

Comparing Electrochemical and Biological Water Splitting

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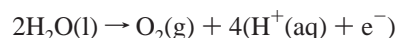
On the basis of density functional theory calculations, we compare the free energies of key intermediates in the water splitting reaction over transition metal oxide surfaces to those of the Mn cluster in photo system II. In spite of the very different environments in the enzyme system and on the inorganic catalyst surface of an acidic electrolysis cell, the thermochemical features of the catalysts can be directly compared. We suggest a simple test for a thermochemically optimal catalyst. We show that, although both the RuO₂ surface and the Mn cluster in photo system II are quite close to optimal, the biological catalyst appears to be best.

Electrochemical water splitting is a key process in hydrogen production from sunlight, either by first using a photovoltaic cell to generate an electrostatic potential followed by electrolysis or in an integrated process such as the Graetzel cell.¹ At the anode, water is split and molecular oxygen evolves together with protons and electrons. At the cathode, molecular hydrogen is produced by recombination of the protons and electrons. The anode reaction is found to be associated with slow kinetics, and an effective catalyst for the oxygen evolution reaction is needed. The best anode catalysts known today is RuO₂^{2,3} sometimes mixed with IrO₂.^{4,5}

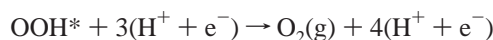
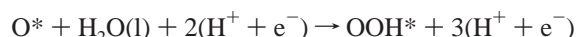
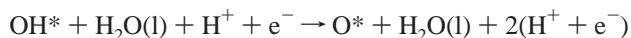
The water splitting and oxygen evolution process has a biological analogue in photosynthesis. The catalytically active part of the photo system II enzyme is a Mn–O cluster.^{6,7} This cluster is the result of evolution through billions of years, and it is likely to be a highly effective catalyst system.

In the present letter, we make a comparison between the catalytically active sites of the inorganic and biological water splitting catalysts. We do that using a simple scheme developed for understanding trends in the electrocatalytic activity.^{8,9} Using density functional theory calculations, we estimate the free energy of key intermediates in the reaction and show that the two kinds of water splitting reactions can be described in the same framework. We introduce the concept of the thermochemically optimal catalyst and show that, although the best known inorganic catalyst, RuO₂, is quite close to optimal, the model of the biological system is even closer. This finding gives some hope that better inorganic electrocatalysts can be found. It may also indicate why the Mn cluster is unique in biology.

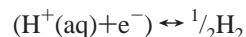
In the following, we consider the free energies of the intermediates in the oxygen evolution reaction as a function of the electron potential. The free energy is obtained on the basis of density functional theory calculations as outlined in refs 8 and 9. The reaction can be written



On the surfaces, we have found that a likely reaction pathway is the following:⁹



In all of the calculations, we refer the free energy of (H⁺(aq) + e[−]) to that of gas-phase H₂ by using that at standard conditions (298 K, pH = 0, p_{H2} = 1 bar) the free energy change for the reaction



is $\Delta G = eU$, where U is the electrode potential relative to the standard hydrogen electrode.⁸

The free energy of the intermediates on rutile RuO₂ (110) surface is shown in Figure 1 for three different potentials: the open cell potential, 0 V, the equilibrium potential, 1.23 V, and the lowest potential, 1.60 V, at which there is no reaction step where the free energy change is positive. At potentials where all reaction steps are downhill in free energy, we consider the total reaction facile, since at potentials where one or more of the elementary reaction steps are uphill an extra activation free energy develops, slowing down the reaction. We note that there are additional activation barriers associated with the formation of the oxygen–oxygen bond.¹⁰ There could also be barriers for the proton/electron-transfer reactions. A negative reaction free energy for all reaction steps is therefore not a sufficient criterion for a facile reaction, and the following analysis concentrating

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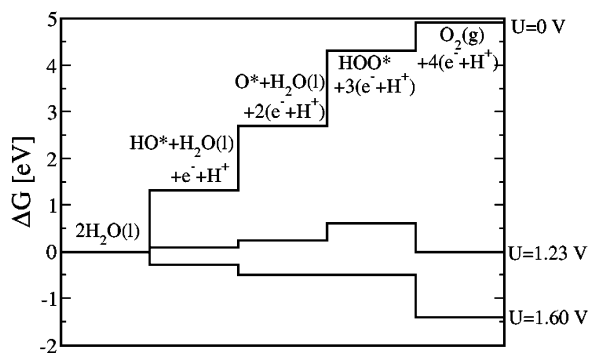


Figure 1. Calculated free energies for intermediates of the oxygen evolution reaction on RuO_2 at three potentials (relative to the standard hydrogen electrode): zero potential ($U = 0$ V), the equilibrium potential ($U = 1.23$ V), and the lowest potential at which all steps are downhill in free energy ($U = 1.60$ V).

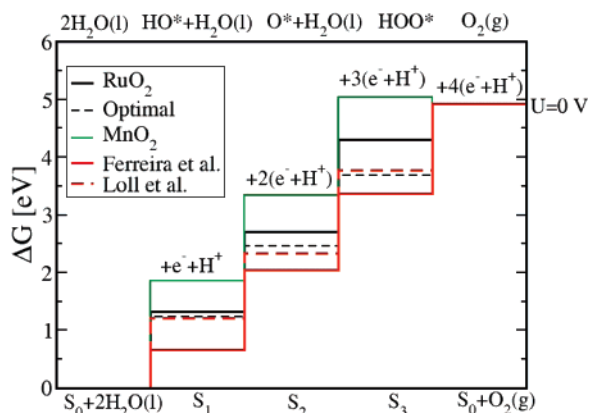


Figure 2. Relative free energies for intermediates along the oxygen evolution reaction for RuO_2 (black, solid line), the optimal catalyst (dashed black line), MnO_2 (green line), and energies from ref 10 for two different X-ray structures of the Mn-cluster found in enzymes (red line represents the Ferreira et al.⁶ structure and red dashed line represents the Loll et al.⁷ structure).

on reaction free energies will therefore only establish a minimum set of requirements for a facile reaction.

For simplicity, we term the difference between the lowest potential where all steps are downhill and the equilibrium potential the theoretical overpotential η_T . The results of DFT calculations shown in Figure 1 give a value of $\eta_T = 1.60 - 1.23$ V = 0.37 V. The low value of η_T shows that the calculations describe the experimentally established fact that RuO_2 surfaces are good water splitting catalysts.^{2–5}

The perfect oxygen evolution catalyst should be able to facilitate water oxidation just above the equilibrium potential (where the over all reaction free energy is just becoming negative). In the present analysis, this would require all oxidation steps to have reaction free energies of zero at the equilibrium potential. This is equivalent to having all reaction free energies of the same magnitude at zero potential. In Figure 2, we show the free energy profile of such a catalyst. We will refer to this as the thermochemically optimal catalyst. It can be seen in Figure 2 that RuO_2 is quite close to the optimum, except for the third step, which gives rise to the overpotential, η_T .

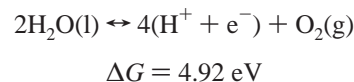
Now we attempt to include data for the Mn cluster active site of PSII.¹⁰ In these calculations, four different oxidation states S_0 – S_3 for the Mn cluster are considered, and these states are not directly the same as for the surface reaction. In the biological Mn cluster, protons and electrons are transferred to P_{680}^+ , which defines the chemical potential of the hydrogen atoms in the enzyme. For a full catalytic cycle, the total change in free energy

TABLE 1: Translation of Chemical Reference System^a

	ΔG^{10} [eV]		ΔG^\ominus vs SHE
$S_0 + 2\text{H}_2\text{O}(\text{l})$	0 (0)	0×1.73 V	0
$S_1 + \text{H}^+ + \text{e}^-$	-1.07 (-0.53)	$\text{e} \times 1.73$ V	0.66 (1.20)
$S_2 + 2(\text{H}^+ + \text{e}^-)$	-1.42 (-1.13)	$2\text{e} \times 1.73$ V	2.04 (2.33)
$S_3 + 3(\text{H}^+ + \text{e}^-)$	-1.81 (-1.41)	$3\text{e} \times 1.73$ V	3.37 (3.77)
$S_0 + \text{O}_2(\text{g}) - 2\text{H}_2\text{O}(\text{l})$	-1.99 (-1.99)	5.91 eV	4.92 (4.92)
$+ 4(\text{H}^+ + \text{e}^-)$			

^a The energies from ref 10 in eV for the different oxidation states of the Mn cluster. Ferreira et al. structure⁶ (Loll et al. structure⁷) are listed in the different rows. (1) In the first column the relative free energies are listed with the chemical potential of $\text{H}^+ + \text{e}^-$ defined by P_{680}^+ . (2) In the second column shows the change in potential between the P_{680}^+ and the standard hydrogen electrode calculated based on the change in energy for the full catalytic cycle: $(4.92 - -1.99 \text{ eV})/4\text{e} = 1.73$ V per $(\text{H}^+ + \text{e}^-)$. (3) In the third column is the chemical potential of $\text{H}^+ + \text{e}^-$ changed to that of the standard hydrogen electrode (SHE). This means that the change in free energy is ΔG^\ominus .

is -46.0 kcal/mol (-1.99 eV) including zero-point energy. We would like to apply the standard hydrogen electrode as reference for the hydrogen chemical potential as done above. At standard conditions, the change in free energy for the full catalytic cycle is



The procedure used for shifting the reference is shown in Table 1. Having the same reference for the inorganic oxide surfaces and the Mn cluster in enzymes, it is possible to compare the two systems directly. We note that the calculations for the inorganic and biological catalysts have been done using different exchange-correlation functionals. The calculations on the surfaces have been done with RPBE and the Mn clusters with B3LYP. For the comparisons we make here, it is only the relative heights of the reaction free energy steps for a given system (determining η_T) that is important. Since the reference is water and molecular hydrogen, all of the states have the same number of bonds, which means that most of the systematic error and difference between functionals cancels. Between RPBE and PW91, the η_T for RuO_2 is only changed with 0.03 V. The differences in functionals are therefore not a primary concern for this property.

Calculations have been performed¹⁰ for two different experimentally determined structures of the Mn cluster: the Ferreira et al. structure⁶ and the Loll et al. structure.⁷ The two structures give quite similar results giving theoretical overpotentials (at pH = 0) of $\eta_T = 0.32$ and 0.21 V, respectively. Both values are smaller than that of RuO_2 .

Given the composition of the active site in the biological catalyst, it is interesting to include a $\text{MnO}_2(110)$ surface in the present analysis. We have done similar calculations for this compound (see Figure 2), showing, in agreement with experiment,³ that it is a fairly good catalyst for oxygen evolution, however, not as good as RuO_2 .

The present analysis, Figure 2, indicates that the structure from Loll et al. is closer to optimal than the structure of Ferreira et al. However, both structures of the biological catalyst are closer to the thermochemically optimal catalysts than the best inorganic electrocatalysts. Although there is considerable uncertainty in the DFT calculations, this gives hope that we can find better inorganic electrocatalysts for the water splitting reaction. One lead in this direction is the observation that the

active cluster in the enzyme has larger flexibility of oxidation site and geometry which cannot be matched by the rigid oxide surface.

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