Quantifying Uncertainty in Activity Volcano Relationships for Oxygen Evolution Reaction

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Motivation

- Water Splitting- key process in hydrogen production from sunlight and other sources of electricity.
- Current major hydrogen source is steam reforming of fossil fuel which generates GHG – CO_2 as by-product.

Formation Energies of Bulk Rutile dioxides

- It is important to ascertain the accuracy of DFT calculations with BEEF-vdW exchange correlation for the formation energies of Rutile dioxides.
- Hence we compared the DFT-BEEF-vdW calculations of formation energies with the experimentally obtained values from the electrochemical series.
- Poor DFT description of the O_2 molecule was avoided by using H_2O rather than O_2 as the reference for oxygen on the calculation of the heat of formation.[1] Following reaction was used:

$$M \ (bulk) + 2H_2O \ (l) \rightarrow MO_2 \ (bulk) + 2 \ H_2 \ (g)$$
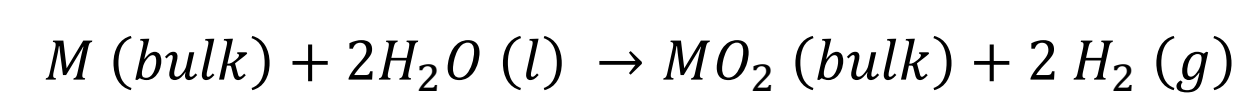
$$\Delta G_{form} = G[MO_2 \ (bulk)] + 2G[H_2 \ (g)] - \{G[M \ (bulk)] + 2G[H_2O \ (l) \ ]\}$$
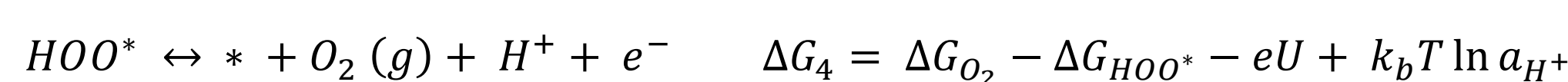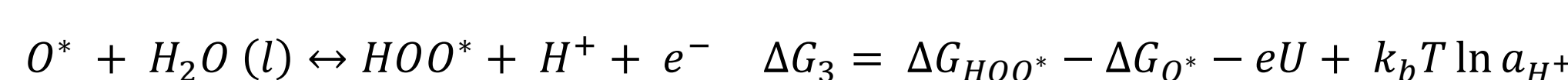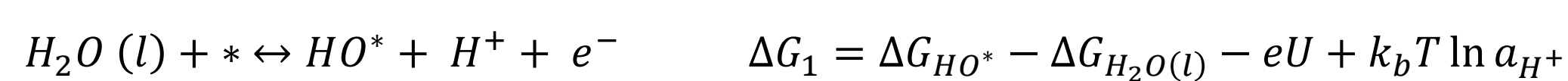
- For bulk crystals the entropy (S) and zero-point energy (ZPE) effects have been neglected as at room temperature, these values are negligible.
- The experimental change in free energy is found via the dissolution potentials of these two reactions :

$$M \ (bulk) \leftrightarrow M^{n+} + ne^-$$

$$MO_2 \ (bulk) + 4H^+ + (4-n)e^- \leftrightarrow M^{n+} + 2H_2O \ (l)$$
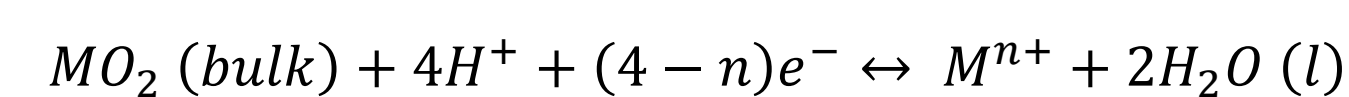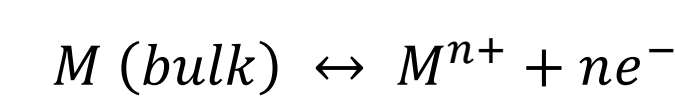
- Figure 1 shows the calculated ΔG_{form} for a large number of rutile metal dioxide as a function of the experimental values (ΔG_{expt}) extracted from the above equations (electrochemical series)[2-4] .

Oxygen Evolution Reaction

- Following four electron reaction transfer is used for the describing the reaction mechanism:

$$H_2O \ (l) + * \leftrightarrow HO^* + H^+ + e^- \quad \Delta G_1 = \Delta G_{HO^*} - \Delta G_{H_2O(l)} - eU + k_bT \ln a_{H^+}$$

$$HO^* \leftrightarrow O^* + H^+ + e^- \quad \Delta G_2 = \Delta G_{O^*} - \Delta G_{HO^*} - eU + k_bT \ln a_{H^+}$$

$$O^* + H_2O \ (l) \leftrightarrow HOO^* + H^+ + e^- \quad \Delta G_3 = \Delta G_{HOO^*} - \Delta G_{O^*} - eU + k_bT \ln a_{H^+}$$

$$HOO^* \leftrightarrow * + O_2 \ (g) + H^+ + e^- \quad \Delta G_4 = \Delta G_{O_2} - \Delta G_{HOO^*} - eU + k_bT \ln a_{H^+}$$

- ΔG_{1-4} has been calculated using computational Standard Hydrogen Electrode (SHE). Hence the proton and an electron is replaced with half a hydrogen molecule at U = 0 V vs. SHE.
- The free energies vary in the same way with pH and U, hence the potential determining step is independent of the pH and U. Therefore, the analysis performed for the free energies is at Standard Conditions (pH=0, T=298.15 K) and U=0.
- Potential determining step is defined as the last step to become downhill in the free energy as the potential increases, i.e., the specific reaction step in the four-step mechanism with the largest ΔG:

$$G^{OER} = \max[\Delta G_1^0, \Delta G_2^0, \Delta G_3^0, \Delta G_4^0]$$

- Overpotential which is independent of pH, at standard conditions is given by:

$$\eta^{OER} = \left(\frac{G^{OER}}{e}\right) - 1.23 \ V$$
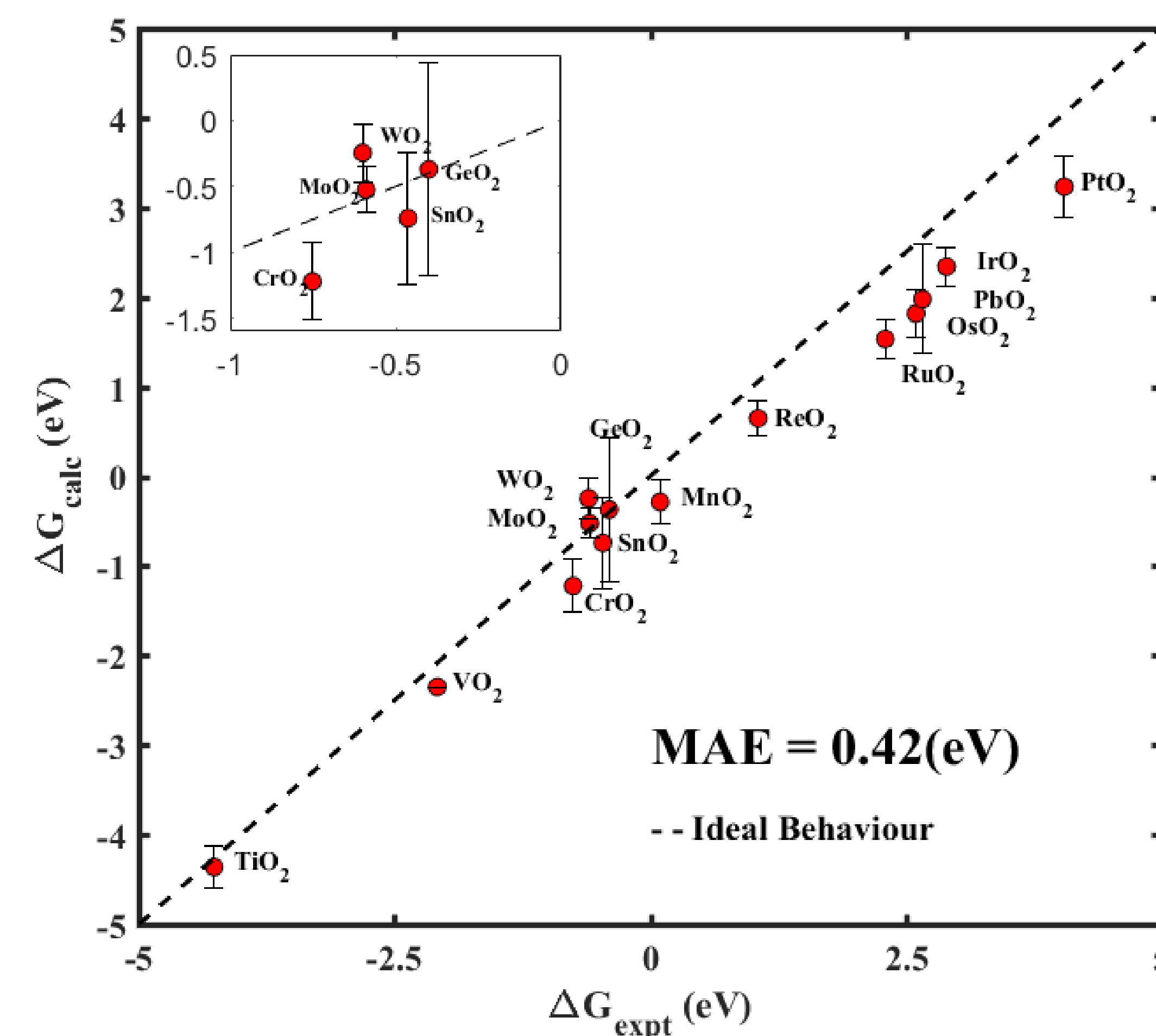
Results

Figure 1. Calculated formation energies of various representative rutile metal dioxides as a function of the experimental values extracted from the electrochemical series.[2-4] A mean absolute error =MAE =$(\sum_i^n (y_i - x_i))/n$ with respect to the experimental values was found to be 0.416 eV using BEEF-vdW exchange correlation. A MAE of 0.29 eV had been reported earlier using RPBE exchange correlation.
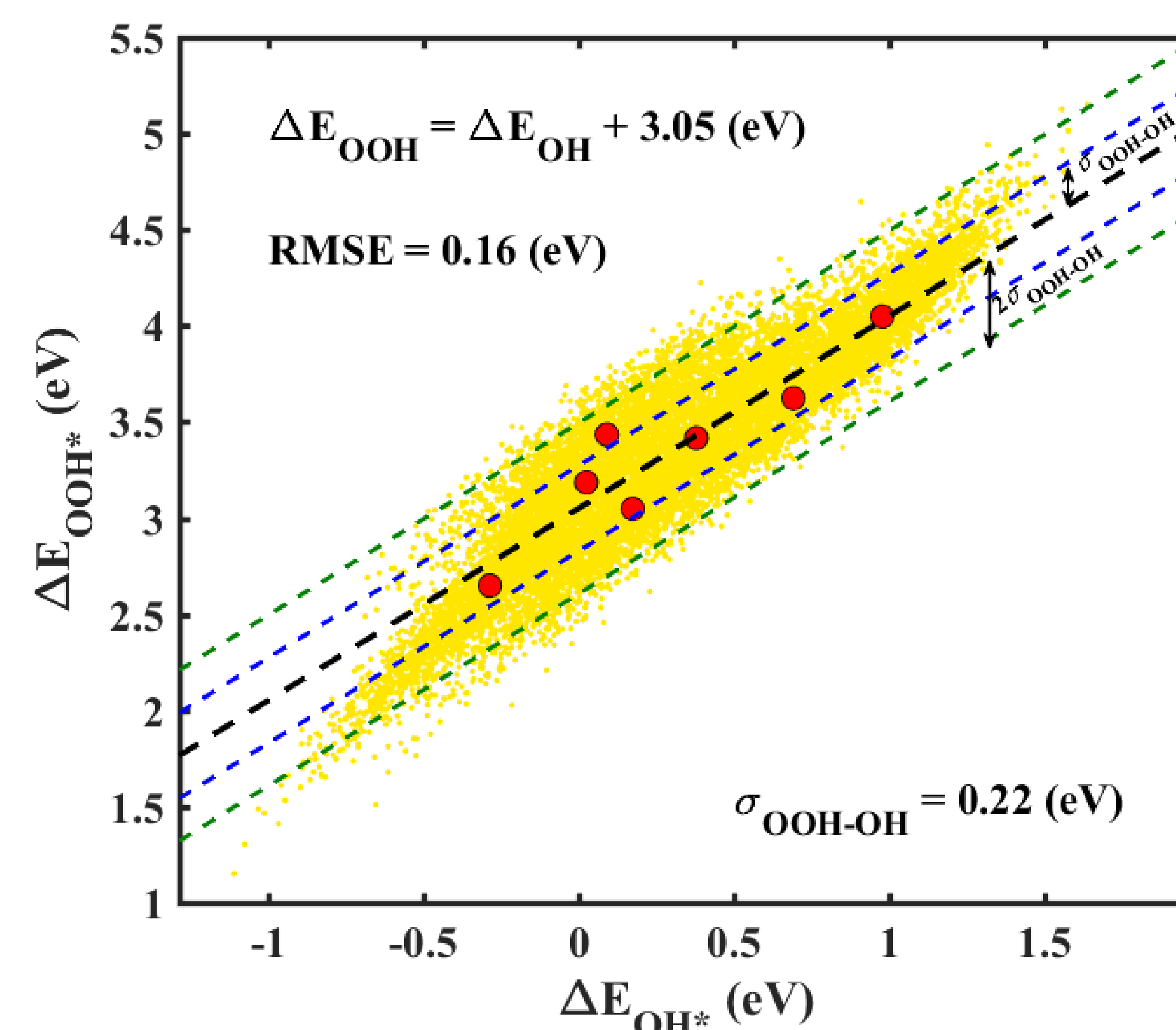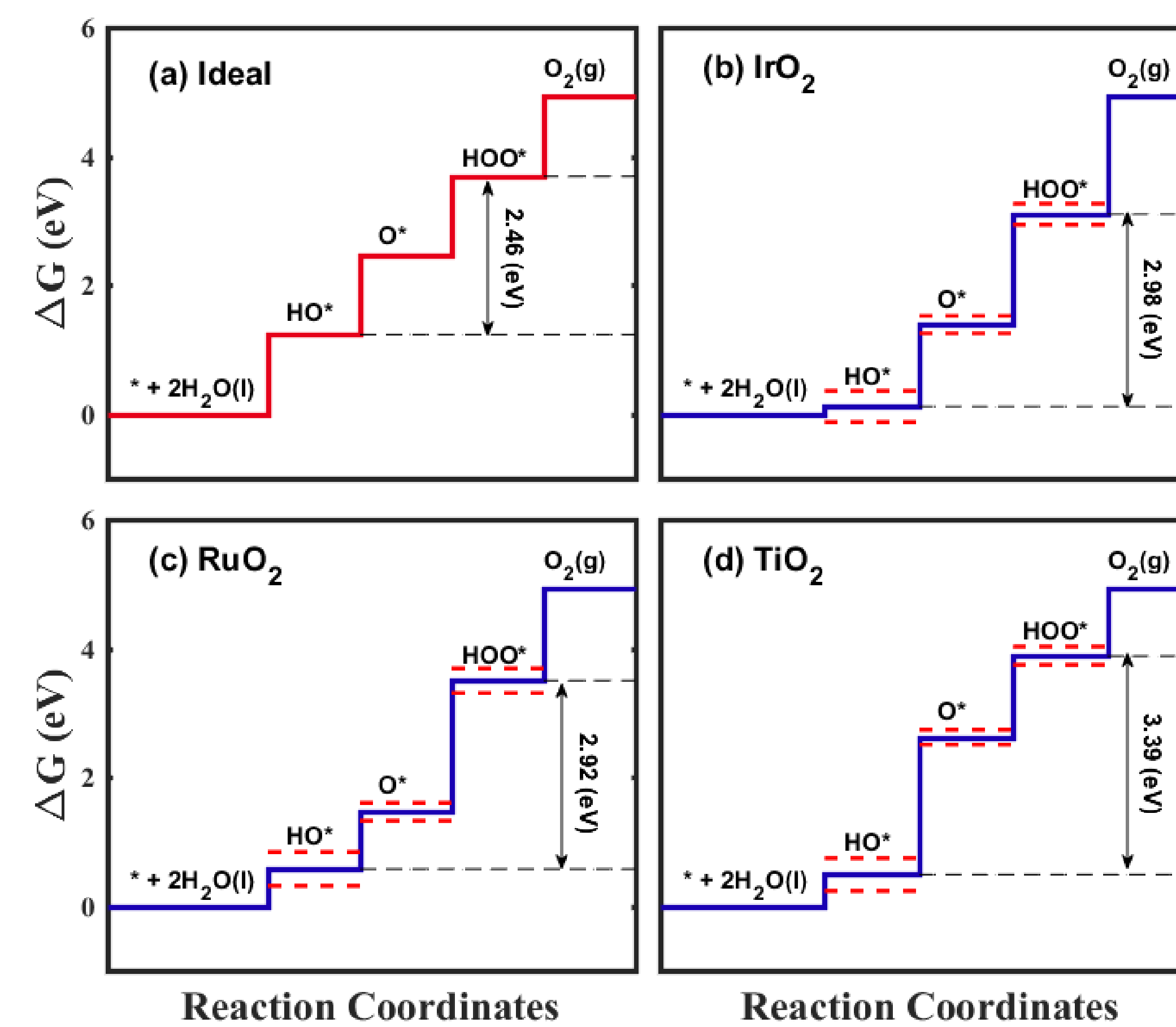

Figure 2. Standard Free energy diagram for the OER at zero potential (U=0) at pH = 0 and T = 298.15 K for: (a) Ideal Catalyst, (b) IrO_2 , (c) RuO_2 , (d) TiO_2. Fall all the real catalysts (b,c,d), $\Delta G_{O^*}^0 - \Delta G_{HO^*}^0$ is approximately constant with an average value of 3.0503 eV, where as the optimum value (ideal) is 2.46 eV. The dashed (red) lines represent the uncertainty in the respective free energies using BEEF-vdW exchange correlation.

Figure 3. Adsorption energy of HOO^* plotted against the adsorption energy of HO^* on rutile metal dioxide (110) surface. The red dots represent the calculated adsorption energies for various surfaces while the yellow dots represent the respective ensemble of energies generated. The scaling line (black dashed) has the equation: $\Delta E_{OOH} = \Delta E_{OH} + 3.0503 \ (eV)$. The blue and green dashed lines represent one and two standard deviations ($\sigma_{(OH^*-OOH^*)}$ and $2 \times \sigma_{(OH^*-OOH^*)}$).
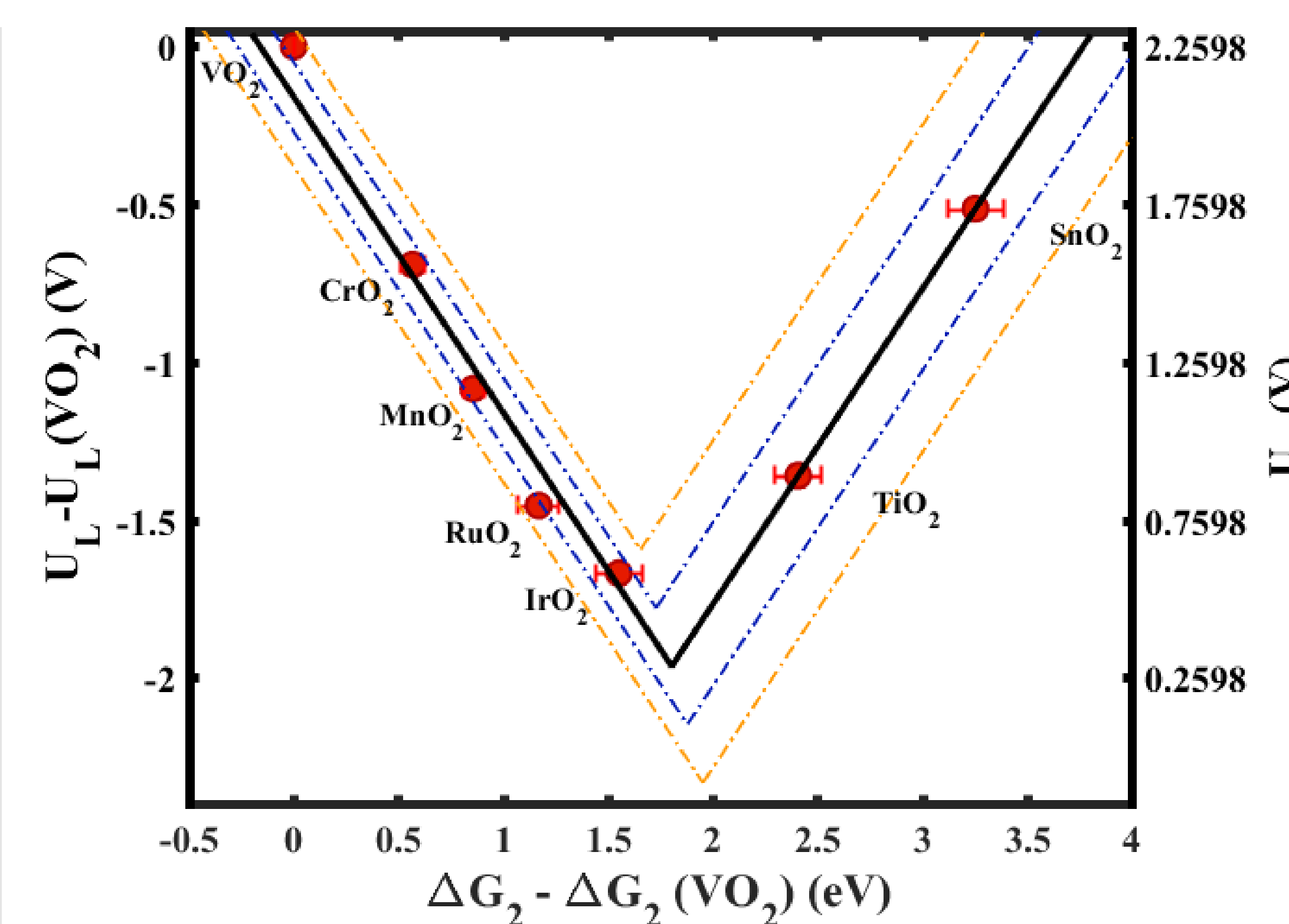

Figure 4. Volcano plot as a result of the unique descriptor for the OER activity. The negative values of overpotential were plotted against free energy difference ($\Delta G_{O^*}^0 - \Delta G_{HO^*}^0$). The errorbars represent the uncertainty in the difference of the free energies.

Scaling Relations

- A correlated energy phenomenon has been observed on metal oxide surfaces as a result of scaling relations between the intermediates.[5-6]
- From figure 2 and figure 3, it can be seen that the free energy difference between HO^* and HOO^* is almost constant, independent of the binding strength of the surface.
- Following relation is found:

$$\Delta E_{OOH} = \Delta E_{OH} + 3.0503 \ (eV)$$

- BEEF-vdW Energy ensemble is used to get the standard deviation of the intercept which is found to be 0.2221 eV.

Descriptor and Activity Volcano

- Given the constant difference between the HO^* and HOO^* levels, the difference ($\Delta G_{O^*}^0 - \Delta G_{HO^*}^0$) can be used as a unique descriptor for the OER activity.
- This means that either step (2) or step (3) is the potential determining equation:

$$G^{OER} = \max[\Delta G_2^0, \Delta G_3^0] = \max[(\Delta G_{O^*}^0 - \Delta G_{HO^*}^0), (\Delta G_{HOO^*}^0 - \Delta G_{O^*}^0)]$$

$$\approx \max[((\Delta G_{O^*}^0 - \Delta G_{HO^*}^0), 3.2 - (\Delta G_{O^*}^0 - \Delta G_{HO^*}^0)]$$

$$\eta^{OER} = \{\max[((\Delta G_{O^*}^0 - \Delta G_{HO^*}^0), 3.2 - (\Delta G_{HO^*}^0)]/e\} - 1.23 \ V$$

- Plotting η^{OER} as a function of $\Delta G_{O^*}^0 - \Delta G_{HO^*}^0$ leads to a volcano relationship independent of the catalyst material (Figure 4).

Adsorption Site
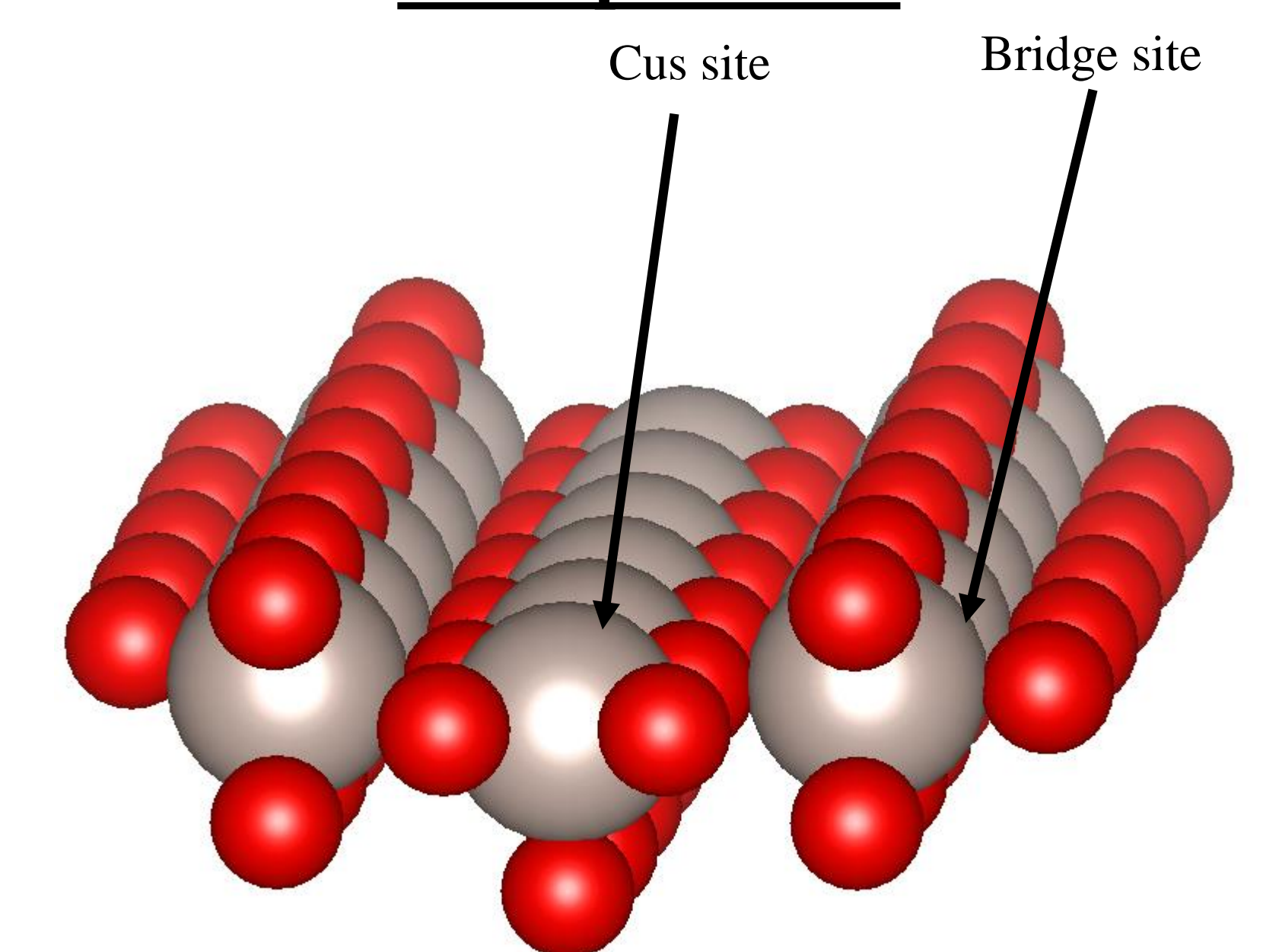
- Figure 5. Visualization of the considered surface structure of rutile metal dioxide (110 facet). Rutile-like stoichiometric surface (110) for MO_2 with M = Ir, Ru, Ti, Mn, Cr, Sn, V. Red and grey spheres represent O and metal atoms respectively. Bridges are inactive sites and are covered with oxygen while the cus site is active sites (cus).

References

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