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Chapter 6

Summary, conclusion and outlook

6.1 Summary

6.1.1 Introduction

There are several drawbacks that are associated with the use of fossil fuels in energy production. Their low rate of formation makes their use unsustainable since they are consumed much faster than they are regenerated. This also means that burning fossil fuels leads to a build-up of CO₂ in the atmosphere which drives climate change.^[1] It is therefore imperative that a transition is made in the near future from fossil fuels to sustainable energy sources.^[1-3] In order to achieve power generation based solely on sustainable sources on a global scale, utilization of solar energy is essential since other sustainable energy sources like wind cannot provide sufficient power for the entire planet.^[1]

While the conversion of solar energy into electricity via photovoltaics is already possible, the transportation and storage of the collected energy remains problematic. Batteries are costly and have a low energy density compared to chemical fuels^[4] and not all technologies can be easily adapted from fuel to electricity. Therefore new technologies are required, for the conversion of solar energy into a chemical fuel, in order to achieve widespread utilization of solar energy as the primary source of energy.

Nature is able to generate biomass from CO₂, sunlight and water through photosynthesis with O₂ being the only by-product. However, the reactions involved in photosynthesis are highly complex. Therefore, artificial solar-to-fuel conversion schemes necessarily have to be simpler processes like the splitting of water into dihydrogen and dioxygen. In order to achieve water splitting, efficient and robust catalysts are required for both the hydrogen evolution reaction and the oxygen evolution reaction. Between the hydrogen evolution reaction and the oxygen evolution reaction, the latter, also commonly referred to as water oxidation, is substantially more difficult to catalyze. The water oxidation reaction involves the rearrangement of four electrons and four protons which results in a kinetically very challenging reaction.^[5] As a result, catalyzing the water oxidation reaction has been a research topic of great interest for over a decade now and a wide range of different catalysts, both homogeneous and heterogeneous, has been developed.^[6-7]

In chapter 1 of this thesis an overview is provided over the progress in homogeneous water oxidation catalysis with emphasis on iron-based water oxidation catalysts in particular. Additionally, the use of chemical oxidants in large

excess – currently the standard methodology for studying potential water oxidation catalysts – is discussed critically in comparison with electrochemistry as an alternative methodology.

6.1.2 Structure-activity relationships of iron-based electrocatalysts for the water oxidation reaction

In this thesis, iron-based water oxidation catalysts are described, based on the three different ligand platforms cyclam, bpmcn and Hbbpya (with bpmcn = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-cyclohexane-1,2-diamine; Hbbpya = *N,N*-bis(2,2'-bipyrid-6-yl)amine and cyclam = 1,4,8,11-tetraazacyclotetradecane) (Fig. 6.1).

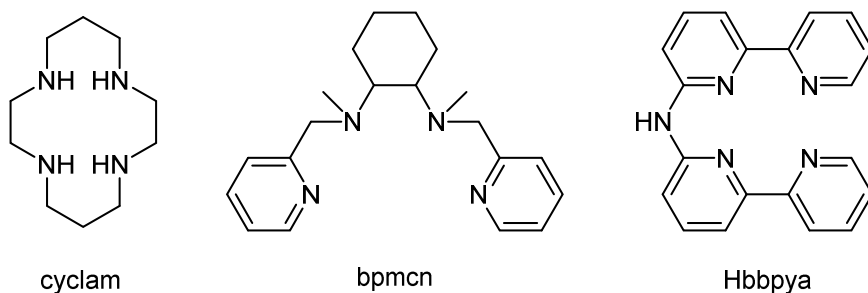


Figure 6.1: Structures of the three ligand platforms used in the iron-based water oxidation catalysts described in this thesis: 1,4,8,11-tetraazacyclotetradecane (cyclam, left), *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-cyclohexane-1,2-diamine (bpmcn, middle) *N,N*-bis(2,2'-bipyrid-6-yl)amine (Hbbpya, right).

In chapter 2, three complexes based on the macrocyclic cyclam ligand are described (Fig. 6.2). The complexes *cis*-[Fe(cyclam)Cl₂]Cl and *trans*-[Fe(cyclam)Cl₂] are both based on the same ligand and differ only in their coordination-geometry.

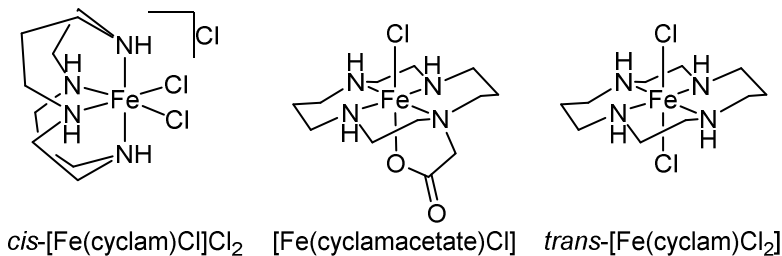


Figure 6.2: Structures of the three cyclam-based complexes discussed in chapter 2.

The complex [Fe(cyclamacetate)Cl] features a modified cyclam ligand which has an additional acetate group that can coordinate in axial position on the iron

centre, resulting in a pentadentate ligand. The results of CV experiments in 0.1 M NaClO₄ electrolyte solution showed that the Fe^{II/III} redox couples of *cis*-[Fe(cyclam)Cl₂]Cl and [Fe(cyclamacetate)Cl] lie at considerably more cathodic potentials than the Fe^{II/III} redox couple of *trans*-[Fe(cyclam)Cl₂]. On-line electrochemical mass spectrometry (OLEMS) measurements of all three complexes showed that *cis*-[Fe(cyclam)Cl₂]Cl and [Fe(cyclamacetate)Cl] are capable of catalyzing water oxidation with an onset potential of oxygen evolution at about 1.8 V. *Trans*-[Fe(cyclam)Cl₂] on the other hand was found to be catalytically inactive at potentials up to 2.0 V. This comparison shows that the electronic structure of a complex is crucial for enabling catalytic activity at lower overpotentials. Having an Fe^{II/III} redox couple at a lower potential is indicative of a structure in which more electron density is donated from the ligand to the metal centre which should help to stabilize the high oxidation states which are required to achieve water oxidation.

The results of the OLEMS experiments presented in chapter 2 also show that considerable amounts of CO₂ are being formed for all three complexes with an onset of CO₂ formation below that of the onset of O₂ evolution. This observation could indicate a weakness of cyclam as a ligand platform for reactions under strongly oxidizing conditions.

6.1.3 The role of the electrode surface in electrocatalytic homogeneous water oxidation

Due to the use of a carbon-based working electrode in the experiments described in chapter 2, it is difficult to unambiguously determine the electrode or the cyclam ligand as the source of the CO₂ formation. The presence of chloride ions in the structures of all three cyclam-based complexes prohibits the use of other electrode materials such as gold since the gold oxide layer formed at the surface of the electrode at high potentials is unstable in the presence of halide ions. This leads to a large oxidative background current which makes interpretation of the voltammograms difficult (see Fig. 2.2, chapter 2). These limitations have been addressed in the follow-up work described in chapter 3.

In chapter 3 the synthesis and characterization of a new dinuclear iron complex based on the ligand Hbbpya is described. The complex was designed based upon the results described in chapter 2. The polypyridyl-type ligand Hbbpya is expected to be more robust towards oxidation than the aliphatic cyclam ligand. Additionally, the compatibility of the complex with different electrode materials

was ensured by avoiding the use of halide ions. The electrochemical experiments described in chapter 3 with the complex $[(\text{MeOH})\text{Fe}(\text{Hbbpya})-\mu\text{-O}-(\text{Hbbpya})\text{Fe}(\text{MeOH})](\text{OTf})_4$ revealed two main results: I) when using a pyrolytic graphite (PG) working electrode, substantial amounts of CO_2 are detected in OLEMS experiments while little to no CO_2 formation is observed in OLEMS experiments with a gold working electrode and II) using a working electrode made up of graphitic carbon results in a substantially lower overpotential for oxygen evolution catalyzed by the $\text{Fe}(\text{Hbbpya})$ complex compared to working electrodes made up of gold or non-graphitic carbon.

CO_2 formation has already been described in literature to occur in experiments with carbon-based electrodes under the harsh conditions required for electrocatalytic water oxidation.^[8] However, the first direct evidence for the carbon electrode being the source of the CO_2 is provided by the difference in CO_2 formation between a PG working electrode and a gold working electrode in the OLEMS experiments described in chapter 3.

The difference in oxygen evolution behaviour of the $\text{Fe}(\text{Hbbpya})$ complex between a PG working electrode and a gold working electrode suggests different mechanisms of the oxygen evolution reaction by the complex for graphitic and non-graphitic electrode materials. π - π -stacking interactions between the complex and the surface of an sp^2 carbon electrode could be a possible explanation for this phenomenon because of the presence of an extended aromatic system in the Hbbpya ligand. To the best of our knowledge, this is the first evidence for a clear substrate influence of the electrode material in electrocatalytic water oxidation.

The results described in chapter 4 showed two indications for the involvement of the surface of a gold working electrode in the resulting electrochemistry of the complexes $\text{H}_4\text{-}\alpha\text{-}[\text{Fe}(\text{bpmcn})(\text{OTf})_2]$ and $\text{D}_4\text{-}\alpha\text{-}[\text{Fe}(\text{bpmcn})(\text{OTf})_2]$: I) The peak current at 2.0 V increased between scans in CV experiments in which the potential was cycled repeatedly over the gold oxide formation and reduction area and II) the first scan was markedly different from subsequent scans in an OLEMS experiment between 1.3 and 2.0 V in terms of the current profile as well as O_2 and CO_2 mass traces. While the underlying mechanism for these observations could not yet be determined conclusively, the evidence points to a connection to gold oxide formation processes at the electrode surface. Other explanations such as the formation of surface deposits under high potential conditions could be ruled out through control experiments with an electrochemical quartz crystal microbalance (EQCM) in combination with cyclic voltammetry.

6.1.4 Challenges in benchmarking of homogeneous electrocatalysts for the water oxidation reaction

The results described in section 6.1.3 regarding the influence of the electrode surface on the results of electrochemical water oxidation catalysis are not only of fundamental interest for the understanding of the processes involved in electrocatalytic water oxidation on a molecular level and the design of improved water oxidation systems. Beyond that, the results also have very important implications for attempts at benchmarking water oxidation catalysts with regards to future applications in water splitting.

The formation of CO₂ from carbon-based working electrodes is an undesired side reaction. Not only does this represent a challenge for applications in sustainable energy production, it also means that potential formation of CO₂ must be accounted for when investigating the kinetics of catalysis with carbon-based working electrodes. Additionally, the formation of CO₂ from the electrode material implies that the surface of a carbon-based working electrode changes constantly under oxidative electrocatalytic conditions.

The dynamic behaviour observed in experiments with a gold working electrode described in chapter 4 also represents a significant obstacle for obtaining reliable benchmark values when gold is used as an electrode material. Therefore, the interplay between complexes in solution and the electrode surface was explored further as is described in chapter 5.

The results of a series of CV experiments show that both PG and gold working electrodes behave differently in the presence and in the absence of metal complexes in the electrolyte solution. A PG working electrode showed an onset of CO₂ formation at a lower potential in the presence of metal complexes compared to blank experiments. This means that metal complexes which are capable of catalyzing the water oxidation reaction also catalyze the oxidation of carbon-based electrodes to CO₂. In the case of a gold working electrode, the presence of metal complexes in solution resulted in changes to the gold oxide formation and reduction pattern in the voltammogram of the gold background. Even though the nature of those changes and the mechanism through which they are induced remains unclear, these results show that the presence of metal complexes in solution influences the surface structure of a gold working electrode. This leads us to conclude that there must be substantial electronic interaction between the complexes and the electrode surface which goes beyond simple outer sphere electron transfer.

While the results of chapter 3 show that the choice of electrode material can significantly influence the electrochemical behaviour of a given complex, the results of chapters 4 and 5 show that dynamic processes at the surface of a working electrode can lead to changes over time in electrochemical experiments. These results demonstrate the importance of considering the electrode material as part of the electrocatalytic system.

6.2 General conclusions

The results of the work presented in this thesis show that coordination complexes based on iron can be made to work as electrocatalysts for the water oxidation reaction. We found that in order to achieve robust and efficient water oxidation electrocatalysis based on iron, it is important to not only find a stable ligand platform but to also control the electronic structure of the complex (chapter 2).

Considering that benchmarking of catalysts is an important part of the development of new catalysts, the interactions between homogeneous electrocatalysts and the surface of the working electrode need to be considered carefully, which so far has been largely ignored in literature. The interactions between the electrocatalyst and the surface of the working electrode can have important consequences, both for the catalytic behaviour of the catalyst (chapters 3 and 4) and for the electrode material itself (chapter 5). As a result, useful comparisons between different electrocatalysts can only be made when the same electrode material is used in each case. Additionally, electrocatalysts should be studied with several different electrode materials whenever possible to assess to which extent the electrode surface might be involved in catalysis. While some catalysts may experience a beneficial influence from a certain electrode material such as graphitic carbon (chapter 3) the same is not necessarily true for other catalysts in combination with the same electrode material (chapter 4).

In order to obtain an estimation of the relative catalytic activities of the catalysts reported in this thesis, in table 6.1 we compare the $(I_{\text{cat}}/I_{\text{p}})^2$ values (cf. Appendix B) of the complexes *cis*-[Fe(cyclam)Cl₂]Cl (chapter 2), [(MeOH)Fe(Hbbpya)-μ-O-(Hbbpya)Fe(MeOH)](OTf)₄ (chapter 3) and H₄-α-[Fe(bpmcn)(OTf)₂] (chapter 4). Keeping in mind the aforementioned challenges in determining reliable benchmark values, the data is derived from CV experiments with graphitic working electrodes for each catalyst. This allows us to use O₂ to CO₂ ratios from OLEMS measurements as an indicator of the relative amount of current caused by oxygen evolution for each complex. Since the O₂ to CO₂ ratios fall within the same

order of magnitude for all three complexes, the $(I_{\text{cat}}/I_{\text{p}})^2$ values suggest that the Fe(Hbbpya) complex is the most active electrocatalyst described in this thesis. Considering that the ratio of O₂ to CO₂ only represents a rough estimation of the faradaic efficiency, we refrain from assigning definitive catalytic turnover frequencies to any of the $(I_{\text{cat}}/I_{\text{p}})^2$ values.

In terms of catalytic overpotential the Fe(Hbbpya) complex reported in chapter 3 clearly stands out as having the lowest onset potential of water oxidation with respect to the thermodynamic standard potential for the water oxidation reaction of 1.23 V vs. RHE. The complexes *cis*-[Fe(cyclam)Cl₂]Cl and α -[Fe(bpmcn)(OTf)₂] showed onsets of water oxidation around 1.8 V (Fig. 2.6, chapter 2 and Fig. 4.13, chapter 4) while the Fe(Hbbpya) complex showed oxygen evolution at potentials as low as 1.6 V (Fig. 3.6, chapter 3).

Table 6.1: Benchmark values for selected water oxidation catalysts described in this thesis[†]

Catalyst	E [V]	$(I_{\text{cat}}/I_{\text{p}})^2$	O ₂ /CO ₂ Ion current*
<i>cis</i> -[Fe(cyclam)Cl ₂]Cl	2.0	3×10^2 ^[a]	2.8±0.8
H ₄ - α -[Fe(bpmcn)(OTf) ₂]	2.0	1×10^2 ^[b]	2.0±0.2
[((MeOH)Fe(Hbbpya)) ₂ - μ -O](OTf) ₄	2.0	7×10^2 ^[c]	2.5±0.4
[((MeOH)Fe(Hbbpya)) ₂ - μ -O](OTf) ₄	1.75	1×10^2 ^[c]	8.7±1.4

^a based on data from figure 2.4b, chapter 2; ^b based on data from a CV experiment with 1.1 mM α -[Fe(bpmcn)(OTf)₂] in a 0.1 M NaClO₄ electrolyte solution recorded between 0.0 and 2.0 V vs. RHE with a GC working electrode at 10 mV/s; ^c based on data from figure 3.5b, chapter 3.

[†]All $(I_{\text{cat}}/I_{\text{p}})^2$ values were determined from the 2nd scan of a CV experiment of each respective catalyst, measured between 0.0 and 2.0 V vs. RHE at a scan rate of 10 mV/s. Electrochemical experiments with [((MeOH)Fe(Hbbpya))₂- μ -O](OTf)₄ were performed at half the catalyst concentration of the experiments with *cis*-[Fe(cyclam)Cl₂]Cl and H₄- α -[Fe(bpmcn)(OTf)₂] to ensure the same concentration of iron centres in each case.

*The values for the ratios of $m/z = 32$ to $m/z = 44$ ion currents at 2.0 V vs. RHE were determined by taking the average over all available datasets for each catalyst. The value of the ratio of $m/z = 32$ to $m/z = 44$ ion currents for [((MeOH)Fe(Hbbpya))₂- μ -O](OTf)₄ at 1.75 V vs. RHE was determined by averaging the ion currents over the range of 1.70–1.80 V vs. RHE for each available dataset and then taking the average over all datasets. The errors represent the largest deviation from the average that was measured. Background correction was performed by assuming an exponential decay fit for all ion current traces.

6.3 Outlook & Perspectives

Based on the results obtained over the last few years, it is now established that iron complexes can function as electrocatalysts for the water oxidation reaction.^{[9-}

^{11]} To further improve the efficiency of homogeneous iron-based water oxidation electrocatalysts, targeted variations of the electronic properties of ligands are needed to control the redox potential of the crucial high oxidation state

intermediates in order to achieve low overpotential catalysis. A similar approach has already been successfully employed for long established ruthenium-based catalysts.^[12] Accordingly, a systematic experimental study of differently substituted ligands guided by theoretical calculations could be helpful for finding low overpotential iron-based electrocatalysts.

The incorporation of additional functional groups could further improve the catalytic activity, once the energy barrier for reaching the highest oxidation state intermediates is sufficiently low. When the O–O bond formation step is rate determining, facilitating this step could lead to an improved catalytic performance.^[13] In a water nucleophilic attack mechanism, the O–O bond formation involves a high-energy intermediate in the form of $[M-O-OH_2]$. Proton shuttles can lower the energy barrier associated with the O–O bond formation step by abstracting a proton from the incoming water molecule, thus avoiding the formation of this energetically unfavourable intermediate (Fig. 6.3).^[13-14] The proton shuttle in this case can be an external base such as phosphate or acetate buffer which is present in excess,^[13] a pending basic group in the second coordination sphere of the metal centre^[15] or a neighbouring ligand at the metal centre^[16].

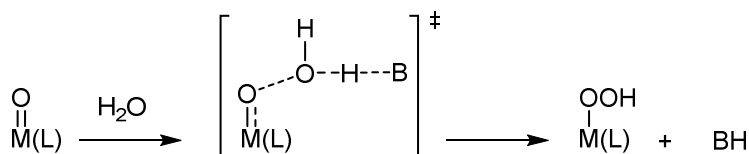


Figure 6.3: Schematic representation of a general water nucleophilic attack mechanism involving a proton acceptor B (with M = metal, L = ligand)

The experiments described in chapters 3-5 of this thesis provide evidence for considerable interactions between dissolved complexes and the surface of the working electrode in electrocatalytic applications. Further research is still required in order to obtain a better understanding of the mutual influence between the surface of the electrode material and the electrochemistry of complexes in solution. The combination of electrochemical measurements with online spectroscopic measurements would be desirable to obtain a better understanding of the extent of electronic interactions between the Fe(Hbbpya) catalyst and the surface of graphitic electrodes. Graphene-based carbon electrodes could potentially prove to be suitable substrates for combining, for example, cyclic voltammetry and UV-vis spectroscopy.

In the case of gold working electrodes, surface-enhanced Raman spectroscopy (SERS) in combination with ^{18}O isotopically labeled water could be used to gain insight into the fate of the oxide layer on the electrode surface at potentials above 1.3 V vs. RHE in the presence of metal complexes in solution. Additionally, surface characterization techniques such as *in situ* and *ex situ* microscopy will be required to understand the apparent restructuring processes that take place at the surface of gold electrodes in the presence of metal complexes

6.4 References

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