

7. Summary

In this thesis I will describe my contributions to the field of molecular water oxidation catalysis. In **Chapter 1** a broad introduction into the field of water oxidation catalysis is given, starting off with the societal relevance of this research in relation to climate change and renewable energy storage. **Chapter 2** discusses scaling relations in molecular catalysts for water oxidation and their influence on the fundamental minimal overpotential that can be achieved depending on the mechanism by which the water oxidation catalyst operates. In **Chapter 3** an iridium water oxidation catalyst is described that oxidatively anchors to a metal oxide surface, resulting in robust anodes. **Chapter 4** discusses a molecular nickel complex that is active in water oxidation catalysis, and depending on the pH and potential decomposes and deposits an active catalyst layer on the electrode. In **Chapter 5** chemical oxidants are used to discover trends in molecular nickel complexes for water oxidation. In **Chapter 6** a novel ligand framework is presented that forms iron complexes that result in high turnover numbers and frequencies in iron-catalyzed water oxidation.

In **Chapter 1** we discuss several strategies to prevent further global warming and reduce dependence on fossil fuels. It is clear that a transition to renewable energy will be necessary. The potentially largest renewable energy sources, wind and solar, are both intermittent. To account for this intermittency, at least part of the energy will have to be stored. One promising option is to store this energy in the form of chemical bonds. This can lead to high energy density fuels, which can be easily stored and transported, and can also be used for heavy mobile applications. To store energy in a chemical bond a thermodynamically uphill reaction has to be performed (Figure 7.1). Catalysts will have to be employed for the production of these renewable fuels to minimize energy losses. Hydrogen (H_2) or carbon-based fuels can be produced by proton reduction and CO_2 reduction, respectively. Water oxidation, as counter redox reaction, can supply the required electrons and protons. In this thesis I will focus on the use of molecular catalysts for this challenging reaction.

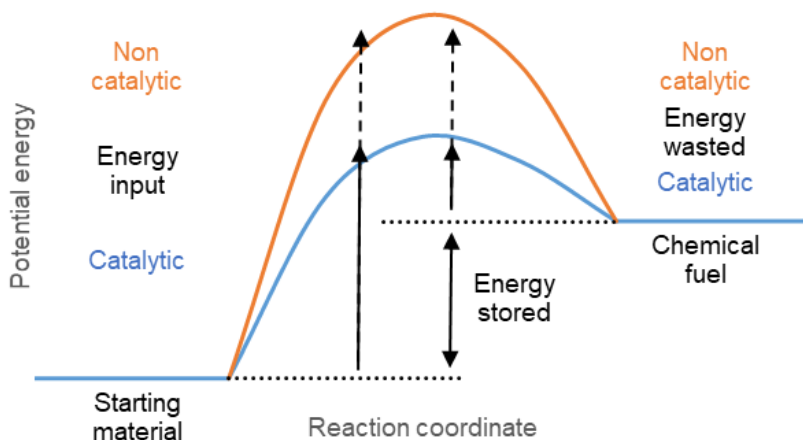


Figure 7.1. Schematic diagram of energy storage.

In the second section of **Chapter 1**, we provide a tutorial on strategies on the development of molecular water oxidation catalysts (WOCs). We start by discussing strategies applied in solution phase, including water oxidation driven by chemical oxidants, photochemical water oxidation and electrochemical water oxidation. Studies with chemical oxidants can give information on structure-activity relationships as well as mechanistic insight. Studies on photochemical water oxidation can be used to probe stability under irradiative conditions. Electrochemical studies can give insight in the oxidation states of a metal complex before catalysis and the (over)potential at which a catalyst operates. Spectro-electrochemical approaches can be very powerful in attaining mechanistic information. To arrive at more practical devices, molecular WOCs can be anchored on electrode surfaces. Common strategies include anchoring on metal oxide surfaces with for instance carboxylic acid groups or the use of large aromatic groups for π - π -stacking on carbon materials. An important consideration for anchoring a catalyst is the reduction of the degrees of freedom, which could have mechanistic implications. Once a catalyst is anchored, electrochemical studies can give information on catalyst stability and performance. In photoelectrochemical water oxidation, a light harvesting moiety will also have to be incorporated. Here, it is important to focus on directional energy transfer to arrive at high quantum efficiencies and catalyst stability. For a full electrolysis or photoelectrochemical cell, the

properties of the cathode are also important.

In the last section of **Chapter 1** we summarize progress in the field of molecular water oxidation catalysts focusing on complexes based on metals covered in this thesis. We start with an overview of trends in ruthenium- and iridium-based WOCs. Generally, these second- and third-row transition metals perform better in terms of turnover numbers and turnover frequencies than their first-row metal counterparts. In addition they often oxidize water at a lower overpotential. However, as first-row transition metals are more abundant and have a lower cost, there are both economical and academic interests to develop first-row transition metal WOCs. There are three fundamental reasons first-row transition metal WOCs generally have lower performance than second- and third-row transition metal WOCs, all associated with the core orbital structure (Figure 7.2). As first-row transition metals bond with smaller d orbitals, there is a lower σ -orbital overlap, and thus faster ligand dissociation. These characteristics lead to less stable complexes due to more dynamic ligand coordination. The second thermodynamic argument is that π -orbital overlap is higher for first-row transition metals, which causes the M=O intermediate to be a thermodynamic sink in the water oxidation reaction. The third reason why first-row transition metals have a lower performance is kinetic in nature. As they have fewer electrons, an oxidation (or reduction) will result in a larger change in ionic radii. This causes a higher reorganizational energy, which in turn leads to slower electron transfer. After discussing these fundamental properties of lower performance of first-row transition metal WOCs in comparison to second- and third-row transition metals, we focus on some trends in iron-based water oxidation and summarize progress on nickel-based WOCs in literature.

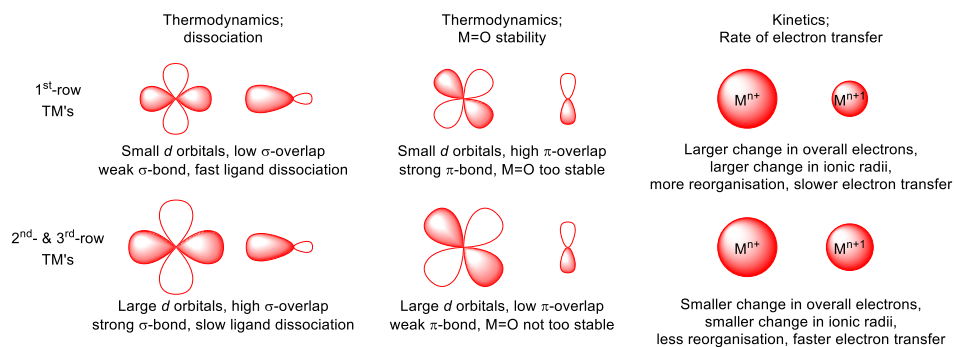


Figure 7.2. Thermodynamic and kinetic characteristics of transition metal complexes.

In **Chapter 2** we highlight the intrinsic influence of the water oxidation mechanism used by molecular catalysts on the theoretically achievable minimal overpotential, based on scaling relationships typically used for heterogeneous catalysts (Figure 7.3). Due to such scaling relationships, catalysts that operate through the water nucleophilic attack (WNA) mechanism have a fundamental minimal overpotential of about 0.3 V, whereas those that follow the dinuclear radical-oxo coupling (ROC) mechanism should in principle be able to operate with a lower overpotential (close to the thermodynamic potential). Therefore, it is recommended to design catalysts operating through the latter mechanism to achieve very efficient water oxidation systems.

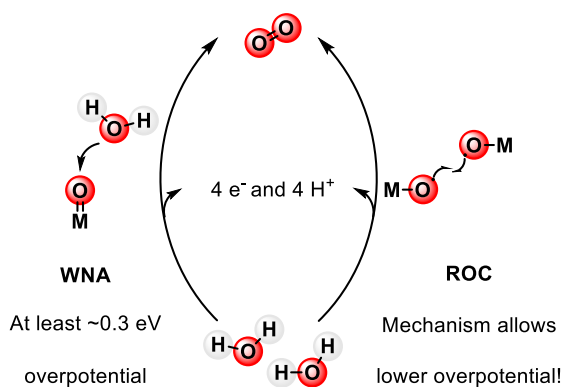


Figure 7.3. Scaling relations dictate a minimal overpotential of 300 mV for catalysts following the water nucleophilic attack mechanism, while the radical-oxo coupling mechanism allows for a lower overpotential.

In **Chapter 3** we focus on deposition of a chemically oxidized molecular iridium precursor on indium-doped tin oxide (ITO) electrodes resulting in robust Ir@ITO anodes (Figure 7.4). Electrochemical experiments reveal that the electrodes exhibit a chemically reversible oxidation wave at 0.7 V vs NHE. The Ir@ITO electrodes show electrochromic behavior, being colorless below 0.7 V and turning blue after the oxidation wave at 0.7 V vs NHE. During water oxidation catalysis at 1.4 V vs NHE, the electrode is again colorless. The Ir@ITO electrodes oxidize water with a current density of 0.5 mA cm⁻² at a potential of 1.4 V vs NHE at pH 2.3. X-ray absorption spectroscopy indicates an iridium(IV) species both before the oxidation wave at 0.7 V vs NHE and during catalytic conditions. These observations suggest that the resting state of the catalyst involves an iridium(IV) species and not, as often assumed, an iridium(III) complex. We propose a redox active substrate/ligand mechanism, which does not affect the formal oxidation state of the iridium center. Our findings are of importance to develop improved iridium-based water oxidation catalysts.

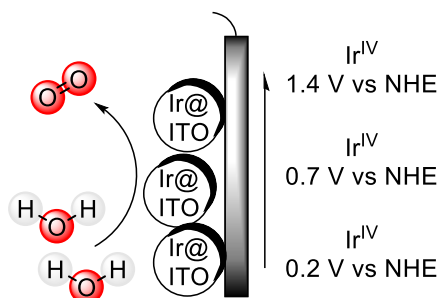


Figure 7.4. Oxidation states of the Ir@ITO WOC.

The development of water oxidation catalysts can be aided by the postulation of design rules. Decomposition of molecular complexes to nanoparticles can complicate the analysis of the reactivity, which in turn can lead to incorrect mechanistic interpretations and design rules. In **Chapter 4** we show that a nickel-based water oxidation catalyst, [Ni^{II}(*meso*-L)](ClO₄)₂ previously reported to operate as a molecular catalyst, decomposes to form a NiO_x layer in a pH 7 phosphate buffer under prolonged catalytic conditions as indicated by controlled potential electrolysis and electrochemical quartz crystal microbalance measurements (Figure 7.5). Interestingly, the formed NiO_x layer desorbs

from the surface of the electrode under less anodic potentials. Therefore, no nickel species can be detected on the electrode after electrolysis. This chapter demonstrates the importance of *in situ* characterization methods for catalyst decomposition and metal oxide layer formation. Catalyst decomposition is strongly pH and buffer dependent as we cannot find an indication of NiO_x layer formation at a pH of 6.5 in phosphate buffer nor in a pH 7 acetate buffer. Under these conditions the activity is ascribed to a molecular catalyst, however, the activity is much lower compared to the *in situ* formed NiO_x layer.

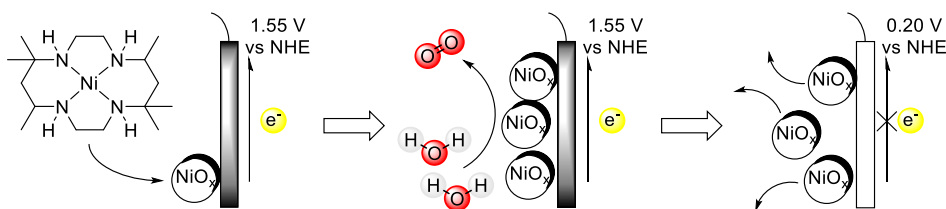


Figure 7.5. The Ni^{II}(*meso*-L)](ClO₄)₂ catalyst decomposes to a NiO_x layer during prolonged water oxidation experiments in a pH 7 phosphate buffer. This heterogeneous layer dominates the catalytic activity in water oxidation. The formed NiO_x deposit desorbs from the electrode surface at less anodic potentials.

In **Chapter 5** we show that chemical oxidants can be used to probe oxygen evolution activity for nickel-based systems and report trends that can improve future ligand design (Figure 7.6). Interestingly, we observe different ligand effects in comparison to other first row-transition metal complexes. For example, nickel complexes with secondary amine donors are more active than with tertiary amine donors, which is the opposite for iron complexes. The incorporation of imine donor groups in a cyclam ligand results in the fastest and most durable nickel catalyst of our series, achieving oxygen evolution turnover numbers up to 380 and turnover frequencies up to 68 min⁻¹ in a pH 5.0 acetate buffer using Oxone as oxidant. Initial kinetic experiments with this catalyst reveal a first order in chemical oxidant and a half order in catalyst. This implies a rate determining oxidation step and with likely a dimeric species breaking up to generate the active catalyst. These findings lay the foundation for the rational design of molecular nickel catalysts for water oxidation, and highlight that catalyst design rules are not generally applicable for different metals.

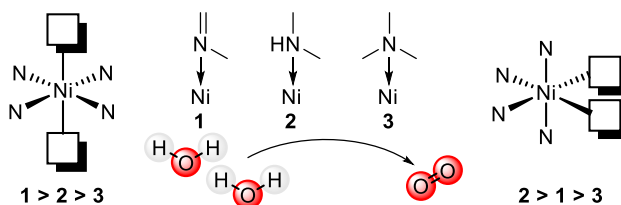


Figure 7.6. Observed structure-activity relationships for molecular nickel-based WOCs.

In **Chapter 6** we report a new multidentate ligand, in which one pyridine donor group is replaced by a more electron donating mesoionic carbene donor group. The formed iron complex leads to greatly enhanced performance in water oxidation catalysis (Figure 7.7). Turnover numbers up to 19000 and turnover frequencies up to 800 min^{-1} are observed during oxygen evolution driven by Oxone as chemical oxidant at pH 6.0. Kinetic studies reveal a first order rate dependence on Oxone and on iron, indicating a rate limiting oxidation step. Initial electrochemical studies demonstrate oxygen evolution at a potential of 1.7 V (vs NHE), with a 200 mV lower onset potential than the parent catalyst reported in literature. This chapter shows the importance of exploring novel ligand structures to move forward in the field of (water oxidation) catalysis.

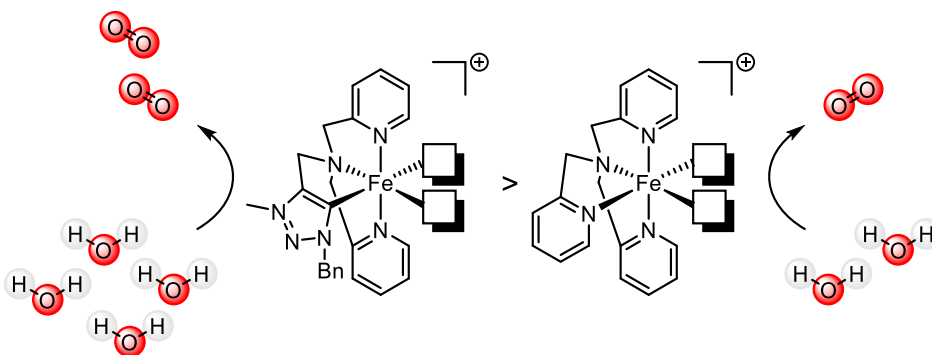


Figure 7.7. Substituting a pyridine donor group for a carbene donor group leads to vastly improved performance for a molecular iron-based WOC.

In this thesis we give a thorough background on molecular water oxidation catalysts. We learn that there are some fundamental reasons why second- and third-row transition metals catalysts perform better than first-row complexes, and that the mechanism at which a water oxidation catalyst

operates can influence the minimal overpotential the catalyst can achieve. We show that *in situ* X-ray absorption spectroscopy can be used to attain mechanistic insight on catalysts anchored to a surface. In addition, electrochemical quartz microbalance measurements can be used to show that under certain catalytic conditions a molecular catalyst, based on nickel, decomposes and forms a metal-oxide layer. This metal-oxide layer is the dominant active species in catalysis. Importantly, this layer desorbs at open circuit potential, preventing *ex situ* detection. Next, we give design rules for nickel-based water oxidation catalysts, which strongly differ from those of other first-row transition metals. Finally, we show that incorporating a mesoionic carbene moiety in a ligand for iron-based water oxidation leads to high catalytic performance. Overall, with this work we hope to encourage the development of first-row transition metal catalysts for water oxidation, with a focus on thorough mechanistic studies and exploring novel ligand frameworks.