The electrochemical reduction of dioxygen and hydrogen peroxide by molecular copper catalysts

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Chapter 6


Summary and outlook

6.1.   Summary

The transition from fossil fuels to renewable energy is one of the most pressing challenges of this century. Many factors play a role in our ability to reduce our carbon footprint, while simultaneously being able to keep up with a growing demand for energy. Methods that allow us to be able to efficiently store electrical energy over longer periods of time are essential. This is especially important due to the intermittent nature of two of the most important renewable energy sources, solar and wind energy. While battery technology has progressed such that it is now the most viable option for powering (short-range) transportation with consumer vehicles, batteries are not easily scalable for large scale energy storage to power the industry. Alternatively, dihydrogen (H_2) generated by water electrolysis can play an important role as a chemical energy carrier, which can be used to store and transport energy. Fuel cells can be used to convert H_2 and O_2 to H_2O, thereby generating an electrical current between the anode and cathode of the fuel cell. However, the half reaction at the cathode, the reduction of O_2 to H_2O, is subject to significant energy losses. This multi-step catalytic reaction involves four protons and four electrons is subject to significant overpotential. Even the best platinum-based catalyst is not able to perform this reaction close to the equilibrium potential of 1.23 V. Developing alternative catalysts that are based on non-precious metals and are able to more efficiently catalyse the electrochemical reduction of dioxygen would increase both the cost and energy efficiency of fuel cells.

In nature, copper plays an important role in the active sites of many redox-active enzymes that are involved in the activation and reduction of dioxygen. Inspired by these natural systems, many molecular copper complexes have been studied for their dioxygen binding and activation reactivity throughout the past decades. Moreover, it has been shown that the multicopper oxidase enzyme Laccase is able to efficiently catalyse the reduction of dioxygen to water. Electrochemical studies on Laccase have shown that the reduction of O_2 to H_2O takes places close to the O_2/H_2O equilibrium potential, with a lower overpotential than the platinum-based heterogenous catalysts currently responsible for the oxygen reduction reaction (ORR) in hydrogen fuel cells. This has led to a significant interest in the use of biomimetic molecular copper complexes as catalysts for the electrochemical ORR. The tris(2-pyridylmethyl)amine) (tmpa) copper complex (Cu-tmpa) and similar derived complexes have been previously studied for the ORR using sacrificial reductants. Initial results suggested that perhaps a dinuclear species is formed during the catalytic reaction. However, the mechanism for the ORR by Cu-tmpa under electrochemical conditions had not been fully clarified yet, nor have the reaction kinetics for the electrochemical ORR been investigated. With the research presented in this thesis, we performed a detailed mechanistic and kinetic analysis of the electrochemical oxygen and hydrogen peroxide reduction reactions by

Cu-tmpa, under aqueous conditions and in an organic electrolyte. Additionally, three additional mononuclear copper complexes were investigated for their catalytic performance with respect to the reduction of O_2 and H_2O_2.

In Chapter 2, the electrochemical analysis of Cu-tmpa as a homogenous electrocatalyst for the ORR is described. Because of the limited stability of Cu-tmpa under acidic conditions and our interest in the catalytic performance under neutral conditions, we performed the electrochemical measurements in an aqueous pH 7 phosphate buffered solution. Due to the fast ligand exchange kinetics associated with copper ions, we first determined the stability of Cu-tmpa under electrochemical conditions via in situ electrochemical quartz crystal microbalance (EQCM) experiments. These revealed that no measurable deposition takes place during the electrocatalytic ORR reaction, thus establishing the homogeneous nature of the catalytic species. Catalyst concentration studies showed a first-order dependence of the catalytic current on the copper concentration, demonstrating that the catalytic mechanism involves a single copper site, as opposed to the previously suggested copper dimer species. Another important aspect for the ORR is the nature of the reaction product and the amount of electrons involved in the catalytic reaction. Using the rotating ring-disk electrode (RRDE) and the resulting Koutecky-Levich analysis, an electron transfer number close to 4 was determined. This showed that H_2O is the primary product in the limiting-current regime. However, in the potential window before the limiting current is reached, a small oxidative current was observed at the ring. By modulating the potential of the Pt ring and varying the catalyst concentration, it was determined that this current response on the Pt ring was caused by the oxidation of H_2O_2. Chronoamperometric measurements confirmed that H_2O_2 is the preferentially formed product at potentials close to the catalytic onset. Indeed, analysis of the Tafel Slopes for the full catalytic potential window showed two distinct catalytic regimes. Using the foot-of-the-wave analysis (FOWA), we were able to determine the catalytic first-order rate constant associated with the partial reduction of O_2 to H_2O_2. This catalytic rate constant was shown to be an order of magnitude larger than the rate constant associated with the full four-electron reduction to H_2O. These results showed that competition between two distinct catalytic cycles takes place during the ORR (see scheme 6.1), in which H_2O_2 is readily replaced in the copper coordination sphere.

Hydrogen peroxide was shown to play a pivotal role in the electrochemical reduction of dioxygen by Cu-tmpa. This shows similarities with the Fenton chemistry observed in several copper-containing enzymes. These enzymes activate and reduce O_2, and under certain conditions produce H_2O_2, or are able to use H_2O_2 as a substrate for the oxidation reactions carried out by these enzymes. Understanding how hydrogen peroxide is activated by these copper enzymes and copper complexes is essential for
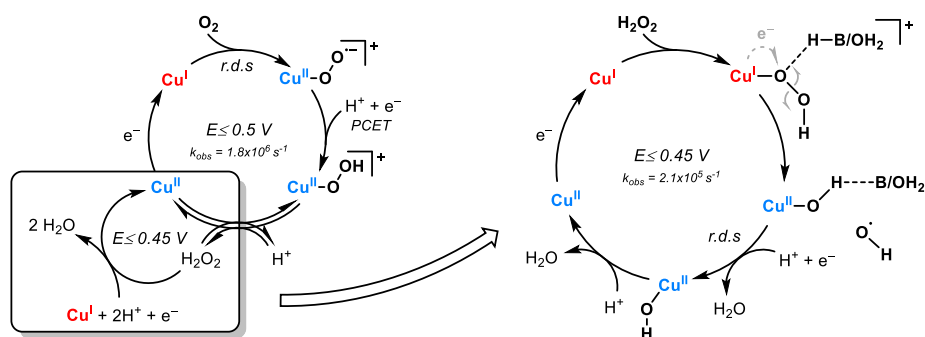
Scheme 6.1. The mechanistic cycles proposed in this thesis (Chapter 2 and 3) for the ORR and HPRR by Cu-tmpa. Here, k_{obs} refer to the rate constants obtained by FOWA.

the design of new selective catalysts for the reduction of O_2 or the electrochemical production of H_2O_2. Therefore, we set out to investigate the electrochemical hydrogen peroxide reduction reaction (HPRR) by Cu-tmpa in neutral aqueous solution, as is described in Chapter 3. The electrochemical HPRR was shown to have a first-order dependence in catalyst concentration, as was also shown to be the case for the ORR as described in Chapter 2. Kinetic studies revealed that the reduction of hydrogen peroxide is significantly slower by at least one order of magnitude than the reduction of dioxygen. By performing the same electrochemical analysis of the catalytic performance of Cu-tmpa in a phosphate buffered D_2O electrolyte solution, we were able to determine the kinetic isotope effect (KIE) associated with the HPRR. Application of the FOWA and the determination of the rate constant through the direct current enhancement (i_{cat}/i_p) at low catalyst concentrations both resulted in lower catalytic rate constants than in non-deuterated electrolyte solution. This translated to a solvent KIE of 1.4 to 1.7 for the HPRR by the copper catalyst. This indicates that an hydrogen or proton transfer is involved in the rate-determining step of the catalytic reaction. Following these results we proposed a mechanism similar to those suggested for the active sites of copper-containing monooxygenases, involving the formation of a Cu^{II}-OH species and a free hydroxyl radical as intermediate species. The overall electrocatalytic mechanisms for the reduction of O_2 and H_2O_2 by Cu-tmpa based on Chapter 2 and 3 is shown in Scheme 6.1.

While we have shown that the reduction of dioxygen by Cu-tmpa under neutral aqueous conditions follows a mononuclear reaction pathway, questions remained regarding the catalytic mechanism in organic solvents. The catalytic mechanism can be significantly affected by the reaction conditions. Different interactions between the solvents and the catalytic species or reaction intermediates, and differences in the nature of the proton source can all play a role. In Chapter 4 we describe the

investigation of the ORR and HPPR by Cu-tmpa in acetonitrile, evaluating the catalytic reactions in several acidic and buffered electrolyte solutions. Of the four different acids that were used, trifluoroacetic acid (HTFA) and dimethylformamidium trifluoromethanesulfonate (HDMF$^+$) resulted in instability and decomposition of the Cu-tmpa complex. No reversible redox couples could be obtained in the presence of either of these two strong acids. For the milder acetic acid (HOAc) and triethylammonium (HNEt$_3^+$) acids, reversible redox couples were observed for Cu-tmpa. Nitriles, such as EtCN and MeCN, act as strong ligands for the reduced Cu^I-tmpa species, competing with the reversible binding of O$_2$. In the case of EtCN, it has previously been shown that the equilibrium constant of formation for [Cu^{II}(O$_2^{\bullet-}$)(tmpa)]$^+$ is only 0.38 M^{-1} at room temperature due to competition with the coordination of the solvent to the copper centre. It is expected that this will have a significant supressing effect on the catalytic ORR rate. Indeed, after studying the reaction kinetics of the electrocatalytic ORR in MeCN using the catalytic current enhancement, we observed a 10^5 times reduction of the observed rate constant k_{obs} compared to the ORR in an aqueous environment. Finally, we were able to show that while the kinetics of the catalytic reactions were significantly slower in MeCN, the overpotential associated with the ORR is more than 100 mV lower in the buffered MeCN solution than in neutral aqueous solution. Interestingly, catalytic rate constants were higher for the HPRR than for the ORR, a clear inversion from the behaviour observed under aqueous conditions. This study has shown that the catalytic mechanism for the reduction of O$_2$ in acetonitrile is largely similar to what we have observed in water, despite the significantly inhibited reaction kinetics due to the involvement of the competitive coordination of acetonitrile.

In Chapter 5, the synthesis and electrochemical analysis of three different pyridylalkylamine copper complexes is described. Here, we varied the distance between the central amine and one of the pyridine arms, thereby varying the amount of strain on the coordination sphere of the copper complex. Additionally, one ligand was synthesized as an analogue to bmpa (bmpa = bis(2-pyridylmethyl)amine), by introducing a non-coordinating furanyl group while maintaining the central tertiary amine, instead of the secondary amine present in bmpa. The largest increase of the redox potential was observed for Cu-bpmpa (bpmpa = bis[(2-pyridyl)methyl]-2-pyridylamine), with a +300 mV higher redox potential than Cu-tmpa. A general trend is observed where an increase in strain on the coordination environment of the Cu centre results in a higher redox potential of the complex. A clear linear scaling relationship between the redox potential and the catalytic rate constants of the reduction of O$_2$ and H$_2$O$_2$ was established. The lower the redox potential of the given copper complex, the higher the catalytic rate constants. In the case of Cu-bpmpa, this also results in a faster HPRR than ORR, contrary to the other complexes that were investigated. This shows

the HPRR and ORR catalytic cycles are not entirely linked, which provides additional confirmation that for mononuclear copper catalyst two separate catalytic cycles take place during the ORR.

6.2.　Outlook

We have identified Cu-tmpa as an excellent electrocatalyst for the ORR, exhibiting exceedingly fast kinetics that resulted in a catalyst able to operate at maximum capacity even at catalyst concentrations in the low micromolar range. However, a significant overpotential (>0.9 V) is associated with the ORR by Cu-tmpa. Attempts to reduce the overpotential by modifying the ligand strain placed on the coordination sphere were successful, but did result in significant decrease of the catalytic rate constants. We have also shown that the catalytic mechanism for the ORR proceeds via a mononuclear catalytic species. This result was obtained both under neutral aqueous conditions and in acetonitrile in the presence of weak acids. Thus, the suggested dimeric $[\{Cu^{II}(tmpa)\}_2(O_2)]^{2+}$ species, which has been shown to form under non-catalytic conditions, and from which the ORR was able to take place, does not form under fully electrocatalytic conditions in the presence of protons. This highlights the necessity to study the catalytic mechanism under electrochemical conditions, when previously published results have been obtained using chemical reductants in stopped-flow experiments.

Furthermore, the apparent stepwise reduction of O_2 to H_2O via H_2O_2 by mononuclear copper catalysts based on the Cu-tmpa structural template shows that the 1.23 V vs RHE standard reduction potential of dioxygen is not the limiting factor in bringing down the overpotential of these catalysts, but the standard reduction potential of 0.695 V vs RHE associated with the partial reduction of O_2 to H_2O_2. This has significant implications for the design of catalysts with even lower overpotentials for the 4–electron reduction of O_2. It points to the need of multinuclear copper catalysts that can avoid the formation of a hydroperoxo intermediate during the catalytic cycle and are instead able to cleave the O–O bond first. In principle, this would call for a catalyst in which two copper centres are spaced at the optimal distance from each other for the bridging of O_2^{2-}, and are connected via a mostly rigid ligand backbone. This can prevent the formation of hydroperoxo species, and thus the formation of H_2O_2. Additionally, the redox potential of the species will also have to be shifted closer to the equilibrium potential of the O_2/H_2O couple to give better overall catalytic performance than mononuclear copper complexes that are able reduce O_2 and H_2O_2 and operate close to the equilibrium potential of the O_2/H_2O_2 couple.