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Summary

This thesis discusses the parameters affecting the catalysis for the electrochemical conversion of water into oxygen. The slow kinetics for the oxygen evolution reaction (OER) is one of the major bottlenecks in the solar energy-to-fuels conversion process, which reduces the efficiency for the photo-electrochemical fuels generation (artificial photosynthesis).

Most of the theoretical and experimental attempts to understand the factors affecting the kinetics for the electrochemical water oxidation to oxygen focus in the properties of the catalysts. Those research efforts concentrate on developing catalysts able to reduce the intrinsic overpotential inherent to the oxygen evolution reaction. Only few research efforts have been devoted to understand the role of the electrolyte in the water oxidation electrocatalysis, which can however strongly affect the OER activity beyond catalyst optimization. This thesis presents a (spectro)-electrochemical study of the factors affecting the kinetics of the water oxidation reaction, not only by looking at the catalysts but also by addressing the role of the electrolyte in the catalytic process. Our experimental approach combines evidence obtained by means of a wide variety of electrochemical techniques such as cyclic and linear sweep voltammetry, potentiostatic and galvanostatic experiments, all under stationary or hydrodynamic conditions. We have also combined these techniques with spectroscopic/spectrometric techniques, particularly surface enhanced Raman spectroscopy (SERS) and online electrochemical mass spectrometry (OLEMS), to respectively monitor the formation of adsorbed intermediates and volatile reaction products. Some of the experimental evidences obtained have been analyzed in the light of results obtained by density functional theory (DFT) calculations, to propose models that allow us to rationalize the reactions occurring on the electrochemical interface, and how they affect the water oxidation kinetics.

The thesis starts in chapter 2 with a joint spectroelectrochemical and computational study of the water oxidation reaction on gold electrodes in acid media. We

study the reactions taking place on the electrode surface prior to the actual oxygen evolution, to understand the role of the 3D structure of the metal oxide in the OER. The experimental and computational results allow us to propose a model for the oxygen evolution reaction on gold electrodes where the surface metal oxide is not innocent but decomposes to produce oxygen during the overall reaction. Gold is nevertheless a very poor catalyst for the oxygen evolution reaction, and therefore it is used as support for other OER catalysts studied in this thesis.

We study the effect of the electrolyte anions and pH on the OER activity of a molecular catalyst in chapter 3. To do this, we performed systematic spectroelectrochemical experiments on an iridium-N-dimethylimidazolin-2-ylidene complex adsorbed on gold electrodes. This chapter compares the water oxidation activity obtained by having the molecular catalyst in solution (by using an auxiliary oxidant), with the electrochemical activity measured on the adsorbed catalyst. This work provides benchmarking criteria that allow one to compare the OER activity on the iridium-based molecular catalyst with heterogeneous catalysts (*i.e*. metal oxides). Moreover, we present conclusive evidences that the electrolyte anions and the pH play a crucial role in the water oxidation catalyzed by the iridium complex, such that the catalytic activity of the iridium-N-dimethylimidazolin-2-ylidene complex can be enhanced 20-fold by carefully selecting the electrolyte anion and the working pH. Furthermore, the work presents *in situ* evidence that the molecular complex does not decompose to iridium oxide during the water oxidation reaction, but rather that it becomes activated by a reversible dimerization process.

The electrochemical water oxidation in alkaline media on oxide catalysts based on earth-abundant materials is revisited in chapters 4 and 5. First, in chapter 4, we provide a joint theoretical-experimental study of the electrocatalysis of the OER on nickel double hydroxides with 3d-transition metal dopants. This study demonstrates that the nature of the active site in the double hydroxides is strongly dependent on the dopant incorporated in the compound. Moreover, this work proposes guidelines that can be employed for the rational design of nickel-based water oxidation catalysts in alkaline media. We continue in chapter 5 with a spectroelectrochemical study of the role of pH on the catalytic activity of nickel oxyhydroxide (NiOOH) towards water oxidation. This study presents evidence of a deprotonation process of the NiOOH towards a negatively charged intermediate (oxo and/or superoxo species) that strongly affects its catalytic activity towards OER. Chapter 5 shows once more that the development of good OER anodes should take into consideration the synergy of the OER catalyst with the electrolyte.

The discussion returns to the acid-based water oxidation electrocatalysis in chapter 6. We present here a new type of oxygen evolution catalyst based on iridium double perovskites. These compounds contain three times less iridium than the IrO_2 benchmarking catalyst but exhibit a more than 3-fold higher catalytic activity, which makes them the most active catalysts for OER in acid media reported to date. The study shows that the 3D arrangement of corner-shared octahedra is a necessary prerequisite for the catalytic activity enhancement of the iridium-based double perovskites and for their chemical stability under anodic working conditions. Our findings regarding the effect of the *A* and *B*-site cations on the catalysis towards water splitting of the iridium based double perovskite suggest that the activity of these compounds might be further improved by carefully selecting the cations at those sites. Our strategy may also be extended to enhance the catalytic activity and chemical stability of ruthenium-containing compounds, with lower content of ruthenium compared with RuO_2.

In summary, this thesis shows that to enhance the kinetics for the oxygen evolution reaction, one should not only look at the catalysts but also consider the synergy between catalyst and electrolyte. A more general approach that considers the electrochemical interface as a whole (electrode + electrolyte) is therefore the most promising route towards optimal activity.