A First-Principles-Based Sub-Lattice Formalism for Predicting Off-Stoichiometry in Materials for Solar Thermochemical Applications: The Example of Ceria

Gopalakrishnan Sai Gautam, Ellen B. Stechel, and Emily A. Carter*

Theoretical models that reliably can predict off-stoichiometry in materials via accurate descriptions of underlying thermodynamics are crucial for energy applications. For example, transition-metal and rare-earth oxides that can tolerate a large number of oxygen vacancies, such as CeO$_2$ and doped CeO$_2$, can split water and carbon dioxide via a two-step, oxide-based solar thermochemical (STC) cycle. The search for new STC materials with a performance superior to that of state-of-the-art CeO$_2$ can benefit from predictions accurately describing the thermodynamics of oxygen vacancies. The sub-lattice formalism, a common tool used to fit experimental data and build temperature-composition phase diagrams, can be useful in this context. Here, sub-lattice models are derived solely from zero-temperature quantum mechanics calculations to estimate fairly accurate temperature- and oxygen-partial-pressure-dependent off-stoichiometries in CeO$_2$ and Zr-doped CeO$_2$. Physical motivations for deriving some of the “excess” sub-lattice model parameters directly from quantum mechanical calculations, instead of fitting to minimize deviations from experimental and/or theoretical data, are identified. Important limitations and approximations of the approach used are specified and extensions to multi-cation oxides are also suggested to help identify novel candidates for water and carbon dioxide splitting and related applications.

1. Introduction

Many energy-relevant materials exhibit off-stoichiometric compositions.$^{[1-8]}$ For example, most electrodes in intercalation batteries$^{[9-13]}$ and semiconductors in non-silicon photovoltaics$^{[14-17]}$ exhibit vacancies and/or other point defects in at least one set of sites (or a sub-lattice) within their structure. Other materials are off-stoichiometric in their equilibrium bulk form, such as FeO (wüstite), which exhibits $\approx$5–10% Fe-vacancies at room temperature.$^{[18,19]}$

Off-stoichiometric oxides can produce renewable fuels and fuel precursors (H$_2$, CO, etc.) via a two-step solar thermochemical (STC) process that splits water (STCH) or CO$_2$ (STCC), as illustrated in Figure 1.$^{[20-25]}$ The first step in a STC cycle is thermal reduction (TR), in which a near-stoichiometric oxide (MO$_x$ in Figure 1) is heated to high temperatures (e.g., $T > 1573$ K) in an environment of low partial pressure of oxygen ($p_{O_2}$) leading to spontaneous oxygen loss and the formation of an oxygen-deficient oxide (MO$_x$ − $\delta$, $\delta > 0$). Prior to the second step, MO$_x$ − $\delta$ is cooled to a lower temperature (e.g., $\approx 873–1373$ K), where the oxide is no longer driven thermodynamically to form oxygen vacancies and the stoichiometric MO$_x$ is stable (or sufficiently metastable). Then, the reduced oxide spontaneously splits steam (or CO$_2$) to generate H$_2$ (or CO) and is re-oxidized to MO$_x$. This step is called the water-splitting (WS) step, which generates hydrogen when steam is introduced (and similarly generates CO when CO$_2$ is present). The gas phase during the WS step is introduced preferably under counter-flow conditions. This is because the gas phase in a stagnant reactor is changed only when the re-oxidation is complete, while, in counter-flow, pure steam is introduced against the oxidized MO$_x$ (or small $\delta$, at low enough temperatures) and is allowed to be reduced progressively as it flows against a progressively reduced oxide. Thus, counter-current conditions are useful in enhancing the thermodynamics of re-oxidation$^{[26,27]}$ by exposing steam at its highest oxidizing potential to MO$_x$ − $\delta$ that typically becomes harder to oxidize as $\delta \to 0$. The source of heat in the TR step often is concentrated sunlight$^{[28]}$, accompanied by heat recuperation while cooling the reduced oxide to the lower temperature. While the current state-of-the-art (SOA) for STCH performance is pure CeO$_2$.$^{[28-32]}$ screening for novel oxides that show superior efficiency is an active area of research$^{[33–42]}$ where theory plays an important role.
One daunting challenge in theoretically screening STCH candidates is to predict accurately the oxygen off-stoichiometries as a function of $T$ and $p_{O_2}$ (Section 2). Specifically, models must capture adequately all entropic contributions\(^\text{[42,43]}\) due to off-stoichiometry, such as vacancies exhibiting configurational entropy within the oxygen and cation sub-lattices in an oxygen-deficient MO\(_{x-\delta}\). Changes in composition also alter vibrational, electronic, and magnetic entropy contributions. Accounting for entropy contributions typically requires extensive calculations, with subsequent post-processing and/or parameterization. For example, configurational entropy in solids usually is evaluated via a “cluster expansion”\(^\text{[44–46]}\) parameterized via density-functional-theory (DFT)-based calculations,\(^\text{[47–52]}\) requiring a large set of input configurations ($\approx$100 for several systems,\(^\text{[53,54]}\) although the exact number of configurations required is highly system-dependent\(^\text{[55–57]}\)) enumerated over large supercells, as well as careful parameterization to ensure predictability. Moreover, generalizing a binary cluster expansion to a ternary or a pseudo-ternary system can incur a dramatically higher computational cost.\(^\text{[58,59]}\) Estimating vibrational entropy, done by calculating the phonon spectrum,\(^\text{[60]}\) also carries significant expense since the number of unique displacements calculated using DFT increases dramatically with larger supercells. Consequently, several STCH theoretical screening studies typically have employed the oxygen vacancy formation energy as a proxy for the enthalpy of reduction ($\Delta H_{\text{red}}$), while not accounting for entropic contributions ($\Delta S_{\text{red}}$) to determine the off-stoichiometry dependence on $T$ and $p_{O_2}$.\(^\text{[38,41]}\) There have been some theoretical studies that have examined specific entropic contributions and their impact for a STCH process.\(^\text{[52,43,51]}\) In any case, given the importance of entropy in high-temperature phenomena such as STCH,\(^\text{[43]}\) the development of first-principles-based thermodynamic models enabling a swift estimation of Gibbs energies for oxides as a function of temperature and off-stoichiometry should advance the fidelity of such screenings. This article presents such a formalism.

In this work, which is illustrated as a workflow in Figure 2, we parameterize a thermodynamic sub-lattice model (Section 3) using a total of 14 distinct DFT-based calculations (computational details in the Experimental Section) to predict oxygen off-stoichiometry in pure CeO\(_2\) under TR and WS conditions, and subsequently validate against an experimentally derived model (Section 4.1). Sub-lattice models or the compound energy formalism (CEF),\(^\text{[61]}\) in the spirit of CALPHAD-style assessments, are used widely to refine temperature-composition phase diagrams, where model parameters are fit to minimize deviations from experimental measurements (see left panel of Figure 2). Here, we utilize the sub-lattice model of Zinkevich et al.,\(^\text{[67]}\) developed from Ce-O experimental data (Section 3.1). We study pure CeO\(_2\) in order to benchmark our predictions for a system with robust experimental data\(^\text{[68]}\) and that is currently the SOA for STCH. We also extend the binary Ce-O model, using another \(\approx 40\) distinct configurations, to describe the ternary Ce-Zr-O system (Sections 3.2 and 4.2) for which no sub-lattice model yet exists. Our first-principles-derived model offers a reliable estimation of oxygen off-stoichiometry under TR and WS conditions for both undoped and Zr-doped CeO\(_2\).

Further, combining DFT with a sub-lattice model enables the identification of underlying physics of model parameters (e.g., “excess” interactions), which otherwise are fit to reproduce experiments. Although DFT previously has supplemented experimental data in constructing sub-lattice models,\(^\text{[65–69,71–77]}\) here we avoid experimental data entirely and parameterize a sub-lattice model solely using DFT to produce an entirely independent theoretical model. Prior examples of sub-lattice models obtained solely from DFT-based data do exist.\(^\text{[72–78]}\) However, such models have been used primarily for intermetallics and not ionic materials (such as Ce-O and Zr-Ce-O) that usually involve several non-charge-neutral “end-members” (Section 3.1) whose energies are not trivial to obtain theoretically. Note that there is an ongoing effort by the developers of FactSage software\(^\text{[79]}\) in building sub-lattice models by combining the 0 K DFT data from the Materials Project database\(^\text{[80]}\) with high-throughput computing\(^\text{[81]}\) and/or machine learning to obtain vibrational entropy as a function of temperature (middle panel in Figure 2). Here, we directly obtain all of our model parameters from 0 K DFT-based calculations (i.e., we approximate Gibbs energies as the total energies at 0 K, or $G \approx E$, see right panel of Figure 2) instead of fitting to an existing data set. We also identify limitations and approximations in our approach, along with possible future improvements. Ultimately, quantum-based sub-lattice models may enable a rapid identification of novel off-stoichiometric candidates for STC and related applications.

2. Thermodynamics of Solar Thermochemical Hydrogen Generation

Because STCH involves the exchange of O-atoms between a solid (MO\(_x\)/MO\(_{x-\delta}\)) and a gas (O\(_2\)/H\(_2\)/H\(_2\)O), estimating the oxygen chemical potential ($\mu_O$) separately in each phase efficiently decouples the thermodynamics of the solid from the gas. While $\mu_O$ of the solid ($\mu_O^s$) and gas ($\mu_O^g$) will be identical when they are in equilibrium ($\mu_O^s = \mu_O^g$), the reduction (re-oxidation) of the solid will be spontaneous when $\mu_O^s$ is higher (lower) than $\mu_O^g$. Formally, under TR/WS conditions, $\mu_O^s$ (TR/WS) is given by Equations (1) and (2):

$$\mu_O^s (\text{TR}) = \mu_O^g + \frac{1}{2} RT \ln \frac{p_{O_2}}{p^v} \quad (1)$$
\[
\mu_0^e (\text{WS}) = G_{\text{H}_2\text{O}} (g) - G_{\text{H}_2} (g) + RT \ln \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} 
\]

where \( \mu_0^e = \frac{1}{2} G_{\text{O}_2} (g) = \frac{1}{2} H_{\text{O}_2} (g) - \frac{1}{2} T S_{\text{O}_2} (g) \) is the oxygen chemical potential of pure \( \text{O}_2 \) gas at a reference pressure, with \( G, H, S \) corresponding to Gibbs energy, enthalpy, and entropy, respectively, \( p \) is the reference pressure, here set to 1 atm. Experimental \( \mu_0^e, G_{\text{H}_2\text{O}}(g), \) and \( G_{\text{H}_2}(g) \) are obtained from the National Institute of Standards and Technology database.\(^{[82]} \) For the solid, \( \mu_0^s \) is the derivative of the Gibbs energy of the oxide (\( G_{\text{MO}_x} \)) with respect to the oxygen concentration \( x \) (Equation (3)), where our DFT-based model estimates \( G_{\text{MO}_x} \) for STC-relevant \( x \) (Section 3).

\[
\mu_0^s = \frac{d G_{\text{MO}_x}}{dx} \quad (3)
\]

Note that increasing the efficiency of a STC cycle requires either exceptionally good heat recovery or small temperature differences between the TR and WS steps,\(^{[27]} \) while practical considerations suggest “reasonable” upper and lower bound temperatures for TR and WS to be \( \approx 1673 \) and \( \approx 873 \) K, respectively. Such considerations also yield a lower bound on \( p_{\text{O}_2} \) during TR to be \( \approx 10 \text{ Pa} \) (\( \approx 10^{-4} \text{ atm} \)) and a \( \text{H}_2: \text{H}_2\text{O} \) product ratio of at least 1:9 in WS (i.e., 10% \( \text{H}_2 \) yield). Thus, the TR and WS conditions of primary interest are \( T = 1673 \text{ K} \) and \( p_{\text{O}_2} = 10 \text{ Pa} \), and \( T = 873 \text{ K} \) and \( p_{\text{H}_2\text{O}} = 9 \text{ Pa} \), respectively. Also, capacity of a given oxide material can be quantified in terms of mmol (or standard units of volume, \( 22.4 \text{ cm}^3 \text{ mmol}^{-1} \)) of gas evolved (either \( \text{O}_2 \) or \( \text{H}_2 \)) per unit of oxide. For example, the TR resulting in an oxygen concentration, \( x = 1.999 \) from stoichiometric-CeO\(_2\) (or an oxygen vacancy concentration, \( \delta = 0.001 \) per CeO\(_2\) formula unit), corresponds to an oxygen evolution capacity of \( \approx 1.5 \text{ mmol (mol atom)}^{-1} \) of oxide (or \( \approx 34 \text{ cm}^3 \text{ (mol atom)}^{-1} \text{ oxide} \)).

Oxides with smaller \( \Delta H_{\text{red}} \), that is, smaller costs to undergo reduction and form oxygen vacancies, tend to exhibit higher oxygen deficiency during TR but potentially lower \( \text{H}_2 \) evolution (relative to the TR oxygen deficiency, due to the lower driving force for oxidation) during WS.\(^{[21,83]} \) On the other hand, lower \( \Delta S_{\text{red}} \) indicates lower driving force to form oxygen vacancies, thereby leading to lower oxygen deficiencies but higher \( \text{H}_2 \) production (relative to TR oxygen deficiency) during WS. Thus, STC efficiency is determined by the ability of \( \text{MO}_x \) to exhibit an optimal \( \Delta H_{\text{red}} \) and \( \Delta S_{\text{red}} \) and to tolerate a wide swing in oxygen off-stoichiometry over TR and WS temperatures. Given \( G_{\text{MO}_x} \) as a function of \( x \) (Equation (3)), \( \Delta H_{\text{red}} \) and \( \Delta S_{\text{red}} \) at a given \( T \) are evaluated (and normalized per O-atom) using Equations (4a) and (4b), respectively, where the angular brackets indicate averaged quantities from \( x \) to \( x - \delta \).

\[
\Delta H_{\text{red}} = \left( -\frac{d G_{\text{MO}_x}}{dx} \right) + \frac{1}{2} H_{\text{O}_2} (g) \quad (4a)
\]

\[
\Delta S_{\text{red}} = \left( -\frac{d S_{\text{MO}_x}}{dx} \right) + \frac{1}{2} S_{\text{O}_2} (g) \quad (4b)
\]

Using the average in Equation (4) yields the \( \Delta H_{\text{red}} \) and \( \Delta S_{\text{red}} \) that is averaged from the stoichiometric (say \( \text{MO}_x \)) to an off-stoichiometric composition, \( \text{MO}_{x-\delta} \), while the derivatives in Equation (4) yield the instantaneous enthalpy and entropy of reduction at a given off-stoichiometric composition, \( \text{MO}_x \). Note that \( \Delta H_{\text{red}} \) as defined in Equation (4a) is a better indicator of the net
heat input required to remove one oxygen and to induce an off-stoichiometry of \( \delta \) than the instantaneous quantity.

3. Solution Thermodynamics Using the Sub-Lattice Formalism

In this section, we briefly introduce the concepts behind the CEF and subsequently define the sub-lattice models for pure and Zr-doped CeO\(_2\). When two components (e.g., pure elements), A and B, form a solution phase (A, B), the Gibbs energy of the solution phase \( G_{A,B} \) can be written as

\[
G_{A,B} = \gamma G_A + \gamma G_B + \Delta G_{\text{mix}}
\]

where \( G_A \) and \( G_B \) are the Gibbs energies of the pure components, also known as end-members, A and B. \( \Delta G_{\text{mix}} \) contains the enthalpic and entropic contributions that lead to the formation of the solution phase from the pure components. Therefore, if the temperature \( (T) \) dependence of \( G_A \) and \( G_B \) and the composition \( (\gamma) \) dependence of \( \Delta G_{\text{mix}} \) are known, then the Gibbs energy of the solution phase can be estimated accurately across the \( T - \gamma \) space, which in turn can be used to calculate the overall A-B phase diagram. However, when multiple components (such as in ternary, quaternary, quinary, etc., systems) form a solution phase, \( \Delta G_{\text{mix}} \) may not be trivial to determine experimentally or calculate theoretically. In this context, the CEF provides a robust thermodynamic framework to estimate the Gibbs energy of a solution phase in multi-component systems, using available experimental and/or theoretical data on chemical potentials, enthalpies, heat capacities, etc. The readers are directed to the literature for further reading about the CEF.

Generalizing Equation (5) for any multi-component system, the Gibbs energy of a given solution phase \( G_{\text{soln}} \) can be written as

\[
G_{\text{soln}} = G_{\text{end-members}} - T S_{\text{soln}} + G_{\text{excess}} + G_{\text{phys}}
\]

where \( G_{\text{end-members}} \) is the sum of the Gibbs energies of the end-members, \( S_{\text{soln}} \) is the configurational entropy of the solution phase, \( G_{\text{excess}} \) is the excess Gibbs energy not captured by the end-members and the configurational entropy contributions, and \( G_{\text{phys}} \) is the Gibbs energy arising from any physical or phase transformations in the solution phase (e.g., a ferromagnetic \( \rightarrow \) paramagnetic transition). \( G_{\text{end-members}} \) for a solution phase with a single sub-lattice is the weighted sum of all of the pure components, that is,

\[
G_{\text{end-members}} = \sum_i \gamma_i G_i
\]

(7)

\( \gamma_i \) is the site fraction, equivalent to the mole fraction in this case, of component \( i \) within the solution phase. When the solution phase exhibits two distinct sub-lattices \( (k, l) \) with two distinct components \( \{A, B\} \), sub-lattice \( k \) and \( \{C, D\} \), sub-lattice \( l \), then \( G_{\text{end-members}} \) is written as

\[
G_{\text{end-members}} = \sum_i \gamma_i \gamma_j \gamma_k \gamma_l G_i
\]

where \( \gamma_i \) in Equation (8) is the site fraction of species \( X \) on sub-lattice \( z \), with \( G_{X,Y} \) representing the Gibbs energy of a configuration with sub-lattices \( k \) and \( l \) completely occupied by components \( X \) and \( Y \), respectively. For higher-order, multi-component, multi-sub-lattice systems, \( G_{\text{end-members}} \) can be generalized in a similar manner.

\[
S_{\text{soln}} = - R \sum \gamma_k \ln \gamma_k
\]

(9)

where \( R \) is the universal gas constant and \( \gamma_k \) is the total number of sites (normalized per formula unit) of sub-lattice \( z \) in the solution phase. Although it is an assumption that configurational entropy exhibits ideal behavior in a multi-component, multi-sub-lattice system, precedence for such sub-lattice models accurately describing phase behavior in several systems does exist.

While the \( G_{\text{phys}} \) component in Equation (6) is included only if there are strong first- or second-order phase transformations or other unique physical changes in the solution phase, \( G_{\text{excess}} \) typically is expressed in terms of binary interaction parameters \( (I) \) using the functional form of Equation (10) for the \( (A, B) \) \( \rightarrow \) \( (C, D) \) system.

\[
G_{\text{excess}} = \sum \gamma_i \gamma_j \gamma_k \gamma_l I_{A,B,C,D}
\]

(10)

Here, each \( I \) term can have both a temperature dependence (typically of the \( a + b T \) functional form) and a concentration dependence that usually is expressed as a Redlich–Kister (RK) power series.

\[
I_{A,B,C,D} = \sum_i \left( \gamma_i - \gamma_j \right) L_{A,B,C,D}
\]

(11)

Note that the \( i \) terms in Equation (11) represent the exponent and an index for the \( \gamma \) and the \( L \) terms, respectively. Although several higher-order RK terms \( (\text{large } i \text{ in } L) \) can be used, the standard practice is to restrict \( i \) to a maximum of 3, and often no more than 1. Note, that in addition to binary terms, higher-order interaction terms \( (i.e., \text{, } L \text{ for ternary, quaternary, etc., interactions}) \) can be employed within the CEF.

3.1. Sub-Lattice Model in CeO\(_2\)

Figure 3 illustrates the sub-lattice model used for fluorite-CeO\(_2\), which is based on stoichiometric-CeO\(_2\), that exhibits the fluorite structure containing one Ce site (Ce sub-lattice) and two oxygen sites (O sub-lattice). Two possible species can occupy each of its two sub-lattices, namely, Ce\(^{4+}\) (green circles/polyhedra in Figure 3) and Ce\(^{3+}\) (orange circles/polyhedra) in the Ce sub-lattice and oxygen (red circles) and vacancies (Va, blue circles) in the O sub-lattice, necessitating a four-component, two-sub-lattice model. As a result, the relevant end-members for CeO\(_2\) within the sub-lattice framework involve all Ce and O sites occupied by: i) Ce\(^{4+}\) and O (stoichiometry of Ce\(^{4+}\)O\(_2\), top left configuration in Figure 3); ii) Ce\(^{3+}\) and O (Ce\(^{3+}\)O\(_2\), top right); iii) Ce\(^{4+}\) and O (Ce\(^{4+}\)O\(_2\), bottom left).
end-member, which simply represents stoichiometric CeO$_2$, is charge-neutral. Thus,
\[ G^e_{\text{CeO}_2} = G^e_{\text{CeO}_2} \]  

(14)

The superscript F in $G^e_{\text{CeO}_2}$ represents the fluorite structure. To estimate the Gibbs energies of non-charge-neutral end-members, the CEF formalism normally uses reference states and/or reciprocal relations.\cite{61,62} For example, $G^e$ for the Ce$^{4+}$/Va$_2$ end-member can be referenced to the Gibbs energies of stoichiometric CeO$_2$ and oxygen gas (i.e., using two charge-neutral reference states), as in Equation (15).

\[ G^e_{\text{CeO}_2} = G^e_{\text{CeO}_2} - G_{\text{O}_2} (g) \]  

(15)

To determine $G^e$ for Ce$^{3+}$ : O and Ce$^{4+}$ : Va end-members, Zinkevich et al.,\cite{67} defined a reference state and reciprocal relation, also used here. Specifically, a combination of Ce$^{3+}$ : O and Ce$^{4+}$ : Va end-members gives rise to a fluorite structure with a charge-neutral stoichiometry of CeO$_2$, that is, 25% of all O sites within the fluorite structure are vacant. Notably, Ce$_2$O$_3$ is a stable oxide within the Ce-O binary system and exhibits a hexagonal structure at 298 K,\cite{90} although the fluorite polymorph can form in a metastable manner at STCH-relevant temperatures.\cite{91}

Mathematically the Ce$_2$O$_3$ reference state is defined as

\[ \frac{1}{2} G^e_{\text{Ce}_2\text{O}_3} = G^e_{\text{CeO}_2} + \frac{3}{4} C_{\text{CeO}_2}^{\text{F}} + \frac{1}{4} G^e_{\text{O}_2} + 2RT \left( \frac{3}{4} \ln 3 + \frac{1}{4} \ln 4 \right) \]  

(16)

where the entropic contribution to $G^e_{\text{CeO}_2}$ arises from the co-existence of O and Va within the O sub-lattice. With three relations defining three of the four end-members, the following reciprocal relation is employed to determine the final end-member. Physically, the reciprocal relation assumes—frankly, without justification—that the energy to evolve O$_2$(g) from the Ce$_3$O$_2$ end-member ($G_{\text{Ce}_3\text{O}_2} - G_{\text{Ce}_2\text{O}_3}$) is equivalent to evolving O$_2$(g) from Ce$_2$O$_3$ ($G_{\text{Ce}_2\text{O}_3} - G_{\text{Ce}_3\text{O}_2}$).

\[ G^e_{\text{Ce}_3\text{O}_2} = G^e_{\text{Ce}_2\text{O}_3} - G^e_{\text{Ce}_2\text{O}_3} \]  

(17)

Apart from $G^e_{\text{end-member}}$ and $S^\text{soln}$ (Equations (12) and (13)), Zinkevich et al.,\cite{67} also utilized binary interaction parameters in defining the excess Gibbs energy (Equation (18)), which was crucial to obtaining an accurate description of all experimental data in their sub-lattice model.

\[ G^e_{\text{excess}} = y_{\text{Ce}^{4+}} y_{\text{O}_2} y_{\text{Va}} L_{\text{Ce}^{4+}\text{O}_2,\text{Va}} + y_{\text{Ce}^{3+}} y_{\text{O}_2} L_{\text{Ce}^{3+}\text{O}_2,\text{Va}} + y_{\text{O}_2} y_{\text{Va}} L_{\text{Ce}^{4+}\text{Va}} \]  

(18)

To minimize the number of excess parameters, Zinkevich et al.,\cite{67} used two unique parameters by setting, again without justification

\[ L_{\text{Ce}^{3+}\text{O}_2,\text{Va}} = L_{\text{Ce}^{4+}\text{O}_2,\text{Va}} = 0; L_{\text{Ce}^{3+}\text{Ce}^{4+}} = L_{\text{Ce}^{4+}\text{Ce}^{4+}} \]  

(19)
Moreover, the authors[67] used the following constant and first-order RK terms to define the interaction parameter (see Section 3.1.1 for further discussion).

\[ L_{\text{Ce}^{3+}, \text{Ce}^{4+}} = L_0^{\text{Ce}^{3+}, \text{Ce}^{4+}} + \left( y_{\text{Ce}^{3+}}^C - y_{\text{Ce}^{4+}}^C \right) L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}} \]  

(20)

Through this work, we will use the notations of \( L_0 \) and \( L_1 \) for \( L_{\text{Ce}^{3+}, \text{Ce}^{4+}} \) and \( L_1^{\text{Ce}^{3+}, \text{Ce}^{4+}} \), respectively. Thus, the excess Gibbs energy has the final functional form as written in Equation (21).

\[ G_{\text{excess}} = y_{\text{Ce}^{3+}} L_0 + \left( y_{\text{Ce}^{3+}}^C - y_{\text{Ce}^{4+}}^C \right) L_1 \]  

(21)

Note that the \( y_{\text{O}}^0 \) and \( y_{\text{O}}^\text{excess} \) site-fractions of Equation (18) drop out in Equation (21), because setting \( L_{\text{Ce}^{3+}, \text{Ce}^{4+}} \) = \( L_{\text{Ce}^{3+}, \text{Ce}^{4+}}^{\text{Va}} \) (Equation (19)) gives rise to a \( y_{\text{O}}^0 + y_{\text{O}}^\text{excess} \) term, which equals 1 always.

Finally, combining \( G_{\text{end-members}} \), \( S_{\text{excess}} \), and \( G_{\text{excess}} \), the Gibbs energy of the fluorite-CeO \( _2 \) phase (\( G_{\text{CeO}_2} \)) can be expressed, as in Equation (22):

\[
G_{\text{CeO}_2} = y_{\text{Ce}^{3+}}^C \left( G_{\text{CeO}_2}^F + \frac{1}{4} G_{\text{O}_2} (g) - 2RT \left( \frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4} \right) \right) + y_{\text{Ce}^{4+}}^C \left( G_{\text{CeO}_2}^F - G_{\text{O}_2} (g) \right) + RT \left( \ln y_{\text{Ce}^{4+}}^C + \ln y_{\text{Ce}^{3+}}^C \right) + 2RT y_{\text{O}}^0 \left( y_{\text{O}}^0 \ln y_{\text{O}}^0 \right) + y_{\text{Ce}^{3+}} y_{\text{Ce}^{4+}} \left( L_0 + \left( y_{\text{Ce}^{3+}}^C - y_{\text{Ce}^{4+}}^C \right) L_1 \right) \]

(22)

Equation (22) can be simplified further by expanding the site-fractions with respect to \( x \), as \( y_{\text{Ce}^{3+}}^C = 2x - 3 \), \( y_{\text{Ce}^{4+}}^C = 4 - 2x \), \( y_{\text{O}}^0 = \frac{x}{2} \), and \( y_{\text{O}}^{\text{excess}} = 1 - \frac{x}{2} \), which ultimately results in Equation (23). The site-fractions are defined such that \( y_{\text{Ce}^{3+}}^C = 1 \), \( y_{\text{Ce}^{3+}} = 0 \), \( y_{\text{O}}^0 = 1 \), and \( y_{\text{O}}^{\text{excess}} = 0 \) at \( x = 2 \) (fully oxidized CeO \( _2 \)) and \( y_{\text{Ce}^{3+}}^C = 0 \), \( y_{\text{Ce}^{4+}}^C = 1 \), \( y_{\text{O}}^0 = 0.75 \), and \( y_{\text{O}}^{\text{excess}} = 0.25 \) at \( x = 1.5 \) (fully reduced CeO \( _1.5 \)).

\[
G_{\text{CeO}_2} = G_{\text{CeO}_2}^F - (4-2x) \left( G_{\text{CeO}_2}^F - G_{\text{CeO}_2}^F_{\text{Na}} \right) + 2RT \left( \frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4} \right) + RT \left( y_{\text{Ce}^{4+}}^C \ln y_{\text{Ce}^{4+}}^C + y_{\text{Ce}^{3+}}^C \ln y_{\text{Ce}^{3+}}^C \right) + 2RT y_{\text{O}}^0 \left( y_{\text{O}}^0 \ln y_{\text{O}}^0 \right) + y_{\text{Ce}^{3+}} y_{\text{Ce}^{4+}} \left( L_0 + \left( y_{\text{Ce}^{3+}}^C - y_{\text{Ce}^{4+}}^C \right) L_1 \right) \]

(23)

After calculating all of the input parameters in Equation (23) (\( G_{\text{CeO}_2}^F \), \( G_{\text{CeO}_2}^F_{\text{Na}} \), \( G_{\text{CeO}_2} (g) \), \( L_0 \), \( L_1 \)), we evaluate with DFT the energies (\( G \approx E \)) of all other binary Ce oxides (e.g., hexagonal-Ce \( _2 \)O \( _3 \)) and also evaluate the lowest Gibbs energy of the solid phase as a function of oxygen composition. Subsequently, the derivative of the lowest Gibbs energy with respect to the oxygen concentration yields the oxygen chemical potential within the solid \( (\mu_{\text{O}}) \), see Equation (3)), which then is equated with the oxygen chemical potential in the gas phase \( (\mu_{\text{O}}^\text{gas}) \) to determine the equilibrium oxygen concentration \( (x_{\text{eq}} = 2 - \delta_{\text{eq}}) \) for a given \( T \) and \( p_{\text{O}_2} \).

\[ x_{\text{eq}} = 2 - \delta_{\text{eq}} \]

3.1.1. Excess Terms

Physically, \( L_0 \) and \( L_1 \) signify the excess interactions between \( \text{Ce}^{3+} \) and \( \text{Ce}^{4+} \) within the Ce sub-lattice due to the presence of \( \text{O} \) vacancies in the O sub-lattice. Specifically, \( L_0 \) and \( L_1 \) exhibit a quadratic and cubic dependence on \( x \) for \( G^F \) in Equation (23) since each \( x \) depends linearly on \( x \). As logarithmic (entropic) terms in Equation (23) contribute to \( \Delta S_{\text{red}} \) (of Equation (4)), \( L_0 \) and \( L_1 \) signify slope and curvature, respectively, of \( \Delta H_{\text{red}} \) as a function of \( x \). \( L_0 \), which represents excess interactions between \( \text{Ce}^{3+} \) and \( \text{Ce}^{4+} \) not captured by the end-members, can be referenced to the theoretically calculated enthalpy (\( \Delta H_{\text{red}} \)) of an isolated oxygen vacancy in stoichiometric CeO \( _2 \) \( (H_{\text{VaO}} \approx E_{\text{VaO}} \) where \( \delta \rightarrow 0; x \rightarrow 2 \)), as illustrated by the solid blue circle in Figure 4. This is because the simultaneous existence (and interactions) of \( \text{Ce}^{3+} \) and \( \text{Ce}^{4+} \) in the Ce sub-lattice is possible physically only when a vacancy exists in the O sub-lattice. On the other hand, \( L_1 \) represents interactions between \( \text{Ce}^{3+} \) and \( \text{Ce}^{4+} \) not captured by both end-members and \( L_0 \), such as additional interactions between multiple oxygen vacancies. We therefore define \( L_1 \) via theoretically calculating the (lowest) energy of two oxygen vacancies.
in stoichiometric CeO$_2$ ($E_{\text{CeO}_2}^{V_{\text{Va}}, x'} \to 2$), as indicated by the red diamond in Figure 4.

Additionally, the calculated $E_{\text{CeO}_2}^{V_{\text{Va}}}$ (and $E_{\text{CeO}_i}^{V_{\text{Va}}}$) have to be scaled appropriately with the energies of the reference structures, since $L_0$ (and $L_1$) represents contributions not captured by the end-member $G^*$ (and $L_0$) terms. Mathematically, $L_0$ is defined in terms of $x$ or $\delta$ as

$$L_0 = \frac{E_{\text{CeO}_2}^{V_{\text{Va}}} - (2x - 3)E_{\text{CeO}_2}^F - (4 - 2x)E_{\text{CeO}_{1.5}}^F}{2(2 - x)};$$

$$L_0 = \frac{E_{\text{CeO}_2}^{V_{\text{Va}}*(x')} - (1 - 6\delta)E_{\text{CeO}_2}^F - 2\delta E_{\text{CeO}_{1.5}}^F}{2\delta}$$

(24)

where the multiplicative factors scaling $E_{\text{CeO}_2}^F$ and $E_{\text{CeO}_i}^F$ arise from the lever rule of thermodynamics, and the denominator ensures that $L_0$ is defined per O-vacancy, that is, $L_0$ represents the slope of $E_{\text{CeO}_2}^{V_{\text{Va}}}$ (Figure 4). The Gibbs energies of the reference CeO$_5^*$ and CeO$_{1.5}$ states in Equation (24) are approximated by their corresponding internal energies ($G \approx E$). The multiplicative factor of 2 in the denominator is to ensure that the $L_0$, as defined here, is compatible with our sub-lattice model defined per the CeO$_2$ formula unit instead of as in Zinkevich et al.\cite{67}, where $L_0$ is defined per Ce$_2$O$_4$ formula unit. Similarly, we define $L_1$ as

$$L_1 = \frac{E_{\text{CeO}_2}^{V_{\text{Va}}} - (2x' - 3)E_{\text{CeO}_2}^F - (4 - 2x')E_{\text{CeO}_{1.5}}^F}{2 - x'};$$

$$L_1 = \frac{E_{\text{CeO}_2}^{V_{\text{Va}}} - (1 - 6\delta)E_{\text{CeO}_2}^F - 4\delta E_{\text{CeO}_{1.5}}^F}{2\delta}$$

(25)

Note that $L_1$, as expressed above, is compatible with our definition of $G_{\text{CeO}_2}$ (Equation (23)), which is normalized per CeO$_2$ formula unit. The factor of 2 multiplying $L_0$ in Equation (25) signifies that there are twice the number of oxygen vacancies in calculating $E_{\text{CeO}_2}^{V_{\text{Va}}*(x')}$ as compared to $E_{\text{CeO}_2}^{V_{\text{Va}}*(x)}$ that is, $2 - x' = (2 - x)/2$.

Hence, $L_1$ captures the excess interactions not already captured by $L_0$ (and the end-members), since $L_1$ will be zero if the introduction of an additional oxygen vacancy is simply equivalent to the energy of two isolated oxygen vacancies.

### 3.2. Sub-Lattice Model in Zr-Doped CeO$_2$

Although sub-lattice models based on experimental data have yet to be developed for Zr-doped CeO$_2$, the CEF is general enough that the model developed for pure CeO$_2$ can be extended for the Zr-doped system, as has been done for similar oxides.\cite{93} With Zr-doping, the Ce sub-lattice will contain three species, namely Ce$^{4+}$, Zr$^{4+}$, and Ce$^{3+}$, while the O sub-lattice contains O and Va. Note that Zr is not redox-active in doped-CeO$_2$, but has been known to reduce $\Delta H_{\text{red}}$ and thereby increase the equilibrium oxygen off-stoichiometry.\cite{30,32,94,95} To account for Zr$^{4+}$ in the Ce sub-lattice, the energies of two additional end-members, namely $G_{\text{Zr}^{4+}, \text{Va}}^*$ (and $G_{\text{Zr}^{4+}, \text{Va}}^*$) need to be evaluated, similar to the end-members of undoped-CeO$_2$. Specifically, we reference $G_{\text{Zr}^{4+}, \text{O}}^*$ to stoichiometric ZrO$_2$ in the fluorite structure, that is,

$$G_{\text{Zr}^{4+}, \text{O}}^* = G_{\text{ZrO}_2}^F$$

(26)

While the ground-state structure of stoichiometric ZrO$_2$ is monoclinic, ZrO$_2$ can exhibit a fluorite structure isostructural with fluorite-CeO$_2$ at higher temperatures.\cite{96} Thus, $G_{\text{ZrO}_2}^F$ can be evaluated using DFT-based calculations ($G_{\text{ZrO}_2}^F \approx E_{\text{ZrO}_2}^F$). Similar to $G_{\text{Zr}^{4+}, \text{Va}}^*$, we define the Gibbs energy of the non-charge-neutral end-member $G_{\text{Zr}^{4+}, \text{Va}}^*$ using O$_2$ (g) as the reference:

$$G_{\text{Zr}^{4+}, \text{Va}} = G_{\text{ZrO}_2}^F - G_{\text{O}_2}^g$$

(27)

The configurational entropy contribution in Zr-doped CeO$_2$ is modified from Equation (13) to be:

$$S_{\text{Zr}^{4+}, \text{Va}} = -R \left( y_{\text{Ce}_{4+}} \ln y_{\text{Ce}_{4+}} + y_{\text{Zr}_{4+}} \ln y_{\text{Zr}_{4+}} + y_{\text{Va}_{0}} \ln y_{\text{Va}_{0}} \right)$$

$$- 2R \left( y_{\text{O}_2}^g \ln y_{\text{O}_2}^g + y_{\text{O}_2}^g \ln y_{\text{O}_2}^g \right)$$

(28)

Additionally, we introduce four excess parameters, all normalized per the (Ce,Zr)O$_2$ formula unit, to describe interactions among: i) binary Ce$^{4+}$-Zr$^{4+}$ ($L_{\text{Ce}_{4+}, \text{Zr}_{4+}}$) referenced to half the Gibbs energy ($\approx E$) of the CeZrO$_2$ fluorite-based superstructure; ii) binary Ce$^{4+}$-Zr$^{4+}$ ($L_{\text{Ce}_{4+}, \text{Zr}_{4+}}$) referenced to one-quarter of the Gibbs energy ($\approx E$) of cubic-Ce$_2$Zr$_2$O$_7$; iii) ternary Ce$^{4+}$-Ce$^{4+}$-Zr$^{4+}$ ($L_{\text{Ce}_{4+}, \text{Zr}_{4+}}$) referenced to a combination of one Zr and one oxygen vacancy within a Ce$_2$O$_7$ supercell; and iv) ternary Ce$^{4+}$-Ce$^{4+}$-Zr$^{4+}$ ($L_{\text{Ce}_{4+}, \text{Zr}_{4+}}$), referenced to one Zr and two oxygen vacancies in a CeO$_2$ supercell. All excess parameters are normed appropriately to the energy scale of the end-members, analogous to Equations (24) and (25). The overall $G_{\text{Zr}^{4+}, \text{O}}$ for Zr-Ce-O ternary, combining $L_0$ and $L_1$ terms for binary Ce-O, is written as in Equation (29):

$$G_{\text{Zr}^{4+}, \text{O}} = y_{\text{Ce}_{4+}} y_{\text{Ce}_{4+}} \left( L_0 + \left( y_{\text{Ce}_{4+}, \text{Zr}_{4+}} - y_{\text{Ce}_{4+}} \right) L_1 \right)$$

$$+ y_{\text{Ce}_{4+}} y_{\text{Zr}_{4+}} \left( L_0 + \left( y_{\text{Ce}_{4+}, \text{Zr}_{4+}} + y_{\text{Zr}_{4+}} \right) L_1 \right)$$

$$+ y_{\text{Ce}_{4+}} y_{\text{Va}_{0}} \left( L_0 + \left( y_{\text{Ce}_{4+}, \text{Va}_{0}} \right) L_1 \right)$$

$$+ y_{\text{Zr}_{4+}} y_{\text{Va}_{0}} \left( L_0 + \left( y_{\text{Zr}_{4+}, \text{Va}_{0}} \right) L_1 \right)$$

(29)

Similar to undoped-CeO$_2$, we evaluate all of the input parameters in Equations (23), (26), and (29) and the energies of all binary and ternary oxides within the Ce-Zr-O system to obtain the lowest Gibbs energy as a function of the oxygen composition (and x$_{eq}$ as a result) at different Ce:Zr ratios in Zr-doped CeO$_2$.

### 4. Results

#### 4.1. Pure CeO$_2$

Figure 5a plots the comparison between experimental (green, data from Zinkevich et al.\cite{67}) and theoretical (red) $\mu_\text{O}_2$ as a
function of $x$ in CeO$_2$ at 298 K for STCH-relevant concentrations (1.5 $\leq x \leq$ 2). The zero of the vertical axis is set to the free energy of O$_2$ (g) at 0 K, i.e., $G_{O_2}(g) \approx E_{O_2}(g) \approx 0$. The change in $H_{O_2}(g)$ from 298 K to 0 K is neglected ($S_{O_2}(g) = 0$ at 0 K), resulting in $\mu_{O_2}^F = -0.31$ eV at 298 K and $\mu_{O_2}^G = 1$ atm from the $-TS_{O_2}(g)$ contribution (Equation (1)). A stable composition in Figure 5a spans a range of $\mu_{O_2}$ (e.g., stoichiometric CeO$_2$ spans $-3.8 \leq \mu_{O_2} \leq 0$ eV, green line), while a constant $\mu_{O_2}$ spanning a range of $x$ indicates a two-phase equilibrium (e.g., CeO$_2$ and Ce$_7$O$_{12}$ co-exist at $\mu_{O_2} = -3.8$ eV). Qualitative agreement exists between the theoretical and experimental variations in $\mu_{O_2}$. For example, both experiments and theory find Ce$_7$O$_{12}$ ($x = 1.71$), which is an ordered, fluorite-based superstructure of reduced-CeO$_2$, to be stable at 298 K in addition to fluorite-CeO$_2$ and hexagonal-Ce$_2$O$_3$. While errors in predicted (versus experimental) $\mu_{O_2}$ for $x < 1.5$ (not relevant to STCH) are due to mixing DFT+U$^{[92,97]}$ (for Ce-oxides) and DFT (for Ce-metal) energies (Experimental Section), the differences in the range of $\mu_{O_2}$ for CeO$_2$ and Ce$_7$O$_{12}$ arise from the specific $U$ value employed$^{[92]}$ and from comparing 0 K energies to experimental enthalpies at 298 K.

Analogous to Figure 5a, we compare theoretical and experimental $\mu_{O_2}$ under STCH-relevant conditions (at 1673 K, Figure 5b) and WS (at 873 K, Figure 5c) conditions. The orange (purple) line in Figure 5b (Figure 5c) corresponds to $p_{O_2} = 10$ Pa ($p_{H_2O} = 10$ Pa) ($p_{H_2O} = 9$). Dashed green and dotted red lines (Figure 5b,c), as well as corresponding annotations, indicate equilibrium oxygen off-stoichiometries ($x_{eq}$) in CeO$_2$ from the experimental and theoretical models, respectively ($\mu_{O_2}^L = \mu_{O_2}^S \equiv \mu_{O_2}^{(0)}$). For example, under TR, the experimental and theoretical models estimate $x_{eq} \approx 1.986$ and $\approx 1.988$, respectively, equivalent at $\delta_{eq} = 0.014$ and 0.012 (Figure 5b and its inset). Similarly, $x_{eq} \approx 1.999$ in both theory and experimental models under WS (Figure 5c).

The robust agreement between the theoretical and experimental models at small off-stoichiometries ($x > 1.975$) degrades at smaller $x$. For example, theory estimates that fluorite-CeO$_2$ should remain stable only up to $\delta \approx 0.075$ ($x \approx 1.925$), while experiments indicate a maximum $\delta \approx 0.31$ ($x \approx 1.69$, inset of Figure 5b). The wide discrepancy at lower $x$ originates in the artificial stabilization of Ce$_7$O$_{12}$ at 1673 K due to the neglect of vibrational entropy within the theoretical model (Ce$_7$O$_{12}$ is not stable beyond 1321 K experimentally$^{[67]}$). Fluorite-CeO$_2$ is stable up to $\delta \approx 0.13$ ($x \approx 1.87$) in the theoretical model when Ce$_7$O$_{12}$ is not included as a competing phase (dotted blue line in Figure 5b). The fair agreement between theoretical and experimental models at low oxygen off-stoichiometry for TR and WS (Figure 5b,c) relevant conditions highlights that vibrational entropy differences within solid phases, at the corresponding temperatures, can be neglected$^{[98]}$ for practical STCH, providing a sufficiently accurate and less expensive approach.

Figure 5d displays variations in $\frac{dH_{Ox}}{dx}$, related to $\Delta H_{red}$ via Equation (4), versus $x$ at 1673 K, where solid (dashed) lines indicate quantities from the experimental (theoretical) model. The robust agreement between the theoretical and experimental models at small off-stoichiometries ($x > 1.975$) degrades at smaller $x$. For example, theory estimates that fluorite-CeO$_2$ should remain stable only up to $\delta \approx 0.075$ ($x \approx 1.925$), while experiments indicate a maximum $\delta \approx 0.31$ ($x \approx 1.69$, inset of Figure 5b). The wide discrepancy at lower $x$ originates in the artificial stabilization of Ce$_7$O$_{12}$ at 1673 K due to the neglect of vibrational entropy within the theoretical model (Ce$_7$O$_{12}$ is not stable beyond 1321 K experimentally$^{[67]}$). Fluorite-CeO$_2$ is stable up to $\delta \approx 0.13$ ($x \approx 1.87$) in the theoretical model when Ce$_7$O$_{12}$ is not included as a competing phase (dotted blue line in Figure 5b). The fair agreement between theoretical and experimental models at low oxygen off-stoichiometry for TR and WS (Figure 5b,c) relevant conditions highlights that vibrational entropy differences within solid phases, at the corresponding temperatures, can be neglected$^{[98]}$ for practical STCH, providing a sufficiently accurate and less expensive approach.
formation of competing phases (e.g., hexagonal-Ce₂O₃) is not considered in Figure 5d to ensure a direct comparison of the theoretical and experimental models. Blue, red, and green lines in Figure 5d signify, respectively, that \( H^{\text{CeO}_2} \) contains no excess interaction terms (\( L_0 \) or \( L_1 \)), only \( L_0 \), and both \( L_0 \) and \( L_1 \). \( \frac{dH^{\text{CeO}_2}}{dx} \) therefore is independent of \( x \) without the excess terms, and \( L_0 \) and \( L_1 \) add a slope and a curvature, respectively (Equation (23)). Significantly, \( \frac{dH^{\text{CeO}_2}}{dx} \) is the isolated oxygen vacancy formation energy in stoichiometric CeO₂ as \( x \to 2 \), where the theoretical-model-predicted value of \( \approx 4.15 \text{ eV} \) agrees well with the experimental-model-predicted \( \approx 4.33 \text{ eV} \). Additionally, the concave curvature of both the experimental and theoretical \( \frac{dH^{\text{CeO}_2}}{dx} \) (green) highlights that the oxygen vacancies become progressively easier to create as \( x \) decreases from 2 (up to \( x \approx 1.85 \)), a unique feature of pure-CeO₂ compared to doped-CeO₂ and several oxide perovskites.\(^{(83)}\)

When \( x \ll 1.85 \), \( \frac{dH^{\text{CeO}_2}}{dx} \) becomes significantly more negative and oxygen vacancies become harder to create.

Figure 5e shows \( x_{eq} \) versus \( T \) at TR-relevant \( p_{O_2} = 10 \text{ Pa} \) (solid lines and solid diamonds) and at \( p_{O_2} = 10^{-12} \text{ Pa} \) (dashed lines and hollow diamonds), where \( x_{eq} \) is calculated only from theoretical (solid and hollow diamonds) and experimental (solid and dashed curves) models without considering competing Ce-oxides. We also plot \( x_{eq} \) adding just \( L_0 \) (red diamonds), and adding both \( L_0 \) and \( L_1 \) (green diamonds) to the overall \( G^{\text{CeO}_2} \) (Equation (23)), while the experimental model is plotted including both \( L_0 \) and \( L_1 \). Interestingly, adding \( L_1 \) hardly changes the theoretically predicted \( x_{eq} \) under both \( p_{O_2} = 10 \) and \( 10^{-12} \text{ Pa} \) and across temperatures, with a maximum deviation (at 1473 K, \( 10^{-12} \text{ Pa} \)) of \( <10 \% \) in \( x \) per CeO₂. Theoretical predictions (including that of \( L_0 \) and \( L_1 \)) agree well with experimental \( x_{eq} \) at \( p_{O_2} = 10 \text{ Pa} \), highlighted by a maximum deviation of \( \approx 0.02 \text{ per CeO}_2 \) (theoretical CeO₂ theory versus experimental CeO₂, \( \text{at} \) 1873 K). Theory deviates significantly from experiment at \( p_{O_2} = 10^{-12} \text{ Pa} \), especially at intermediate temperatures (1273–1473 K), for example, \( x_{eq}^{\text{theory}} \approx 1.92 \) (green diamond) and \( x_{eq}^{\text{experiment}} \approx 1.84 \) at 1273 K. This dramatic deviation is due to the high concavity of the experimental \( \frac{dH^{\text{CeO}_2}}{dx} \) curve (solid green line in Figure 5d) for \( 1.7 < x < 1.9 \).

4.2. Zr-Doped CeO₂

Similar to Figure 5b,c, we plot the theoretical \( \mu_O \) as a function of \( x \) in Zr-doped CeO₂ at Zr-contents of 0\% (pure-CeO₂, red curves), 10\% (dashed green), 20\% (dash-dot blue), and 30\% (dotted brown) in Figure 6. Panels a and b correspond to TR (1673 K) and WS (973 K) conditions, where the orange and purple lines indicate \( p_{O_2} = 10 \text{ Pa and } \frac{p_{H_2O}}{p_{H_2}} = 9 \), respectively. Additionally, increasing Zr-content also destabilizes the oxide without any oxygen off-stoichiometry, that is, (Ce₂ZrO₄) domains. The prediction of phase separation is in qualitative agreement with the observed sublimation of CeO₂ at temperatures above 1600 K.\(^{(89)}\) HITEMP and TGA measurements can provide accurate measurements when \( p_{O_2} \) is well-controlled,\(^{(108)}\) and often will be the only measurements available for theory to compare with.

Notably, as Zr-content increases, the net reduction (and the extent of stable oxygen off-stoichiometry) of Zr-doped CeO₂ increases under TR conditions, in qualitative agreement with experiments.\(^{(10,11,99)}\) For example, at 1673 K and \( p_{O_2} = 10 \text{ Pa, } x_{eq} \approx 1.988, 1.985, \) and 1.982 at 0\%, 10\%, and 20\% Zr-doping, respectively. Additionally, increasing Zr-content also destabilizes the oxide without any oxygen off-stoichiometry, that is, (Ce₂ZrO₄) domains. The prediction of phase separation is in qualitative agreement with experimental observations of surface segregation of ZrO₂, in conjunction with selective sublimation of CeO₂, upon thermal sublimation.

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Figure 6. Theoretical oxygen chemical potentials, as a function of \( x \) in CeₐZr₁₋ₓOₓ at Zr doping levels of 0\% (solid red), 10\% (dashed green), 20\% (dash-dot blue), and 30\% (dotted brown). a) TR (1673 K) and b) WS (973 K) conditions, where the orange and purple lines indicate \( p_{O_2} = 10 \text{ Pa and } \frac{p_{H_2O}}{p_{H_2}} = 9 \), respectively.
reduction at 1683 K in Ce0.85Zr0.15O2. Thus, large-scale doping of Zr within CeO2 will be counter-productive to reduce reaction (and subsequent re-oxidation) under reasonable STCH conditions. However, Zr-addition does stabilize larger off-stoichiometric compositions, under highly reducing conditions (e.g., Ce0.7Zr0.3O1.9 is stable at μ0 Ω ~ 4.08 eV).

Interestingly, none of the Zr-doped configurations are stable thermodynamically at 873 K, and the doped oxide should phase separate into CeO and ZrO2 domains. This may be a cause for the poor long-term cyclability of Zr-doped CeO2 compared to pure-CeO2, as Zr4+ ions are known to exhibit long-range diffusion and segregation within the fluorite structure under STCH conditions. Hence, to compare quantitatively pure and doped CeO2, we chose the WS temperature to be 973 K in Figure 6b instead of 873 K used in Figure 5c. Among the various Zr-dopant concentrations considered (i.e., 10%, 20%, and 30%), only the 10% Zr-doped fluoride phase is stable at 973 K and yields x ≈ 1.996 as compared to ≈ 1.997 for pure-CeO2. Thus, higher Zr-doped contents should phase separate into Ce0.9Zr0.1O and ZrO2 domains at 973 K. Nevertheless, higher Zr-doped compositions may also exist in a metastable manner at 973 K (or 873 K) without explicitly forming Ce-rich and ZrO2 domains due to kinetic barriers, which are difficult to quantify theoretically or experimentally. Note that relying on kinetic barriers for materials that will have to cycle over very many cycles probably would not be a wise strategy.

5. Discussion

In this work, we have constructed a sub-lattice model (Figures 3 and 4), parameterized entirely using 0 K DFT-based calculations (Figure 2) for undoped and Zr-doped CeO2, which form the SOA for water and/or CO2 splitting under a STC cycle (Figure 1). Specifically, we based our theoretical model (Section 3 and Figure 3) on the sub-lattice framework for undoped CeO2 that was built and fit to experimental data by Zinkevich et al. Subsequently, we extended our model to make predictions on the ternary Ce-Zr-O system. Importantly, our theoretical model’s predictions are in fair agreement with experimental observations for both undoped and Zr-doped CeO2 (Figures 5 and 6), with a high degree of quantitative accuracy at low oxygen off-stoichiometries under TR and WS conditions. Our work highlights that fully DFT-based sub-lattice models, upon careful validation, can enable the discovery and optimization of candidate off-stoichiometric oxides for STC applications.

The CEF approximation often benefits from error cancellation. Ideal solution configurational entropy for all sub-lattices is a major assumption, especially in systems with a short-range order and/or binding between different species (e.g., Ce3+, dopant, and oxygen vacancies); entropy overestimates can cancel within the excess terms. In the case of CeO2, the electrostatic attraction between Ce3+ and oxygen vacancies will dominate at low temperatures. Hence, the Ce4+ formed should be “adjacent” to the oxygen vacancies which we indeed observe in our 0 K calculations (see Figure S1, Supporting Information). However, at higher temperatures (especially the range of interest for STCH, 873–1673 K), gains in configurational entropy can offset such Ce3+-oxygen vacancy binding. Hence, the sub-lattice model in this work (and in Zinkevich et al.) uses the assumption of ideal mixing between the Ce3+ and Ce4+ in the Ce sub-lattice and between oxygen ions and vacancies in the oxygen sub-lattice. Despite the assumption of ideal mixing potentially leading to an overestimation of the configurational entropy, subtle error cancellation enables the sub-lattice model to reliably model the CeO2 system, as highlighted by the good predictions of the experimental model by Zinkevich et al. versus measurements. Indeed, multiple examples exist of sub-lattice models yielding robust phase diagrams while using ideal solution entropy. The error cancellation alluded to here should occur between the excess terms and the configurational entropy, which can be understood within the framework of a regular solution model. Note that the L0 term is analogous to the mixing enthalpy (Hmix) in a regular solution. A negative (positive) value of Hmix in a regular solution favors clustering (phase separation) of the individual components, while the ideal solution entropy is a random solution. Hence, errors in overestimating Smix can cancel the over (under) estimation of Hmix, leading to a physically reasonable description of the underlying solution phase. Such error cancellation also seems to benefit the theoretical model, as highlighted by the robust agreement between the theoretical and experimental models in this work.

In general, a good estimate of the “enthalpy of mixing” and ideal solution entropy is sufficient to describe chemical systems that behave in a regular or sub-regular-solution-like manner. In the case of sub-lattice models, usage of L0 and L1 excess terms, such as in the case of CeO2, is approximately equivalent to a sub-regular model. This probably explains why using 0 K vacancy formation energies to obtain L0 and L1 (i.e., a robust estimate of the enthalpy of mixing), in conjunction with ideal solution of mixing within the Ce and O sub-lattices yields fairly accurate estimates of off-stoichiometry at higher temperatures. Although we used the lowest-energy oxygen vacancy configurations in CeO2 to obtain both L0 and L1, the effect of including both excess terms does not seem to have a compounding effect in increasing or decreasing the excess Gibbs energy (Figure 5d) across oxygen concentrations. For example, L0 (L1) increases (decreases) the absolute value of dHdx in Figure 5d, particularly at low oxygen off-stoichiometries (x ≥ 1.9), which corresponds to decreasing (increasing) the energy required to form oxygen vacancies in CeO2. Thus, at low oxygen deficiencies, L0 and L1 contribute in contrasting manners to the overall excess Gibbs energy, which might mitigate any error in over- or under-estimating the excess interactions. To account for short-range interactions between Ce3+ and oxygen vacancies, particularly at low temperatures, modified sub-lattice models that account for short-range order and/or binding can be used. However, obtaining enthalpy and/or entropy estimates for phases including short-range order and/or binding using DFT-based calculations can incur significant computational expense.

Having energies of non-charge-neutral end-members referenced to neutral phases or constrained via reciprocal relationships also are approximations within the CEF. Errors from these approximations will affect model quality. Nevertheless, models built on experimental data nominally retain a high degree of predictability provided the fit is good. Although a preliminary examination of our model’s predictability was done here (Figure 5e), the general applicability of theoretical models for...
more complicated materials and different thermodynamic conditions requires further evaluation.

The degradation of the agreement between theoretical and experimental models at large off-stoichiometries in undoped CeO$_2$ (Figure 5b, x < 1.975) can be attributed to the lack of vibrational entropy contributions associated with the spurious stabilization of Ce-O$_2$ under TR conditions. Although better quantitative agreement with experiments is possible if vibrational entropy is explicitly included,[51,52,98,103–105] the increase in computational expense can be prohibitive. Specifically, phonon calculations for the reference states (CeO$_2$, CeO$_{1.5}$, and O$_2$), the competing Ce-oxides (Ce$_7$O$_{12}$, hexagonal-Ce$_2$O$_3$), and all possible x in off-stoichiometric CeO$_x$ (in principle) would be needed. A prior study constructing a DFT-based cluster expansion on CeO$_2$ indeed did report better agreement with experiments when vibrational entropy contributions at CeO$_2$ and CeO$_{1.91}$ were included.[51]

The focus in the present work, though, was to compare the accuracy of sub-lattice models based on “simple and cheap” 0 K DFT-based calculations against qualitative and quantitative experimental trends. It is not surprising that more accurate predictions can be obtained via theoretical models with higher degrees of complexity and costs of computation,[72] but such accurate methods are not practical for materials screening.

Nevertheless, we have included an estimate of the errors that can arise in μ$_T$ predictions and without including the T dependence of G$_{\text{CeO}_2}$, G$_{\text{CeO}_{1.5}}$, I$_0$ and I$_L$ in Section S1, Supporting Information.

The availability of an experimental model guided our CEF parameterization. However, in systems without such models, rules and procedures must be formalized to build theoretical models. Conventional “rules of thumb” exist,[61,62] such as minimizing the number of excess parameters, employing only charge-neutral reference states, and utilizing charge-preserving reciprocal relations. To build reliable theoretical models for higher-component systems (e.g., STC-relevant ternary/quaternary/quinary oxide perovskites[38,41]), such rules of thumb will be crucial because the number of end-members (and hence reference states) required to construct a model will increase with increasing components. For example, ternary-LaMnO$_3$ (versus binary-CeO$_2$) requires 24 (versus four) end-members and five (versus three) reference configurations,[106] when going beyond simpler descriptors such as the energy difference between the perovskite and brownmillerite phases.[34,107] Excess parameters in theoretical models must be estimated with a physical justification and the values appropriately normed so as to ensure robust predictability. Rigorous quantification of errors in both experimental and theoretical model predictions will add insight and guide future work.

6. Conclusion

STC processes offering sustainable pathways to fuels require oxides tolerant to significant oxygen off-stoichiometry over a wide T and p$_O_2$ range. Consequently, any theoretical framework for screening STC candidates must describe off-stoichiometry well and demonstrate predictive capability. Here, we parameterized a thermodynamic sub-lattice model solely using quantum calculations and we demonstrated its ability to predict equilibrium oxygen off-stoichiometries under STC-relevant conditions, validated against SOA undoped and Zr-doped CeO$_2$. Specifically, we calculated energies of reference states and excess parameters needed to build a CEF model and benchmarked our predictions against a model fit to experimental data. We identified a physical way to estimate directly the excess parameters, which conventionally are fit to experimental and/or theoretical data. Similar theoretical models, after careful validation, will be useful for discovering novel off-stoichiometric materials for STC and related applications.

7. Experimental Section

Computational Methods: All DFT calculations were done spin-polarized using the Vienna ab initio simulation package, utilizing the all-electron, frozen-core, projector augmented-wave theory.[108–110] The plane-wave basis, expanded up to a kinetic energy cutoff of 520 eV, was sampled on a dense Γ-point-centered k-point mesh (with a spacing of ±0.03 Å$^{-1}$) for all oxide structures. The total energies were converged to 0.01 meV and the atomic forces were converged to <0.03 eV Å$^{-1}$ similar to computational parameters used in our earlier work.[92] The starting structures of all binary and ternary Ce- and Zr-oxides were taken from the Inorganic Crystal Structure Database.[111] Electron exchange-correlation (XC) was described using the strongly constrained and appropriately normed (SCAN) functional,[112] with a Hubbard U[97] correction of 2 eV added to the Ce’s 4f orbitals to correct for spurious self-interaction errors common within transition-metal and rare-earth oxides. The choice of U value was based on our previous study that benchmarked oxidation energies of metal oxides, including binary Ce-oxides.[71] A U to Zr was not added since it nominally was present in its +4-oxidation state and hence does not contain open-shell d electrons. Additionally, a U correction was not added to calculate the total energies of any elemental species (Ce/Zr/O2), as it was not appropriate for metals or molecules.

Note that we prefer to use the SCAN+U framework instead of the previously employed[113,114] local density approximation (LDA)[115] +U or a generalized gradient approximation (GGA)[116] +U for two reasons: i) SCAN is a more accurate and more well-founded functional than LDA/GGA since it satisfies all 17 known constraints of a XC functional[112] and ii) the absolute U correction required with SCAN is normally lower compared to LDA/GGA, consistent with SCAN containing more of the correct XC physics.[92]

All possible symmetry-distinct oxygen-vacancy configurations were enumerated within the conventional CeO$_{1.5}$ unit cell to evaluate the energy of CeO$_{1.5}$ and we used the lowest energy obtained. For estimating E$_{O_2}$(g), an isolated oxygen molecule was placed in an asymmetric 15 Å × 16 Å × 17 Å cell to obtain the triplet electronic ground state of O$_2$. The oxygen vacancy formation energy in CeO$_2$ and Zr-doped CeO$_2$ (to define L$_0$ and L$_0^{Ce_{1.5},Ce_{4+},Zr_{4+}}$, respectively) was calculated using a 2 × 2 × 2 supercell of the conventional fluorite structure. For estimating the vacancy-vacancy interaction energy (to define L$_1$ and L$_1^{Ce_{1.5},Ce_{4+},Zr_{4+}}$), all of the symmetry-distinct configurations of two vacancies were enumerated within the 2 × 2 × 2 supercell and we used the lowest energy among the considered configurations. Finally, the pymatgen[117] toolkit was used to construct the Ce-O$_2$ (and Ce-Zr-O$_2$) phase diagram and determine the oxygen chemical potential in the solid phase (μ$_O$$_2$) as a function of T. Unless specified otherwise, Gibbs energies of all stoichiometric (G$_{\text{CeO}_2}$, G$_{\text{CeO}_{1.5}}$, G$_{\text{CeO}_{2.5}}$, G$_{\text{ZrO}_2}$, G$_{\text{Ce}_2\text{Zr}_2\text{O}_7}$) structures (Equations (5) and (26)) were approximated as internal energies (E) calculated at 0 K (e.g., G$_{\text{CeO}_2}$ = E$_{\text{CeO}_2}$(theory)). For O$_2$(g), its enthalpy (H$_O_2$(g)) was approximated as the total energy of an isolated O$_2$ molecule at 0 K (E$_{O_2}$(g)).
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

density functional theory, off-stoichiometric materials, solar thermochemical water splitting, sub-lattice models, thermodynamic modeling

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