The role and analysis of molecular systems in electrocatalysis
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Chapter 6

Summary and conclusion

6.1   Summary

The storage of electricity that is generated via renewable sources is one of the great challenges of the future because there is no technology available yet that is able to replace all fossil fuel driven processes. As discussed in Chapter 1, water electrolysis into H_2 and O_2 is a method to store electricity, but the half reaction that concerns the oxidation of H_2O to O_2, and *vice versa,* is accompanied with large energy losses. Even the best electrocatalysts to date have to operate far from the equilibrium potential to obtain sufficiently high currents. Electrocatalytic studies of molecular catalytic systems can contribute to reduce overpotentials in several ways. Structural mimics of the active site of highly active enzymes can be synthesized and/or the ligand(s) of molecular complexes can be systematically adjusted to induce differences in the electronic and geometric properties of the metal active site to boost its reactivity. For example, the molecular copper complexes for O_2 reduction that have been described in this thesis are partly inspired on the active site of the enzyme laccase. Laccases performs oxygen reduction close to the equilibrium potential of 1.23 V by utilizing a trinuclear copper active site. Mechanistic structure–activity studies of the (modified) molecular complexes can reveal which factors improve catalysis. On the other hand, molecular systems are generally far less stable than heterogeneous electrocatalysts. In most cases, high ligand exchange rates or ligand degradation due to reactive intermediates lead to metallic or metal oxide deposits on the electrode. With this in mind, there are several tools to attribute the kinetics, product selectivity and stability of these molecular systems under electrocatalytic conditions. Rate constants may be obtained with the current enhancement method and/or the foot of the wave analysis (FOWA). The rotating ring disk electrode (RRDE) setup is a powerful tool to determine product selectivity, for example the selectivity of the O_2 reduction reaction (ORR) to either H_2O_2 or H_2O as product, especially when combined with other tools to quantitatively determine the product distribution. Finally, the stability of molecular systems can be assessed with a range of electrochemical tools such as electrochemical quartz crystal microbalance (EQCM), but also surface sensitive techniques such as X-ray photoelectron spectroscopy (XPS). We have used these tools to investigate several molecular systems. Chapters 2 and 3 discuss molecular complexes that decompose to a heterogeneous active species and the subsequent effect on electrocatalytic water oxidation or ORR, respectively. Also, we have studied molecular copper complexes for the ORR for which we changed the ligand which resulted in a different selectivity (Chapter 4) and/or affected the onset potential and catalytic rate (Chapter 5).

The best electrolyzers to date use iridium oxide as catalyst to oxidize water to O_2. Nevertheless, the overpotential at which these electrolyzers have to operate is still significantly large. Moreover, iridium oxide is expensive and scarce to such an extent, that the current technology will not be able to replace all fossil fuel driven processes. For that reason, molecular iridium complexes can be interesting platforms to study whether ligand effects can increase the activity of iridium and reduce catalyst loadings. A significant portion of studies involving molecular catalysts have been performed with sacrificial reagents, in which the oxidative power for O_2 evolution is delivered by reagents such as $((NH_4)_2[Ce(NO_3)_6])$ and $NaIO_4$. In a previous study that used sacrificial reagents, the turnover frequency (TOF) of a series of Cp* (Cp* = pentamethylcyclopentadienyl) iridium complexes bearing hydroxylpicolinate ligands was found to be the highest for the complex with an unsubstituted picolinate ligand. In Chapter 2, the electrochemical evaluation of the water oxidation activity of these complexes is described. We found with EQCM studies that these complexes, under electrochemical conditions, form a deposit on the electrode that was characterized by XPS. Bulk electrolysis revealed that the Cp* ligand of the parent complexes was oxidatively degraded because breakdown products were found in the electrolyte with ^{1}H nuclear magnetic resonance (NMR) spectroscopy. Interestingly, the XPS studies showed that the influence of the ligand on the electronic environment of the iridium was stronger for the parent complexes than for the corresponding deposits on the electrode. Minimal differences between the electronic properties of the iridium in the deposit were found. Correspondingly, a minimal difference in water oxidation activity of these deposits was observed as well without a clear structure–activity relationship. Equally, other known iridium complexes with different ligand systems were also found to deposit material on the electrode. XPS studies showed that the spectra of these deposits differed only marginally from the spectra of the deposits formed by the iridium picolinate complexes. Likewise, a minimal variation in water oxidation activity of these deposits was observed. In contrast, the deposit formed by ligand-free $[Ir(OH)_6]^{2-}$ produces water oxidation currents that are almost 2 orders of magnitude larger. Based on these results, we suggested that the iridium complexes oxidatively degrade to a small IrO_x type cluster that contains just a few iridium atoms but also some ligand (or residues thereof). The ligand (or residue), might inhibit the water oxidation activity but may be used to prevent catalyst deactivation and, more importantly, prevent aggregation of active iridium sites which could be beneficial for lowering the iridium loading in electrolyzers.

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Fuel cells are able to generate electricity by the reaction of H_2 and O_2 to H_2O. However, the energy output is limited due to the fact that even state-of-the-art catalysts cannot reduce O_2 close to the equilibrium potential of 1.23 V. Some electrochemical studies into laccase have suggested that this enzyme can perform the ORR close to the equilibrium potential. Inspired on the enzymatic active site that contains a trinuclear copper cluster, many molecular copper complexes for oxygen reduction have been reported. Interestingly, one specific dinuclear copper complex (**Cu(DAT)**) with two bridging 3,5-diamino-1,2,4-triazole (DAT) ligands was reported with a remarkably low overpotential and high activity and was therefore seen as the benchmark for ORR by molecular copper complexes. Notably, the active catalyst used in that study was prepared by mixing a copper salt, the triazole ligand, and a carbon support without any proof that **Cu(DAT)** was actually present as active species. Therefore, we set out to investigate the ORR activity of **Cu(DAT)** as is elaborated in Chapter 3. We found that **Cu(DAT)** precipitates out of aqueous solutions when coordinating anions are used either in the source of the copper salt or in the electrolyte. Therefore, our electrochemical studies were performed with *in situ* generated complex that was prepared from $Cu(CF_3SO_3)_2$ and in $NaClO_4$ as supporting electrolyte. This way, we were able to start with a homogeneous, dinuclear copper complex which was characterized with EPR (electron paramagnetic resonance) and UV-vis spectroscopy. We found with EQCM that the complex forms a deposit on the electrode under electrochemical conditions. We characterized this as a Cu^o deposit with XPS. Thus, the complex itself was found to be unstable under electrochemical conditions. Furthermore, we have shown with EPR and XPS characterization that the previously reported active catalyst (the mixture of carbon support, a copper salt, and DAT) is not **Cu(DAT)**, but in fact the very same Cu^o deposit. Studies with a Cu^o electrode in the presence of the triazole ligand showed that this ligand inhibits corrosion of Cu^o at higher potentials than without the presence of the triazole. This explains why the active species formed by the complex (the Cu^o deposit) did not show any stripping peaks at higher potentials within the catalytic potential window. Even though the molecular system disintegrates, this finding shows that the ligand still beneficially influences the electrocatalysis. This study signifies the need for proper characterization of the active species so that catalyst are not wrongfully benchmarked to molecular systems that are not stable under electrocatalytic conditions.

The electrocatalytic reduction of O_2 can be either the 4 electron reduction to H_2O or the 2 electron reduction to H_2O_2. The electrochemical production of H_2O_2 by the ORR is a promising on-site alternative for the current bulk production method

via the energy intensive and wasteful anthraquinone process which still accounts for over 90% of the worldwide production of H_2O_2. In that retrospect, we studied a water-soluble dinuclear copper complex (**Cu_2(btmpa)**) that bears the btmpa ligand (btmpa = 6,6'-bis[[bis(2-pyridylmethyl)amino]methyl]-2,2'-bipyridine) that links two Cu^{II} sites via the central bipyridine moiety. This complex can be considered as the dinuclear version of the mononuclear copper complex (**Cu(tmpa)**) bearing the tmpa ligand (tmpa = tris(2-pyridylmethyl)amine). **Cu(tmpa)** was previously found to reduce O_2 with a TOF up to 10^6 s^{-1} in a stepwise mechanism with H_2O_2 as intermediate. In Chapter 4, we show that **Cu_2(btmpa)** has very different properties as compared to **Cu(tmpa)**. Characterization by EPR and SQUID (superconducting quantum interference device) showed that the Cu^{II} centers do not antiferromagnetically couple and that each Cu^{II} has a distorted octahedral geometry as opposed to **Cu(tmpa)** that has a trigonal bipyramidal geometry. This difference has a large impact on the electrochemistry of **Cu_2(btmpa)**. First of all, the $Cu^{I/II}$ redox couple potential of both Cu^{II} centra of **Cu_2(btmpa)** shifted 0.3 V positively with respect to **Cu(tmpa)** due to bipyridine moiety of the btmpa ligand which is less able to donate electrons to the Cu^{II} centra of **Cu_2(btmpa)**. Moreover, we found that O_2 reduction was more sluggish as compared to the O_2 reduction by **Cu(tmpa)**. The most important finding was that H_2O_2 (over-)reduction is hindered to such an extent that the selectivity for H_2O_2 was up to 90% according to RRDE measurements. This lead us to investigate the Faradaic efficiency for H_2O_2 in long, bulk electrolysis experiments using a rotating disk electrode. We found that RRDE is not a suitable method for the measurement of the Faradaic efficiency. Instead, a photometric based method that determines the concentration of H_2O_2 by its reaction with an peroxidase enzyme was used to determine the Faradaic efficiency. In the first half hour of bulk electrolysis at 0.0 V, we found that the complex has a Faradaic efficiency up to 80% for the production of H_2O_2. Moreover, potential dependent adsorption of the complex on the electrode surface, as suggested by EQCM measurements, resulted in the accumulation of active catalyst and thereby a steady increase of the catalytic current in the first 20 to 30 minutes. The most important finding of this study, was that we were able to retain a Faradaic efficiency between 60 and 70% for 2 hours by preventing over-reduction of H_2O_2. At higher H_2O_2 concentrations, **Cu_2(btmpa)** is most likely more prone to disintegrate to Cu^o. Consequently, the formed Cu^o deposit over-reduces H_2O_2 to H_2O which lowers the Faradaic efficiency. However, by briefly applying stripping potentials in regular intervals during the bulk electrolysis of O_2, we were able to strip accumulated Cu^o and prevent over-reduction of H_2O_2. The research presented in Chapter 4 is the first intensive study into the long term

production of H_2O_2 by a molecular system showing that optimization of potentials and stripping intervals is beneficial to optimally use this intrinsically highly selective molecular system for the production of H_2O_2.

The mononuclear **Cu(tmpa)** complex was also the inspiration for Chapter 5. In this chapter, the effect of electron donating groups (EDG's) or electron withdrawing groups (EWG's) on the reactivity of **Cu(tmpa)** was explored. NH_2 (EDG), Cl, and CF_3 (both EWG's) substituents were placed at the *para* position of the coordinating pyridines of the tmpa ligand. The resulting effect that the substituted ligand has on the electronic character of the complex can be best described with the Hammett parameter, because a linear correlation between this parameter and the $E_{1/2}$ of $Cu^{I/II}$ redox couple was found for the complexes. Interestingly, the onset potential of O_2 reduction did not change for the complexes with EWG's with respect to **Cu(tmpa)**, even though the corresponding $E_{1/2}$ of the complex had shifted 100 mV more positive in the case of CF_3 as substituent. Additionally, we found that the rate of catalysis was the highest with Cl substituents, whereas CF_3 substituents did not affect the rate with respect to **Cu(tmpa)**. The reduction of Cu^{II} to Cu^I and the subsequent coordination of O_2 to the reduced Cu^I complex to form the $Cu^{II}-O_2^{\bullet-}$ superoxo species are very fast with respect to the scan rate of a cyclic voltammogram, because the TOF of O_2 reduction by **Cu(tmpa)** is very high (10^6 s^{-1}). Therefore, we believe that the Cu^I complex can be considered as a transient species in a fast equilibrium with both Cu^{II} and $Cu^{II}-O_2^{\bullet-}$ and that the observed rate determining step is Cu^{II} to $Cu^{II}-O_2^{\bullet-}$. In addition, the potential determining step is determined by the $E_{1/2}$ of the Cu^{II} to $Cu^{II}-O_2^{\bullet-}$ reduction. As the electron ends up in an orbital at a remote position from the ligand, the ligand does not affect the onset potential significantly. The rate is most likely determined by the binding constant of O_2 to the complex for which π-backbonding plays an important role. The reduction of H_2O_2 is significantly different from O_2 reduction. Here, we found that EWG's increase the onset potential and increase the rate of H_2O_2 reduction. This is not a unique finding, but can be regarded as unusual as many studies find that a decrease of the overpotential is accompanied by a lower rate. Of note, the highest rate was again obtained with the complex that had Cl groups as substituent. As opposed to the CF_3 group, the Cl group can delocalize electrons from p orbitals and thus have secondary effects on, for example, π-backbonding that are not entirely captured by the Hammett parameter. The structure–activity study presented in this chapter shows that this type of study yields valuable insight into the (apparent) mechanism and can help to beneficially increase the reactivity of molecular systems.

6.2   Conclusion and outlook

The high tunability of molecular complexes is an ideal toolbox to study (electro)catalytic reactions. A variety of options, such as structure–activity studies, can greatly aid the understanding of catalytic mechanism. Chapters 4 and 5 both took inspiration from the mononuclear **Cu(tmpa)** complex and show that catalysis can be significantly altered by inducing a different geometry (Chapter 4) or by changing the electronic nature of the complex by introducing EDG's and EWG's on the ligand (Chapter 5). Specifically, we were able to improve the electrochemical reduction of H_2O_2 by a simultaneous increase of the catalytic rate and onset potential by introducing EWG's on the tmpa ligand of moleculer **Cu(tmpa)** type complexes. The increase of the onset potential could be expected from the Hammett parameter of the corresponding complexes as this correlates to the $E_{1/2}$ of the complexes. As opposed to fast reduction of H_2O_2, we found that **Cu₂(btmpa)** is a highly selective catalyst for the O_2 to H_2O_2 reduction due to hindered H_2O_2 over-reduction. There is no clear explanation why the selectivity differs significantly from **Cu(tmpa)** with the current understanding of the H_2O_2 reduction mechanism. Interesting to note, is that **Cu₂(btmpa)** had the highest $E_{1/2}$ of the $Cu^{I/II}$ of all complexes studied in Chapters 4 and 5 while this had no clear effect on the onset potential, rate or selectivity of O_2 and H_2O_2 reduction with respect to the findings of Chapter 5. Clearly, the difference in rigidity leading to a different geometry has a large impact on electron transfer rates and therefore on the rate of catalysis. Whereas the observed differences in rate and electron transfer induced by the electronic differences of the complexes in Chapter 5 were small, **Cu₂(btmpa)** has a far slower electron transfer due to geometrical constraints that has a large impact on catalysis with respect to **Cu(tmpa)**. In general, the **Cu(tmpa)** type complexes of Chapter 5 displayed fast O_2 and H_2O_2 reduction. The trigonal bipyramidal Cu^{II} geometry and the easy transition to a tetragonal geometry of the corresponding Cu^{I} complex makes that the Cu^{II} to Cu^{I} reduction occurs via fast electron transfer. The flexibility of the pyridine arms of the tmpa ligand facilitate the coordination and release of the tertiary amine to establish these two preferred geometries. On the other hand, the btmpa ligand of **Cu₂(btmpa)** has a strained bipyridine moiety. The rigidity of this moiety leads to an elongation of both of the Cu–N bonds of the bipyridine to avoid steric hindrance between the two Cu centers of **Cu₂(btmpa)**. This leads to a distorted octahedral geometry which is not the optimal geometry for Cu^{II}. In addition, a transition to a tetragonal geometry, preferred for Cu^{I}, is more cumbersome. As a result, the electron transfer to form the Cu^{I} complex is slow. In turn, the slow electron transfer

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significantly lowers the O_2 reduction rate and diminished the H_2O_2 over-reduction. Steric hindrance cannot explain the difference in reactivity because H_2O_2 and O_2 can be considered as comparable in size. An explanation might be that the reorganization required for the reduction of H_2O_2 is more complex than the reorganization of O_2 which encompasses O_2 coordination after Cu^{II} to Cu^I reduction to form the superoxo radical species. In O_2 and H_2O_2 reduction, the strain of the btmpa ligand slows down any required reorganization, but may have a larger impact on H_2O_2 catalysis where reorganization might entail more than merely the reduction of Cu^{II} to Cu^I. Another option would be that any radical species generated due to the splitting of the O–O bond of H_2O_2 degrades the ligand of **Cu₂(btmpa)**. However, this should lead to a quick depletion of the catalytic activity which is not observed and therefore less likely. In contrast, **Cu(tmpa)** type complexes have an open site available due to the tetragonal geometry of the Cu^I complex where coordinated H_2O_2 is not in close proximity with any of the pyridines. Overall, the ability of **Cu(tmpa)** (and related complexes) to adopt a trigonal bipyramidal Cu^{II} complex and easily transition to a tetragonal Cu^I complex allows for very fast O_2 and H_2O_2 reduction to form H_2O. The rate can mildly be improved by placing electron withdrawing groups on the ligand. Mostly, catalysis will be mass-transport limited. On the other hand, for selectively obtaining H_2O_2, steric hindrance caused by a rigid moiety in the ligand seems to be important. As a consequence, O_2 reduction to H_2O_2 will be kinetically hindered instead of mass transport limited and thus requires more catalyst material.

The stability of molecular complexes is always seen as a problem since decomposition of the parent complex can kill the activity, or any observed reactivity might be incorrectly linked to the structure of the complex. Of note, the production of H_2O_2 uses anthraquinones as redox mediator which only have a few turnovers but is still considered as acceptable since >90% of H_2O_2 is prepared via this inefficient process. Chapters 2 and 3 emphasize that thorough studies with multiple methods are required to observe and characterize any active species arising from the decomposition driven deposition of material on the electrode. Even though the molecular systems studied were not the active species, they did form a deposit on the electrode that was active. Interestingly, we found that the ligands used still could influence the activity of the complexes (Chapter 2) and prevent corrosion of the active species under the studied conditions (Chapter 3). This shows that the effect of ligands might still perturbate the activity and stability of heterogeneous bulk catalysts. As discussed in Chapter 1, ligands are actively used to improve the reactivity of, for example, nanoparticles by utilizing the knowledge obtained from catalytic studies with molecular systems. Moreover, the results from Chapter 4

accentuate that the negative consequences of catalyst decomposition (in this case H_2O_2 over-reduction) can be counteracted. First of all, knowledge about the decomposition is vital. Not only in this thesis, but also in other reports, it is shown that copper complexes are prone to decompose to Cu^o deposits. An important aspect is the binding strength of the ligand. The complex discussed in Chapter 3 has a ligand which has only one chelating site per copper atom and thus readily loses its ligand to form Cu^o. On the other hand, the complexes in Chapter 4 and 5 have three to four chelating sites per copper atom that greatly enhances the stability. Due to the higher binding strength of the ligand, Cu^o deposits are less likely to form and can be removed during bulk electrolysis by applying high stripping potentials and thereby retain the high Faradaic efficiency for H_2O_2 production by **Cu₂(btmpa)** (Chapter 4). In conclusion, the research presented in this thesis concerns the assessment of the stability of molecular complexes, identification of the active species, and uncovering factors that improve the reactivity of molecular systems in electrocatalytic reactions. Together, the research allows for a better understanding of the mechanism to improve electrocatalysts that are important for the future energy infrastructure.

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