

Supporting Information

Reduction enthalpy and charge distribution of substituted ferrites and doped ceria for thermochemical water and carbon dioxide splitting with DFT+U

Dimitrios A. Dimitrakis, Nikolaos I. Tsongidis, Athanasios G. Konstandopoulos

S1. Calculation of the chemical potential of oxygen

The chemical potential of an Oxygen atom, μ_{O} , is taken to be half of the calculated total energy of a free, isolated, spin polarized oxygen molecule (triplet) with the GGA-PBE method, using a supercell of $12 \times 12 \times 12 \text{Å}^3$, a cutoff energy of 520eV, forces criterion of under 0.001eV/Å, electronic ground state convergence of 10^{-7} eV and the PAW PBE O potential supplied with VASP version 4.6.

Because GGA is known to significantly overestimate the binding energy of O_2 even by more than 1.5eV [1-3], a correction was applied to the O_2 total energy, by comparing the calculated binding energy to the experimental value of 5.12eV [4,5].

We calculate a binding energy of 6.65eV, which is higher than the experimental value by +1.53eV. This correction is applied to the oxygen molecule total energy bringing it higher to -8.32eV, which lies close to previous GGA calculations [2]. A zero point energy correction has not been considered in the present study.

The correction follows equations (S1)-(S3):

$$BE_{\text{calc}} = 2E_{\text{Oat}} - E_{\text{O2mol}} \quad (\text{S1})$$

$$E_{\text{corr}} = BE_{\text{calc}} - BE_{\text{exp}} \quad (\text{S2})$$

$$E_{\text{O2corr}} = E_{\text{O2mol}} + E_{\text{corr}} \quad (\text{S3})$$

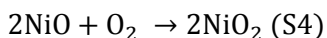
where, BE_{calc} is the calculated binding energy of the oxygen molecule, E_{Oat} is the total energy of a single oxygen atom, E_{O2mol} is the total energy of an oxygen molecule, E_{corr} is the correction applied, defined as the difference between the calculated binding energy and the experimental binding energy BE_{exp} , and E_{O2corr} is the corrected oxygen molecule total energy used in the calculations.

S2. Hubbard term (U)

The approach of Dudarev et al. [6] is used in this study, with a single effective interaction parameter, U-J, to define the on-site Coulomb interaction, in which the U parameter and the exchange parameter J are combined under a spherically average, named simply as U.

In order to determine the optimum U value for each transition and rare earth metal evaluated in the current work, parametric studies with respect to discrete U values (1 to 8 eV with a step of 1 eV) were undertaken aiming to generate results, namely lattice parameters, partial magnetic moments, band gaps and heats of formation of the most stable oxides of the selected elements. This database was utilized to set the computation parameters of the complex mixed metal oxides tested.

The heat of formation of the oxides is calculated with the following rationale as presented in the equations (S4)-(S6), using nickel (II) oxide oxidation reaction to nickel (IV) oxide as an example:



$$\Delta H_{\text{rxn}}^{\text{DFT}} = 2 \cdot (E_{\text{totNiO}_2})_{\text{calc}} - 2 \cdot (E_{\text{totNiO}})_{\text{calc}} - (E_{\text{totO}_2})_{\text{calc}} \quad (\text{S5a})$$

$$\Delta H_{\text{rxn}}^{\text{exp}} = 2 \cdot (\Delta H_f^{\circ} \text{NiO}_2)_{\text{exp}} - 2 \cdot (\Delta H_f^{\circ} \text{NiO})_{\text{exp}} \quad (\text{S5b})$$

$$\Delta H_{\text{rxn}}^{\text{DFT}} = \Delta H_{\text{rxn}}^{\text{exp}} \quad (\text{S6a})$$

$$\Delta H_f^{\circ} \text{NiO} = (\Delta H_f^{\circ} \text{NiO}_2)_{\text{exp}} - (E_{\text{tot}} \text{NiO}_2)_{\text{calc}} + (E_{\text{tot}} \text{NiO})_{\text{calc}} + \frac{1}{2} (E_{\text{tot}} \text{O}_2)_{\text{calc}} \quad (\text{S6b})$$

Where $\Delta H_f^{\circ} \text{NiO}$ is the calculated heat of formation of NiO, $(\Delta H_f^{\circ} \text{NiO}_2)_{\text{exp}}$ the experimental heat of formation of NiO₂, $(E_{\text{tot}} \text{NiO}_2)_{\text{calc}}$ and $(E_{\text{tot}} \text{NiO})_{\text{calc}}$ the calculated total electronic energies of NiO₂ and NiO, respectively, as obtained by VASP results and, finally, $(E_{\text{tot}} \text{O}_2)_{\text{calc}}$ the corrected energy of an O₂ molecule.

In the cases of Fe, Co, Ni and Ce, parametric studies have been carried out and compared with the available experimental data (Tables S1, and S2 for the U that gives values closest to experiment). A simple stable oxide structure for each element is selected and a structure relaxation is performed with a cutoff energy of 400eV and a k-mesh of 0.5/Å for the primitive unit cell. This translates into (4x4x4), (4x3x4) and (3x3x3) k-meshes in Brillouin Zone for NiO, CoO and Fe₃O₄/CeO₂ respectively. Magnetism was also included according to experimental data. After the relaxation calculations for each U value, single point energy calculations are performed. The results of each parameter with respect to the U values are presented in Figure S1 a-d. The reference values are depicted by dashed lines, while the computational by points of different shape and color. The selected U values that give the best correlation to experimental values for all parameters are shown in Table S3.

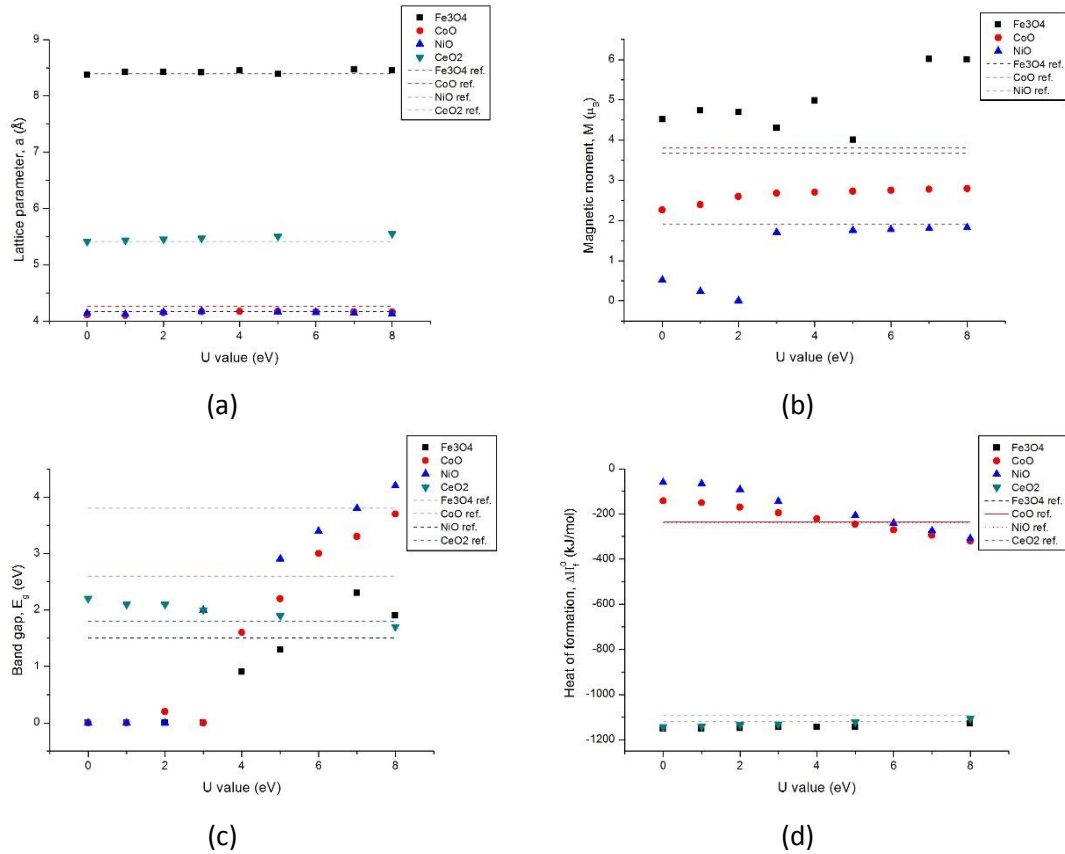


Figure S1 a) Lattice parameter, b) Magnetic moment, c) Band gap, d) Heat of formation vs. U value

Table S1. Calculated lattice parameters (Å) and magnetic moments M (μ_B) for optimum U

Oxide	Lattice parameter a (Å)			Magnetic moments M (μ_B)		
	LDA or GGA	DFT + U	Expt.	LDA or GGA	DFT + U	Expt.
Fe ₃ O ₄	8.375	8.388	8.396[7]	4.5	4.0	3.7[11,12]
CoO	4.114	4.172	4.260[8]	2.3	2.7	3.8[13]
NiO	4.141	4.141	4.170[9]	0.5	1.8	1.9[13]
CeO ₂	5.414	5.507	5.410[10]	0.0	0.0	0.0[14]

Table S2. Calculated band gaps E_g (eV) and heat of formation ΔH_f^0 (eV) for optimum U

Oxide	Band gap E _g (eV)			Heat of formation (kJ/mol)		
	LDA or GGA	DFT + U	Expt.	LDA or GGA	DFT + U	Expt.
Fe ₃ O ₄	0.0	1.3	1.5[15]	-1151.5	-1145.2	-1120.9[18]
CoO	0.0	2.2	2.6[16]	-141.6	-245.9	-236.9[19]
NiO	0.0	3.8	3.8[16]	-60.5	-274.5	-240.3[19]
CeO ₂	2.2	1.9	1.8[17]	-1143.9	-1121.3	-1090.4[20]

For elements Zr, Gd and Hf, due to lack of readily available experimental thermodynamic data of their more rare oxides which would enable us to compare the heat of formation, U values were directly adopted from literature studies (Table S3).

Table S3. Selected U values

Selected U (eV)	Element						
	Fe	Co	Ni	Ce	Zr	Gd	Hf
	5	5	7	5	4[21]	6[22]	4[21]

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