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Molecular catalytic system for efficient water splitting

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Surface Electrocatalytic Assembly for Water Oxidation at High Turnover and Rate

ABSTRACT

The development surface catalytic electrochemical assembly for water oxidation is important for application in electro- and photo-driven devices for fuel generation. This chapter describes the extension of the mono-site ruthenium derived molecular complexes in chapter 3 for use in an electrochemical system and discloses a highly competent immobilized mono-site ruthenium molecular catalytic assembly for water oxidation and oxygen evolution. This catalytic system mimics the photosystem-II (PS-II) in producing hundred thousands of rapid turnovers for dioxygen by four proton coupled electron transfer (PCET) steps. In neutral water, the catalyst generates $>3 \times 10^5$ turnovers for dioxygen at a frequency of ~ 7 per second and more than 6×10^5 turnovers at $\sim 5.33 \text{ sec}^{-1}$ in aqueous acids were realized. The catalyst cycles through $\text{Ru}^{\text{III/IV}}-\text{Ru}^{\text{III/IV/II}}$ states while maintaining an overall charge +2. This leads to a water splitting device with the highest turnover numbers achieved till date for a molecular catalyst. A turnover rate up to 80 per second was achieved during full cell water electrolysis between 1.8–2.2 V (vs. NHE).

Based on: K.S. Joya and H.J.M. de Groot, 2011 (*submitted*)

4.1. INTRODUCTION

The quest for a greener future through clean and affordable energy, fuel and electricity, using renewable natural resources, has become one of the most urgent challenges, spurred by worries about global warming, climate change and fuel scarcity [1,2]. The production of hydrogen or low-carbon based fuels from catalytic water splitting using solar energy represents an attractive potential solution for environmentally clean energy carriers [3-5]. However, the design and implementation of a stable four-electron transfer catalytic system for efficient water oxidation operating at high catalytic turnover number (TON) and frequency (TOF), with low activation barrier, moderate overpotential and high current density is a challenging hurdle along the way [6-10]. Principles laid down in natural photosystem-II have manifested guidance for the synthetic design, where a consecutive proton coupled electron transfer regime enables the accumulation of four redox equivalents that circumvent high energy intermediates during the multi-electron water oxidation cycle [11,12].

In spite of the elucidation of the photosynthetic machinery, there is as yet no artificial equivalent, capable of constructing a four-step PCET pathway, separating electrons and protons from water to produce oxygen at a high rate for hundred thousands of cycles [13-18]. During last few years, a growing interest in light driven and electrocatalytic water splitting has triggered the scientific interest towards the construction of an efficient system with a robust oxygen evolving complex (OEC). In this pursuit, various molecular complexes [17-20] and inorganic oxide materials [21-23] have been scrutinized for effective water oxidation, but they were far behind in mimicking the TON and TOF performance of PS-II. Also the few electrochemical molecular catalysis systems that have been reported show a low rate and small current densities for oxygen evolution [24-26].

From a mechanistic standpoint, formation of molecular oxygen is realized by the extraction of four electrons and protons in four PCET steps from two water molecules at the anode [12]. The total free energy change between H₂O and the

reaction products, O_2 and H_2 , is 4.92 eV (see chapter 1 for details). An ideal water oxidation catalyst operates at an equilibrium potential of 1.23 eV for each PCET step and photosynthesis is thought to work very close to this optimum [27,28]. In mononuclear artificial systems, the maximum oxygen evolution activity is considered to be limited due to a minimum overpotential of ~ 0.4 V when proceeding through an HOO^* intermediate, and there is a constant difference of 3.2 ± 0.1 eV in the affinity between the HOO^* and the HO^* intermediates [11,27]. However, recently reported mono-site ruthenium catalysts are unable to construct a four step PCET mechanism, and the HOO^* intermediate is formed at high potential from a $[Ru^V=O]^{3+}$ species which is generated by an electron transfer step in a non-PCET rate limiting step [18,29].

In this chapter, the synthesis and analysis of a highly efficient and apparently robust immobilized electro-assisted catalytic water splitting system is described that generates hundred thousands turnover at a rapid rate, both in neutral solution and aqueous acids (Fig. 4.1).

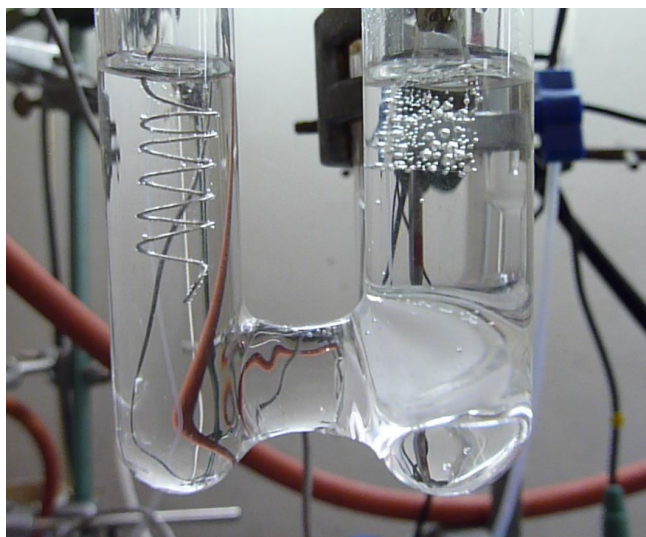


Figure 4.1. Experimental demonstration of oxygen generation (bubbles) by Cat.**Ru**- PO_3H_2 or Cat.**Ru**- $COOH$ catalyst anchored on ITO electrode surface via linker molecules ($L = COOH$ or PO_3H_2) to drive electro-assisted water oxidation.

The catalysts are easy accessible mononuclear ruthenium complexes with alkyl substituted benzene or cyclopentadiene and a heterocyclic 2,2'-bipyridine (bpy) ligand [30]. The complexes can be immobilized on conducting oxide surfaces via anchoring groups like COOH or PO₃H₂ and electrochemical analyses provide converging evidence that the catalysts operate by a four-step PCET mechanism for water oxidation at a moderate overpotential. The onset of oxygen evolution in aqueous acid (pH=1) is just above 1.83 V (vs. NHE) and at *ca.* 1.45 V (vs. NHE) in neutral solution. Catalytic induction of the complex by aqua exchange produces an electronic bias that brings the catalyst redox potential into the regime for PCET water oxidation while reducing the proton affinity at the same time. A mechanism is proposed where the catalyst cycles through Ru^{II/III/IV}–Ru^{III/IV/II} states while maintaining an overall divalent positively charged complex during the water oxidation pathway.

4.2. RESULTS AND DISCUSSION

4.2.1. Synthesis and Characterization

The *p*-cymene-Ru derived 4,4'-dicarboxylic (H₂dcabpy) or 4,4'-diphosphonic acid (H₄dphbpy) modified 2,2'-bipyridine complexes [(H₂dcabpy)Ru^{II}(cy)Cl]⁺ (**Ru**–COOH) and [(H₄dphbpy)Ru^{II}(cy)Cl]⁺ (**Ru**–PO₃H₂), and their aqua version catalysts [(H₂dcabpy)Ru^{II}(cy)-OH₂]²⁺ (Cat.**Ru**–COOH) and [(H₄dphbpy)Ru^{II}(cy)-OH₂]²⁺ (Cat.**Ru**–PO₃H₂), were obtained by procedures described in Materials and Methods, and characterized by proton NMR spectra and elemental analysis (see subsection 4.4.1). The X-ray structure of the related complexes reveals a trans configuration of the dinitrogen ligand with respect to the aromatic moiety [31,32]. The aqua versions Cat.**Ru**–PO₃H₂ and Cat.**Ru**–COOH are readily obtained by stirring with the stoichiometric aliquots of aqueous AgNO₃ or silver hexafluorophosphate in methanol water mixture. Similar to the complexes described in chapter 3, the *in situ* aqua exchange for [(H₂dcabpy)Ru^{II}(cy)Cl]⁺ complex in the presence of water is also followed by UV-vis studies indicating

spectral changes for colour change from orange-yellow to bright-yellow, corresponding with an absorption band shift from 412 nm to 399 nm (Fig. A4.2). Above pH=8, the complex starts to turn brown ascribed to the deprotonation of the OH₂ moiety and the solution darkens upon further increase of the pH.

4.2.2. Electrochemistry and Oxygen Evolution

The CV of the linker modified [(cy)Ru^{II}(L₂-bpy)OH₂]²⁺ catalyst shows clean polarization waves for the [Ru^{III}-(OH)]²⁺/[Ru^{II}-(OH₂)]²⁺ and [Ru^{IV}(=O)]²⁺/[Ru^{III}-(OH)]²⁺ redox pairs in aqueous solution (Fig. 4.2). In aqueous acid, the current waves for the first two oxidations appear at E_{1/2} ca. 0.60 V and 1.18 V (vs. NHE) respectively. For E > 1.5 V (vs. NHE) the current rises due to the formation of the [Ru^{III}-(OOH)]²⁺ species from [Ru^{IV}(=O)]²⁺ on second aqua ligation and following [Ru^{IV}-(OO)]²⁺/[Ru^{III}-(OOH)]²⁺ with subsequent oxygen release at E > 1.83 V (vs. NHE), observed as bubbles on the working electrode during forward scans. In neutral solution, [Ru^{III}-(OH)]²⁺/[Ru^{II}-(OH₂)]²⁺ and [Ru^{IV}(=O)]²⁺/[Ru^{III}-(OH)]²⁺ pairs appear at E_{1/2} ~ 0.22 V and E_{1/2} ~ 0.77 V (vs. NHE), respectively, with weaker signals resembling Cat.**Ru**-bpy as described in section 3.2.2 [33,34]. The electrochemical findings in aqueous acid and neutral solution validate the Nernst behaviour for [Ru^{III}-(OH)]²⁺/[Ru^{II}-(OH₂)]²⁺ and [Ru^{IV}(=O)]²⁺/[Ru^{III}-(OH)]²⁺ transitions by two consecutive PCET steps [29]. The [Ru^{III}-(OOH)]²⁺/[Ru^{IV}(=O)]²⁺ transition in the neutral phase occurs at E_{1/2} ca. 1.42 V (vs. NHE) while the reverse scan reveals the reduction wave for [Ru^{IV}(=O)]²⁺/[Ru^{III}-(OOH)]²⁺ at ca. 1.36 V (vs. NHE). This confirms the Nernst behaviour for the [Ru^{III}-(OOH)]²⁺/[Ru^{IV}(=O)]²⁺ transition, which implies a third consecutive PCET step along the reaction coordinate describing the catalytic mechanism. Since the steps are very similar as for the homogeneous catalysts in chapter 3, there is very little effect of the linker on the catalytic function.

The stepwise oxidation of [Ru^{II}-OH₂]²⁺ into [Ru^{III}-(OH)]²⁺ and [Ru^{IV}(=O)]²⁺ in acidic solution is also monitored spectro-electrochemically at 0.63 V and 1.22 V (vs. NHE) for a sample at higher concentration to make the optical absorption

detectable. The third oxidation step of the catalyst occurs *ca.* 1.75 V (vs. NHE) and is accompanied by a colour change (inset Fig. 4.2). Repeating the scans in neutral solution generates similar spectral shifts for consecutive oxidation at 0.27 V, 0.82 V and 1.43 V (vs. NHE) respectively. The absorption spectra for $[\text{Ru}^{\text{III}}\text{-(OH)}]^{2+}$ and $[\text{Ru}^{\text{II}}\text{-(OH)}_2]^{2+}$ are entirely recovered during reduction from $[\text{Ru}^{\text{IV}}\text{=O}]^{2+}$ or $[\text{Ru}^{\text{III}}\text{-(OH)}]^{2+}$ for the reverse scan, at cathodic peak potentials of 1.05 V and 0.51 V, respectively. This points to sturdiness and reversible kinetics of the electrocatalytic system [9,25].

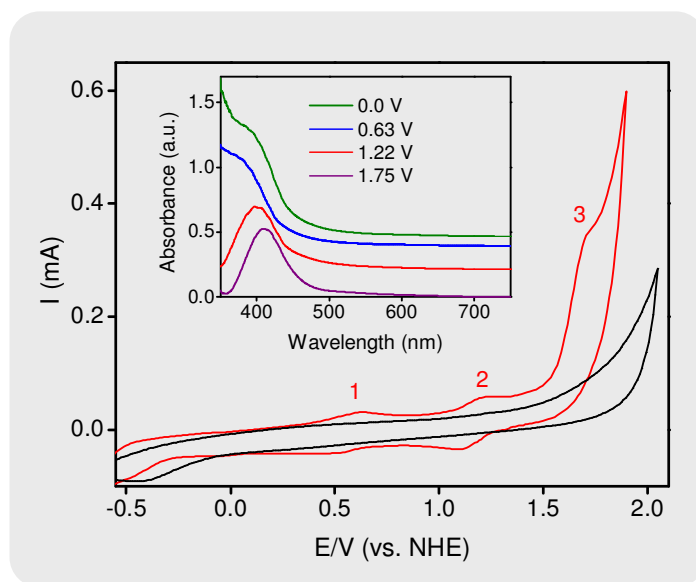


Figure 4.2. Cyclic voltammograms of $[(\text{cy})\text{Ru}(\text{dcabpy})\text{-(OH)}_2]^{2+}$ complex (2 mM) at a glassy carbon (GC) disk in 0.1 M HNO_3 solution showing oxidation waves for (1) $[\text{Ru}^{\text{III}}\text{-(OH)}]^{2+}/[\text{Ru}^{\text{II}}\text{-(OH)}_2]^{2+}$, (2) $[\text{Ru}^{\text{IV}}\text{=O}]^{2+}/[\text{Ru}^{\text{III}}\text{-(OH)}]^{2+}$ and (3) $[\text{Ru}^{\text{III}}\text{-(OOH)}]^{2+}/[\text{Ru}^{\text{IV}}\text{=O}]^{2+}$ (red line) and a blank CV trace for a glassy carbon (GC) disk measured under similar conditions (black line). (E/V vs. NHE, scan rate was 100 mV/sec, GC disk diameter $d=5$ mm). The inset shows spectro-electrochemical investigation of the Cat.**Ru**-COOH in 0.1 M HNO_3 solution. The UV-vis spectra were recorded at 0.0V and following electrolysis at 0.63 V (blue line); 1.22 V (red line) and 1.75 V (purple line). (The catalyst concentration was ~ 8.5 μM).

The onset of oxygen evolution for a Cat.**Ru**-COOH modified ITO electrode initiates just above 1.41 V (vs. NHE) in neutral phosphate buffer solution. On the other hand, the oxygen generation starts at *ca.* 1.87 V (vs. NHE) in 0.1 M aqueous

acid (Fig. 4.3). After the oxygen onset in neutral solution, the current density rises sharply and reaches $>3 \text{ mA/cm}^2$ at just 1.55 V. ITO is considered a relatively inert electrode [8-10], and this observation provides strong evidence for an excellent and fast rate catalytic performance of the system for electrolysis of neutral water. Since the overpotential closely matches the behaviour of the catalyst measured on the glassy carbon electrode, it is unlikely that the complex decomposes on the surface. In addition, similar type of surface enhancement has been observed by Meyer's group for $[(\text{N-N})\text{Ru}^{\text{II}}(\text{terpy})-(\text{OH}_2)]^{n+}$ and $[(\text{N-N})\text{Ru}^{\text{II}}(\text{Mebimpy})-(\text{OH}_2)]^{n+}$ catalysts [25,26]. Further cycling of the potential for the surface anchored catalyst in neutral buffer solution causes the current density to attain a value $>14 \text{ mA/cm}^2$ at *ca.* 1.95 V vs. NHE (Fig. 4.3). The current density increase is accompanied by a rapid rise of the oxygen generation at the Cat.**Ru**–COOH modified indium-doped tin oxide (ITO) electrode with simultaneous hydrogen evolution at the Pt counter electrode.

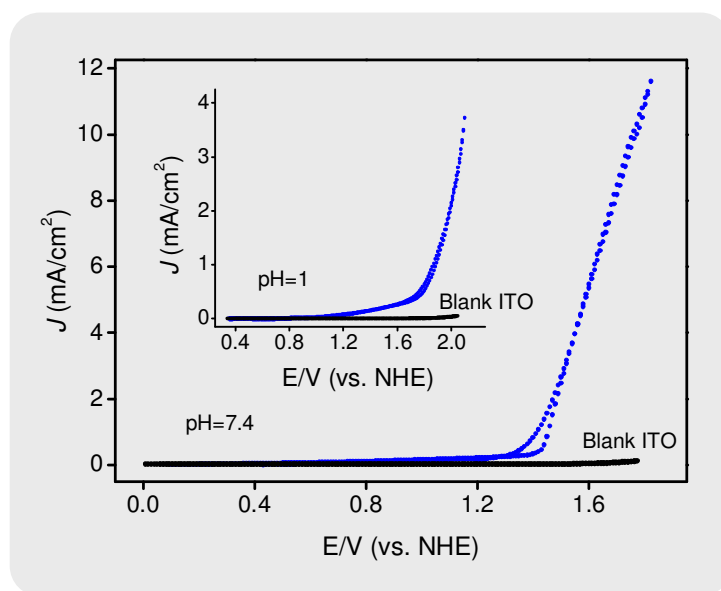


Figure 4.3. Cyclic voltammograms for a Cat.**Ru**–COOH modified ITO electrode (Cat/ITO) showing the oxygen onset current wave in 0.1 M aqueous phosphate buffer (pH=7.4) that was deoxygenated prior to performing the experiment. The inset represents the CV for the onset current wave in 0.1 M H_2SO_4 solution under similar conditions. (Scan rate was 50 mV/sec, ITO area $A=1 \text{ cm}^2$, catalyst loading $1.51\text{--}1.65 \times 10^{-10} \text{ mol/cm}^2$).

At higher potential (above 1.80 V vs. NHE) in neutral solution, the rapid increase of the current density with applied potential gradually levels off (Fig. 4.3 and Fig. A4.3). Meanwhile, an abundant stream of oxygen bubbles leaves from the ITO electrode surface. It is remarkable that the first conversion step, the oxidation of the $[\text{Ru}^{\text{II}}-(\text{OH}_2)]^{2+}$ into $[\text{Ru}^{\text{III}}-(\text{OH})]^{2+}$ appears at a lower potential, at *ca.* ~0.60 V (vs. NHE) than for the recently reported $E_{1/2} > 0.90$ V (vs. NHE) for mono site ruthenium catalysts [18,34]. The oxygen evolution CV's at high current densities of 4 and 12 mA/cm² for the immobilized complexes on ITO in acidic and neutral pH solutions are remarkably reproducible, indicating good stability of the surface anchored catalyst under electrochemical conditions (Fig. 4.3). This is in line with the high TOF and TON for the electrocatalytic systems. The CV data for the electrodes in acidic solution and in neutral media provide converging evidence that the electrochemical redox behaviour of the $[(\text{cy})\text{Ru}^{\text{II}}(\text{dcabpy})\text{OH}_2]^{2+}$ catalyst comprises multiple pH dependent oxidations and exhibits also a shift in the oxygen onset potential while going from an acidic phase to a neutral solution (Fig. 4.3).

4.2.3. Pourbaix Diagram and Free Energy Profile

The Pourbaix diagram constructed for the various ruthenium transitions in the Cat.**Ru**-COOH is shown in Figure 4.4. A ~60 mV/pH shift of the equilibrium point for water oxidation is detected for positive potential scanning in aqueous solution over a wide pH range, from 2 to 12. This shows that the limiting step is a PCET process for water oxidation. The pH-dependence of the transition from the $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ to the $[\text{Ru}^{\text{III}}-\text{OOH}]^{2+}$ intermediate indicates the Nernst behaviour of the $[\text{Ru}^{\text{III}}-(\text{OOH})]^{2+}/[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ couple that determines the overpotential of the system. The PCET formation of $[\text{Ru}^{\text{III}}-\text{OOH}]^{2+}$ from $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ was not yet observed for a mono site molecular water oxidation catalyst [18,25]. For instance, in recently reported mononuclear complexes the rate-limiting step is independent of pH and is thought to involve the formation of a high energy $[\text{Ru}^{\text{V}}=\text{O}]^{3+}$ intermediate via a non-PCET step by one electron oxidation of $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ above 1.75 V (vs. NHE) prior to second OH_2 insertion [25,26]. In this scheme, a subsequent OH_2

attack is rate limiting for O-O bond formation and is followed by release of a proton [29].

In contrast, for catalyst Cat.**Ru**-COOH the oxygen generation occurs at less overpotential in neutral or higher pH aqueous solutions by following a ~ 60 mV/pH slope due to the PCET conversion of the ruthenium couple $[\text{Ru}^{\text{III}}(\text{OOH})]^{2+}/[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$. In neutral solution, the water catalysis by the $[(\text{cy})\text{Ru}^{\text{II}}(\text{dcabpy})\text{OH}_2]^{2+}$ complex starts just above 1.41 V (vs. NHE) and the limiting step is the formation of the $[\text{Ru}^{\text{III}}(\text{OOH})]^{2+}$ species with a standard free energy difference of $\Delta G=1.83$ eV (pH=0) and at an overpotential $\Delta V=0.60$ V for the full electrolysis reaction. Since this overpotential is quite close to the minimum overpotential of 0.4 V, there is near-optimal positioning of $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ intermediate with respect to the free energy levels of $[\text{Ru}^{\text{III}}(\text{OH})]^{2+}$ and $[\text{Ru}^{\text{III}}(\text{OOH})]^{2+}$ complexes [27,28].

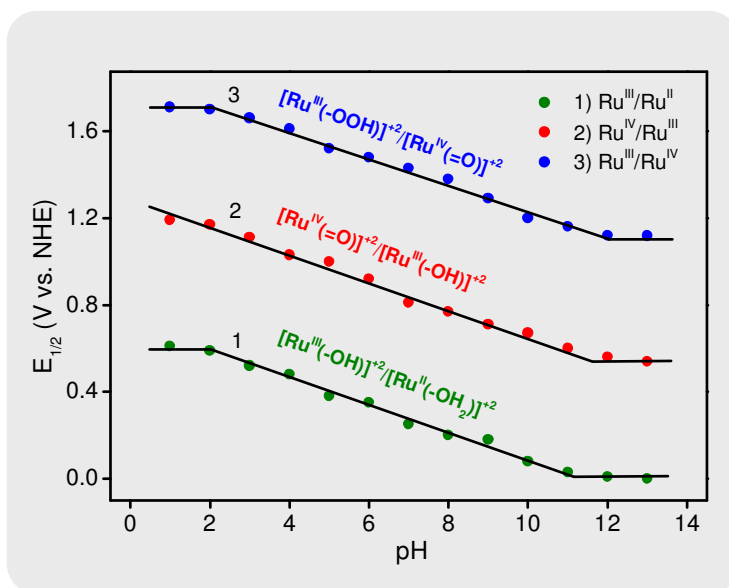


Figure 4.4. Pourbaix diagram for Cat.**Ru**-COOH showing $[\text{Ru}^{\text{III}}(\text{OH})]^{2+}/[\text{Ru}^{\text{II}}(\text{OH}_2)]^{2+}$, $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}/[\text{Ru}^{\text{III}}(\text{OH})]^{2+}$ and $[\text{Ru}^{\text{III}}(\text{OOH})]^{2+}/[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ couples generated at a glassy carbon disk (diameter $d=5\text{mm}$) working electrode in 0.1 M aqueous solutions.

From the Pourbaix diagram (Fig. 4.4), the electrochemical polarization for $[\text{Ru}^{\text{III}}-(\text{OH})]^{2+}/[\text{Ru}^{\text{II}}-(\text{OH}_2)]^{2+}$, $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}/[\text{Ru}^{\text{III}}-(\text{OH})]^{2+}$ and $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}/[\text{Ru}^{\text{III}}-(\text{OOH})]^{2+}$ at pH=7 translates into the standard free energy differences of 0.67 eV, 1.27 eV and 1.83 eV respectively, in a pH-independent reference frame. Hence the difference in affinity between the $[\text{Ru}^{\text{III}}-(\text{OH})]^{2+}$ and $[\text{Ru}^{\text{III}}-(\text{OOH})]^{2+}$ intermediate is 3.10 eV, which is well within the range of 3.2 ± 0.1 eV calculated by Rosmeissl and Nørskov [28,35]. As the standard free energy difference for the whole water splitting process is 4.92 eV, a potential difference of 1.15 eV is calculated for the last step towards oxygen evolution involving the $[\text{Ru}^{\text{IV}}-(\text{OO})]^{2+}/[\text{Ru}^{\text{III}}-(\text{OOH})]^{2+}$ intermediate, which is not potential limiting.

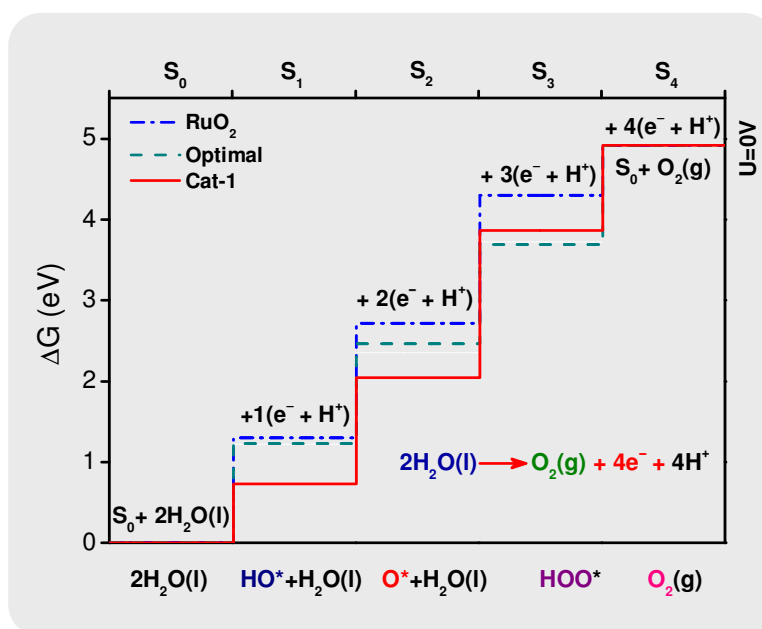


Figure 4.5. Relative Gibbs free energies (ΔG) of reactive species and intermediates, S_0 - S_4 (horizontal lines) during catalytic water splitting and oxygen generation for $[(\text{cy})\text{Ru}^{\text{II}}(\text{dcabpy})\text{OH}_2]^{2+}$ (Cat-1), compared with the free energy profiles for RuO_2 , and the reaction coordinate for the optimal catalyst with four steps each of 1.23 eV [27,28].

Since the complex $[(\text{cy})\text{Ru}^{\text{II}}(\text{dcabpy})\text{OH}_2]^{2+}$ exhibits a pH-dependent feature with the characteristic slope of ~ 60 mV/pH and produces the catalytic intermediates independent of proton chemical potential, the chemical reference system can be

changed to obtain a universal description of the cycle in terms of its free energy profile along a reaction coordinate that is delineated by the catalytic intermediates in 1.1-1.4 and 1.5-1.8 in chapter 1 [27,35].

The total free energy change for the water oxidation by Cat.**Ru**-COOH complex is $\Delta G=4.92$ eV, which is distributed over the four steps between sequential intermediates, S_1 - S_4 , as described above. The free energy profile is compared with the standard free energies of the three intermediates in RuO_2 that were calculated with DFT, and with an optimal water oxidation catalyst with $\Delta G = 1.23$ eV for each of four steps, which is very similar to the profile of the natural PS-II (Fig. 4.5) [11,27]. Catalytic water oxidation can proceed at the lowest potential when all steps are downhill. For RuO_2 this requires a minimum overpotential of ~ 0.4 V [27], while the Cat.**Ru**-COOH modified ITO operates at a moderate overpotential of just ~ 0.6 V for thousands of cycles and represents a very good artificial system for water splitting.

4.2.4. Catalytic Water Splitting and Oxygen Evolution

The steady state catalytic water electrolysis experiments were performed with the Cat.**Ru**-COOH modified ITO electrode, both in acidic and neutral pH solutions in an electrolysis cell with separate anodic and cathodic compartments. In aqueous acids, a turnover number of more than 6.7×10^5 in 35 hours was achieved at *ca.* 1.89 V (vs. NHE) with a turnover frequency of ~ 5.33 moles of oxygen per mole of catalyst per second. The current density was >1.7 mA/cm² in the beginning and dropped to ~ 1.65 mA/cm² after 13 hours (Fig. 4.6a). The average current density during the whole experiment over 35 hours was >1.6 mA/cm². The oxygen generation was monitored *in situ* with a calibrated oxygen electrode as described in the previous chapter [25]. More than 800 μmol of oxygen was produced in 30 hours during water oxidation with a Cat.**Ru**-COOH modified ITO electrode in a 0.1 M acidic solution (inset Fig. 4.6a).

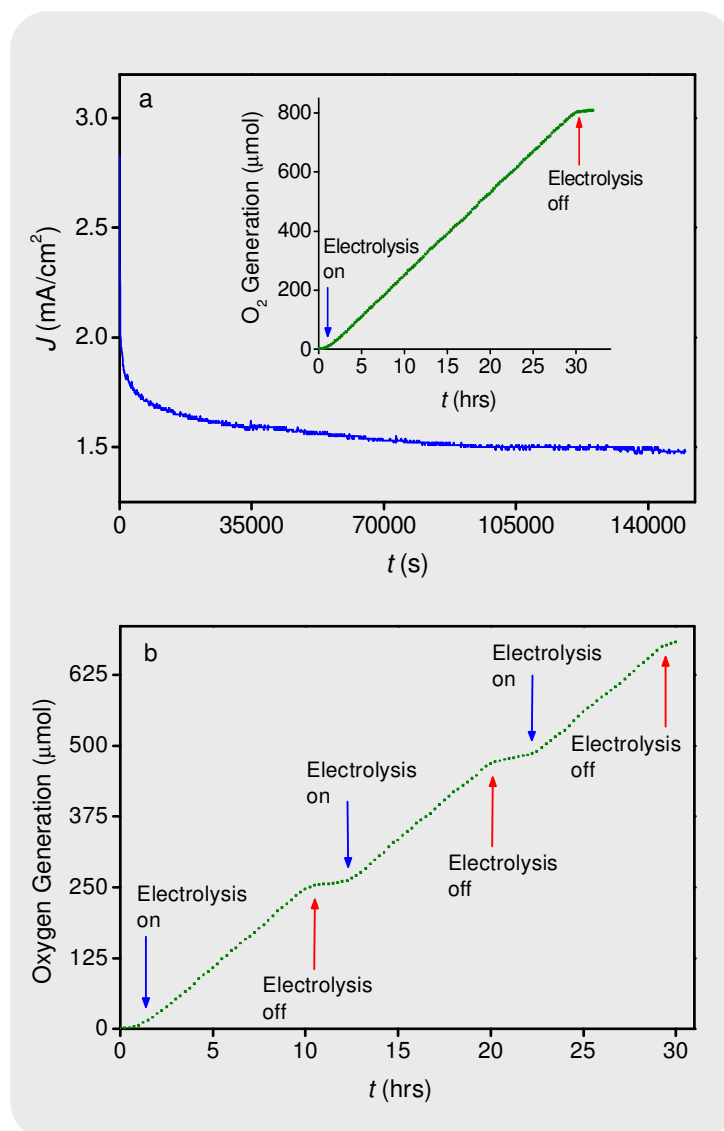


Figure 4.6. (a) Controlled-potential water electrolysis (current density mA/cm² vs. time) with the Cat.**Ru**-COOH modified ITO electrode in deoxygenated aqueous 0.1 M H₂SO₄ at ca. 1.89 V (vs. NHE). The inset shows oxygen generation (in μmol) vs. time for prolonged water electrolysis under similar conditions. (b) Successive initiation of water electrolysis (10 hours) and termination (2 hours) with the Cat.**Ru**-COOH modified ITO electrode in deoxygenated aqueous 0.1 M H₂SO₄ at ca. 1.89 V (vs. NHE). ITO area $A=1$ cm², (catalyst loading ~ 1.51 – 1.65×10^{-10} mol/cm²). (The blue arrows mark the beginning of electrolysis and red arrows point to termination of the electrolysis).

In order to monitor the stability of the catalytic system for intermittent operation, successive electrolysis experiments were performed for consecutive time intervals with the Cat.**Ru**-COOH modified ITO electrode in 0.1 M acidic aqueous solutions. Figure 4.6b shows the activity of the catalyst for three electrolysis runs, with a 2 hours break after 8 and 9 hours of catalytic operation. The rate of oxygen generation remains almost the same for each electrolysis step. This indicates good stability and surface activity of the immobilized Cat.**Ru**-COOH complex in the acidic environment. Also when the system is not being operated for a while, the catalyst stays active and efficient when electrolysis is initiated again.

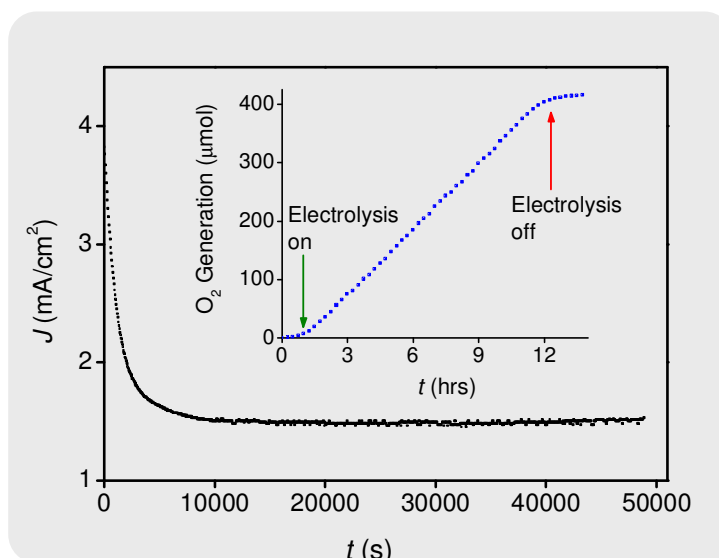


Figure 4.7. Controlled-potential water electrolysis (current mA/cm² vs. time) with the Cat.**Ru**-COOH modified ITO electrode in deoxygenated aqueous 0.1M phosphate buffer solution (pH ~ 7.1) at ca. 1.45 V (vs. NHE). The inset shows oxygen generation (in μmol) vs. time for prolonged water electrolysis under similar conditions. ITO area A=1 cm², (catalyst loading $\sim 1.51\text{--}1.65 \times 10^{-10}$ mol/cm²). (The green arrow indicates the beginning of electrolysis and red arrow point to termination of the electrolysis).

The Cat.**Ru**-COOH modified ITO generates more than 3.1×10^5 turnovers for molecular oxygen at ca. 1.5 V (vs. NHE) in only 12 hours, at a turnover rate of ~ 7.14 moles of oxygen per mole of catalyst per second during electrocatalysis of a

neutral aqueous solution containing 0.1 M phosphate buffer (inset Fig. 4.7). Under steady state conditions, the average current density was more than 1.5 mA/cm^2 (Fig. 4.7). The above numbers are larger than observed for a cobalt phosphate catalyst on an ITO electrode under similar conditions in neutral phosphate buffer solution, *i.e.* $9 \text{ } \mu\text{mol}$ of oxygen per hour with a current density of $\sim 1 \text{ mA/cm}^2$ at an overpotential of 0.41 V at $\text{pH}=7$ [10]. For the Cat.**Ru**-COOH modified ITO, the current was stable for more than 15 hours and a stream of oxygen bubbles was running off the catalyst modified ITO electrode with simultaneous hydrogen bubbles generation at the Pt cathode. More than $400 \text{ } \mu\text{mol}$ of oxygen was produced in 11 hours in neutral phosphate buffer solution (inset Fig. 4.7).

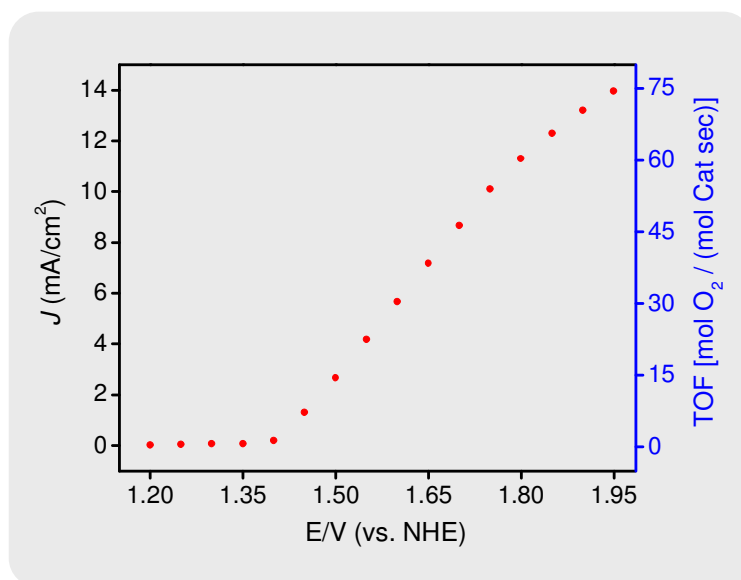


Figure 4.8. TOF (mol O₂ per mol catalyst per second) and oxygen generation (μmol per hour) against the applied potential at the Cat.**Ru**-COOH modified ITO electrode in deoxygenated aqueous in 0.1 M phosphate buffer solution ($\text{pH}\sim 7.4$). ITO area $A=1 \text{ cm}^2$, (catalyst loading $\sim 1.51\text{--}1.65 \times 10^{-10} \text{ mol/cm}^2$).

In the potential cycling catalytic water oxidation experiments, it was also noticed that the oxygen evolution initiates above 1.41 V (vs. NHE) in the neutral phase and the current density rises almost linearly up to 10 mA/cm^2 with increasing potential until $E = 1.77 \text{ V}$ vs. NHE (Fig. 4.8). This is accompanied by an increase

of the oxygen generation at the Cat.**Ru**–COOH modified ITO electrode, along with enhanced hydrogen evolution at the Pt counter electrode. At higher potential the current density gradually levels off, while an abundant stream of oxygen bubbles is leaving from the ITO surface (Fig. A4.3). The three-parameter relation in Figure 4.8 also shows a linear increase in the TOF of the catalytic system with the applied electrode potential until 1.75 V (vs. NHE). Approximately 350 μmol of oxygen per hour is produced by water oxidation at an oxygen generation rate of >60 mol per mol of catalyst per second, with a current density of ~ 11 mA/cm^2 (Fig. A4.3).

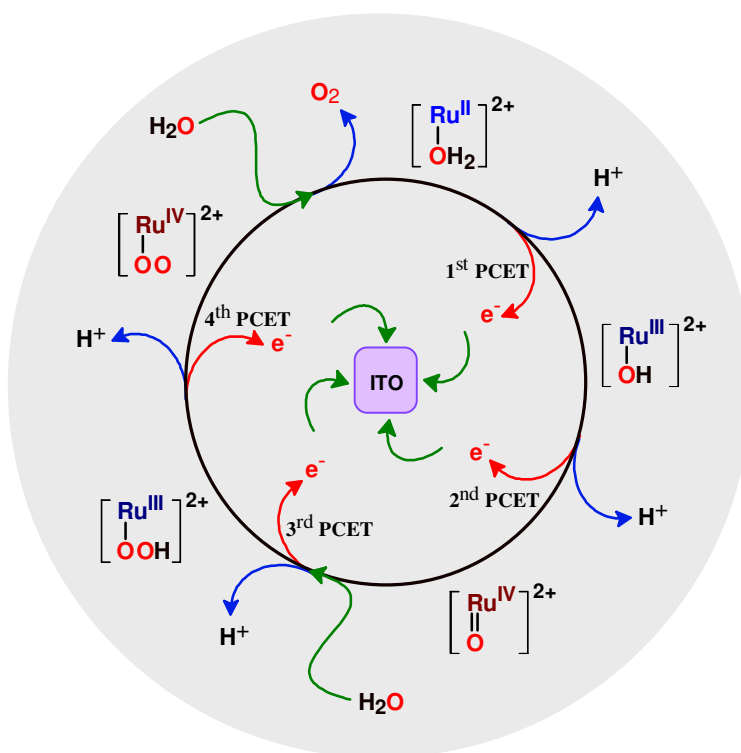
4.2.5. Catalytic Mechanism for Water Oxidation

On the basis of electrochemical investigations and potential vs. pH behaviour of Cat.**Ru**–COOH complex, a pentacyclic mechanism for catalytic water oxidation (Scheme 1) is deduced that proceeds along the reaction coordinate depicted in Figure 4.5. A double positive charge is maintained in successive proton coupled electron transfer steps, similar to the modified S-cycle for PS-II [11,12]. Induction of the catalyst is accomplished by the exchange of the chloride anion by a H_2O molecule. This produces a $[\text{Ru}^{\text{II}}(-\text{OH}_2)]^{2+}$ complex that can equilibrate its electron and proton affinities and bridge between the electrode and the surrounding medium via the aqua ligation. $[\text{Ru}^{\text{III}}(-\text{OH})]^{2+}/[\text{Ru}^{\text{II}}(-\text{OH}_2)]^{2+}$ and $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}/[\text{Ru}^{\text{III}}(-\text{OH})]^{2+}$ transitions are realized by two successive proton coupled electron transfer oxidation steps after aqua induction in the first half of the water oxidation cycle [18,29].

The CV's show a pH dependent potential for the $E_{1/2}$ of the $[\text{Ru}^{\text{III}}(-\text{OH})]^{2+}/[\text{Ru}^{\text{II}}(-\text{OH}_2)]^{2+}$, $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}/[\text{Ru}^{\text{III}}(-\text{OH})]^{2+}$ couples, higher potential $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}/[\text{Ru}^{\text{III}}(-\text{OOH})]^{2+}$ species and oxygen onset potential during water oxidation (Figs. 4.2-4.4). Apparently the $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ complex is not converted into a longer living $[\text{Ru}^{\text{V}}(=\text{O})]^{3+}$ intermediate before second water ligation, the mechanism reported earlier for single site catalysts [25,26]. The addition of the second water molecule with the complex $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ probably produces a short lived $[\text{Ru}^{\text{II}}(-\text{O}_2\text{H}_2)]^{2+}$ type intermediate that enables the balancing of proton and electron affinities at the beginning of the second half of the catalytic cycle [18].

This then undergoes a third consecutive PCET conversion into $[\text{Ru}^{\text{III}}(-\text{OOH})]^{2+}$, as shown by a slope of ~ 60 mV/pH (Fig. 4.4). In this way the formation of $[\text{Ru}^{\text{V}}(=\text{O})]^{3+}$ or other higher oxidation ruthenium intermediates that would arise when the non-protic $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ intermediate is oxidized prior to addition of a second water molecule, can be avoided [18,25]. Apparently, the water coordination with $[\text{Ru}^{\text{IV}}(=\text{O})]^{2+}$ is not rate-limiting, and it is probably facilitated by the wide angle between bpy-Ru and the small multifunctional *p*-cymene that might switch back and forth its topology [36].

Scheme 4.1. Proposed pentacycle catalytic mechanism for water oxidation and oxygen evolution by $[(\text{cy})\text{Ru}^{\text{II}}(\text{L}_2\text{bpy})-\text{OH}_2]$ type complexes (L_2 is COOH or PO_3H_2). Red arrows represent four electron removal steps, each coupled with a proton transfer (blue arrows) and green arrows indicate electron transfer to ITO electrode via the linker. Characteristic for the mechanism is a complex with overall charge +2 and alternating Ru oxidation states $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}} - \text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}/\text{Ru}^{\text{II}}$ that are enabled by rapid, non rate-limiting oxidation processes, following association of a second water molecule and internal rearrangements and subsequent exchange of O_2 by H_2O .



This mediates the electron affinity of the system with its charge stabilization properties to allow for both the coordination of a second OH₂ in an octahedral Ru surrounding and rapid PCET interconversion to a [Ru^{III}-(OOH)]²⁺ species by lowering the barrier for this process. Thus, the surface anchored Cat.**Ru**-COOH eliminates the need for an increase of the redox potential by increasing the valence state of the Ru site and the entire complex without ejection of a proton. The different rate-limiting ruthenium couples in the catalyst [(cy)Ru^{II}(dcabpy)OH₂]²⁺ all show for the slope of ~60 mV/pH that is characteristic for reversible kinetics at the glassy carbon electrode, even at higher pH up to 12 and for none of the steps there is an underlying mechanism delaying proton transfer and affecting the kinetics. This matches the PCET characteristics of the natural PS-II system and of RuO₂ [11,27]. It represents a compelling advantage of the Cat.**Ru**-COOH complex over earlier molecular water oxidation complexes, and allows for a catalytic cycle of kinetically reversible proton coupled electron transfer regime while maintaining a divalent complex throughout the cycle, according to the mechanism proposed in Scheme 4.1.

4.3. CONCLUSIONS

In conclusion, a surface immobilized mononuclear ruthenium complex for electro-driven water oxidation, based on a stable, easy accessible and highly efficient mono catalytic site system, is discussed in this chapter. The complex appears electrocatalytically active and robust when anchored to the electrode surface by a linker group. A catalyst modified ITO electrode in neutral solution generated more than 400 μmol of oxygen in 11 hours in a controlled-potential water electrolysis experiment at relatively low overpotential with a current density >1.5 mA/cm². The catalyst turnovers were more than 3.1×10⁵ in 12 hours, at a turnover rate of ~7.14 moles of oxygen per mole of catalyst per second. In another set of experiments in aqueous acids, the oxygen generation turnover numbers were more than 6×10⁵ in 35 hours with turnover frequencies of ~5.33 per second. One cm² of electrode

covered with catalyst produced 800 μmol of oxygen in 30 hours of water electrolysis at a current density of $\sim 1.65 \text{ mA/cm}^2$. The catalytic system is capable of generating $\sim 450 \text{ } \mu\text{mol}$ of oxygen per hour in neutral water at an oxygen generation rate up to 80 per mol of catalyst per second, with a current density of $> 14 \text{ mA/cm}^2$. The above numbers are in excess of values reported for other known molecular catalysts for homogeneous and electrocatalytic oxygen evolution [18,24-26]. This study describes thus a good oxygen generation catalytic system for neutral and acidic water electro-oxidation and opens new doors towards efficient, stable and easy accessible water splitting assemblies for clean fuel generation.

Although we do not have access yet to detailed spectroscopic data for the catalyst on ITO, the CV analyses provide converging evidence that the catalyst is intact and active on the ITO surface. First, there is a catalytic effect at less overpotential than for the bare ITO that gives a water oxidation indication only at $> 2.5 \text{ V}$ (vs. NHE); second, the magnitude of the overpotential does not correspond with the overpotential for the most common decomposition product RuO_2 ; third, the magnitude of the overpotential is essentially the same as for the catalyst on the glassy carbon electrode; fourth, there is pH dependence and it is essentially the same over a range from 1-10.5 as for the catalyst on the glassy carbon electrode. On the other hand, it is sometimes difficult to identify the first two ruthenium transitions for the very small amount of catalyst in contact with the ITO surface [25,26], which can be attributed to slow electrode kinetics [18,25]. The ITO electrode is a mixture of two oxides and chemically different from the inert glassy carbon for which (i) the Nernst behaviour of the intermediates was determined and (ii) enhanced catalysis relative to the catalyst in solution was already observed. Although the bare ITO does not give a polarization response (Fig 4.3) [9,25], it is in principle possible that complex mechanisms involving a combination of molecular and semiconductor electronic processes at the interface between the catalyst and the ITO occur. After continuous operation for many hours, inactive spots develop on the electrode at the locations where oxygen bubbles were generated. Since ITO is a relatively inert electrode and the blank electrode does not

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give an electrocatalytic response, these spots were attributed to inactivation or deterioration of the catalyst, possibly involving breakdown of the cymene that is thought to undergo ligation switching in every cycle in the proposed mechanism of Scheme 4.1.

In this way nicely the fundamental chemical paradox of water splitting transpires, that a durable system requires sturdiness, while multi electron catalysis requires flexibility. Apparently the molecular catalytic system for efficient water splitting discussed here offers an attractive compromise in this respect, with its high TON's and TOF's that exceed the values reported thus far for other catalytic systems. Further validation of the system and resolving the mechanism that makes that the interface of catalyst and electrode allow the rapid switching of the electronic properties for many cycles will have to be investigated by time resolved spectroelectrochemical studies in a future step.

4.4. MATERIALS AND METHODS

Unless otherwise specified, the solutions were prepared in ultra-pure water (Millipore MilliQ® A10 gradient, 18.2 MΩ cm, 2–4 ppb total organic content). The electrochemical measurements were carried out in carefully Ar-purged deoxygenated aqueous solutions at room temperature. Compounds, ligands and catalyst complexes were synthesized in argon/nitrogen atmosphere. ITO coated glass slides (10 cm × 2.5 cm), [RuCl₂(*p*-cymene)]₂ dimer and RuCl₃·*n*H₂O were obtained from Sigma-Aldrich Co., and used as received. 4,4'-dicarboxylic acid-2,2'-bipyridine (H₂dcabpy) and 4,4'-diphosphonic acid-2,2'-bipyridine (H₄dphbpy) were prepared using literature procedures [37,38]. ¹H NMR spectra and UV-vis measurements are conducted as described in the previous chapter.

General procedures for glassware and cell cleaning, electrodes type and preparation, and instrumentation for electrochemical measurements are described in section 3.4. ITO coated glass slides (1 cm × 2.5 cm, exposed surface area 1.0 cm²) were used as a working electrode (WE) for the surface bound electro-catalytic

CV studies. The catalytic water electrolysis and oxygen evolution measurement investigations were carried out in a three electrode double junction H-type glass cell where the reference electrode chamber was separated by a very fine porosity glass frit. In catalytic water electrolysis, the WE was ITO with the specification mentioned above. Platinum wire (thickness 1 mm), shaped into a spiral, was used as a counter electrode (CE). The catalytic oxygen evolution was measured *in situ* using a calibrated oxygen electrode connected with a digital O₂ meter (YSI, Inc., Model 550A).

Prior to the water splitting investigation and oxygen measurements experiments, the aqueous solutions were purged with high-purity argon (Linde Gas, 6.0) for at least 30 min before each measurement. The whole cell assembly was airtight and care was taken to prevent any passage of air and oxygen into the test solution in the cell. Oxygen elimination from the continuously Ar-bubbled aqueous solutions was carefully verified by scanning the freshly polished Pt disk (diameter d=3 mm, embedded in PTFE) electrode on RDE assembly from 500-2500 rpm until no oxygen detection was observed.

Immobilization of the catalyst on ITO coated glass slides (1 cm × 2.5 cm) was accomplished by soaking the electrode (4-8 hours) in 0.1 mM stock solution of catalyst in either pure deoxygenated water or 0.1M aqueous HNO₃. For controlled –potential water electrolysis studies, a 15-25 µL aliquot of 0.01 mM catalyst stock solution was placed on the ITO coated glass electrode to obtain the catalyst loading of $\sim 1.5 - 2.5 \times 10^{-10}$ mol/cm². The density of electrocatalytically active species per cm² of ITO surface was estimated from the CV's. The voltammograms for Ru^{III}/Ru^{II} transition between 0.40 and 0.85 V (Fig. A4.4) were integrated after background current correction according to equation 4.1:

$$\rho_{cat} = \frac{\int (I_{cat} - I_0) dV}{AS e_0} \left[\frac{\text{el.sp.}}{\text{cm}^2} \right], \quad (4.1)$$

and converted into number of moles of the catalyst per cm^2 of the electrode [25,26]. Here ρ_{cat} is number of electrocatalytically active species per electrode area (el.sp./cm^2), I_{cat} and I_0 is catalytic and background currents, respectively, V is potential, A is area (1 cm^2), S is scan rate (100 mV/sec) and e_0 is the elementary charge. The ITO, after each surface modification, was dried and the catalyst modified ITO slides were put inside a groove ($1.1 \text{ mm} \times 5 \text{ mm}$) of a stainless steel rod (length $l=18 \text{ cm}$ and diameter $d=0.5 \text{ cm}$) and fixed with Parafilm or Teflon tape. In some cases, a crocodile clip was used to hold the catalyst coated ITO glass slide for electrocatalytic water oxidation experiments.

Synthesis

4.4.1. Chloro complex $[(\text{cy})\text{Ru}^{\text{II}}(\text{H}_2\text{dcabpy})\text{Cl}]\text{Cl}$ (**Ru-COOH**)

4,4'-dicarboxylic acid-2,2'-bipyridine (H_2dcabpy : 0.244 g, 1.0 mmol) was dissolved in 0.5 mL water containing NaOH (0.08 g, 2.0 mmol) and MeOH (25 mL) was added to it. This mixture was poured into a stirred mixture of $[\text{RuCl}_2(p\text{-cymene})]_2$ dimer (0.362 g, 0.5 mmol) in absolute MeOH (20 mL). The whole reaction mixture was further stirred for 2 hours at 40-45 °C. The solution was cooled to room temperature and pH was lowered to 1-2 by addition of 0.5 M HCl. The free ligand was filtered off and the solvent mixture was evaporated under vacuum. The solid orange chloro complex $[(\text{cy})\text{Ru}^{\text{II}}(\text{H}_2\text{dcabpy})\text{Cl}]\text{Cl}$ thus obtained was re-precipitated from MeOH or acetone by addition of ether/hexane. Yield 0.43 g, 78 %. ^1H NMR (CD_3OD , 295 K, δ ppm, J Hz): 9.66 (d, 2H, $\text{H}^{6,6'}$ _{dcabpy}, J 5.76); 8.99 (s, 2H, $\text{H}^{3,3'}$ _{dcabpy}); 8.22 (dd, 2H, $\text{H}^{5,5'}$ _{dcabpy}, J 1.49, J 5.79); 6.19 (d, 2H, $\text{Ar}_{p\text{-cy}}$, J 6.33); 5.95 (d, 2H, $\text{Ar}_{p\text{-cy}}$, J 6.33); 2.66 (sep, 1H, $-\text{CH}(\text{CH}_3)_2$ _{$p\text{-cy}$}); 2.27 (s, 3H, CH_3 _{$p\text{-cy}$}); 1.06 (d, 6H, $-\text{CH}(\text{CH}_3)_2$ _{$p\text{-cy}$} , J 6.91), Analysis found: C, 45.56%; H, 4.41%; N, 4.85%. Calculated: C, 45.74%; H, 4.36%; N, 4.86% for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_4\text{Ru}_1\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$ complex.

4.4.2. Chloro Complex [(cy)Ru^{II}(H₄dphbpy)Cl]Cl (**Ru**-PO₃H₂)

The chloro complex [(cy)Ru^{II}(H₄dphbpy)Cl]Cl was prepared in a similar manner as described above (section 4.4.1) using 4,4'- diphosphonic acid -2,2'-bipyridine (H₄dphbpy: 0.316 g, 1.0 mmol) in 0.5 mL water containing NaOH (0.16 g, 4.0 mmol) instead of 4,4'-dicarboxylic acid-2,2'-bipyridine. Yield 0.41 g, 66 %. ¹H NMR (CD₃OD, 295 K, δ ppm, *J* Hz): 9.29 (d, 2H, H^{6,6'}_{dphbpy}, *J* 6.11); 8.81 (s, 2H, H^{3,3'}_{dphbpy}); 7.97 (dd, 2H, H^{5,5'}_{dphbpy}, *J* 2.01, *J* 6.15); 6.12 (d, 2H, Ar_{*p*-cy}, *J* 6.37); 5.87 (d, 2H, Ar_{*p*-cy}, *J* 6.37); 2.65 (sep, 1H, -CH(CH₃)₂_{*p*-cy}); 2.21 (s, 3H, CH₃_{*p*-cy}); 1.03 (d, 6H, -CH(CH₃)₂_{*p*-cy}, *J* 6.91), Analysis found: C, 38.08%; H, 3.16%; N, 4.86%. Calculated: C, 38.60%; H, 3.89%; N, 4.50% for C₂₀H₂₄N₂O₆P₂RuCl₂ complex.

4.4.3. Catalyst Complex [(cy)Ru^{II}(H₂dcabpy)-OH₂]²⁺ (Cat.**Ru**-COOH)

The chloro complex [(cy)Ru^{II}(H₂dcabpy)Cl]Cl was converted into the aqua (OH₂) catalyst [(cy)Ru^{II}(H₂dcabpy)-OH₂]²⁺ by stirring with aqueous solution containing 2.1 eq. of AgNO₃ or silver hexafluorophosphate in methanol (1:1, H₂O/MeOH) for 30 minutes. The white precipitates were filtered off and the solvent mixture was evaporated under vacuum. The yellow solid aqua complex thus obtained was reprecipitated from acetone or MeOH by addition of ether/hexane.

4.4.4. Catalyst Complex [(cy)Ru^{II}(H₄dphbpy)-OH₂]²⁺ (Cat.**Ru**-PO₃H₂)

The bright yellow aqua complex [(cy)Ru^{II}(H₄dphbpy)-OH₂]²⁺ was prepared in a similar manner as described above (section 4.4.3) using chloro complex of 4,4'-diphosphonic acid -2,2'-bipyridine instead of 4,4'-dicarboxylic acid-2,2'-bipyridine.

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Appendix A4

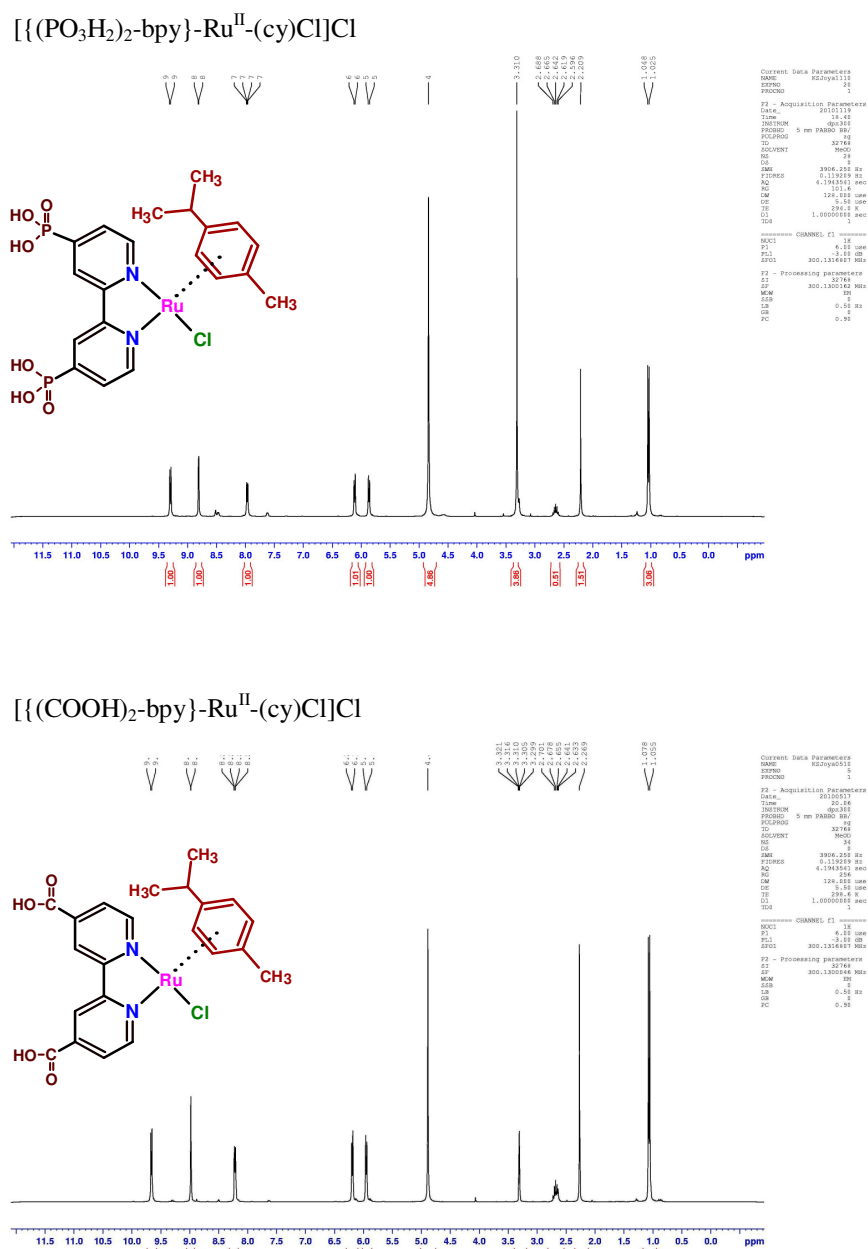


Figure A4.1. Proton-NMR spectra of the water oxidation complexes, **Ru-PO₃H₂** and **Ru-COOH**.

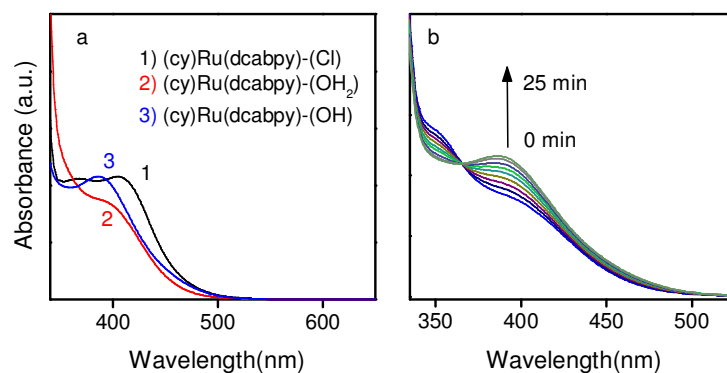


Figure A4.2. (a) Electronic absorption spectra of $[(\text{cy})\text{Ru}(\text{dcabpy})-(\text{Cl})]^+$, $[(\text{cy})\text{Ru}(\text{dcabpy})-(\text{OH}_2)]^{2+}$ and $[(\text{cy})\text{Ru}(\text{dcabpy})-(\text{OH})]^+$ complexes and (b) conversion of $[(\text{cy})\text{Ru}(\text{dcabpy})-(\text{OH}_2)]^{2+}$ into $[(\text{cy})\text{Ru}(\text{dcabpy})-(\text{OH})]^+$ complex in 0.5 M NaOH. (The concentration of all complexes is 7.5×10^{-5} M).

Figure A4.3.

Relation between the applied electrolysis potential, oxygen evolution rate (μmol per hour) and TOF (O_2 mol per mol of catalyst per second) for the Cat.**Ru**-COOH modified ITO electrode in deoxygenated aqueous 0.1M phosphate buffer solution (pH $\sim$ 7.1). (E/V vs. NHE, ITO area $A=1 \text{ cm}^2$, catalyst loading $\sim 1.51\text{--}1.65 \times 10^{-10} \text{ mol/cm}^2$).

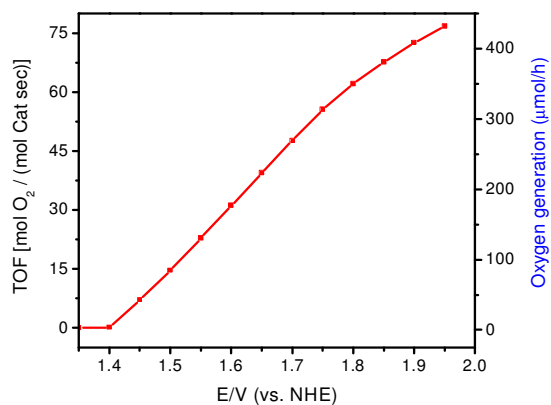


Figure A4.4.
CV's for blank ITO and
Cat.**Ru**-COOH/ITO system.
The number of active
catalytic species were
estimated by integrating
peak area for the Ru(III/II)
transition in deoxygenated
aqueous 0.1 M HNO₃. Scan
rate was 100 mV/sec, ITO
area A=1 cm².

