

Supporting Information

The Effect of Defect Interactions on the Reductions of Doped Ceria

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Mass action law for interacting defects

The change of the Gibbs energy of the doped lattice due to reduction can be expressed as:

$$\Delta G_R = \Delta G_{\text{Ce}'} + \Delta G_V + \Delta G_{\text{O}_2} - k_B T \Delta S_{\text{conf}} + \Delta G_{\text{inter}}$$

This includes:

- The contributions from the formation of polarons, vacancies and oxygen molecules:

$$\Delta G_{\text{Ce}'} = N_{\text{Ce}'} \cdot g_{\text{Ce}'}$$

$$\Delta G_V = N_V \cdot g_V$$

$$\Delta G_{\text{O}_2} = N_{\text{O}_2} \cdot \mu_{\text{O}_2}$$

where $N_{\text{Ce}'}$, N_V , N_{O_2} are the number of polarons, oxygen vacancies, and oxygen molecules, respectively.

- The ideal configurational entropy with the contributions before and after reduction:

$$\Delta S_{\text{conf}} = \ln \frac{(N_{\text{cation}})!}{(N_{\text{cation}} - N_{\text{Ce}'} - N_{\text{dot}})! N_{\text{Ce}'}! N_{\text{dot}}!} + \ln \frac{(N_{\text{anion}})!}{(N_{\text{anion}} - N_V - N_{\text{V,dot}})! (N_V + N_{\text{V,dot}})!} \\ - \ln \frac{(N_{\text{cation}})!}{(N_{\text{cation}} - N_{\text{dot}})! N_{\text{dot}}!} - \ln \frac{(N_{\text{anion}})!}{(N_{\text{anion}} - N_{\text{V,dot}})! N_{\text{V,dot}}!}$$

Where N_{dot} and $N_{\text{V,dot}}$ are the number of dopant ions on cerium sites and the number of oxygen vacancies introduced by doping, respectively and N_{cation} and N_{anion} are the total number of cations or anions.

- ΔG_{inter} , which refers to the total change of Gibbs energy due to defect interactions.

Due to charge neutrality and site balance, the constraints $2N_V = N_{\text{Ce}'}$, $2N_{\text{V,dot}} = N_{\text{dot}}$, and $N_V = 2N_{\text{O}_2}$ can be used and the equation rewritten in terms of the number of oxygen vacancies N_V using the relation $N_{\text{cation}} = \frac{1}{2} N_{\text{anion}} = N_{\text{CeO}_2}$ and $\Delta_r g = 2g_{\text{Ce}'} + g_V + 0.5\mu_{\text{O}_2}$:

$$\begin{aligned}
\Delta G_R &= N_V \cdot \Delta_r g \\
&- k_B T \ln \frac{(N_{\text{CeO}_2})!}{(N_{\text{CeO}_2} - 2N_V - N_{\text{dot}})!(2N_V)! N_{\text{dot}}!} \\
&- k_B T \ln \frac{(2N_{\text{CeO}_2})!}{(2N_{\text{CeO}_2} - N_V - N_{\text{V,dot}})!(N_V + N_{\text{V,dot}})!} \\
&+ k_B T \ln \frac{(N_{\text{CeO}_2})!}{(N_{\text{CeO}_2} - N_{\text{dot}})! N_{\text{dot}}!} + k_B T \ln \frac{(2N_{\text{CeO}_2})!}{(2N_{\text{CeO}_2} - N_{\text{V,dot}})! N_{\text{V,dot}}!} \\
&+ \Delta G_{\text{inter}}
\end{aligned}$$

Minimizing this term with respect to N_V yields:

$$\begin{aligned}
\frac{\partial \Delta G_R}{\partial N_V} &= \Delta_r g + 2k_B T \ln \frac{2N_V}{N_{\text{CeO}_2} - 2N_V - N_{\text{dot}}} \\
&+ k_B T \ln \frac{N_V}{2N_{\text{CeO}_2} - N_V - N_{\text{V,dot}}} + \frac{\partial \Delta G_{\text{inter}}}{\partial N_V} \stackrel{\text{def}}{=} 0
\end{aligned}$$

Using again the previous constraints and introducing the lattice mole fraction $\frac{N_{\text{Ce}'}}{N_{\text{CeO}_2}} = [\text{Ce}']$ and

$\frac{N_V}{N_{\text{CeO}_2}} = [\text{V}_{\text{O}}^{\bullet}] = \delta$ leads to:

$$\Delta_r g + 2k_B T \ln \frac{[\text{Ce}'_{\text{Ce}}]}{[\text{Ce}^x_{\text{Ce}}]} + k_B T \ln \frac{[\text{V}_{\text{O}}^{\bullet}]}{[\text{O}_{\text{O}}^x]} + \frac{\partial \Delta_r g^{\text{int}}(T, \delta, N_{\text{dot}})}{\partial \delta} = 0$$

Rearranging results in:

$$\frac{[\text{V}_{\text{O}}^{\bullet}][\text{Ce}'_{\text{Ce}}]^2}{[\text{O}_{\text{O}}^x][\text{Ce}^x_{\text{Ce}}]^2} = \exp\left(-\frac{\Delta_r g}{k_B T}\right) \exp\left(-\frac{\partial \Delta_r g^{\text{int}}}{k_B T \partial \delta}\right)$$

or

$$\frac{[\text{V}_{\text{O}}^{\bullet}][\text{Ce}'_{\text{Ce}}]^2}{[\text{O}_{\text{O}}^x][\text{Ce}^x_{\text{Ce}}]^2} p_{\text{O}_2}^{\frac{1}{2}} = \exp\left(-\frac{\Delta_r g^\circ}{k_B T}\right) \exp\left(-\frac{\partial \Delta_r g^{\text{int}}}{k_B T \partial \delta}\right) = K(T) \cdot K_{\text{int}}(T, \delta)$$

$\Delta_r g^\circ$ is the standard Gibbs energy of reduction and $\Delta_r g^{\text{int}}$ is the additional contribution per formula unit due to defect interactions. Neglecting volume changes in the solid, the approximation $\Delta_r g^{\text{int}} \approx \Delta_r f^{\text{int}}$ is applicable and we obtain

$$\frac{[\text{V}_{\text{O}}^{\bullet}][\text{Ce}'_{\text{Ce}}]^2}{[\text{O}_{\text{O}}^x][\text{Ce}^x_{\text{Ce}}]^2} p_{\text{O}_2}^{\frac{1}{2}} = \exp\left(-\frac{\Delta_r g^\circ}{k_B T}\right) \exp\left(-\frac{\partial \Delta_r f^{\text{int}}}{k_B T \partial \delta}\right) = K(T) \cdot K_{\text{int}}(T, \delta)$$

Calculation of $\Delta_r u^{\text{int}}$ and $\Delta_r f^{\text{int}}$

The Metropolis Monte Carlo algorithm samples a sequence of states in thermodynamic equilibrium with the probability of each state being proportional to the respective Boltzman factor:

$$m \cdot M(E, T) = \Omega(E) \cdot \exp\left(\frac{-E}{k_B T}\right)$$

Here, $M(E, T)$ is the sampled distribution, $\Omega(E)$ is the total configurational space, and m is a proportionality constant. The interaction contribution to the internal energy per formula unit u^{int} is then just the average of the sampled states:

$$u^{\text{int}} = \frac{1}{2} \cdot \langle \sum_i \sum_j E_{ij} \rangle_{\text{MCS}} / N_{\text{CeO}_2} = \langle M(E, T) \rangle_E / N_{\text{CeO}_2}$$

The contribution to the internal energy of reduction $\Delta_r u^{\text{int}}$ is given by the difference between stoichiometric and non-stoichiometric composition.

However, as only a small part of the configurational space is sampled and the proportionality constant m is not known, the direct evaluation of the partition function and the free energy is not possible.

This problem is circumvented with the approach by Valleau and Card¹ where the sampled distribution $M(E, T_{\text{min}})$ is connected to the random, non-interacting distribution $\Omega^*(E)$ by a series of bridging distributions. The bridging distributions are defined by their temperatures that are given by the factor $\alpha = T_{\text{min}}/T$. For $\alpha = 1$ the desired distribution is obtained and for $\alpha = 0$ the random distribution is sampled. From the overlap of subsequent distributions, the individual factor m'_i can be obtained and the free energy of interaction, i.e. the difference between the interacting and the non-interacting system can be calculated from:

$$F_{\text{int}} = -k_B T \cdot \sum \ln(m'_i)$$

The contribution to the free energy of reduction $\Delta_r f^{\text{int}}$ is given by the difference between stoichiometric and non-stoichiometric composition.

Energy parameters

Pair interaction energies were taken from refs.^{2,3}. These energies were calculated with DFT+U using the PBE functional and $U_{\text{eff}} = 5$ eV.

Trivalent Cation interactions

Table 1: Pair interactions for trivalent cations in eV.

RE ³⁺	RE' _{Ce} - V _O ^{••} 1NN	RE' _{Ce} - V _O ^{••} 2NN	RE' _{Ce} - Ce' _{Ce} 1NN
Sc	-0.75	-0.22	0.1
Lu	-0.48	-0.12	0.1
Y	-0.35	-0.14	0.1
Gd	-0.29	-0.13	0.1
Sm	-0.24	-0.14	0.1
Nd	-0.18	-0.17	0.1
Ce	-0.14	-0.19	0.1
La	-0.12	-0.20	0.1

Vacancy-vacancy interactions

Table 2: Pair interactions between two vacancies, depending on the distance. 3 NN(a) and 3 NN(b) differentiate interactions without and with a cation position between the vacancies.

Neighbor position	interaction / eV
1 NN	0.90
2 NN	0.33
3 NN(a)	0.32
3 NN(b)	0.46
4 NN	0.34

Zirconium ion interactions

Table 3: Interactions for defect pairs containing zirconium ions in ceria.

Defect pair	interaction / eV
$\text{Zr}_{\text{Ce}}^{\times} - \text{V}_{\text{O}}^{\bullet\bullet}$ 1NN	-0.6
$\text{Zr}_{\text{Ce}}^{\times} - \text{V}_{\text{O}}^{\bullet\bullet}$ 2NN	-0.05
$\text{Zr}_{\text{Ce}}^{\times} - \text{Zr}_{\text{Ce}}^{\times}$ 1NN	-0.01
$\text{Zr}_{\text{Ce}}^{\times} - \text{Y}'_{\text{Ce}}$ 1NN	0.0
$\text{Zr}_{\text{Ce}}^{\times} - \text{Gd}'_{\text{Ce}}$ 1NN	0.0
$\text{Zr}_{\text{Ce}}^{\times} - \text{Ce}'_{\text{Ce}}$ 1NN	0.0

References

1. J. P. Valleau, *The Journal of Chemical Physics*, 1972, **57**, 5457.
2. S. Grieshammer, M. Nakayama and M. Martin, *Phys. Chem. Chem. Phys.*, 2016, **18**, 3804–3811.
3. S. Grieshammer, *J Phys Chem C*, 2017, **121**, 15078-15084.