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Molecular catalytic system for efficient water splitting

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SUMMARY

The focus of this dissertation is the development of synthetic molecular water oxidation catalysts that are easily accessible and stable in light and moisture, with efficient oxygen generation capability at high rate in integrated electrochemical assemblies. While making hydrogen from water is important, it is not the only future target, since the protons released from water splitting could be effectively utilized in systems for CO₂ reduction into useful products and low carbon fuels like methanol and formic acid.

This research manuscript begins with **Chapter 1** that introduces the concept of the present and future global energy requirements, fossil based power supply, automotive transportation and its relation to the alarming level of carbon dioxide in the earth's atmosphere. The mechanism of water oxidation and a new model of the Mn₄CaO_x cluster in the PS-II is described that can be helpful in designing new synthetic molecular catalytic systems. The emphasis is on the revision of literature on evolutionary stages in the chemistry of water splitting by various kinds of molecular complexes. After a brief discussion of early research dealing with binuclear manganese and ruthenium complexes of dinitrogen ligands, this chapter describes the polypyridyl ligand based Ru and Mn complexes that were synthesized later in the 20th century, along with a few mono nuclear analogues. This is followed by a view on electro-assisted water oxidation systems with immobilized molecular catalysts. The chapter concludes with summing up the challenges in the field and outlines the scope of the thesis and the structure of this research work.

Advanced electrochemical techniques for catalytic water oxidation studies, have been implemented on an existing tri-ruthenium catalyst and are presented in **Chapter 2**. Oxygen formation at a Ru-red/Au_{disk} and detection by a platinum ring is investigated with a rotating ring-disk electrode assembly that was not used before for studying oxygen evolution by a molecular catalyst. The chapter also describes a successful application of *in situ* surface-enhanced Raman spectroscopy for catalyst transitions at the electrode-electrolyte interface and shows that the formation of

some type of oxide of metal during catalysis cannot be excluded. Finally, online electrochemical mass spectrometry analyses are applied that validate oxygen evolution for Ru-red adsorbed on the gold electrode.

After validating the electrochemical techniques, the next step of this project was to design and synthesize new bio-inspired water oxidation complexes containing a single catalytic site, aiming for a consecutive four-step proton coupled electron transfer (PCET) catalytic cycle for oxygen evolution. A new class of mononuclear ruthenium *p*-cymene derived half sandwiched aqua complexes with dinitrogen ligands for homogeneous catalysis is reported in **Chapter 3**. The complexes are synthesized in good yield and purity by stirring the ingredients in an alkanol mixture at ambient temperature. The catalytic induction was performed with Ag salts in aqueous solution. Using an external catalyst activator, the molecular complexes show activity for water oxidation by generating a fair amount of TON's for molecular oxygen. Their electrochemistry reveals an important feature of following a four PCET step reaction coordinate, as evidenced by the pH dependent behaviour of the intermediates shown in the Pourbaix diagram (Figure 3.3). The catalysts undergo rapid aqua exchange in the catalyst induction step and facilitate the insertion of the second OH₂ without transforming into a higher oxidation state [Ru^V(=O)]³⁺ complex.

The surface immobilized catalytic system derived from the mono ruthenium complexes for electrochemical water oxidation is discussed in **Chapter 4**. The dinitrogen 2,2'-bipyridine ligand as mentioned in chapter 3, was modified with electrode linker groups like –COOH or –PO₃H₂ as anchoring sites for the indium-doped tin oxide (ITO) coated glass surface. The [(L₂bpy)Ru^{II}(cy)-OH₂]²⁺ catalyst modified ITO assembly also shows a PCET behaviour in aqueous solution at pH up to 12. CV's obtained for oxygen evolution reveal the onset potential at *ca.* 1.45 V in neutral solution and >1.83 V (vs. NHE) for the acidic electrolytes. The controlled-potential water electro-splitting was conducted in deoxygenated solution revealing remarkable efficiency and stability under electrochemical conditions. During neutral water catalysis, more than 400 μmol of oxygen was produced in 11

hours with a current density $>1.5 \text{ mA/cm}^2$. With a TOF of ~ 7.14 moles of oxygen per mole of catalyst per second, the catalyst turnovers were more than 3.1×10^5 in 12 hours. On the other hand, in aqueous acids, the turnover numbers were in excess of 6×10^5 in 35 hours at a rate of ~ 5.33 per second. More than $800 \text{ }\mu\text{mol}$ of oxygen is generated in 30 hours with one cm^2 of ITO/Cat system at a current density of $\sim 1.65 \text{ mA/cm}^2$. Further increase of the potential up to 2.20 V (vs. NHE) results in $\sim 450 \text{ }\mu\text{mol}$ of oxygen per hour in neutral water at a rate up to 80 mol O_2 per mol of catalyst per second, with a current density of $>14 \text{ mA/cm}^2$. The investigation thus discloses a catalytic system with tremendously high turnover number at rapid rate of oxygen evolution for an electrochemical water oxidation assembly based on a single metal molecular oxygen evolving complex.

The next target of the project was to explore the mono-site iridium complexes for electrochemical water oxidation as these were not tested before on electrode surfaces. A homogeneous catalysis study was conducted with three aqua induced iridium-Cp* complexes, $[(\text{bpy})\text{Ir}^{\text{III}}(\text{Cp}^*)\text{-OH}_2]^{2+}$ (Cat.**Ir**-bpy), $[(\text{phen})\text{Ir}^{\text{III}}(\text{Cp}^*)\text{-OH}_2]^{2+}$ (Cat.**Ir**-phen) and $[(\text{bpm})\text{Ir}^{\text{III}}(\text{Cp}^*)\text{-OH}_2]^{2+}$ (Cat.**Ir**-bpm) as detailed in **Chapter 5**. The study reveals that the $[(\text{Cp}^*)\text{-Ir}^{\text{III}}\text{-(N-N)-OH}_2]^{2+}$ catalysts are twice as efficient as their chloro analogues, reported earlier by another group. A pre-aqua insertion prevented the initial lag period. The iridium catalyst with bpy motif was also modified with $-\text{COOH}$ and $-\text{PO}_3\text{H}_2$ units for immobilization at the inert oxide anode. The complexes Cat.**Ir**- PO_3H_2 and Cat.**Ir**- COOH on ITO generate molecular oxygen for several hours during controlled-potential water electrolysis. The overall catalyst turnover numbers were in excess of 2.1×10^5 in 12 hours at a turnover rate of ~ 6.5 moles of oxygen per mole of catalyst per second. The initial current densities were more than 1.7 mA/cm^2 and the system produces $>350 \text{ }\mu\text{mol}$ of molecular oxygen during half a day catalytic operation. This study is important to pave the way for photo-electrocatalytic systems with immobilized mono iridium complexes for water splitting and hydrogen generation.

To conclude, this thesis, entitled “Molecular Catalytic System for Efficient Water Splitting” provides an account of a class of mono catalytic centre molecular complexes for homogeneous water oxidation, as well as surface electrochemical oxygen evolving assemblies, based on ruthenium and iridium catalysts. It is anticipated that the study presented here introduces new possibilities for efficient and stable water splitting catalytic systems for clean fuel generation leading towards a greener energy technology and sustainable future.