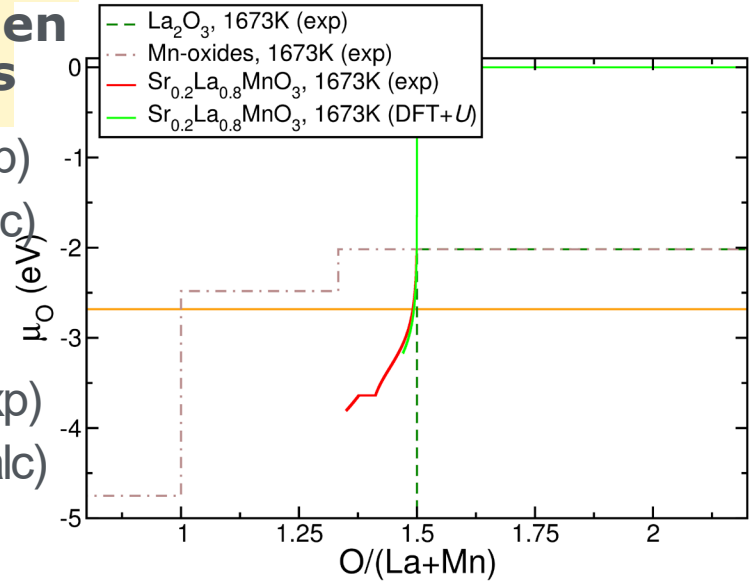
Accomplishments & Progress

$La_{1-x}Sr_xMnO_3$: Computation vs. Experiment

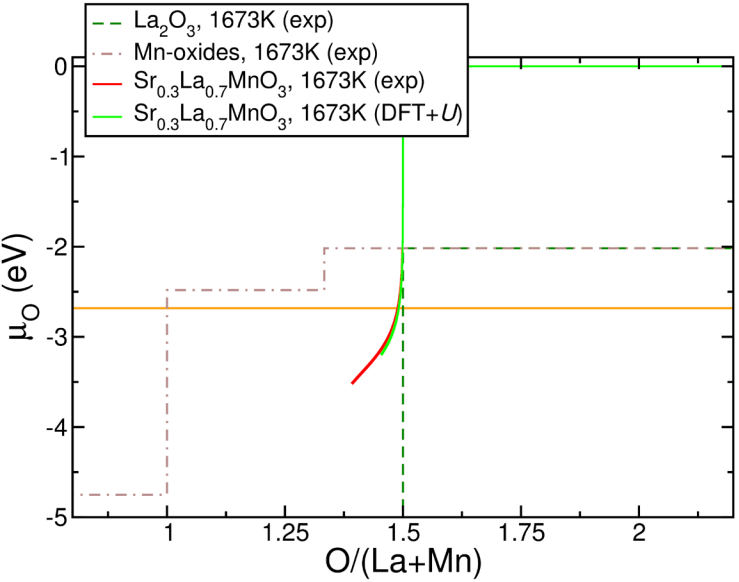
Equilibrium oxygen concentrations



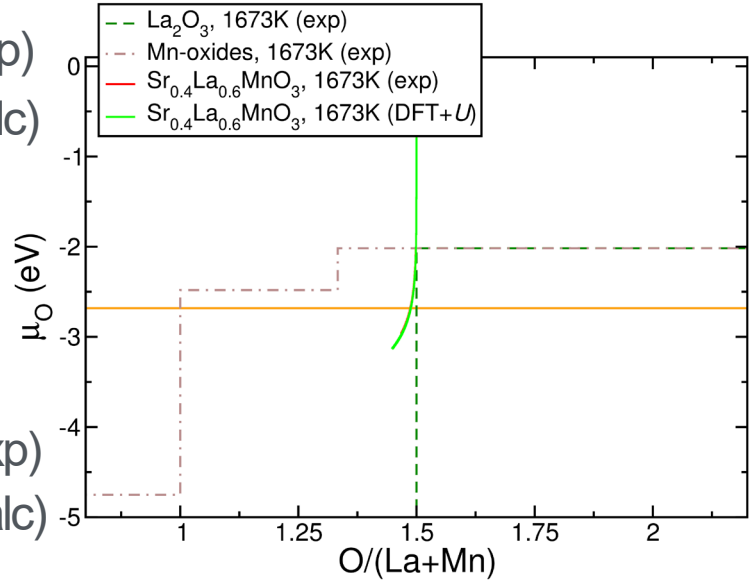
$La_{0.9}Sr_{0.1}MnO_{2.988}$ (exp)
$La_{0.9}Sr_{0.1}MnO_{2.992}$ (calc)



$La_{0.8}Sr_{0.2}MnO_{2.982}$ (exp)
$La_{0.8}Sr_{0.2}MnO_{2.987}$ (calc)



$La_{0.7}Sr_{0.3}MnO_{2.978}$ (exp)
$La_{0.7}Sr_{0.3}MnO_{2.982}$ (calc)



$La_{0.6}Sr_{0.4}MnO_{2.974}$ (exp)
$La_{0.6}Sr_{0.4}MnO_{2.975}$ (calc)

Experimental data from Grundy *et al.*, **CALPHAD 2004**, 28, 191

Approach: Bayesian inference of thermodynamic model parameters

- Bayes' rule updates prior belief in parameter values (λ) with data (d), to obtain posterior belief in the parameter values

$$p(\lambda|d,\mathcal{M}) = \frac{p(d|\lambda,\mathcal{M})p(\lambda,\mathcal{M})}{p(d|\mathcal{M})}$$

- Considered 4 models in transformed variables:

$$z = -\ln(\delta)$$

$$u = \frac{1}{2} ln\left(\frac{P_{O_2,\mathrm{amb}}}{P_{O_2}}\right)$$

$$\beta = \left(\frac{T_{\mathrm{ref}}}{T}\right)$$

$$P_{O_2,\mathrm{amb}} = 0.20946\ Atm$$

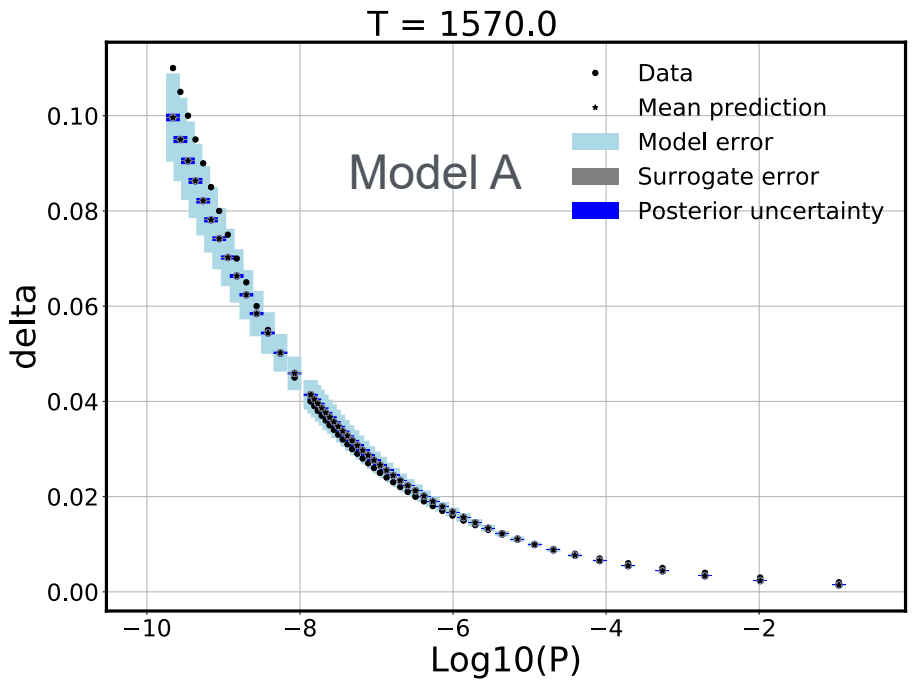
$$T_{\mathrm{ref}} = 1073.15\ K$$

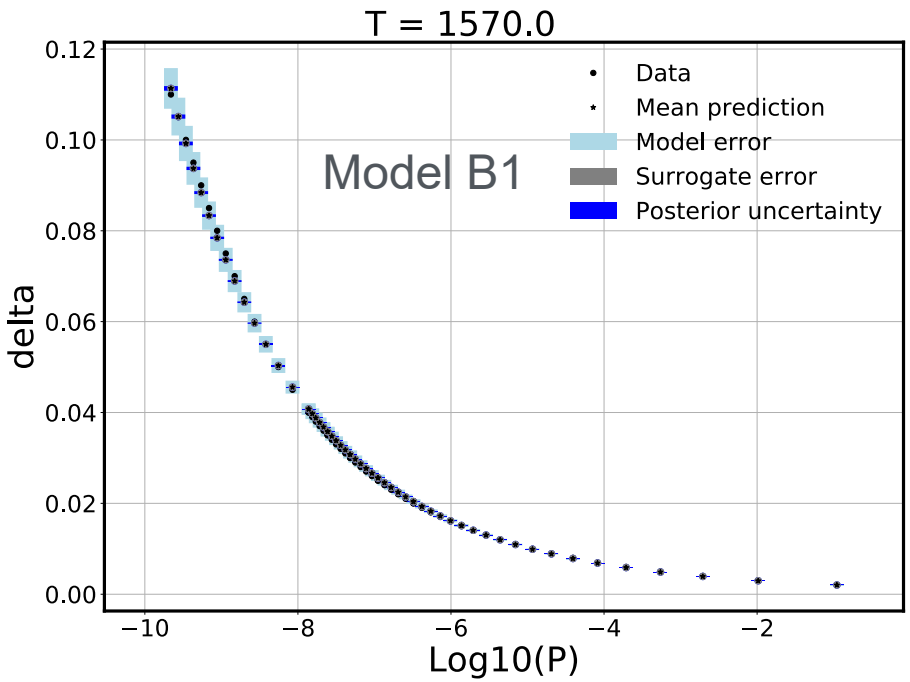
$$z = \frac{z_{\mathrm{ref}} + f_{10}(1-\beta) + f_{20}u + f_{30}u(1-\beta)}{1 + f_{11}(1-\beta) + f_{21}u + f_{31}u(1-\beta)}$$

Model A: f_{11}= f_{21}= f_{30}= f_{31}= 0
Model B1: f_{11}= f_{30}= f_{31}= 0
Model B2: f_{30}= f_{31}= 0
Model C: all parameters are active

- Bayesian inference done in (δ,p,T) space, using a Gaussian noise model on δ

Accomplishments





- Model error embedded in z_{ref}, f_{10} and f_{20} for models A and B1
- Model error is the largest contribution to predictive uncertainty

Model error captures the difference between data and predictions