# Catalysis of the electrochemical water oxidation to oxygen

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# Chapter 1

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## Introduction

### 1.1. Overview

This work was performed in the framework of the project C1.8 of the BioSolar Cells open innovation consortium that focuses on studying the mechanism of water oxidation catalysis on both oxide and molecular catalysts. The fundamental insights obtained from the water oxidation electrocatalysis can be potentially used to develop devices to convert solar energy into fuels (artificial photosynthesis).

To develop our fundamental understanding of water oxidation, this thesis presents a (spectro)electrochemical study of the water oxidation reaction (also known as oxygen evolution reaction, OER), which is the anodic reaction in the water splitting process ($H_2O \rightarrow H_2 + 1/2O_2$).[1-4] This process will have important economic and environmental implications in the near future because it is one of the most promising alternatives to store solar energy, which is one of the fundamental steps in the development of a sustainable energy-based society.[1,3,5-8] The sun is by far the largest exploitable energy resource, which irradiates the earth in one hour with enough power ($4.3 \times 10^{21}$ J) to supply the needs of the whole planet in one year.[1] However, the daily, seasonal and regional intermittence of solar light makes the large scale utilization of this resource unfeasible.[1,3,8,9] Therefore, in a society where solar energy is meant to be the major powering source, there must exist efficient technologies to store the irradiated solar power and that can straightforwardly dispatch it to the end user on demand.[1,6,10]

Conversion of solar energy into fuels (hydrocarbons, alcohols, hydrogen, etc.) is a very attractive approach to perform the solar energy storage, which can be potentially integrated in a distribution system to overcome the availability problem.[1,3,5,6] The water splitting process plays a central role in the solar-to-fuel conversion process because in all approaches for the generation of solar fuels, water is oxidized to oxygen releasing protons that in combination with the photo-generated electrons are used to drive the fuel production.[1,3,5,6,9-11] This clearly points out the importance of the water splitting process for the solar energy-to-fuel conversion process towards the development of a sustainable society, and underscores the relevance of the studies performed in this thesis.

The solar-to-fuel conversion requires the oxidation of water to oxygen. However, the kinetics for this reaction is slow, reducing significantly the efficiency of the generation of fuels.[2,4,5,9,11] The next section will revisit the thermodynamic reasons behind the slow kinetics of the water oxidation reaction and will outline the research challenges in order to develop better catalysts.

## 1.2. Electrocatalysis for the water oxidation reaction

The oxidation of water to oxygen is a complex electrochemical reaction involving the transfer of four electrons and four protons, and the most accepted mechanism through which the reaction proceeds is summarized in equations (1) – (4) for the reaction occurring in acid media, and in equations (5) – (8) for the case of alkaline media.[4,12,13]

In acid media:

$$H_2O + * \rightarrow OH_{ads} + H^+ + e^- \tag{1}$$

$$OH_{ads} \rightarrow O_{ads} + H^+ + e^- \tag{2}$$

$$O_{ads} + H_2O \rightarrow OOH_{ads} + H^+ + e^- \tag{3}$$

$$OOH_{ads} \rightarrow O_2 + H^+ + e^- + * \tag{4}$$

In alkaline media:

$$OH^- + * \rightarrow OH_{ads} + e^- \tag{5}$$

$$OH_{ads} + OH^- \rightarrow O_{ads} + H_2O + e^- \tag{6}$$

$$O_{ads} + OH^- \rightarrow OOH_{ads} + e^- \tag{7}$$

$$OOH_{ads} + OH^- \rightarrow O_2 + H_2O + e^- + * \tag{8}$$

The * in equations (1) – (8) denotes a catalytically active surface site.

Koper revisited the thermodynamic aspects that limit the kinetics of the oxygen reduction reaction (ORR) and its anodic counterpart, the oxygen evolution reaction.[14] His major conclusion was that when all the separate steps involved in the reaction mechanism have the same zero free energy, the overall reaction may proceed at the thermodynamic equilibrium potential of 1.23 V vs. RHE. However, it is known that the binding energies of the intermediates involved in the ORR/OER are strongly correlated,[12,13] and the difference between the binding energy of the OH intermediate and the OOH is a constant value (*ca.* 3.04 – 3.2 *eV*), that exceeds the ideal condition of 2.46 *eV*. This fact introduces a thermodynamic limitation that hinders the optimization process to sub-optimal catalysts with non-zero (thermodynamic) overpotential[14] as it is shown in Figure 1.

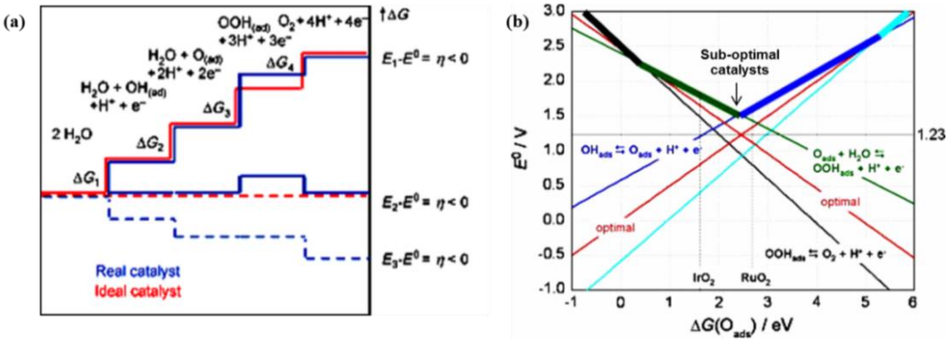

**Figure 1.** a) Chemisorption energy of the intermediates (horizontal lines) of the OER versus the reaction coordinate. Blue lines and red lines indicate energetics of a real (typical) catalyst and an ideal catalyst, respectively, at three different electrode potentials. Dashed lines indicate energetics at the electrode potential where all thermochemical barriers disappear (“thermochemical overpotential”); $\Delta G_i$ denotes the free reaction energy of the two elementary reaction steps. The red ideal case corresponds to a catalyst that can drive the reaction with zero (thermodynamic) overpotential. Figure adapted from reference 4. b) Plot of the equilibrium potentials for the reaction described in equations (1) – (4) for the OER in acid media as a function of the chemisorption energy of oxygen on the catalysts $\Delta G(O_{ads})$. The relative positions of the best OER catalysts in acid media ($RuO_2$ and $IrO_2$) are shown as reference. Figure adapted from reference 14.

The major future challenge in electrocatalysis for OER and ORR is to find materials able to circumvent the thermodynamic scaling relationship between the reaction intermediates, in order to stabilize the hydroperoxo species without affecting the individual stabilities of the hydroxyl and oxygen. Man *et al.* have suggested the design of three-dimensional active sites that can further stabilize the OOH intermediates without affecting the other reactive species on the surface.[15] A recent joint theoretical-experimental work from the groups of Ktril and Rossmeisl reported an attempt to break the thermodynamic limitations for the OER reaction.[16] Their computational DFT results indicated that the incorporation of nickel or cobalt in the structure of $RuO_2$ catalysts activates a proton donor-acceptor functionality on the conventionally inactive bridge surface sites of the ruthenia, and this enhances the OER activity of $RuO_2$. The predicted OER onset potential for these compounds is in the range of 0.1 – 0.3 V. They prepared the Ni and Co modified $RuO_2$ materials and measured the activity for oxygen evolution, and their experimental results showed that the current densities attributed to OER at 1.6 V vs. RHE on the modified ruthenia can be up to 30-fold higher than the values measured on the unmodified material.

Electrocatalysts based on transition metal oxides are among the most extensively studied materials due to their inherent chemical stability under the working conditions for the water oxidation reaction.[4,17,18] Iridium and ruthenium oxides are the most active catalysts for the water oxidation reaction in acid media.[17,19,20] $IrO_2$ is the only one having long term stability for acid-based electrolysis, and it is the material of use for OER anodes in acid-based industrial processes. [21,22] However, iridium is one of the rarest metals on the earth so it is prohibitively expensive to be used for large-scale applications like solar light harvesting for the generation of sustainable energy. For the electrochemical oxidation of water in alkaline media there are cheaper alternatives to $IrO_2$, based on earth abundant 3d transition metal oxides, which have higher catalytic activity towards OER than the expensive iridium oxide option[19,23-27]. However, the lack of efficient separation membranes suitable to work in alkaline electrolyzers and the low conductivity of the electrolytes typically used in such devices reduces the efficiency of solar-to-fuel.

Molecular catalysts have also been used as OER catalysts, in an attempt to mimic the natural photosynthetic compounds.[4,11,28,29] These compounds are relatively easy to tailor both electronically and structurally to obtain fundamental understanding on how these factors affect the activity, which is not straightforward in the case of metal oxides. There are large number of compounds that can drive the water oxidation reaction at high rate, which translate into high values for the turnover frequency (TOF) and the turnover number (TON). Sun's group reported recently a family of ruthenium-based molecular compounds with a TOF of 300 mol $O_2$ $mol_{catalyst}^{-1}$ $s^{-1}$, which is one of the few molecular catalysts able to catalyze the OER at a comparable rate to the natural photosynthesis II system.[30] Actually, there is a great variety of molecular catalysts based on Ir, Mn, Fe, Co that can also drive the electrochemical water oxidation at relatively high rates.[28,29] One of the major drawbacks in the utilization of OER molecular catalysts is their high tendency to decompose during the process, leading to the formation of the corresponding metal oxide, which then acts as the real active catalyst towards OER.[11,29,31,32] Moreover, the OER activity of these compounds is typically measured by using sacrificial oxidants, which makes it difficult to properly define the OER overpotential, and complicates the definition of clear benchmarking criteria.

## 1.3. Outline of this thesis

This thesis addresses the various experimental factors affecting the kinetics of the water oxidation reaction, not only by looking at the catalyst but also by revisiting the role of the electrolyte in the reaction kinetics. Our approach allows us to propose some guidelines for the rational development of catalysts able to efficiently catalyze the electrochemical water oxidation reaction, both in acid and alkaline media.

We start in chapter 2 by a spectroelectrochemical study of the water oxidation reaction on gold electrodes in acid media, to understand the surface processes that take place in the metal oxide, prior the actual oxygen evolution, and to obtain insight about the role of the 3D structure of the oxide in the overall reaction. The results of this study allows us to propose a model for the oxygen evolution reaction where the gold oxide formed on the electrode surface is not innocent in the electrocatalytic water oxidation, but decomposes to produce oxygen in the overall water oxidation process. Still, gold is a poor catalyst for the water oxidation, and hence it is used as electrode material to support the other OER catalysts studied in this thesis.

In chapter 3 we present a spectroelectrochemical study of the electrolyte influence on the OER activity of an iridium-based molecular catalyst immobilized on a gold electrode in acid media. This chapter shows a systematic way to correlate the OER activity measured in homogeneous catalysis experiments with the activity of heterogeneous catalysts, to provide clear benchmarking criteria. We provide evidence that the molecular catalyst does not decompose to iridium oxide during the water oxidation reaction but it becomes activated by a reversible dimerization process.

We also study the electrocatalysis towards OER in alkaline media on earth-abundant materials. Chapter 4 presents a study of the OER electrocatalysis on nickel double hydroxides doped with 3d transition metals immobilized on gold in alkaline media. The results of this study demonstrate that the nature of the active site in the double hydroxides is strongly dependent on the dopant incorporated in the compound. The study provides guidelines that can be employed for the rational design of nickel-based water oxidation catalysts in alkaline media.

Chapter 5 continues the study of the OER electrocatalysis in alkaline media. This chapter presents a spectroelectrochemical study on the effect of pH on the catalytic activity of nickel oxyhydroxide. We provide evidence of a deprotonation process of the NiOOH towards a negatively charge surface intermediate (oxo / superoxo species) that strongly affects its catalytic activity towards OER. The evidence in this chapter shows once more that the development of good OER anodes should take into consideration the synergy of the OER catalyst with the electrolyte.

Finally, in chapter 6 we return to the acid-based OER electrocatalysis. We present a new type of OER catalyst based on iridium double perovskites to drive the reaction in acid media. These compounds contain three times less iridium than the $IrO_2$ benchmarking catalyst and exhibit more than 3-fold higher catalytic activity, which makes them the most active catalysts for OER in acid media reported to date.

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