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 (E. Stechel)
Co-PI, Princeton University (E. Carter & S. Gopalakrishnan
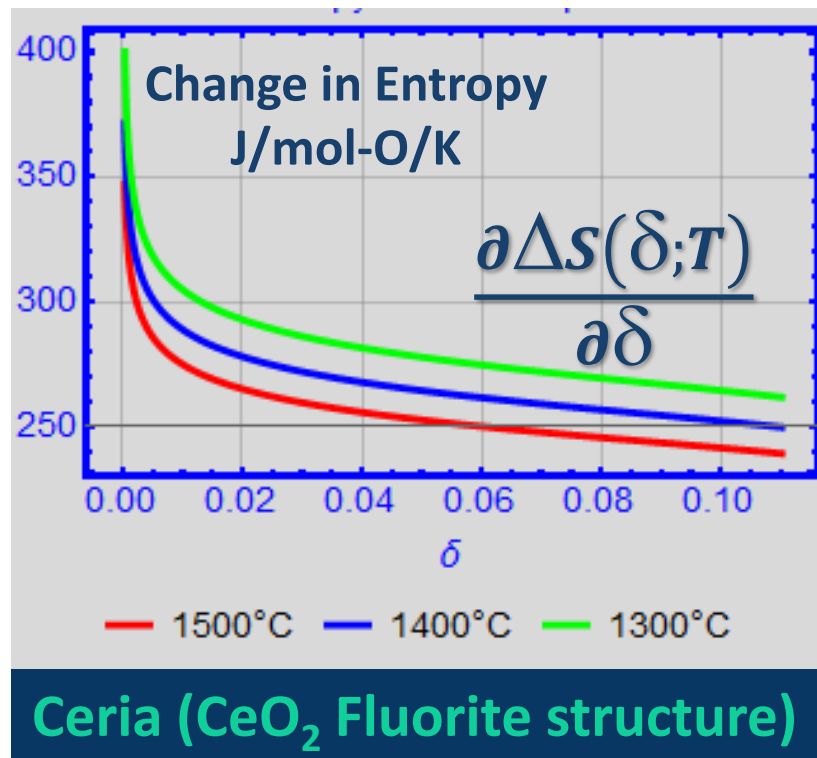
Project Vision

Accurate (enough) first principles calculations of the oxygen chemical potential for complex mixed ionic electronic (off-stoichiometric) up to doubly substituted perovskite solid solutions from which we can extract the thermodynamics and provide inverse design principles.

Project Impact

We aim to contribute to materials discovery for improved STCH materials. We aim to offer strategies to boost solar to hydrogen thermal efficiency, as well as to provide experimentalists with crucial input to synthesize, validate, and perform further testing on promising candidates. We aim to determine best possible, thermodynamically consistent targets depending on operating conditions to guide systems design.

Award #	EE0008090
Start Date	10/01/2018
Yr 1 End Date	03/31/2019
Project End Date	TBD
Total DOE Share	$629,748
Total Cost Share	$72,464
Yr 1 Funding*	$249,971

Change in Entropy J/mol-O/K

$$\frac{\partial \Delta s(\delta; T)}{\partial \delta}$$

— 1500°C — 1400°C — 1300°C

Ceria (CeO$_2$ Fluorite structure)

Approach- Summary

Project Motivation

Inverse design criteria to optimize the search for better materials for STCH do not exist – want to determine the optimum ∆H of reduction while achieving maximum vacancy solubility windows.

Key Impact

Metric	State of the Art	Proposed
T_R	Reduction temperature > 1500°C	Reduction temperature < 1450°C
$\Delta\delta$	Reduction Capacity $\Delta\delta \sim 0.03$ per cation	Reduction Capacity $\Delta\delta > 0.15$ per cation Or best possible at practical partial pressures
Error	N/A	20% accurate chemical potentials over relevant operating window

Barriers

- **Direct comparison** theory & experiment is difficult
- **Open shells and disorder**, difficult to calculate
- Calculating **CALPHAD** models without experimental input is very difficult.
- Determining the "equation of state" **off-stoichiometry** δ **as a function of the oxygen chemical potentia**l has never been attempted.

Partnerships

Dean Emily Carter, Princeton University
Dr. Sai Gopalakrishnan, Princeton Univ.
Node Experts at SNL and NREL
Expertise: developing new DFT+U capabilities, complex oxides, calculating chemical potentials in complex disordered materials, uncertainty quantification
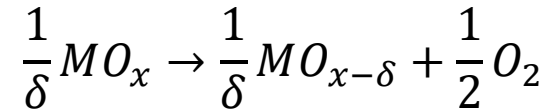**Specific capabilities:** functionals (SCAN+U), Computational CALPHAD (and cluster model as needed)
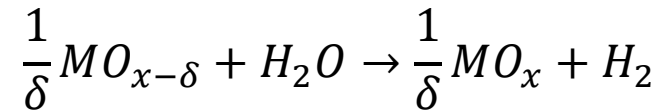
Approach: Innovation
Background
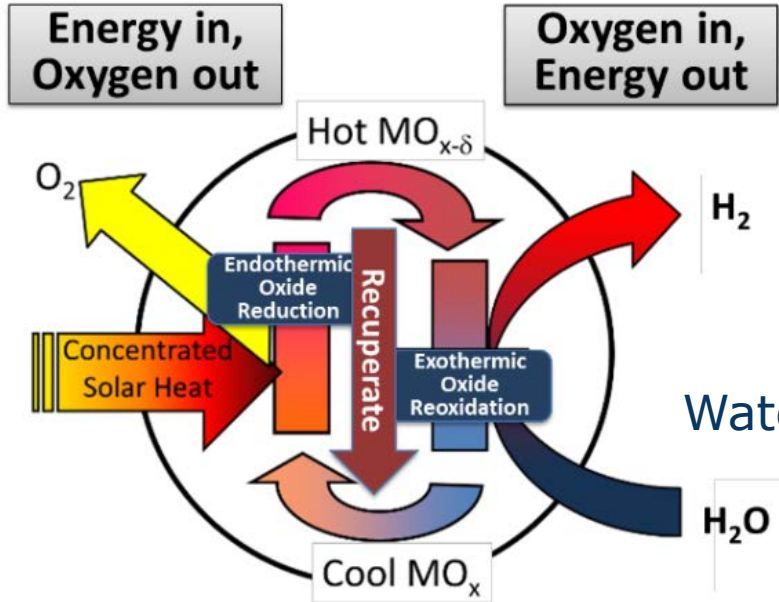
Thermal reduction (TR): High T, low pO_2

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

Endothermic

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

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

Exothermic

TR and WS reactions are thermodynamically feasible, if,

$$\Delta G_{TR} = \left(\frac{1}{\delta}\right)G^{MO_{x-\delta}} + \left(\frac{1}{2}\right)G^{O_2} - \left(\frac{1}{\delta}\right)G^{MO_x} \leq 0$$

$$\Delta G_{WS} = \left(\frac{1}{\delta}\right)G^{MO_{x-\delta}} + G^{H_2O} - \left(\frac{1}{\delta}\right)G^{MO_x} - G^{H_2} \leq 0$$

Both expressions have solid and gas phase energetics.

We decouple the solid from the gas-phase thermodynamics?

Approach: Innovation
Thermal reduction energetics

$$\left(\frac{1}{\delta}\right) MO_x \rightarrow \left(\frac{1}{\delta}\right) MO_{x-\delta} + \left(\frac{1}{2}\right) O_2$$

Target T: $\leq$ 1673.15 K, pO_2: $\geq$ 10 Pa

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

$$\Delta G_{TR} = \left(\frac{1}{\delta}\right) G^{MO_{x-\delta}} + \left(\frac{1}{2}\right) G^{O_2} - \left(\frac{1}{\delta}\right) G^{MO_x} \leq 0$$

Rearrangement of terms

$$\left(\frac{1}{2}\right) G^{O_2} \leq \left(\frac{1}{\delta}\right) G^{MO_x} - \left(\frac{1}{\delta}\right) G^{MO_{x-\delta}}$$

Chemical potential of oxygen in gas stream

$$\mu_O^{O_2,gas} = \left(\frac{1}{2}\right) G^{O_2} = \frac{1}{2}(H^{O_2} - TS^{O_2} + RT \ln pO_2)$$

H and *S* are *T* dependent

Chemical potential of oxygen in solid

$$\delta \times \mu_O^{MO_x - MO_{x-\delta},solid} = G^{MO_x} - G^{MO_{x-\delta}}$$

$$= H^{MO_x} - H^{MO_{x-\delta}} - T(S^{MO_x} - S^{MO_{x-\delta}})$$

$$\approx \Delta H_f^{MO_x} - \Delta H_f^{MO_{x-\delta}} - T(S^{MO_x} - S^{MO_{x-\delta}})$$

Main *T* dependence is from *S* terms

Reduction is spontaneous, if $\mu_O^{O_2,gas} \leq \mu_O^{MO_x - MO_{x-\delta},solid}$

Approach: Innovation
Calculate oxygen chemical potential (μ_O)

▸ μ_O of gas phase components (H_2O, H_2, and O_2) can be obtained from experimental data

  – Available at the National Institute of Standards and Technology (NIST)

▸ μ_O of the solid phase requires calculating the Gibbs energy as a function of temperature

  – Density functional theory (DFT+U) based approaches can yield good estimates for enthalpy, but estimating entropy is non-trivial

  – We aim to construct "simple" thermodynamic models to reasonably estimate Gibbs energies.

▸ Validate models with available data

  – Systems of interest: CeO_2, $(Ce,Zr)O_2$, $La_{1-x}Sr_xMnO_3$, other perovskites (up to doubly substituted) and possibly fluorites

Approach Innovation:
Comprehensive uncertainty management

▸ Overall goal is to predict thermodynamic efficiency given the thermodynamics of a material and a fixed operating cycle with specified uncertainty.

▸ SNL UQ (Uncertainty Quantification) HydroGEN 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

Approach: Innovation
Bayesian inference of thermodynamic fits

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

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

▸ Used transformed variables (δ,pO$_2$,T) $\rightarrow$ (z,u,β)

$$z = -ln(\delta);$$
$$u = \frac{1}{2}ln\left(\frac{P_{O_2,\mathrm{amb}}}{P_{O_2}}\right)$$
$$\beta = \left(\frac{T_{\mathrm{ref}}}{T}\right)$$
$$P_{O_2,\mathrm{amb}} = 0.20946\ Atm$$
$$T_{\mathrm{ref}} = 1073.15\ K$$

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

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

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 efficiency, and management of the uncertainties.

- "**Good fit**" with the HydroGEN Consortium R&D model

  — **Uncertainty Quantification (SNL)** 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 (NREL)

    • Facilitate validation of DFT+U predictions and further testing of candidates

  — **HT-XRD** and Complementary **Thermal Analysis (SNL)**

    • Facilitate experimental determination of the oxygen chemical potential, μ_O

  — Laser Heated **Stagnation Flow Reactor (SNL)**

    • 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
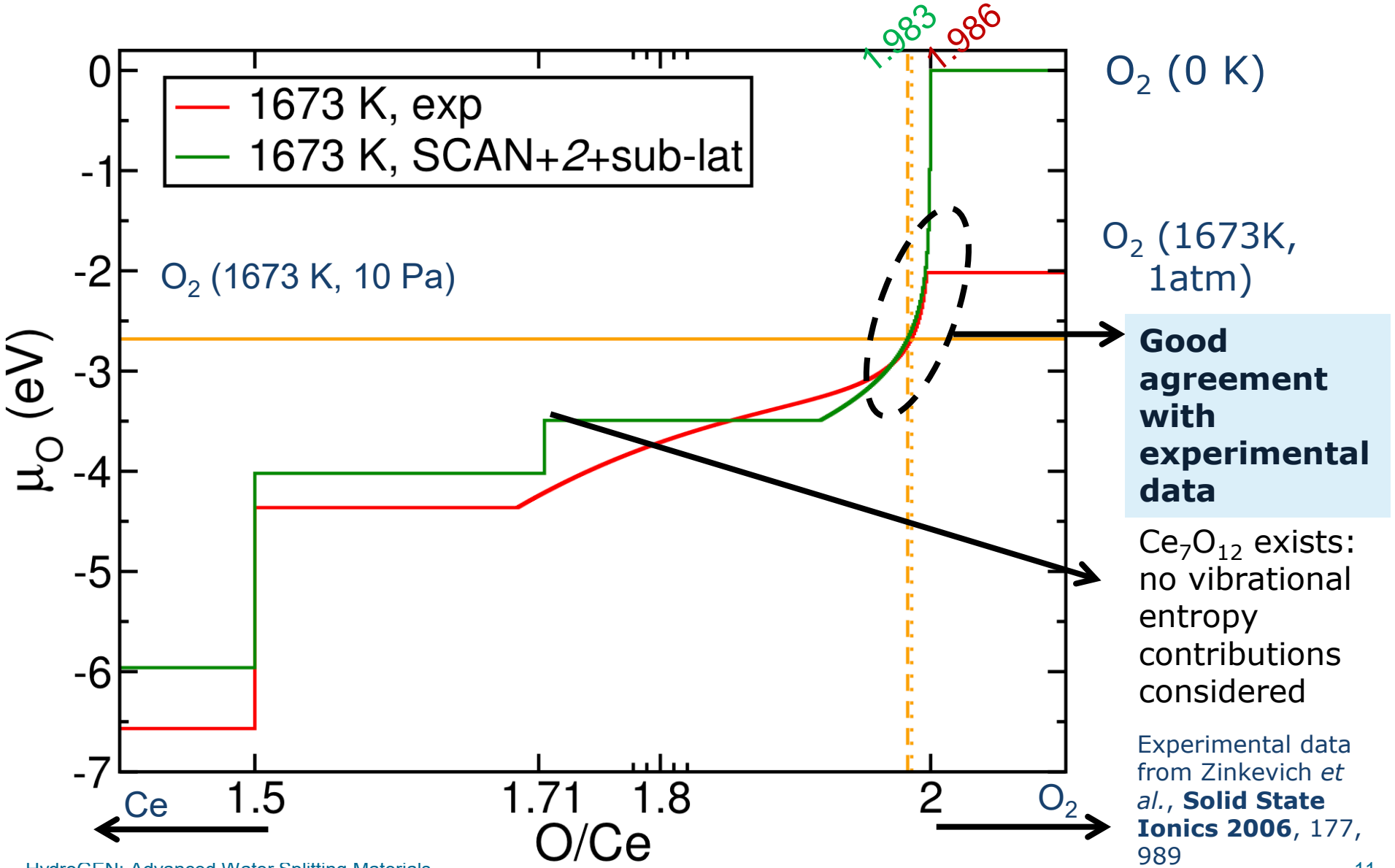
Accomplishments & Progress

- Go/No-Go due 3/31/2019
  - Predictive power demonstrated
  - two candidates with thermodynamic response maps completed and submitted to the consortium; Synthesized in collaboration with NREL Node
  - X-ray diffraction (SNL) measures structure, phase purity, and lattice constants
  - Compare to computational predictions with measured lattice constants
    - Goal 10% agreement
  - μ_O calculated and compared with experiment (two SNL Nodes)
    - **Goal: 20% agreement between derived thermodynamics and inferred from the measurements**
    - **Enthalpy and 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 from DFT+U.
  - The GNG provides confidence in using computation for screening
  - Making the connection to an operating cycle connects materials to technology.
  - The Uncertainty Quantification answers the question how good do measurements or computation have to be to differentiate between materials.

- On track to providing a screening tool that predicts STH efficiency and thermodynamic constraints on the operating cycle from computation.
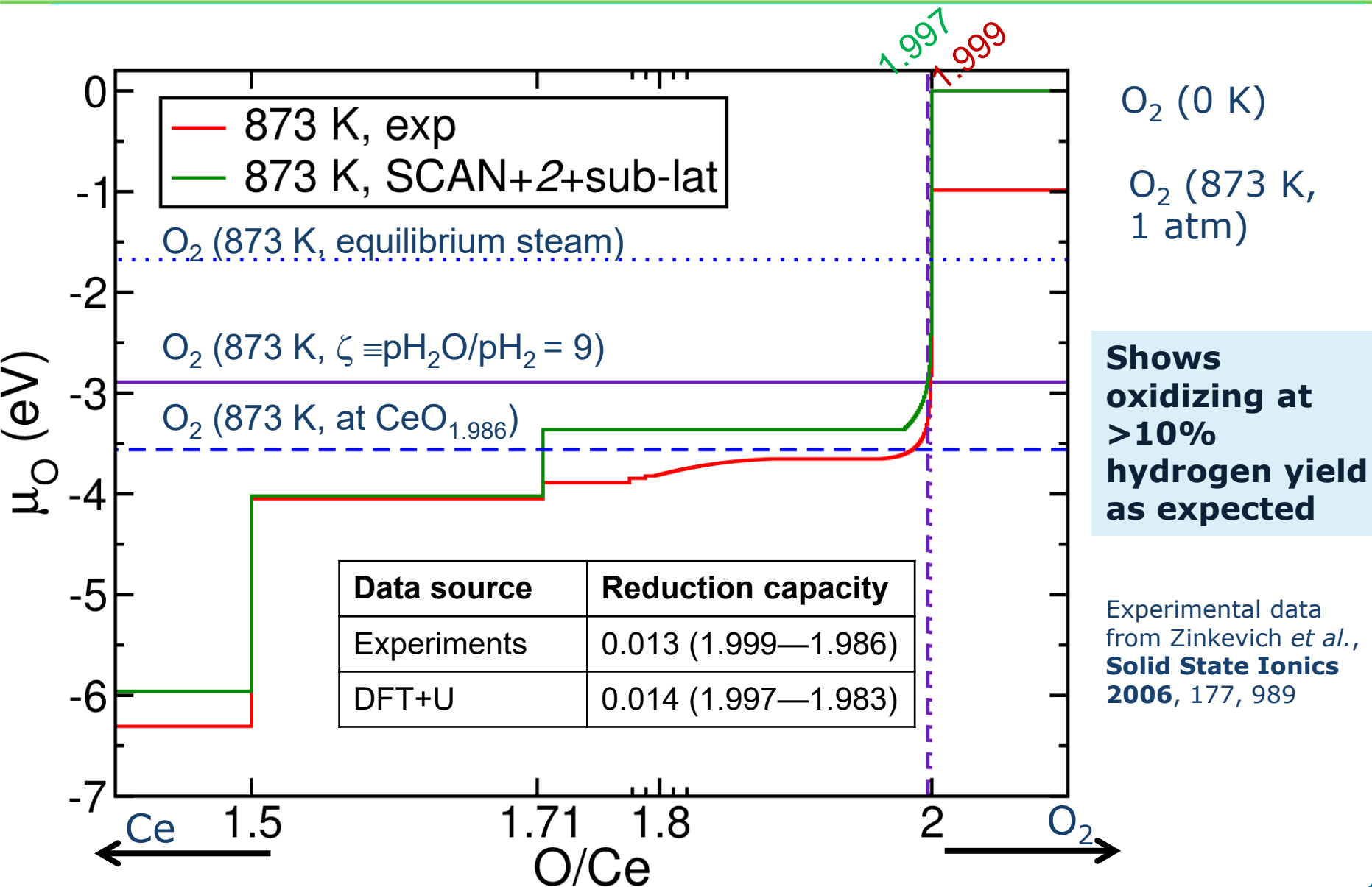
Good agreement with experimental data

Ce$_7$O$_{12}$ exists: no vibrational entropy contributions considered

Experimental data from Zinkevich *et al.*, **Solid State Ionics 2006**, 177, 989

O$_2$ (0 K)

O$_2$ (873 K, 1 atm)

Shows oxidizing at >10% hydrogen yield as expected

Experimental data from Zinkevich *et al.*, **Solid State Ionics 2006**, 177, 989

Data source	Reduction capacity
Experiments	0.013 (1.999—1.986)
DFT+U	0.014 (1.997—1.983)

Accomplishments & Progress
Zr-doped CeO$_2$: DFT+U vs. Experiment

Oxygen off-stoichiometry

Composition	Reducing conditions (1673 K, 10 Pa)		Co-current Oxidizing conditions (873 K, $pH_2O/pH_2 = 9$)	
	Exp.	DFT+U	Exp.	DFT+U
CeO$_2$	0.014	0.017	0.001	0.003
Ce$_{0.9}$Zr$_{0.1}$O$_2$	0.035	0.029	0.015	0.009
Ce$_{0.8}$Zr$_{0.2}$O$_2$	0.05	0.046	0.037	0.025

Fair agreement between experiments and theoretical predictions

Experimental oxygen off-stoichiometric data available:
Hao *et al.*, **Chem. Mater. 2014**, 26, 6073

No thermodynamic assessments available for Zr-Ce-O ternary system
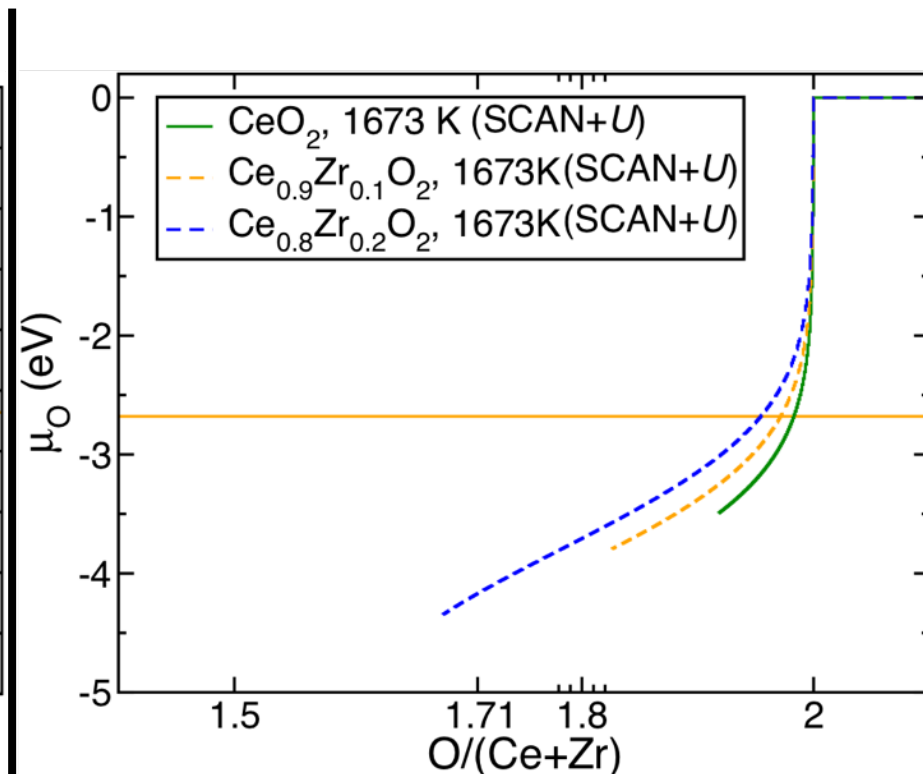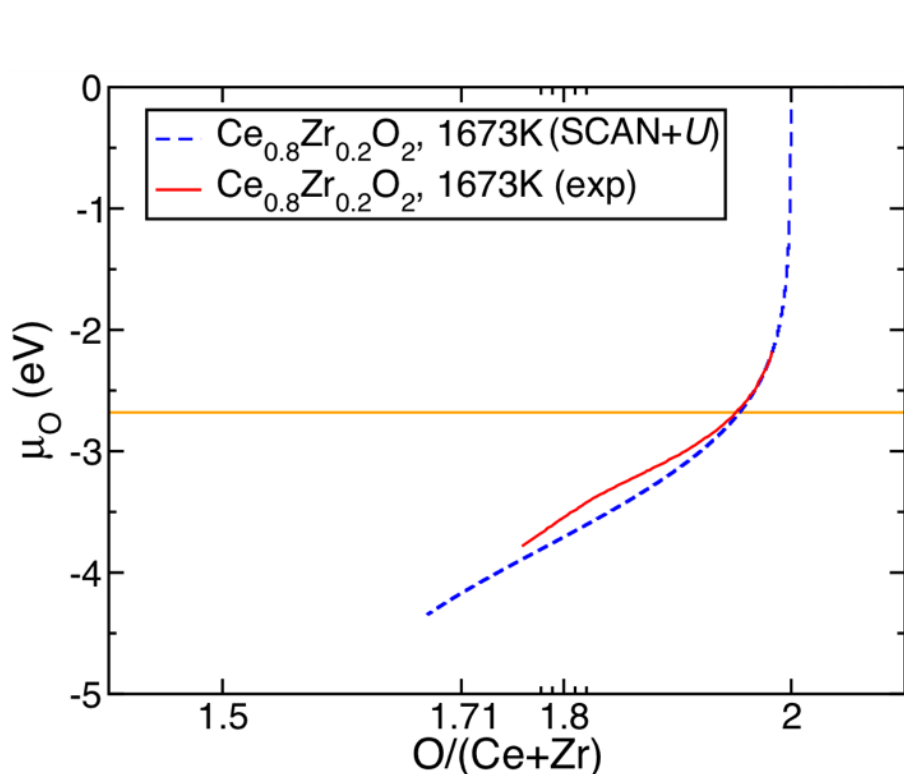
Fair agreement in off-stoichiometric data away from target conditions

**Increased reducibility of CeO_2 with Zr-doping, consistent with experiments**

Experimental data: Hao *et al.*, **Chem. Mater. 2014**, 26, 6073

Collaboration Effectiveness: With Node Expert Bert Debusschere, SNL

- Fit δ as a function of temperature and partial pressure of O_2 for Ceria

- All marginal distributions are unimodal and well defined, indicating the parameters are well-informed by the data (taken from Zinkevich)

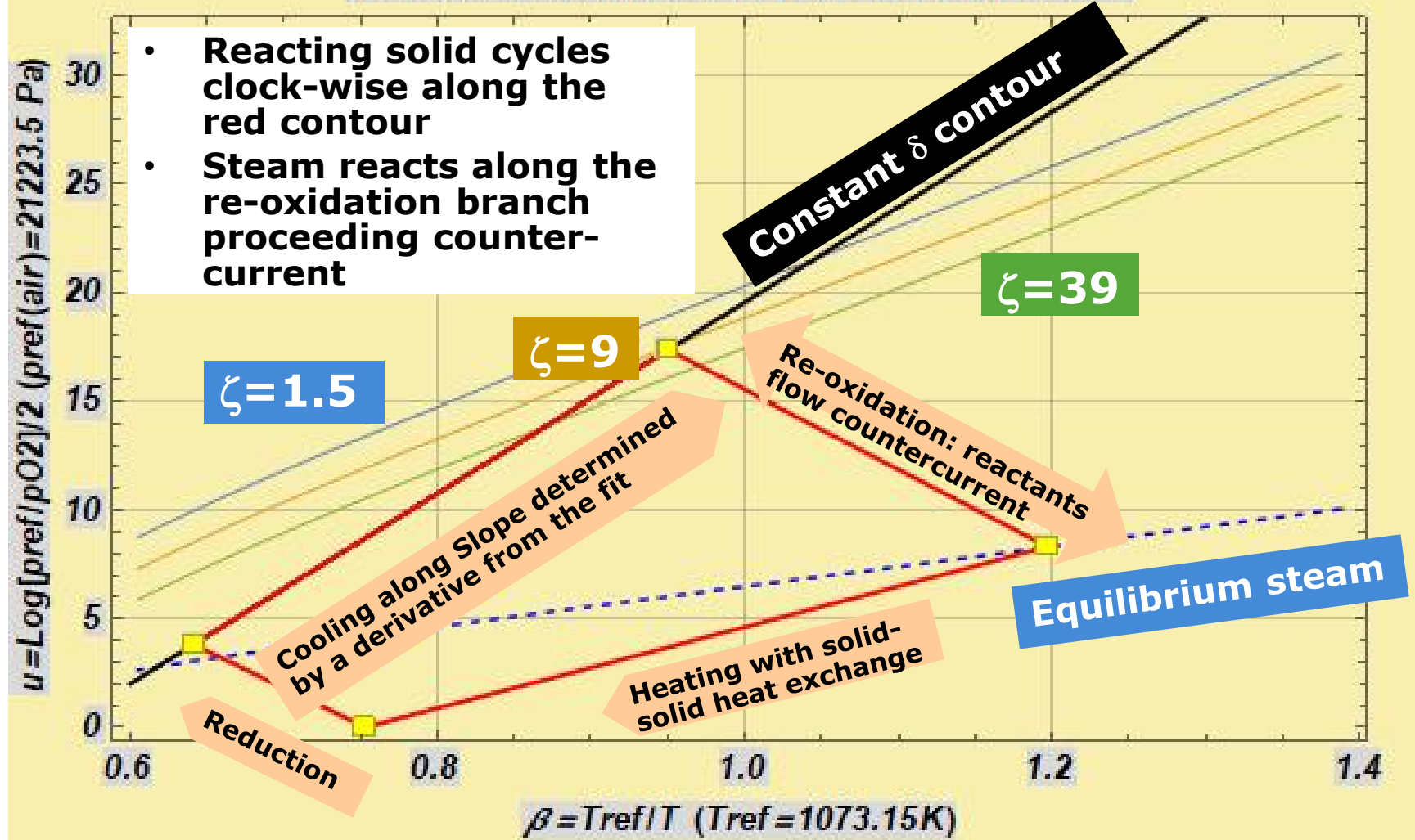- Cross correlations show strong dependencies between some of the parameters

Sigma is the standard deviation of the Gaussian noise model
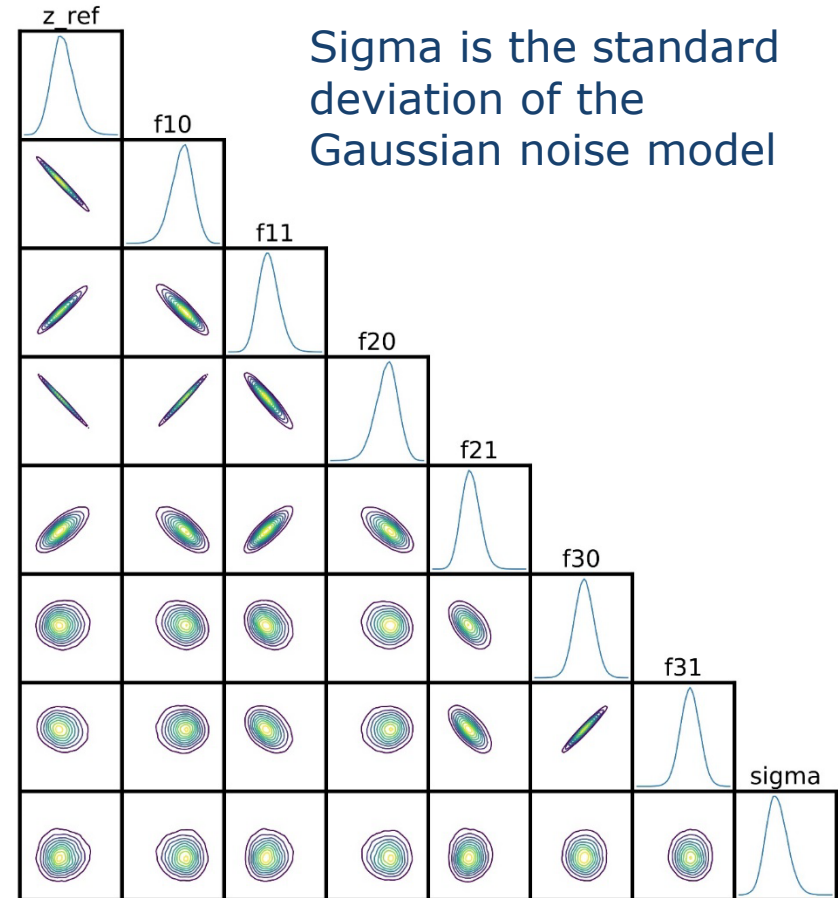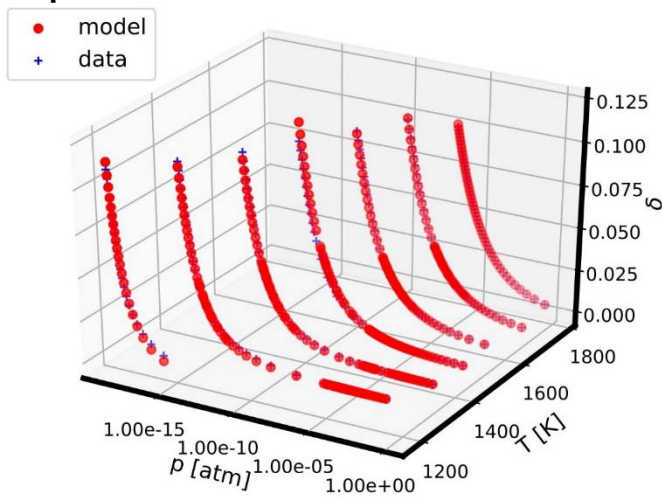
All the thermodynamics can be derived from this function and known gas phase thermodynamics

Reduction at 1400 C, 10 Pa, ∂H=391.5 kJ/mol-O

- **Reacting solid cycles clock-wise along the red contour**
- **Steam reacts along the re-oxidation branch proceeding counter-current**

Constant δ contour

ζ=39

ζ=9

ζ=1.5

Cooling along Slope determined by a derivative from the fit

Re-oxidation: reactants flow countercurrent

Equilibrium steam

Heating with solid-solid heat exchange

Reduction

u=Log[pref/pO2]2 (pref(air)=21223.5 Pa)

β=Tref/T (Tref =1073.15K)

Oxidizing conditions constrained by ζ and effectiveness of heat exchange

Milestone Status

Milestone Schedule							
			Task Completion Date (Project Quarter)				
Milestone #	Project Milestones	Type	Original Planned	Revised Planned	Actual	Percent Complete	Progress Notes
1.1	Computational framework adapted for perovskites and fluorites) and reduced model defined.	Milestone	12/31/2017		12/31/2017	100%	Completed
2.1	Computational accuracy on $(Ce,Zr)O_2$ and $(La,Sr)MnO_3$ validated - at least 10% accuracy achieved and trends with substitution and off-stoichiometry strictly correct.	Milestone	3/31/2018	5/31/2018		80%	On-going
3.2	Trends on desirable chemical potential map determined, in other words an inverse design target defined.	Milestone	6/30/2018	7/31/2018		20%	On-going.
4.1	Significant Progress milestone: Stability map on tertiary perovskites produced - at least 2 candidate classes and stability limits identified.	Milestone	9/30/2018			0%	Not started.
5.1	Preliminary results on a chemical potential map completed and results verified.	Milestone	12/31/2018			20%	Not started.
G/NG	**Go/No-Go: Predictive power demonstrated**	**Go/No-Go**	**3/31/2019**			**20%**	**Not started.**

Collaboration: Effectiveness
It takes a "village"

Computation

Experiment

Operating Cycle

HT-XRD + Thermal Analysis
SNL:Coker

UQ (SNL) Debusschere **See Slide 15**

$$\frac{dH}{d\delta} =$$

$$\beta\frac{d\mu_O}{d\beta} = T\frac{dS}{d\delta}$$

Synthesis & Defect Eng'ing.
NREL: Ginley

Calculate μ_O as function of δ and T

DFT+U

μ_O

Stagna-tion Flow SNL: McDaniel

Fit to data δ as function of T and pO_2; i.e., μ_O
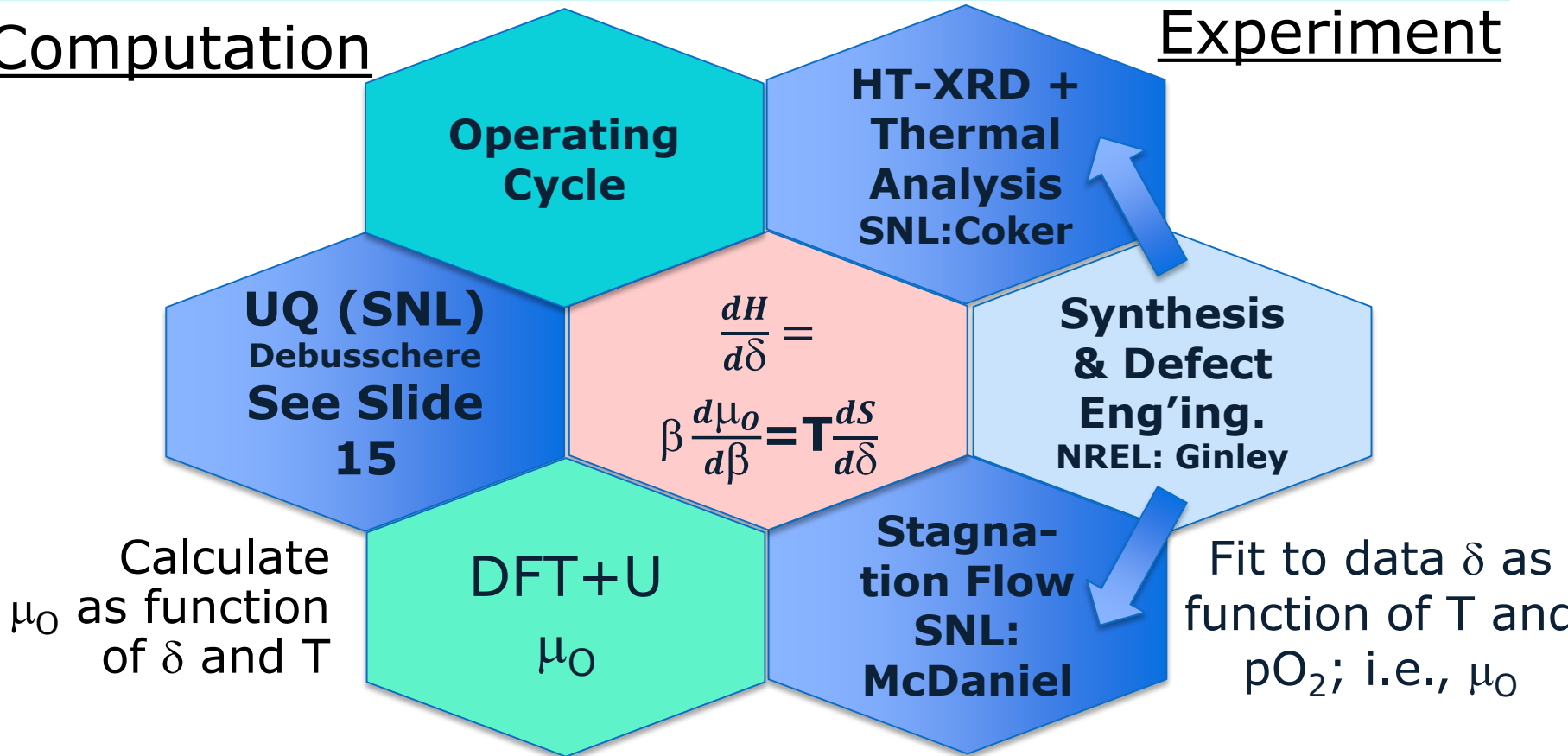
All the important thermodynamics is encompassed in the oxygen chem. pot.
Extensive interactions with the UQ node as reported; initial interactions with the experimental nodes (too early for results)
Will incorporate all DFT+U results and fits for δ into the data hub
Will participate in the DFT+U working group when organized by 2B project

Proposed Future Work
Remaining Challenges and Barriers

‣ Benchmark $SrMnO_3$, ternary of relevance in $(La,Sr)MnO_3$
  – Generalize and validate the sub-lattice formalism for $(La,Sr)MnO_3$
‣ Identification of right reference states crucial for using the sub-lattice model
  – General rules, if possible, need to be formulated
‣ Validate sub-lattice formalism for quaternary $(La,Sr)MnO_3$
‣ After validation, screen for better candidates
  – Estimate capacities using DFT+U calculations + sub-lattice formalism
‣ Identify key performance limiting factors
‣ Formulate design rules that would clearly differentiate good candidates and enable swift screening
‣ Derive screening model relating the thermodynamics (oxygen chemical potential) to efficiency
‣ Uncertainty Quantification
  – Characterization of model error, explore for best model – tradeoff between accuracy and simplicity
  – Propagation of model error into thermodynamic properties
  – Propagation of uncertainties trough cycle efficiency model
  – Determination of measurement / DFT+U accuracy needed to obtain desired confidence in process efficiency

Project Summary

- Construction of chemical potential maps is useful to decouple the energetic contributions of the gas and solid phases in a thermochemical cycle

- Prediction of chemical potentials in solid phases is not trivial
  - Construction of sub-lattice models, with energy values from DFT+U, seems to be a promising way forward
  - Good agreement with experimental data for binary (CeO_2) and ternary {(Ce,Zr)O_2 and $LaMnO_3$} systems
  - Note: Ce-Zr-O ternary and almost any candidate not already explored do not have a full thermodynamic assessments (CALPHAD models) available

- We have developed a way to extract the chemical potential from experimental data numerically, which can be used to validate computation.

- We are developing a methodology for uncertainty quantification to determine how accurate is accurate enough (either experiment or computation) and provide uncertainty bands to differentiate between materials.

- Next: Identify inverse design criteria and candidate materials.
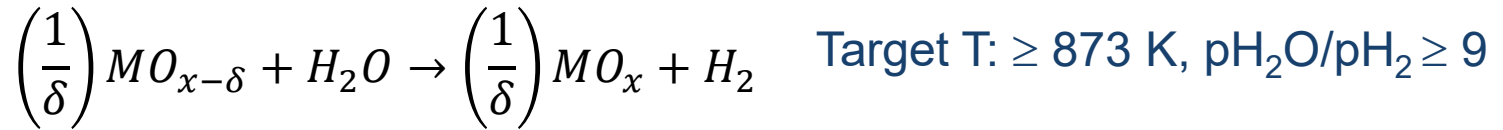
Thank you for your attention

Technical Back-Up Slides

Approach: Innovation
Water splitting energetics

$$\left(\frac{1}{\delta}\right) MO_{x-\delta} + H_2O \rightarrow \left(\frac{1}{\delta}\right) MO_x + H_2$$

Target T: $\geq$ 873 K, $pH_2O/pH_2 \geq 9$

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

$$\Delta G_{WS} = \left(\frac{1}{\delta}\right) G^{MO_x} + G^{H_2} - \left(\frac{1}{\delta}\right) G^{MO_{x-\delta}} - G^{H_2O} \leq 0$$

Rearrangement of terms

$$\left(\frac{1}{\delta}\right) G^{MO_x} - \left(\frac{1}{\delta}\right) G^{MO_{x-\delta}} \leq G^{H_2O} - G^{H_2}$$

Chemical potential of oxygen in solid

$$\delta \times \mu_O^{MO_x - MO_{x-\delta}, solid} = G^{MO_x} - G^{MO_{x-\delta}}$$

$$= H^{MO_x} - H^{MO_{x-\delta}} - T(S^{MO_x} - S^{MO_{x-\delta}})$$

$$\approx \Delta H_f^{MO_x} - \Delta H_f^{MO_{x-\delta}} - T(S^{MO_x} - S^{MO_{x-\delta}})$$

Main T dependence is from S terms

Chemical potential of oxygen in gas stream

$$\mu_O^{H_2O - H_2, gas} = G^{H_2O} - G^{H_2}$$

$$= H^{H_2O} - H^{H_2} - T(S^{H_2O} - S^{H_2}) + RT \ln \frac{p_{H_2O}}{p_{H_2}}$$

$$\approx \Delta H_f^{H_2O} - T(S^{H_2O} - S^{H_2}) + RT \ln \frac{p_{H_2O}}{p_{H_2}}$$

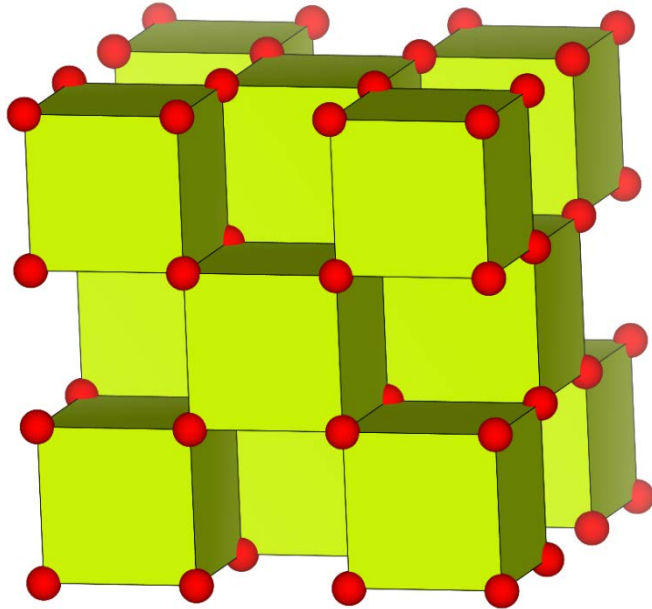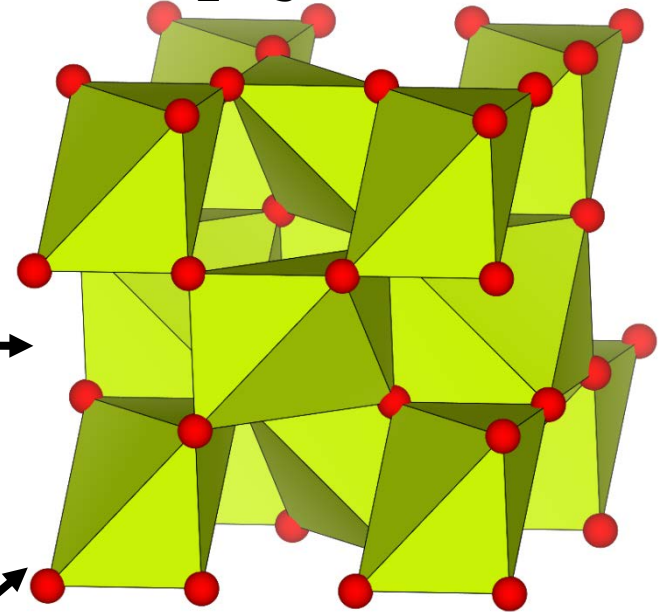Water splitting is spontaneous, if $\mu_O^{MO_x - MO_{x-\delta}, solid} \leq \mu_O^{H_2O - H_2, gas}$

CeO$_2$ (Fluorite)

Ce$_2$O$_3$ (Fluorite)

Oxygen-deficiency
O-Va sub-lattice
Va= Vacancy

Ce^{4+} → Ce^{3+}
Ce sub-lattice

Gibbs energy of CeO$_{2-\delta}$ in fluorite (F) phase

Hypothetical structures, energies calculated via setting references

$$G^F_{CeO_{2-\delta}} = y_{Ce^{4+}}y_O G^0_{Ce^{4+}:O} + y_{Ce^{3+}}y_O G^0_{Ce^{3+}:O} + y_{Ce^{4+}}y_{Va} G^0_{Ce^{4+}:Va} + y_{Ce^{3+}}y_{Va} G^0_{Ce^{3+}:Va} +$$
$$RT\left(y_{Ce^{4+}} \ln y_{Ce^{4+}} + y_{Ce^{3+}} \ln y_{Ce^{3+}}\right) + 2RT\left(y_O \ln y_O + y_{Va} \ln y_{Va}\right) + G^F_{excess}$$

Configuration entropy set to ideal solution behavior

y= **Site fraction**
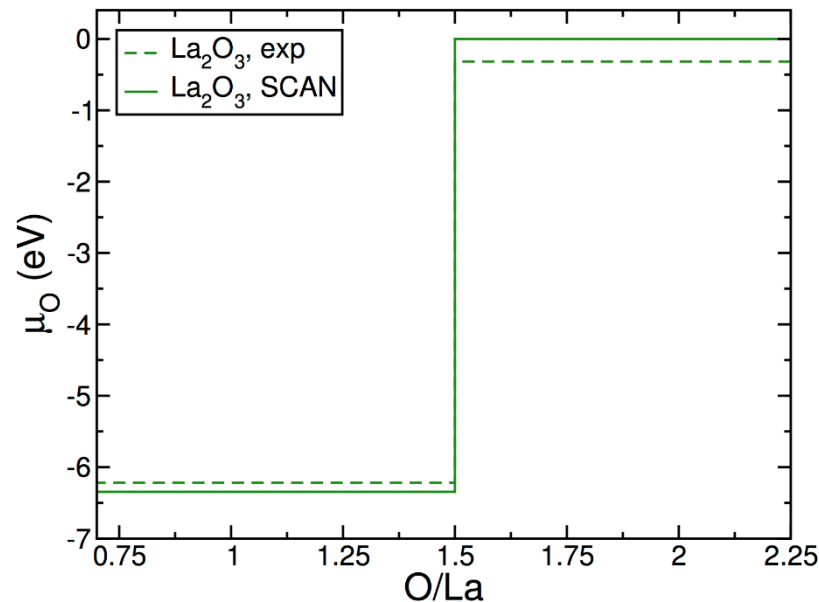
Correction term

Energies evaluated via DFT+U
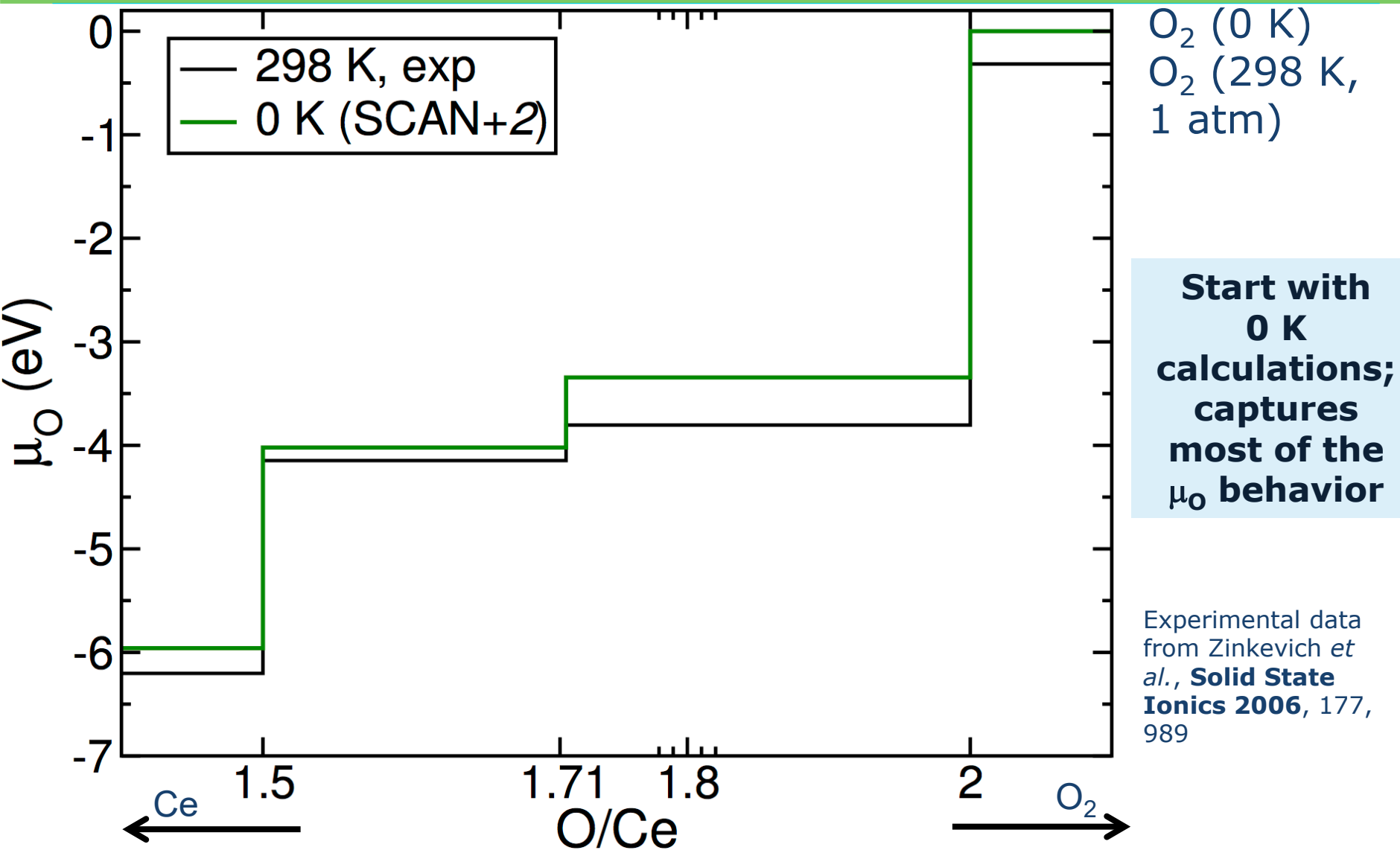
O$_2$ (0 K)
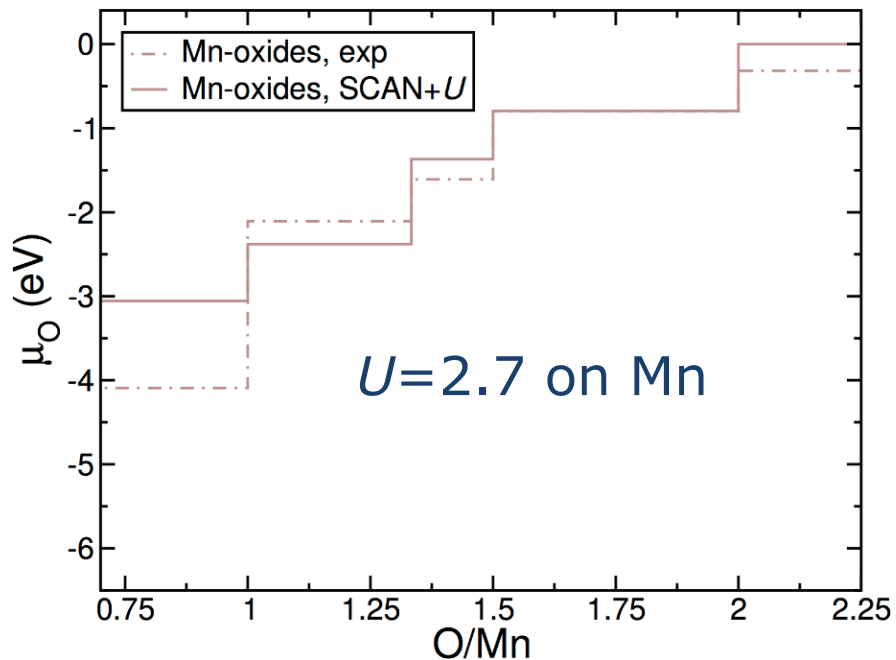O$_2$ (298 K, 1 atm)

Start with 0 K calculations; captures most of the μ_O behavior

Experimental data from Zinkevich *et al.*, **Solid State Ionics 2006**, 177, 989

U=2.7 on Mn

Need to benchmark ternary LaMnO$_3$ before proceeding to quaternary (La,Sr)MnO$_3$

Experimental data from Grundy *et al.*, **J. Phase Equilib. Diffus. 2005**, 26, 131

$U = 2.7$ on Mn

O$_2$ (0 K)

O$_2$ (1673 K, 10 Pa)

Prerequisite to computing quaternary and above

Experimental data from Grundy *et al.*, **J. Phase Equilib. Diffus. 2005**, 26, 131

Source	Off-stoichiometry
Exp.	0.002 (LaMnO$_{2.998}$)
DFT+U	0.008 (LaMnO$_{2.992}$)

Legend:
- La$_2$O$_3$, 1673K (exp)
- Mn-oxides, 1673K (exp)
- LaMnO$_{3-z}$, 1673K (exp)
- LaMnO$_{3-z}$, 1673K (SCAN+U)

Axes: μ_O (eV) vs. O/(La+Mn)

La/Mn   O$_2$