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Chapter 1

Introduction

In this chapter, the challenges which need to be overcome in order to move away from energy production relying on the unsustainable consumption of fossil fuels and towards a future of sustainable energy are discussed. In this context, recent advancements in the development of homogeneous water oxidation catalysts are outlined with a focus on catalysts based on first-row transition metals in general and iron in particular. Two aspects that receive particular attention are the importance of understanding structure-activity relationships in homogeneous water oxidation catalysis and the advantages and disadvantages of different methodologies for studying such catalysts. The latter aspect is explored by comparing the use of chemical oxidants – which is still a widely used standard in the field – to electrochemical techniques. This chapter is completed by a brief outline of the work presented in this thesis.

1.1 Challenges to overcome for a sustainable future

In 2014, humanity consumed a global total of 109 613 TWh of energy.^[1] With the growth of modern societies, this global annual energy consumption is only going to increase in the future.^[2] To meet this demand, energy production currently largely relies on the burning of fossil fuels,^[1] which is problematic in several ways. Fossil fuels are formed in nature through extremely slow processes over millions of years and are therefore effectively finite as the rate of replenishment is much lower than the rate of consumption. Furthermore, burning these fuels releases – among other pollutants – the carbon stored within them in the form of CO₂, raising the atmospheric levels of CO₂ and thereby contributing to anthropogenic climate change.^[3] The gravity of these problems makes the development of new technologies, which allow us to move away from fossil fuels and towards a future of sustainable energy, one of the key challenges for science in the 21st century.^[4] While there are several sustainable sources of energy available such as wind, tides and geothermal heat, sunlight is the only sustainable source of energy which can be harvested in sufficient quantities to build a sustainable energy infrastructure on a global scale.^[2] This makes solar energy a prime candidate for a long term solution to the impending energy crisis.

The technology for the conversion of solar energy to electricity already exists in the form of photovoltaics. However, fluctuations in the availability of sunlight due to clouds and day/night cycles and the uneven distribution of sunlight across the globe mean that additional technologies are required to not only capture energy from sunlight but to also store it. Ideally, solar energy would be stored in the form of chemical bonds through a solar-to-fuel conversion process since (liquid) fuels have considerably higher energy densities than other storage media such as batteries.^[5] Moreover, not all existing technologies can be easily adapted from fuel to electricity.

Currently, the most promising approach to generating chemical fuels from solar energy is to oxidize water to produce oxygen and reduction equivalents in the form of protons and electrons. Water as a starting material is available in large quantities and O₂ as the only byproduct is environmentally friendly. The protons and electrons generated in such a process could subsequently be used for example to produce hydrogen gas or to generate more traditional carbon-based fuels through CO₂ reduction.

1.2 Natural vs. artificial photosynthesis

The formation of a chemical fuel from solar energy is sometimes referred to as “artificial photosynthesis”, due to its conceptual analogy to the natural process of photosynthesis.^[6-8] In natural photosynthesis, green plants and cyanobacteria use sunlight to generate biomass from CO₂ and water, releasing O₂ in the process. Natural photosynthesis is a highly complex process which can be divided into reactions which require light and reactions that occur in the dark. One of the essential pieces in the light-dependent part of photosynthesis is the oxygen evolving complex (OEC) in photosystem II (PSII). According to the best structural information currently available, the OEC contains four manganese centres, linked by bridging oxygen ligands, and one calcium ion which together form an Mn₄CaO₅ cluster.^[9] While the exact mechanism is still a matter of some debate,^[10-15] the OEC is capable of splitting water into oxygen as well as protons and electrons with remarkable efficiency. For the OEC itself, an overpotential of about 20 mV has been reported with respect to the thermodynamic standard potential for water splitting of 1.23 V.^[16] However, when energy transport across the entire photosystem is taken into account, an effective overpotential for oxygen evolution of around 300-400 mV has been determined.^[17-18] Similarly, the measured turnover frequency also depends on the exact conditions such as the intensity of the light and whether the measurement is conducted under *in vivo* or *in vitro* conditions. Accordingly, turnover frequencies of the order of 10¹ s⁻¹ to 10³ s⁻¹ have been reported.^[18-20] Combined with turnover numbers of the order of 10⁵^[21] this results in a net lifetime for PSII on the scale of minutes to hours,^[22] after which PSII is so damaged from oxidative degradation that it is broken down and rebuilt inside the cell.

The electrons which are freed in the process of water oxidation are stored in the form of NADPH for the subsequent fixation of CO₂ in the form of carbohydrates in the light-independent part of photosynthesis.^[23]

Since the complexity of natural photosynthesis is clearly beyond the scope of current human-made technology, viable candidates for artificial photosynthesis are much simpler processes such as the splitting of water into hydrogen and oxygen.

The overall water splitting reaction consists of two parts, the oxidation of water and the reduction of protons, both of which need to be catalyzed (Fig. 1.1).

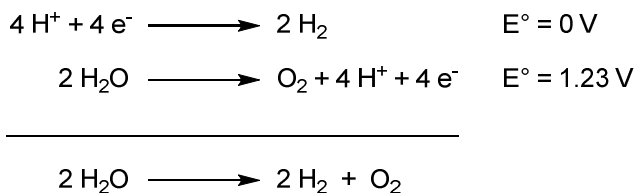


Figure 1.1: Schematic representation of the overall water splitting reaction and its two half-reactions with their respective thermodynamic standard potentials.

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Proton reduction is catalyzed very efficiently at virtually no overpotential by platinum metal.^[24-25] Since platinum is a relatively scarce material, several other proton reduction catalysts based on more abundant materials have been and still are being developed.^[26] Water oxidation on the other hand is a more complicated reaction as each turnover requires the rearrangement of four protons and four electrons, as well as the formation of an O–O bond, resulting in a kinetically very challenging reaction with several intermediates.^[27] Because of these challenges, water oxidation is widely considered to be the bottleneck in developing water splitting processes.^[28] Therefore water oxidation catalysis is still very much a research topic of great interest even after decades of research in this area.

Over the years, both homogeneous and heterogeneous catalysts for the water oxidation reaction have been developed with both areas having unique individual and often complementary strengths and weaknesses.^[29] Heterogeneous catalysts in the form of e.g. metal oxides tend to be inherently more robust under strongly oxidizing conditions, resulting in generally higher turnover numbers compared to homogeneous catalysts. Homogeneous catalysts in the form of metal complexes on the other hand are more flexible in terms of their electronic and steric structures which makes it easier to employ rational design strategies. Additionally, the nature of active sites in heterogeneous catalysts is often poorly understood and their density on the catalyst surface is generally low whereas for homogeneous catalysts each individual complex in principle represents an active site which can be studied through spectroscopic techniques. Therefore, the main goal in homogeneous water oxidation catalysis is to understand structure-activity relationships of transition metal complexes for water oxidation.

1.3 Homogenous water oxidation catalysts

The first example of a homogeneous water oxidation catalyst was published in 1982 by T. J. Meyer and co-workers.^[30] The reported dimeric ruthenium complex $[(\text{H}_2\text{O})\text{Ru}(\text{bpy})_2-\mu\text{-O}-(\text{bpy})_2\text{Ru}(\text{H}_2\text{O})]$ (with bpy = bipyridine) is now commonly

known as the “blue dimer” thanks to its characteristic blue colour. Since the water oxidation reaction requires the catalyst to cycle through a fairly wide range of oxidation states and also due to the multinuclear nature of the OEC in PSII it was not until 2005 that it was realized that mononuclear complexes could also catalyze the water oxidation reaction.^[31] Since then the field of homogeneous water oxidation catalysis has grown exponentially and a vast variety of different catalysts has been developed, based on many different transition metals, most prominently Ru,^[31-39] Ir,^[40-42] Fe,^[43-58] Mn,^[59-61] Co,^[62-67] Ni,^[68-69] and Cu^[70-74]. Even an example of an organic, metal-free water oxidation catalyst has been reported.^[75]

Of those aforementioned transition metals, catalysts based on ruthenium and iridium clearly stand out as being the most active ones in terms of turnover numbers, turnover frequencies and overpotentials. For ruthenium-based catalysts, turnover numbers as high as 10^5 - 10^6 have been reported.^[39, 76] In terms of turnover frequencies, Llobet and co-workers determined the theoretical maximum TOF for their ruthenium-based system via foot-of-the-wave analysis and found values ranging from 8.000 to 50.000 s^{-1} depending on the pH of the electrolyte solution.^[38] Meanwhile, Crabtree and Brudvig have reported an iridium-based water oxidation system operating extremely close to the thermodynamic standard potential of water oxidation of 1.23 V.^[42] From Tafel plots they extrapolated the onset potential of their catalyst to be only 14 mV above 1.23 V. While such a low overpotential is exceptional even for iridium-based systems, other iridium-based systems have also been shown to operate at comparatively low overpotentials of less than 200 mV.^[77]

In contrast to these excellent results, water oxidation catalysts based on the first-row transition metals Fe, Mn, Co, Ni and Cu generally yield considerably lower turnover frequencies and turnover numbers. Most of these systems operate at turnover frequencies below $1 s^{-1}$ and show turnover numbers of the order of 10^0 - 10^2 .^[78] While a few exceptions exist, they all come with their own drawbacks. The Fe(bpmcn) system (with bpmcn = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-cyclohexane-1,2-diamine) (Fig 1.2, left) reported by Costas et al. showed TON of >1000 under the right conditions but the corresponding TOF was low at only $0.06 s^{-1}$.^[47] More recently, Masaoka et al. reported a pentanuclear iron-based water oxidation catalyst (Fig. 1.2, middle) with an impressive TOF of $1.900 s^{-1}$ and an estimated TON of $>10^7$.^[50] However, this pentanuclear iron catalyst was found to be active only in acetonitrile solutions containing small amounts of water. In more water rich or aqueous environments the catalyst was found to be inactive.

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For those first-row transition metal based catalysts that were studied electrochemically, overpotentials generally exceed 500 mV and faradaic efficiencies – if reported – are low.^[43, 45, 53, 58, 64]

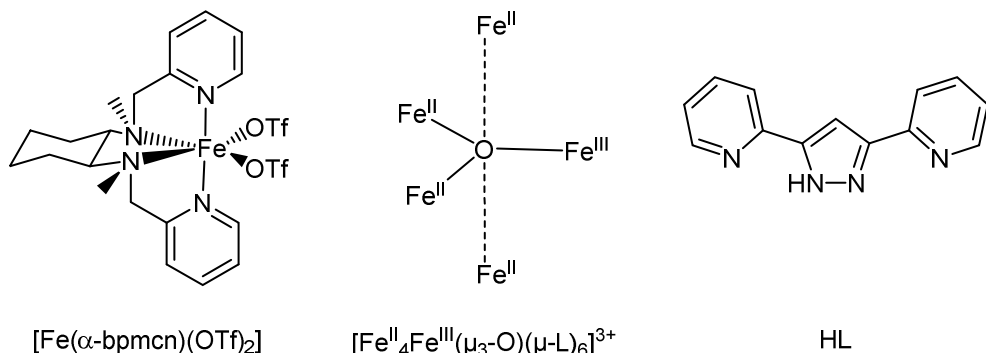
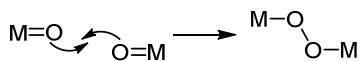


Figure 1.2: Schematic representations of the structures of $\text{Fe}(\text{bpmcn})$ (left) and the pentanuclear iron cluster reported by Masaoka et al. (middle) and the ligand bridging the iron centres in the pentanuclear complex (right).

One concern that is always present when working with molecular catalysts under the harsh conditions that are required to achieve water oxidation, is the possibility of *in situ* formation of heterogeneous material as the true catalytically active species.^[29] Accordingly, heterogeneous materials formed from homogeneous iron,^[79] manganese,^[80] cobalt,^[81] copper^[82] and iridium^[83] precursors have all been shown to be catalytically active. Consequently, one may falsely assume that one is studying an active homogeneous water oxidation catalyst when in fact minute amounts of heterogeneous material are being formed *in situ* which are responsible for part or even all of the observed catalytic activity.^[79] When one wants to study the structure-activity relationships of homogeneous catalytic systems, it is therefore paramount to establish the molecular integrity of supposedly homogeneous water oxidation catalysts as part of routine experiments.

For those systems which have been found to be indeed molecular in nature, extensive investigations have revealed two dominant mechanistic pathways for the O–O bond formation step: (i) an intermolecular recombination of two metal oxo-species and (ii) a nucleophilic attack of water at the oxo ligand in a metal oxo intermediate (Fig. 1.3).^[84-88]

- Bi-molecular O–O bond formation



- O–O bond formation via nucleophilic attack of water

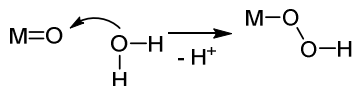


Figure 1.3: Schematic overview of the two main mechanisms of the O–O bond formation step in catalytic water oxidation (with M = metal)

Interestingly, the aforementioned ruthenium-based blue dimer was found to not undergo oxide coupling as one might expect based on the dinuclear structure. Instead, the mechanism is thought to proceed via a nucleophilic attack of water at one of the ruthenium oxo-sites in the $[\text{Ru}^{\text{V}}\text{O}(\text{L})-\mu\text{-O}-(\text{L})\text{Ru}^{\text{V}}\text{O}]$ intermediate which is aided by the abstraction of a proton from the incoming water molecule by the neighbouring ruthenium oxo-site (Fig. 1.4).^[89] In fact, most homogeneous water oxidation catalysts are thought to catalyze water oxidation via a water nucleophilic attack mechanism.^[84-88] An intermolecular recombination-type mechanism has so far only been found for a few ruthenium-based systems.^[88]

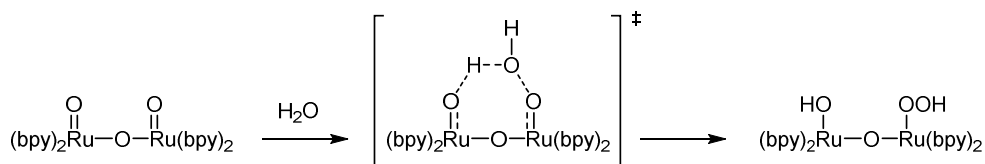


Figure 1.4: Proposed mechanism of the O–O bond formation step of the blue dimer catalyst

1.4 Iron-based water oxidation catalysts

Even though water oxidation catalysts based on ruthenium and iridium show very promising results, the scarcity of these elements is prohibitive for a widespread application in solar fuels production. As a result, more and more attention has been given in recent years to the search for alternative catalysts based on more affordable and abundant first-row transition metals. Out of those first-row transition metals, iron is a prime candidate for the development of new water oxidation catalysts. Iron has a rich redox chemistry as is apparent from the availability of a wide range of accessible oxidation states from –IV to +VII.^[90-91] Additionally, iron is present in many enzymes and metalloproteins found in

oxygen binding and oxygen transport systems in nature. However, while ruthenium and iridium tend to form predominantly low-spin complexes due to their position in the second and third row of the d-block, iron complexes are much more likely to adopt high-spin states. As a consequence, iron complexes tend to have more electron density in orbitals that are anti-bonding with respect to the metal–ligand bond, resulting in considerably faster ligand exchange kinetics for iron complexes compared to ruthenium and iridium.^[92] This fundamental difference might explain at least in parts why first-row transition metal complexes in general and iron complexes in particular are generally deactivated significantly faster during water oxidation catalysis than iridium and ruthenium complexes, resulting in lower turnover numbers.

One of the first examples of homogeneous iron-based water oxidation catalysts that was reported in literature is comprised of the Fe-TAML complexes (TAML = tetra-amido macrocyclic ligand) (Fig. 1.5) which were developed by Collins et al.^[46]

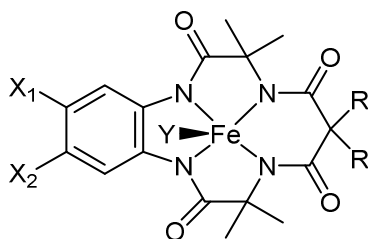


Figure 1.5: Schematic representation of the structure of the Fe(TAML) system developed by Collins et al. with $X_1 = \text{H, NO}_2, \text{Cl}$; $X_2 = \text{H, Cl}$; $\text{R} = \text{CH}_3, (\text{CH}_2)_2, \text{F}$; $\text{Y} = \text{H}_2\text{O}$

The TAML ligand platform was developed from rational ligand design to achieve maximum stability under strongly oxidative conditions. While the best Fe-TAML complex for water oxidation showed high initial-rate turnover frequencies of 1.3 s^{-1} when driven by the sacrificial oxidant cerium(IV) ammonium nitrate (CAN), the activity was short-lived with only 16 turnovers. Several suggestions have been made about the cause of this rapid deactivation. Experimental studies conducted on a series of TAML complexes demonstrated that demetalation can occur in acidic media.^[93] As a result, the loss of activity could at least in part be caused by degradation of the complex due to local acidification through protons generated in the water oxidation reaction. Theoretical calculations suggest the formation of a ligand-centered radical species which opens up degradation pathways.^[94]

Substantially higher turnover numbers were reported in 2011 by Costas et al. for their Fe(bpmcn) complex.^[47] In the presence of excess CAN the complex

generated oxygen with a TOF of 0.23 s^{-1} for around 360 turnovers. By using periodate as the oxidant, instead of CAN, to drive the reaction the turnover number could be increased to around 1000 albeit at a lower rate of 0.06 s^{-1} . One of the key findings Costas and co-workers reported was that the catalytic activity strongly depends on the coordination geometry of the complex. According to their results, iron complexes bearing neutral ligands with four nitrogen donor groups are active water oxidation catalysts if the complex has two available coordination sites in *cis*-position to each other. On the other hand, complexes with two available coordination sites in *trans*-position or complexes with only one available coordination site were found to be catalytically inactive (Fig. 1.6).

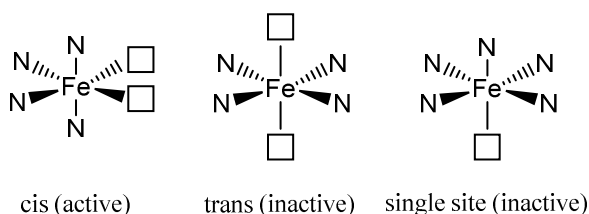


Figure 1.6: Schematic representation of the findings of Fillol et al. regarding the correlation between the coordination geometry of a complex and its catalytic activity towards water oxidation.

This finding was rationalized by invoking a mechanism which proceeds via an iron(V) oxo-hydroxo species (Fig. 1.7). In the proposed mechanism, the rate-limiting step is the O–O bond formation in the form of a nucleophilic attack of a water molecule at the oxo-ligand. This step is assumed to be facilitated by the abstraction of a proton from the incoming water molecule by the neighbouring hydroxo-ligand which acts as an internal base. The proposed mechanism was subsequently supported by DFT calculations.^[95] The authors found that for the case of a *cis*-geometry the involvement of the neighbouring hydroxo-ligand indeed helps in the nucleophilic attack of water by accepting a proton from the incoming water molecule, leading to a reduced energy barrier of the O–O bond formation step compared to the *trans*-geometry for which O–O bond formation was found to be feasible only at significantly higher potentials.

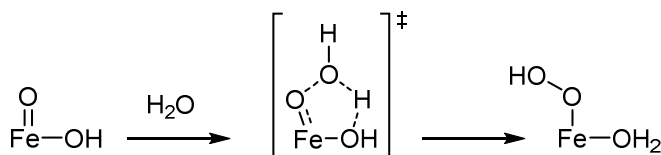


Figure 1.7: Proposed mechanism of the O–O bond formation step of the Fe(bpmcn) catalyst

However, in 2015 Fillol and co-workers published a follow-up report in which they presented evidence for the formation of a Fe- μ -O-Ce species upon addition of stoichiometric amounts of CAN to the catalyst, raising questions about the actual mechanism under catalytic conditions in the presence of CAN.^[96]

1.5 Chemical oxidants vs. electrochemistry

1 In order to achieve water oxidation, a driving force is needed which is strong enough to enable catalytic turnover. While water oxidation can in principle be driven chemically, photochemically and electrochemically, not all of these approaches are equally easy to implement. For the purpose of routine testing of new potential catalysts in the lab, the use of chemical oxidants to drive the catalyst is particularly attractive due to its ease of practical execution. Several chemical oxidants such as CAN or periodate are known to be capable of driving water oxidation catalysts^[97] and all that is required is to add an aqueous solution of the catalyst to an aqueous solution containing excess oxidant. The oxygen that is generated can be detected either in solution with the help of a Clark-type oxygen sensor or via headspace GC analysis. Because of this simplicity, chemical oxidants have been and still are routinely used for testing catalysts for the water oxidation reaction despite the fact that the results of such tests can only be considered very preliminary. The cost and waste associated with the use of stoichiometric amounts of chemical oxidants would make such a process economically unviable. Furthermore the original goal of producing a chemical fuel is also not achieved.

Unfortunately, the use of chemical oxidants is not without problems, even for mere routine testing purposes. The oxidants are generally only stable in a narrow pH region (e.g. around pH 1 for CAN) which means that the studies cannot necessarily be conducted at the pH which is most suitable for the catalyst. Furthermore, the potential which is applied in these cases is poorly defined. In the case of CAN, the potential is given by the relative concentration of Ce^{IV} to Ce^{III} according to the Nernst equation. At the beginning of the reaction, when only Ce^{IV} is present, the potential is therefore theoretically infinite. As the reaction proceeds and Ce^{III} is formed while Ce^{IV} is consumed, the potential also shifts over time. Therefore it is hardly possible to assess the overpotential of any given catalyst under such conditions. Finally, there has been more and more evidence in recent years which casts serious doubt about the nature of such chemical oxidants as mere innocent one-electron acceptors. In several cases it could be shown that

the oxidant is directly involved in the reaction mechanism.^[96, 98-102] Therefore, the results obtained with chemical oxidants cannot be reliably generalized until one has established that the catalyst also functions in the absence of the oxidant, for example under electrochemical conditions.

An alternative method for the routine testing of water oxidation catalysts is by use of electrochemistry. Results obtained under electrochemical conditions are much more meaningful with respect to an actual application since the ambiguity caused by the presence of chemical oxidants is eliminated. Since it is already possible to convert solar energy into electricity via photovoltaics, a catalyst that works under electrochemical conditions could in principle be incorporated into a water splitting device that is driven by solar energy. In addition to this, electrochemistry also offers very practical advantages over the use of chemical oxidants such as more freedom in terms of reaction conditions (e.g. pH of the electrolyte) and much more precise control over the applied potential.

One aspect in electrochemical studies of water oxidation catalysts that has so far been largely overlooked in published literature is the role of the electrode material itself. In principle, electron transfer between the electrode and the catalyst can proceed via an outer sphere mechanism or an inner sphere mechanism. In the case of an outer sphere mechanism one would expect only a small influence of the electrode material. However, in the case of an inner sphere mechanism involving specific adsorption of the catalyst on the electrode surface a much more significant influence of the electrode material is to be expected. Despite the potentially significant influence of the electrode material on the catalytic results, only very few reports exist in literature in which the role of the electrode surface is discussed.^[42, 75]

1.6 Aim and outline of this thesis

The goal of the research presented in this thesis is to provide insight into the redox behaviour of iron-based water oxidation catalysts, in particular under electrochemical conditions as opposed to conditions involving chemical oxidants. The intention behind this goal is to achieve a better understanding of what is required to make an active water oxidation catalyst. These requirements are assessed critically in this thesis by investigating the catalytic activities of different iron complexes under electrochemical conditions with respect to the structural and electronic properties of the complexes. Additionally, contributions from the

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interplay of the electrode surface and the catalyst in solution receive strong consideration.

In chapter 2, three structurally related iron complexes are described for their capabilities in water oxidation catalysis. All three complexes have been studied electrochemically in both unbuffered electrolyte media and in the presence of a pH buffer. Their redox chemistry is investigated by cyclic voltammetry while their water oxidation capabilities have been studied with the help of on-line electrochemical mass spectrometry. Particular emphasis was also placed on obtaining evidence for the integrity of the molecular nature of the catalyst under operando conditions. The results for all three complexes are then compared to obtain insight into structure-activity relationships.

Following the findings of chapter 2, the synthesis and characterization of a second generation iron-based water oxidation catalyst in the form of a dinuclear iron complex is described in chapter 3. Avoiding halide ions in the structure of the complex allowed us to study the complex with several different electrode materials, revealing a strong substrate influence of the electrode material. This effect leads to a significant reduction in the overpotential required to achieve oxygen evolution in the case of electrodes made from graphitic carbon.

In chapter 4, the previously reported benchmark catalyst $\text{Fe}(\text{bpmcn})^{[47]}$ is revisited and investigated from an electrochemical perspective, using methodologies established in chapters 2 and 3. In particular, two isotopologues of the same complex, which have previously been found to display significantly different stabilities when driven with CAN, are compared in terms of their relative stability under electrochemical conditions.

The results discussed in chapters 3 and 4 show clear evidence for significant interactions between the surface of the working electrode and the complex in solution which go well beyond outer sphere electron transfer. Following these findings, the interactions of carbon and gold electrodes with metal complexes in solution have been studied in more detail with respect to the consequences for the electrode material, the results of which are described in chapter 5.

Finally, in chapter 6 a summary of the results discussed in this thesis is presented, followed by general conclusions about electroanalytical studies of iron-based water oxidation catalysts and an outlook for further research.

Parts of this thesis have already been published^[58] while other parts are submitted or in preparation for publication.

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