Heterogenized molecular (pre)catalysts for water oxidation and oxygen reduction

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Chapter 1

Before the large scale use of renewable energy sources can be implemented in our society, the efficient storage of that energy needs to be tackled. The storage of electrical energy in the form of a chemical bond *e.g.* hydrogen or hydrocarbons is a good option for the storage of this renewable energy. Hydrogen can be produced by the electrochemical reduction of protons, which costs energy. This energy can be released by the oxidation of the hydrogen formed. An electrochemical reactions always consists of two half reactions. The water oxidation reaction is a good candidate as second half reaction to complement the proton reduction reaction due to its high redox potential and the non-toxicity of the products, which are oxygen and protons. If the hydrogen is oxidized, oxygen can be reduced to form water. The water oxidation and oxygen reduction reactions are four-electron reactions. As a result the reaction mechanism is complex and difficult to optimize.

There are different types of catalysts which increase the efficiency of the water oxidation and oxygen reduction reactions. In heterogeneous catalysis, the catalyst is in a different phase than the reactant, *e.g.* an electrode (solid) and water (liquid). In homogeneous catalysis, the catalyst and reactant(s) are in the same phase, *e.g.* a molecular complex dissolved in water. Due to the harsh conditions in which water oxidation takes place, the molecular complexes can undergo structural changes and deposit on the electrode surface, effectively making it a heterogeneous catalyst. In extreme cases, a metal oxide catalyst is formed. In the oxygen reduction reaction the ligands of the molecular complex can dissociate from the metallic center and thus form a metallic layer, which is responsible for catalysis. This thesis focuses on the activation of molecular complexes and on strategies to prevent the degradation of molecular complexes in water oxidation and oxygen reduction catalysis.

Chapter 2

In literature there are several examples of molecular iridium precatalysts for water oxidation. Examples are given where the active catalyst will or will not adsorb on the electrode surface. The adsorbed species can either be of molecular nature or be oxidized completely to form IrO_2.

In Chapter 2 a comparison is made between two similar iridium water oxidation catalysts. The catalysts have pyridyl-triazolylidene ligands where a modification is made on the triazolylidene ring. The proton in the one complex is exchanged for an ethoxy moiety. This modification has a drastic influence on the activation of the molecular precatalyst. Water oxidation with a chemical oxidant reveals the highest activity is observed on the complex with the ethoxy moiety. This indicates the electronic properties of the complexes dictate the activity of the molecular complex. Chapter 2 focuses on the electrochemical water oxidation reaction.

Using an Electrochemical Quartz Crystal Microbalance (EQCM) it was established the complexes form a deposit on the surface of the gold working electrode upon applying a potential of 1.8 V *versus* RHE. This is associated with the deposition of the catalytically active species on the surface of the electrode, as the current increases over time the longer 1.8 V is applied. The formation of gaseous products was investigated using Online Electrochemical Mass Spectrometry (OLEMS). The formation of carbon dioxide was observed at a lower potential than the formation of dioxygen in cyclic voltammetry. The formation of CO_2 is an indication of degradation of the ligand backbone, which is observed for iridium complexes before. The (partly oxidized) complexes which are adsorbed on the electrode surface are still of molecular nature, as was established by X-ray Photoelectron Spectroscopy (XPS).

The current work illustrates a small change in the structure of the complex can have a large influence of the catalytic activity and the activation of precatalysts. The challenge for the future lies in determining which factors influence the complete degradation of the complex to IrO_2 and how the molecular complexes form well-defined molecular catalysts for the water oxidation reaction.

Chapter 3

The use of a noble metal such as iridium is not ideal in catalysis due to the high cost and relatively low availability of the metals. The use of a first row transition metal such as copper is much cheaper and more readily available than iridium. The electrochemical activation of the $[Cu^{II}(bdmpza)_2]$ complex ($bdmpza^-$ = bis(3,5-dimethyl-1H-pyrazol-1-yl)acetate) is reported in Chapter 3. The complex is coordinatively saturated, indicating water cannot bind to the complex to begin a water oxidation cycle. Since an alkaline electrolyte is used, the complex does not dissolve in the electrolyte and is dropcasted onto the gold working electrode. Upon applying an oxidizing potential above 1.6 V *versus* RHE an oxidation current is observed. In the backward scan from 2 to 0 V a series of four reduction events between 1.25 and 0.25 V are observed. Upon scanning back to 0 V and oxidizing the electrode again a fifteen fold increase is observed in the second scan. The reduction events are associated with a decrease in mass of the quartz-gold-$[Cu^{II}(bdmpza)_2]$ assembly in EQCM. This is an indication part of the ligand is lost during the reduction events. In the oxidative scan up to 1.2 V a second loss in mass is observed which is associated with the dissolution of copper into the electrolyte. The $[Cu^{II}(bdmpza)_2]$ complex was used in an OLEMS investigation. Upon applying 2.0 V a tiny amount of dioxygen is observed. The oxidation period is followed by reduction at 0 V. Finally a second oxidizing potential is applied, which yields a higher current and dioxygen production. Two pathways in which an active water oxidation catalyst forms can be discerned: an oxidative pathway and a reductive-oxidative pathway. In both pathways the structure of the active catalyst is CuO. Since the active catalyst is the same for both activation pathways, the same maximum activity is expected. However the activation by the oxidative pathway is much slower and thus has not reached the same activity as the reductive pathway.

Chapter 4

In Chapter 4 an investigation of the oxygen reduction reaction with *in situ* generated copper-phenanthroline complexes is discussed. Using Electron Paramagnetic Resonance (EPR) spectroscopy the geometry of the copper complexes which are formed is determined. At a ratio of 1,10-phenanthroline to copper ions of 2:1 up to 10:1 the complex formed *in situ* has a trigonal bipyrimidal geometry around the copper center. At a 10:1 ratio a reversible redox couple is observed in deoxygenated aqueous electrolyte. The reversible redox couple follows the Randles Cevčik relation, indicating the redox couple is a one-electron transfer process. Unfortunately the trigonal bipyrimidal complex does not show any oxygen reduction activity. A 1:1 complex generated *in situ* by addition equimolar amounts of 1,10-phenanthroline and $\mathrm{Cu^{II}}$ is instead an active oxygen reduction catalyst. The 1:1 complex is in the elongated octahedron geometry as is determined by EPR spectroscopy. The complex displays an irreversible redox couple in deoxygenated aqueous electrolyte. Due to the absence of a reversible redox couple the formation of metallic copper layers on the gold working electrode is possible. A new strategy to prevent the deposition of copper on the working electrode is proposed and is reported in Chapter 5.

Chapter 5

The reduction of diazonium compounds ($\mathrm{R{-}N_2^+}$) at an electrode leads to liberation of dinitrogen and the formation of a radical ($\mathrm{R^\bullet}$). The radical can couple to the electrode surface thus forming a relatively strong (covalent) bond. This reduction of diazonium ions in aqueous solution is well-documented for benzene-diazonium and its derivatives.

Copper complexes with 1,10-phenanthroline ligands are only active oxygen reduction catalysts if there is only one 1,10-phenanthroline ligand present on the copper center, as was reported in Chapter 4. The 1,10-phenanthroline-5-diazonium ions are generated *in situ* by the addition of 5-amino-1,10-phenanthroline and sodium nitrite. By the reduction of 1,10-phenanthroline-5-diazonium the 1,10-phenanthroline derivative is immobilized on the electrode surface. The surface coverage is determined by EQCM and is 0.4 nmol cm^{-2}. This equals 18 molecules per 100 Au atoms, whereas 50 molecules should fit a Au (111) surface if the molecules are aligned perfectly. This indicates submonolayer coverage of the molecules. By immobilizing the 1,10-phenanthroline derivative on the working electrode and upon addition of a $\mathrm{Cu^{II}}$ salt in the electrolyte solution, a surface-attached complex is formed.

The oxygen reduction behavior of the $\mathrm{Cu^{II}}$-phen complex immobilized on a gold electrode was determined and compared to different other systems. These involve the bare gold electrode, an electrode modified by the reduction of *in situ* generated 5-bromobenzene-diazonium, the electrode modified by reduction of 5-bromobenzene-diazonium in presence of $\mathrm{Cu^{II}}$and the 1,10-phenanthroline modified electrode in absence of $\mathrm{Cu^{II}}$. In all cases the $\mathrm{Cu^{II}}$-phen is reducing oxygen at the lowest overpotential and the activity is also highest for the $\mathrm{Cu^{II}}$-phen system.

The $\mathrm{Cu^{II}}$-phen system is not very stable. Different redox couples grow into the cyclic voltammogram upon prolonged cycling. These redox couples are associated with the formation of metallic copper on the electrode-complex assembly. XPS results show accumulation of metallic copper on the electrode surface, while an organic layer is still present on the electrode as well.

The immobilized $\mathrm{Cu^{II}}$ complexes described in this chapter is unsuitable for large-scale electrochemical oxygen reduction. However the system can be used for fundamental studies on the oxygen reduction reaction. The difficulty in mechanistic studies on homogeneous electrocatalysis lies in the large portion of catalyst which is inactive. This is due to the largest portion of catalyst being in the bulk of the electrolyte and not close to the electrode surface. By immobilizing the catalyst on the electrode surface all of the catalyst present is doing oxygen reduction at the same time. This allows to watch the complex in action and not while almost all of the catalyst is in its resting state far from the electrode surface. Moreover the rigidity of the immobilized ligands allow for control of the structure of the complex.

The presence of an organic layer on the electrode after oxygen reduction catalysis indicates the immobilized phenanthroline molecules are still present on the electrode surface. By optimizing the concentration of copper ions in solution the formation of metallic copper might be prevented.