Design of homogeneous water oxidation electrocatalysts

Boer, D. den

Citation

Boer, D. den. (2022, December 1). *Design of homogeneous water oxidation electrocatalysts*. Retrieved from https://hdl.handle.net/1887/3492597

Chapter 7

Summary, Conclusion and Outlook

7.1 Summary and Conclusions

The storage of energy is one of the major challenges in the energy transition from fossil fuels to renewable energy. The usage of dihydrogen as an energy carrier is a potential solution for the storage of energy. The advantage of dihydrogen is that it can be produced by water splitting without any emission of pollutants or greenhouse gasses. The overall water-splitting reaction consists of two half reactions, which are the proton reduction and the water oxidation (WO) reaction. Of these two half reactions, the WO reaction is the bottleneck for the overall water splitting process as the reaction consists of multiple intermediates, includes proton- and electron-transfer steps, and the formation of an O–O bond. All of this makes it a complicated reaction, for which it is not easy to find a catalyst that can stabilize all necessary catalytic intermediates equally. Consequently, an additional driving force, i.e. overpotential, is required.

Over the last decades, several homogeneous and heterogeneous water oxidation catalysts (WOCs) have been developed. Most of these catalysts are based on ruthenium and iridium, which are scarce and therefore expensive metals. A cheaper alternative is the utilization of first-row transition metals, such as iron, cobalt, nickel and copper. The research described in this thesis focusses on the design of homogeneous water oxidation electrocatalyst.

In Chapter 1 the developments on designing homogeneous WO electrocatalyst are discussed. Moreover, important lessons learned from Ru- and Ir-based WOCs and additional challenges regarding the homogeneity, ligand stability and activity of first-row transition metal based homogeneous WOCs are summarized.

The development of an efficient electrocatalyst for the WO reaction is hampered by unfavorable scaling relations between catalytic intermediates. Optimization of one particular catalytic intermediate simultaneous results in destabilization of another catalytic intermediate, which results in a constant overpotential. However, homogeneous catalysts allow for tailored ligand design, in which substituents can be introduced on the ligand to tune the electronic structure and stabilize particular catalytic intermediates. Understanding the electronic effects induced by substituents will lead to a clear set of design principles to obtain the best possible performing homogeneous electrocatalysts, similar to the scaling relations in heterogeneous catalysis. To investigate the influence of electron-donating groups (EDGs) or electron-withdrawing groups (EWGs) on the elementary steps in electrochemical WO catalysis, *cis*-$[Ru(bpy)_2(H_2O)]^{2+}$ (bpy = 2,2'-bipyridine) was selected as the scaffold that was modified with methyl, methoxy, chloro and trifluoromethyl groups, which is described in Chapter 2. This catalyst can undergo several electron transfer (ET), proton transfer (PT) and proton-coupled electron transfer (PCET) steps that can all be probed experimentally. For all modified complexes, Pourbaix diagrams were constructed based on cyclic and differential pulse voltammetry. From the Pourbaix diagrams, redox potentials and pK_a values were estimated and it was determined how these values scale compared to the benchmark catalyst. In this Hammett study, we found that the potential of PCET steps are relatively insensitive with respect to the presence of EDGs or EWGs, while the potential of the decoupled ET and PT steps are more heavily affected. However, the influence of the substituents decreases with an increasing oxidation state of the Ru center, due to a lack of d-electrons available at the Ru center for π-backbonding to the bipyridine ligand. Therefore, the potential of the $Ru^{V/VI}$ redox couple appears to be independent of the substituents. Although electronic effects do not decrease the overpotential at which WO catalysis occurs, our studies do show that upon introducing EDGs the pH window wherein the most favorable PCET mechanism (from a thermodynamical point of view) takes place can be extended over a broader pH range. Moreover the implementation of EWGs can shift all oxidation events towards a single thermodynamic potential at which all redox events could occur simultaneously. This illustrates that homogeneous catalysts do not necessarily seem to suffer from linear scaling of the individual redox steps through electronic effects, which offers a significant advantage over heterogeneous catalysis.

A cheaper alternative for the Ru and Ir-based WOCs is the utilization of first-row transition metal based WOCs, as these metals are earth-abundant. First-row transition metals have significantly smaller atomic radii, lower electronegativity and are harder Lewis acids than the second and third-row transition metals. As a consequence, first-row transition metals are less stable in higher oxidation states and suffer from more labile metal-ligand interactions. The utilization of first-row transition metal WOCs is thus challenging compared to Ru and Ir-based WOCs. Due to the different physical properties of the metal center, an alternative WO mechanism is expected for late first-row transition metals instead of the typical water nucleophilic attack and the inter- or intra-molecular radical-oxo coupling pathways, which were previously proposed for Ru-based catalysts. In Chapter 3 the potential mechanistic pathways in Cu-catalyzed WO are discussed. To develop the next generation of efficient WOCs based on first-row transition metals good understanding is required of reaction pathways via which these systems react. In contrast to catalysts based on early transition metals, high-oxidation state metal-oxo species are unlikely intermediates in Cu-catalyzed WO, since π-donation from the oxo ligand to the Cu center is difficult due to the high number of d-electrons in Cu^{II} and Cu^{III} ions. The coordination compound $[Cu^{II}(H\mathbf{L})(OTf)_2]$ (H**L** = *N,N*-bis(2,2’-bipyrid-6-yl)amine) was investigated as a WO catalyst bearing the redox-active H**L** ligand. The compound was studied as a WO catalyst at pH 11.5, at which the deprotonated complex $[Cu^{II}(\mathbf{L}^{-})(H_2O)]^{+}$ is the predominant species in solution. The overall WO mechanism was found to start with two PCET steps. Based on a kinetic study, a 1st-order dependence in catalyst, a 0th-order dependence in phosphate buffer, a kinetic isotope effect of 1.0, a $\Delta H^{\ddagger}$ of 4.49 $kcal{\cdot}mol^{-1}$, a $\Delta S^{\ddagger}$ of –42.6 $cal{\cdot}mol^{-1}{\cdot}K^{-1}$ and a $\Delta G^{\ddagger}$ of 17.2 $kcal{\cdot}mol^{-1}$ were found. A computational study supported the formation of a Cu-oxyl intermediate, $[Cu^{II}(\mathbf{L}^{\bullet})(O^{\bullet})(H_2O)]^{+}$. From this intermediate onwards, formation of the O–O bond proceeds via a single-electron transfer from an approaching hydroxide ion to the ligand (SET-HA mechanism). The Cu^{II} center is proposed to be redox-inactive throughout the mechanism.

Based on the postulated mechanistic pathway in Chapter 3, structure-activity correlations based on the SET-HA mechanism were investigated in more detail. In Chapter 4 a series of Cu complexes is described, bearing modified redox-active ligands based on the 6,6’-bis(2-aminopyridyl)-2,2’-bipyridine ligand scaffold. The effect of the electronic structure and geometry on the redox potentials of the $Cu^{I/II}$ center and ligand-based oxidation of the coordination complex was investigated. The Cu complexes were studied electrochemically in acetonitrile and aqueous solutions. The formation of a delocalized ligand radical was found to be essential to obtain catalytic WO activity. Furthermore, we found that ligand oxidation can be controlled by electronic effects of substituent methoxy groups on various positions in the ligand. This allows us to propose design principles for ligands employed in WOCs that operate via the mechanism proposed in Chapter 3:

1) The redox-active ligand should contain a negative charge of at least –1 or have the ability to oxidize the ligand via PCET whereby a proton is removed from the ligand.
2) The oxidation potential of the redox-active ligands can be controlled by the presence of substituents. To decrease the oxidation potential, the electron density should be directed at the position of the ligand where oxidation occurs.
3) Stabilization of the ligand-based radical upon oxidation of the ligand by electronic or delocalization effects decreases the oxidation potential of the ligand-based oxidation.

Fe- and Cu-based systems in combination with the H**L** ligand showed relatively good results for WO. The ligand was employed in combination with cobalt as described in Chapter 5 and nickel as reported in Chapter 6. The homogeneity of Co-based WOCs has often been under debate over the last decade. A large number of Co-based WOCs have been shown to act as precursors for the formation of CoO_x, which then acts as an efficient heterogeneous WOC. Cyclic voltammetry experiments of aqueous solutions of the coordination compound [Co(H**L**)$(OAc)_2$] revealed that the complex does not remain completely homogeneous over several cycles. In addition, the cobalt-based system was investigated with electrochemical quartz crystal microbalance (EQCM) and X-ray photoelectron spectroscopy. The obtained experimental results were compared with those of heterogeneous CoO_x. Although it is shown that Co(H**L**) interacts with the electrode during electrocatalysis, the formation of CoO_x was not observed. Instead, a molecular deposit of Co(H**L**) was found to be formed on the electrode surface. This study shows that deposition of catalytic material on the electrode surface is not necessarily linked to the decomposition of homogeneous WOCs.

In Chapter 6 the results are reported of the investigation concerning the complex [Ni^{II}(H**L**)$(OTf)_2$] as a WOC under various conditions. This compound was found to be a homogeneous catalyst for the WO reaction at pH 1. The WO mechanism starts with a PCET step involving the redox-active H**L** ligand. A second and third PCET step results in the formation of the active species, $[Ni^{III}(\mathbf{L}^{\bullet})(O^{\bullet})]^{2+}$. A 1st-order dependence in catalyst and a KIE of 1.0 is found. A water nucleophilic attack mechanism is proposed under these acidic conditions. Overall, Ni(H**L**) was found to remain stable and homogeneous under oxidative conditions at pH 1 by bulk electrolysis and EQCM. With this proof of concept, the use of first-row transition metal complexes under acidic conditions opens new opportunities for the design of sustainable electrocatalyst for electrocatalytic WO.

The research described in this thesis provides insight on the influence of electronic effects on homogeneous electrocatalysts and on the interactions between electrocatalyst and the electrode surface. Moreover the studies in this thesis outline design criteria and ideas for a new generation of WOCs, which are essential for efficient and economically viable water splitting.

7.2 Outlook

The results of the work presented in this thesis show that homogeneous electrocatalyst provide an excellent scaffold to study structure-activity relations. For the WO reaction, the advantages and limitations of modifying the electronic structure and the importance homogeneity and operating conditions have been discussed in this thesis.

The employment of the redox-active H**L** ligand with various metals (Co, Ni and Cu) shows that all the complexes do show catalytic activity for the WO reaction (Chapter 3, 5 and 6). The redox-active ligand, which is the common denominator in all these systems, allows for the accumulation of sufficient oxidation equivalents in the WO catalyst without having to go to an unfavorable high oxidation state of the metal center. However, the precise reaction conditions (e.g. pH) where all these catalytic systems operate are highly different. Although this points to a specific influence of the precise reactions conditions on the reactivity of these systems, the origin for these differences are not yet fully understood. Therefore, it would be interesting to systematically explore how catalytic properties are affected by the combination of the ligand, the metal and the selected reaction conditions. The information gained by such studies would ultimately lead us to the design of excellent ligands for WOCs. In addition, it would be useful to study how redox-active ligands are involved in the WO mechanism and O–O bond formation. For example, the H**L** ligand is irreversibly oxidized in combination with various metals. To improve the understanding of the WO mechanism, it is important to understand what kind of species is formed upon oxidation of the ligand and why the oxidized species is stable and not (easily) reduced.

The homogeneity and operating conditions were shown to be of great importance for the performance of WOCs. However, the exact trigger causing a catalyst to decompose or deposit on the electrode surface is often unknown. The interaction between the homogeneous catalyst and the electrode surface is likely of more importance than often is assumed. It would be helpful to investigate the interaction between homogeneous catalysts with various electrode materials in a detailed manner. Such a study should include carbon and metal-based electrodes, as well as conducting and semi-conducting materials, and homogeneous complexes of varying geometry, metal-ligand binding strengths and electronic structure. Understanding these interactions would assist in selecting useful operating conditions to study the catalyst homogenously and to more successfully utilize the catalyst in immobilized form when anchored to the electrode surface.