

**Development and Mechanistic Study of
Copper-Based Water Oxidation Catalysts**

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Abstract

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Water oxidation is a challenging reaction that has great importance for alternative energy and fuel generation. Although several water oxidation catalysts have been discovered, much improvement is needed for the technology to be viable on a global scale. In recent years, there has been focus in the development of catalysts with earth-abundant elements and, subsequently, cobalt, nickel, manganese, and iron catalysts have been reported. This dissertation discusses the discovery and study of the first reported copper-based water oxidation electrocatalyst. This catalyst is a molecular species with bipyridine and hydroxide ligands.

Study of this catalyst has shown that it is among the fastest homogeneous water oxidation catalysts yet reported, with a turnover frequency of $\sim 100 \text{ s}^{-1}$. The catalyst is also relatively robust and can undergo at least 30 turnovers. Solutions of the catalyst are generated easily by reaction of bipyridine and a copper salt in a 1:1 ratio in water, followed by addition of hydroxide to obtain a solution between pH 11 and 13.

The catalytic mechanism has been investigated through spectroscopic analysis to understand the speciation, electrochemical kinetics, a ligand study, and reactivity

studies. While further work is still needed, these investigations have laid the groundwork for a basic understanding of the mechanism.

A phenanthroline-based catalyst has also been successfully immobilized on a pyrolytic graphite electrode through physisorption. The heterogeneous catalyst shows remarkable similarities to its homogeneous counterpart. It operates at the same overpotential and activity level and displays similar pH dependent behavior. This system has important implications for catalyst immobilization in general, which is an important area of study for the development of more industrially relevant catalysts.

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Dedication

To my amazing family

Ima, Aba, and Adam

and always

to Michael

Chapter 1

A General Introduction to Water Oxidation and Copper Chemistry

Water oxidation to dioxygen is a key challenge for the scientific community.¹⁻⁷ Many alternative energy technologies exist and are becoming more prevalent; however some of them, such as solar power and wind power, produce energy only intermittently. For these technologies to sustain our current fuel-based economy, a storage solution is needed. Production of fuels from abundant materials is one possibility. Fuels are, by nature, reductants, so a source of electrons is needed to make them.

Water is a logical source of those electrons. It is an abundant and inexpensive resource, especially if seawater can be used,⁸⁻¹⁰ and electrolytic water oxidation produces only dioxygen as a direct by-product. However, electrolysis of water is very energy intensive and involves a high overpotential (the difference between the practical amount of energy required for a reaction and the thermodynamic potential, which is the theoretical minimum energy required). The kinetic barriers for water oxidation to dioxygen tend to be quite high, due to the required transfer of four protons and four electrons and the formation of an O=O double bond.

Much effort has been devoted to the development of water oxidation catalysts. An ideal catalyst would be inexpensive, robust, have a fast turnover frequency, and operate at a low overpotential. Platinum and oxides of iridium, ruthenium, nickel and other metals have been studied extensively as heterogeneous catalysts,¹¹ with more recent cobalt phosphate,¹² nickel borate¹³ and manganese¹⁴ heterogeneous catalysts

attracting attention as well. There has also been a strong focus on homogeneous catalysts as they are more convenient for mechanistic study, which can lead to greater understanding of these systems and more facile catalyst optimization. Most of the homogeneous studies have focused on ruthenium complexes, but recently a number of other metals have been employed in the design of homogeneous water oxidation catalysts, including iridium, manganese, cobalt, and iron.^{4,14–16} Development of a well-defined, abundant metal catalyst would be a large step forward for this field. Herein, the discovery and exploration of a fast copper-based water oxidation system is reported.

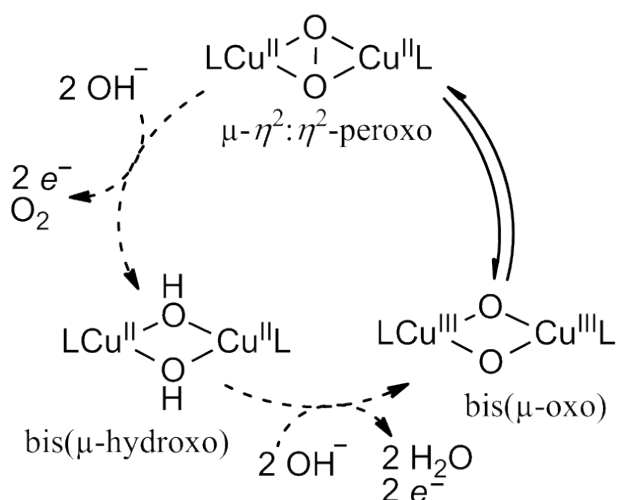
There have been extensive studies in copper-oxygen chemistry, much of it biomimetic chemistry based on enzymes with copper active sites, such as hemocyanin and tyrosinase.^{15–20} Cu(I) complexes with nitrogen ligands will readily react with dioxygen to produce bis(μ -oxo) or μ - η^2 : η^2 -peroxo dimers, generally observed at $< -40^\circ$ C. Often, rapid interconversion takes place between the μ -peroxo and μ -oxo species, which is one of the few examples of facile and reversible O–O bond formation. These complexes are thermally unstable, and often decompose to Cu(II) bis(μ -hydroxo) complexes. When solutions of these copper/ O_2 complexes are warmed to room temperature, they generally decompose to air and temperature stable Cu(II) species, which typically occurs by intramolecular oxidation of the ligand. Cu(II) bis(μ -hydroxo) complexes can be formed by this decomposition.^{21–23} More recently, there has been growing interest in monomeric copper-oxygen species, though there has been less research in this area.

Despite these studies, as well as a large literature studying copper-mediated oxygen reduction chemistry,²⁴ very little work has been done to investigate possible copper-based

water oxidation catalysts. There are two early reports by Elizarova, where a large number of metal salts and complexes were screened for water oxidation, with $\text{Ru}(\text{bpy})^{3+}$ as a chemical oxidant.^{25,26} Although they reported a few turnovers from CuCl_2 , $[\text{Cu}(\text{bpy})_2]\text{Cl}_2$, and $[\text{Cu}(\text{bpy})_3]\text{Cl}_2$, our attempts to replicate their observation resulted in less than a single turnover of O_2 . There have also been some controversial reports of mechanochemical water splitting involve a copper oxide.²⁷⁻²⁹ Since the publication of the $(\text{bpy})\text{Cu}^{2+}$ system described in this dissertation,³⁰ there have been two additional reports of copper-mediated water oxidation by Meyer: one describing simple copper phosphate and carbonate salts³¹ and another with a peptide ligand.³²

The initial motivation behind using copper, was to attempt to run the well-known oxygen activation chemistry in reverse (Scheme 1.1). This envisioned catalytic cycle was based on the dimeric copper chemistry described above. The literature demonstrates precedence for all of the proposed steps except for the removal of two protons and two electrons from the bis(μ -hydroxo) dimer to form the bis(μ -oxo) complex.^{15,21,33} Chris Waidmann, a Mayer Group graduate student, initiated the study of water oxidation with copper complexes by attempting to perform that conversion with β -diketiminato copper complexes.^{34,35} Ultimately, this approach was unsuccessful. In particular, the preparation of bis(μ -hydroxo) complexes led to mixtures of products and there were complications due to oxidant-base incompatibilities.³⁶

Scheme 1.1



While our vision of the catalytic cycle has shifted dramatically from the initial ideas, this work laid the foundation for the approach discussed herein. Care was taken in the selection of the bpy/Cu system, which has been discussed thoroughly in the literature.^{37–41} Most importantly, the oxidant-base incompatibilities led to a shift from use of chemical oxidants in organic solvents to electrochemical study in aqueous media. In the latter system, hydroxide easily serves as the base, while the electrode is the oxidant. Although there are still compatibility concerns under these conditions (i.e., the electrode potential window), they are more easily controlled. Ultimately, electrochemistry has proven to be a very useful tool for probing the copper water oxidation system, and has the added benefit of greater potential industrial applicability.

This change in approach was quite successful. It resulted in discovery of the first copper-based water oxidation electrocatalyst, and one of the fastest homogeneous water oxidation electrocatalysts yet reported. We have discovered that the catalyst can be immobilized without an increase in the overpotential or a decrease in the turnover frequency and have learned a great deal about the mechanism. Although significant

improvements would be required for the copper-based water oxidation catalyst to be commercially viable, it is hoped that the understanding we have gained will allow for optimization of copper catalysts specifically, and water oxidation catalysts in general.

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Chapter 2

Electrocatalysis with (bpy)Cu²⁺ Complexes

Abstract

1:1 Ligand:metal bipyridine complexes of copper are fast, relatively robust electrocatalysts for water oxidation. Electrocatalysis is performed with several supporting electrolytes and two working electrode materials (tin-doped indium oxide and glassy carbon). The turnover frequency is calculated to be 100 s⁻¹ with 30 turnovers observed in a small-volume cell. The Faradaic efficiency is measured to be >90%. Several pieces of evidence indicate that the electrocatalyst remains homogeneous and does not form an electroactive deposit during routine measurements.

2.1 Introduction

Water oxidation is an important challenge in alternative energy research.¹⁻⁴ Although many metals have been tested as potential water oxidation catalysts, with growing interest in using first row, “earth abundant” metals,⁵ copper has not been significantly investigated for water oxidation catalysis. This is particularly surprising, because there is abundant literature about copper-oxygen chemistry,^{6,7} and copper has been long studied as a catalyst for the reverse process: oxygen reduction.⁸ This chapter discusses the discovery of the first electrocatalytic copper-based water oxidation system and the initial study of the catalyst’s capabilities and characteristics. Since water is the most logical solvent for water oxidation chemistry, we focused on development of an aqueous electrocatalyst, using hydroxide as the base and the electrode as the oxidant.

In selecting the best ligand for electrocatalysis, several criteria were considered. A good water oxidation catalyst ligand should be robust in order to withstand the highly oxidative conditions often necessary for water oxidation. It should be easily modified, so that electronic and steric effects can be tuned and studied. Given the potentially global application of water oxidation, the ligand should be inexpensive and easily synthesized. The complexes also should have reasonable solubility in water, given that aqueous solutions are the most logical media for water oxidation.

The 2,2'-bipyridine (bpy) family of ligands fits these criteria. Its aromatic structure makes it fairly robust for an organic ligand, although there are reports of bipyridine activation and oxidation in high-valent complexes, particularly under alkaline conditions.⁹⁻¹² Bpy and related ligands have been widely used in water oxidation catalysts, starting from the blue dimer.¹³⁻¹⁶ It is a ubiquitous ligand in inorganic chemistry, and so myriad modified bpy ligands are commercially available or have syntheses reported in the literature.¹⁷ Our initial focus was on synthesis and use of the $[(\text{bpy})\text{Cu}(\mu\text{-OH})]_2^{2+}$ dimer, in line with our hypothesis that water oxidation chemistry could arise from reversal of well-characterized copper-mediated oxygen activation, which has been studied, mostly, at Cu_2O_2 centers.^{6,7,18} However, it should be noted that, in aqueous solution with labile copper complexes, there are several possible species present. An extensive analysis of the speciation of the catalytic system is reported in Chapter 3.

With initial discovery of a copper-based water oxidation catalyst, two major areas of investigation were emphasized. The first was establishment of catalyst activity and fundamental benchmarks, such as selectivity (Faradaic yield), catalytic rate (turnover frequency), and robustness (turnover numbers). The second was investigating

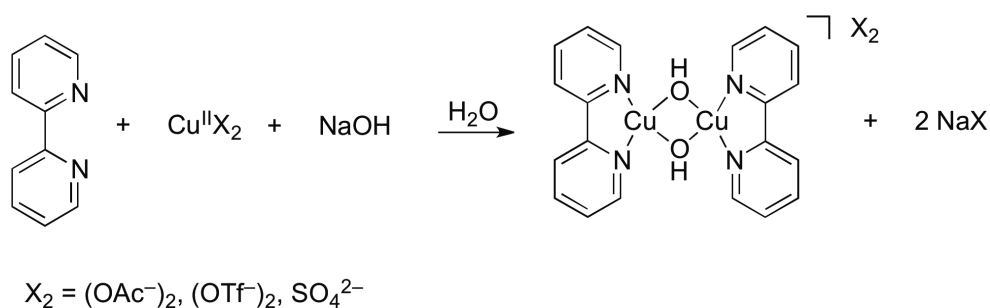
the possibility that the catalyst was not the molecular copper material dissolved in solution, but, instead, dispersed nanoparticles or an electroactive deposit on the electrode surface. Because water oxidation is generally performed under highly oxidizing conditions, decomposition of a starting molecular “catalyst” to catalytically active nanoparticles or deposits is relatively common.^{19,20} Although heterogeneous catalysts are quite useful and will probably provide the eventual solution for water oxidation, it is often easier to study the mechanism of molecular, homogeneous catalysts, which was our primary interest.

2.2 Results and Discussion

2.2.1. *Synthesis of $[(bpy)Cu(OH)]_2^{2+}$ complexes*

Dicopper(II) bis(μ -hydroxo) complexes with bipyridine and phenanthroline (phen) ligands have long been studied, first reported in 1968 in a paper by Woolliams.²¹ These compounds are synthesized simply by dissolving a copper(II) salt in water, adding a single equivalent of ligand, and agitating the solution for 5-10 minutes until the ligand has fully dissolved (Scheme 2.1). If the ligand is added as a solution in an organic solvent such as ethanol or acetonitrile, there is near-immediate formation of the bright blue bpy/Cu^{2+} complex. The dominant species in acidic aqueous solutions is the bis(aquo) complex $[(bpy)Cu(H_2O)_2]^{2+}$.²²⁻²⁴ Upon raising the pH, as described by Woolliams, the dimeric, dicationic bis(μ -hydroxide) copper complex $[(bpy)_2Cu_2(\mu-OH)_2]^{2+}$ is formed. With most starting copper(II) salts $Cu^{II}X_2$, this complex precipitates as a dark blue solid $[(bpy)_2Cu_2(\mu-OH)_2]X_2$ upon addition of hydroxide.

Scheme 2.1



Of the various $[(\text{bpy})_2\text{Cu}_2(\mu\text{-OH})_2]^{2+}$ salts surveyed, only the acetate salt has substantial solubility in water ($> 100 \text{ mM}$). The sulfate and triflate salts have modest solubility ($\leq 1 \text{ mM}$), while the nitrate and tetrafluoroborate are quite insoluble. The UV-vis spectra of the acetate, sulfate and triflate salts are nearly the same at pH 9 and 1 mM $[\text{Cu}]$ (Figure 2.1) implying that there is no substantial anion coordination to copper under these conditions. The ^1H NMR spectrum of the $[(\text{bpy})\text{Cu}(\text{OH})]_2(\text{OAc})_2$ salt shows three broad signals corresponding to three of the four bpy protons, as well as a sharp signal corresponding to acetate (Figure 2.2). Isolated materials were identified as the bis($\mu\text{-OH}$) complexes through elemental analysis. However, these materials rapidly speciate when dissolved in water (see Chapter 3).

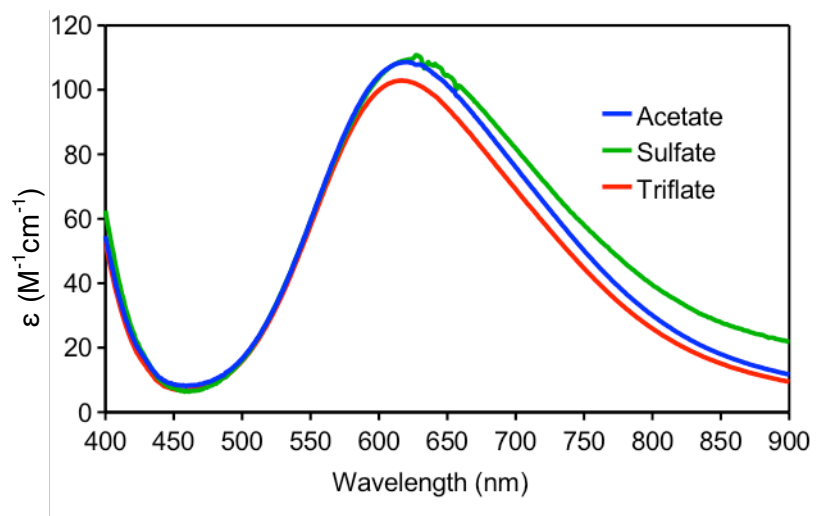


Figure 2.1. UV/Vis spectra of 10 mM [bpyCuOH]₂²⁺ at pH 9 with acetate, sulfate, and triflate anions.

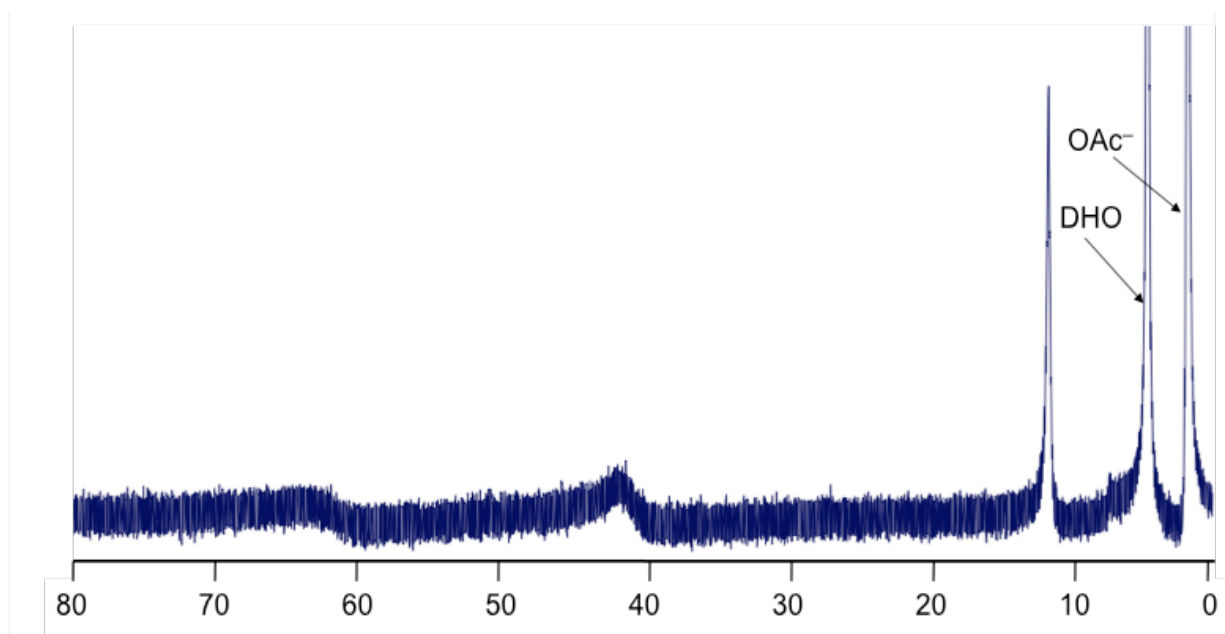


Figure 2.2. ¹H NMR of [bpyCuOH]₂(OAc)₂ in D₂O. The three bipyridine signals at 12, 42, and 62 ppm roughly integrate 1:1:1.

2.2.2 Observing electrocatalysis

Cyclic voltammograms (CVs) of $[(\text{bpy})_2\text{Cu}_2(\mu\text{-OH})_2](\text{OAc})_2$ solutions, using a glassy carbon working electrode and aqueous NaOAc/NaOH electrolyte, show very large anodic (oxidation) currents in alkaline solutions, which increase as the pH increases (Figure 2.3). Peak currents of over 700 mA ($10 \text{ mA}/\text{cm}^2$) at 1 mM copper are much larger than expected for a typical one-electron redox couple. Scanning to negative potentials shows a quasi-reversible one-electron wave, with a peak current (i_p) of 10 mA (Figure 2.3 inset). This wave is assigned to the $\text{Cu}^{\text{II/I}}$ couple. The observation of peak currents ~ 70 times larger than the i_p for the equivalent $1e^-$ couple indicates electrocatalysis, as many more than one electron is being removed from each copper in the vicinity of the electrode.²⁵

To test whether acetate oxidation might be taking place, as occurs in the Kolbe process at higher potentials,²⁶ the cyclic voltammograms of the acetate salt in NaOAc/NaOH buffer were compared with the sulfate and triflate salts in $\text{Na}_2\text{SO}_4/\text{NaOH}$ or NaOTf/NaOH buffers. Very similar electrocatalysis was observed, with slight differences in total current, but identical onset potentials (Figure 2.4). This result indicates that the anion of the electrolyte is not intimately involved in the electrocatalysis, either by being oxidized (sulfate and triflate are not readily oxidized) or by acting as a ligand to Cu (triflate is a very weak ligand).

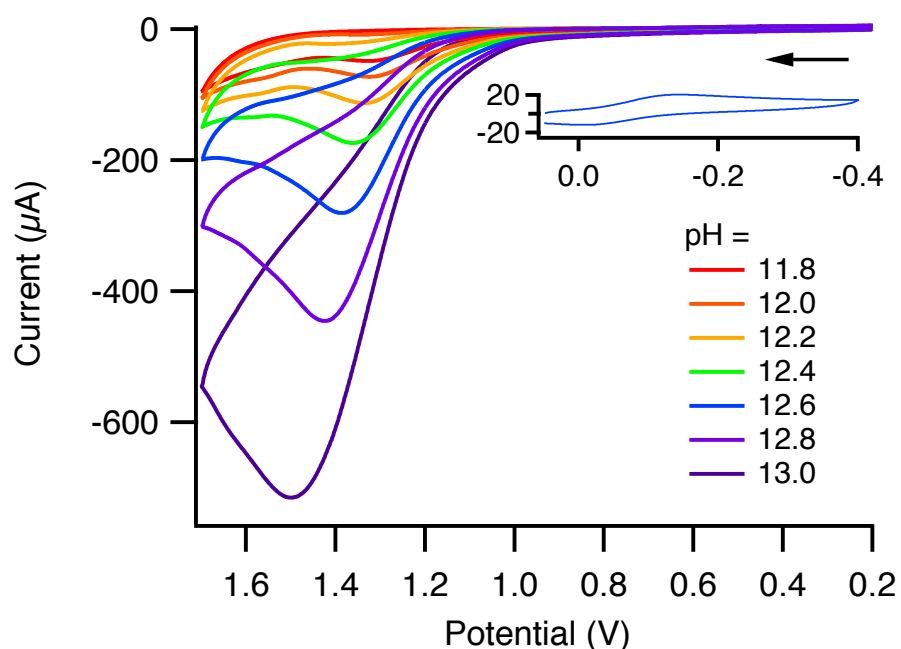


Figure 2.3. CVs of a 0.5 mM solution of $[(bpy)_2Cu_2(\mu-OH)_2](OAc)_2$ show increasing catalytic current as solution is more alkaline. Arrow shows direction of potential sweep. Inset: the $1e^- Cu^{III}$ couple for the same solution, shown to scale. Conditions: 0.1 M electrolyte (NaOAc + NaOH), glassy carbon working electrode, platinum reference electrode, Ag/AgCl reference electrode (adjusted to NHE). Reproduced with permission from Nature Publishing Group.

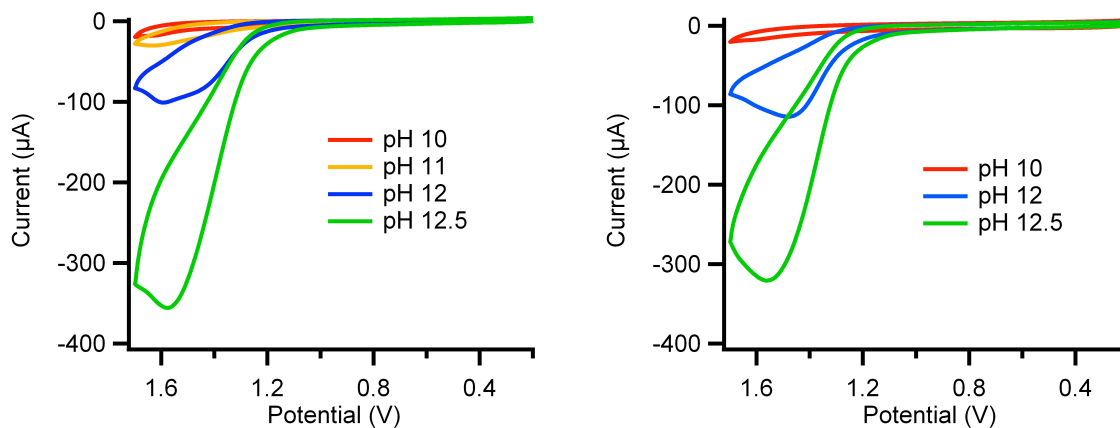


Figure 2.4. Left: Cyclic voltammogram of 0.5 mM $[(bpy)Cu(\mu-OH)]_2(OTf)_2$ in 0.1 M electrolyte (NaOTf + NaOH). Right: Cyclic voltammogram of 0.5 mM $[(bpy)Cu(\mu-OH)]_2(SO_4)$ in 0.1 M electrolyte (Na_2SO_4 + NaOH). Electrodes for all CVs: working, glassy carbon; auxiliary, Pt; reference, Ag/AgCl (adjusted to NHE).

To test whether the electrocatalytic process observed by CV was water oxidation, the dissolved oxygen concentration was monitored during controlled potential electrolysis (CPE) with high surface area reticulated vitreous carbon (RVC) and indium-tin oxide (ITO) electrodes. The monitoring was performed with a fluorescence O_2 probe from Ocean Optics (FOXYTM). A specialized electrochemical cell with a large, gas-tight, TeflonTM cap (Figure 2.5) was constructed in order to prevent atmospheric O_2 from leaking into the chamber and O_2 generated during the experiment from escaping. The cap has air-tight ports for the reference electrode, auxiliary chamber, and a fluorescence O_2 probe. A brass post was threaded through the cap so that the working electrode could be connected on the inside of the cell. The cap also has a gas inlet with a valve, so that the cell can be thoroughly purged with argon before the electrolysis. Argon-sparged electrolyte was introduced by syringe to the cell after the cell was purged, with the whole process monitored with the oxygen probe. Typically, the dissolved oxygen concentration was monitored during electrolysis, with the headspace volume kept to a minimum in order to maximize the amount of oxygen in the aqueous phase. O_2 could also be detected in the headspace.

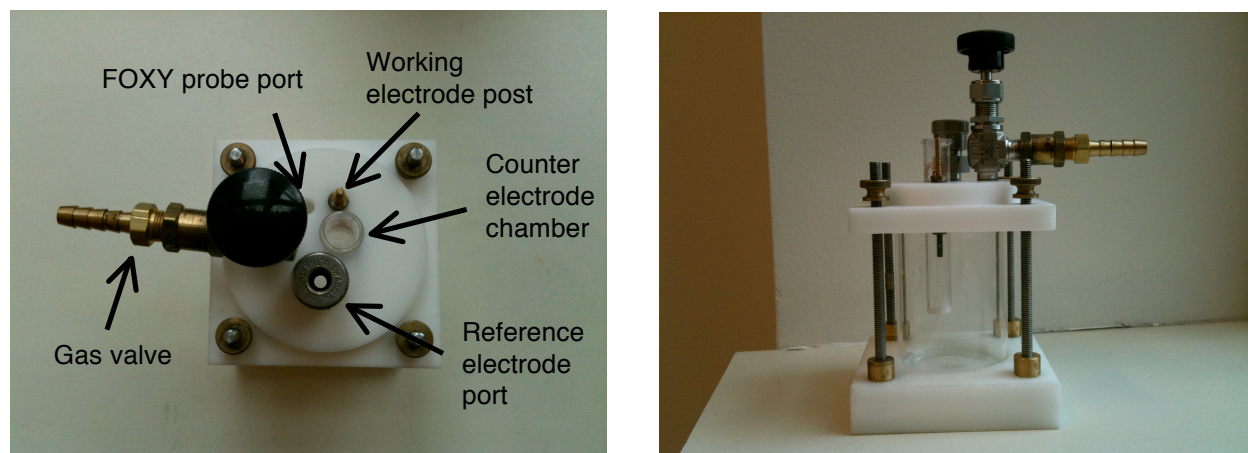


Figure 2.5. Photographs of the gas-tight electrochemical cell used for air-free bulk electrolysis.

CPE was performed at +1.35 V vs. NHE (an overpotential of 860 mV) with the RVC electrode, with 1 mM [(bpy)₂Cu₂(μ-OH)₂](OAc)₂ at pH 12.5 (Figure 2.6). There was a substantial increase in the concentration of dissolved oxygen, from 0 to 550 μM. However, the Faradaic efficiency (with 4 *e*⁻ per O₂) was calculated to be only 35-45%. The control experiments in the absence of copper catalyst revealed similar current levels, but substantially less O₂ generation. Therefore, we hypothesize that, under these highly oxidizing conditions, the carbon electrode was being consumed during CPE, accounting for the low Faradaic efficiency.

We switched the working electrode to unpolished ITO, which is oxidatively much more robust. Similar experiments were performed with this electrode (+1.35 V for 30 minutes with 0.5 mM [(bpy)Cu(OH)]₂(OAc)₂ starting at pH 12.5; see Figure 2.7). Again, substantial O₂ generation was observed with the fluorescence probe. However, one complication with use of the ITO electrode was considerable background production of O₂ under the conditions used. This background O₂ production was taken into account through a simple subtraction of the current and O₂ production in the

absence of catalyst. On ITO, a current of 0.5 mA/cm^2 was sustained for 30 minutes, with a Faradaic efficiency to O_2 of $>90\%$. It is possible that some of the “missing oxygen” escaped the cell due or was in the headspace and, therefore, went unmeasured.

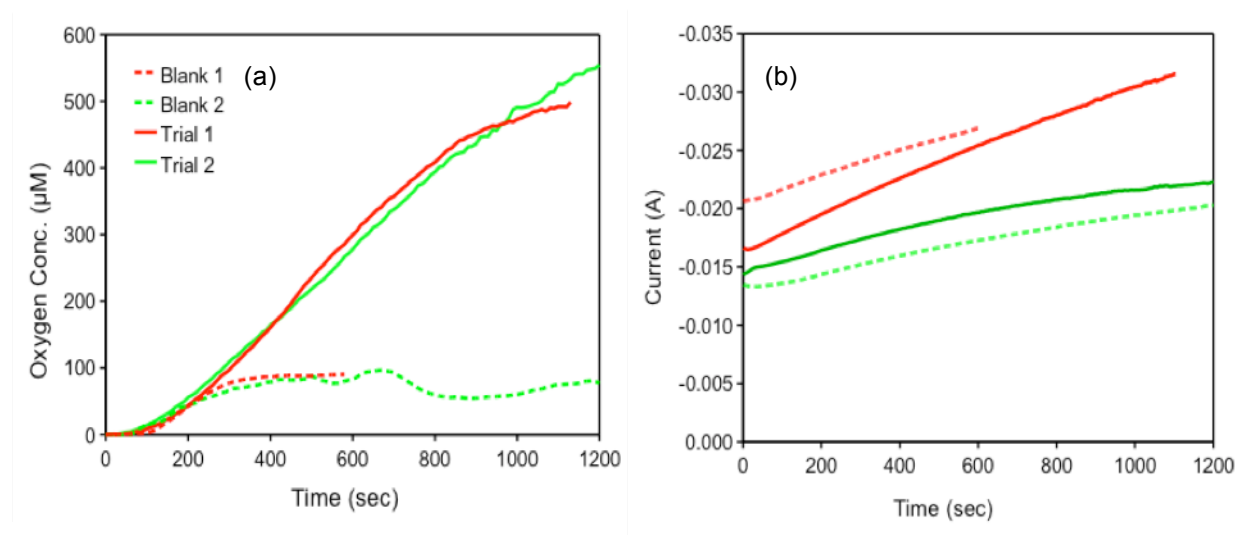


Figure 2.6. CPE at 1.3 V vs. Ag/AgCl. 0.1 M NaOAc, pH 12.5, adjusted with 0.1 M NaOH. “Blank” lines were measured without the presence of Cu, and “trials” included 1 mM $[\text{bpyCuOH}]_2(\text{OAc})_2$. Electrodes: working, RVC; reference, Ag/AgCl; auxiliary, Pt. Lines end where the potential was returned to 0 V.

O_2 was observed electrochemically as well. Upon performing several CVs, in a row, bubbles are observed on the surface of the disk electrode. CVs scanned through the O_2 production wave (following a single or several oxidative CVs) and then reversed to negative potentials show a large current at $\sim -0.2 \text{ V}$ (Figure 2.8). This current is due to reduction of O_2 to O_2^- in basic solution.²⁷ It is much larger than the $\text{Cu}^{\text{II/I}}$ wave (Figure 2.3 inset), which is observed upon initial cathodic scan in O_2 -free solutions, as mentioned above. Scanning through the anodic wave and then sparging the solution with nitrogen removed the large cathodic current, confirming its assignment to the $\text{O}_2^{0/-}$ couple.

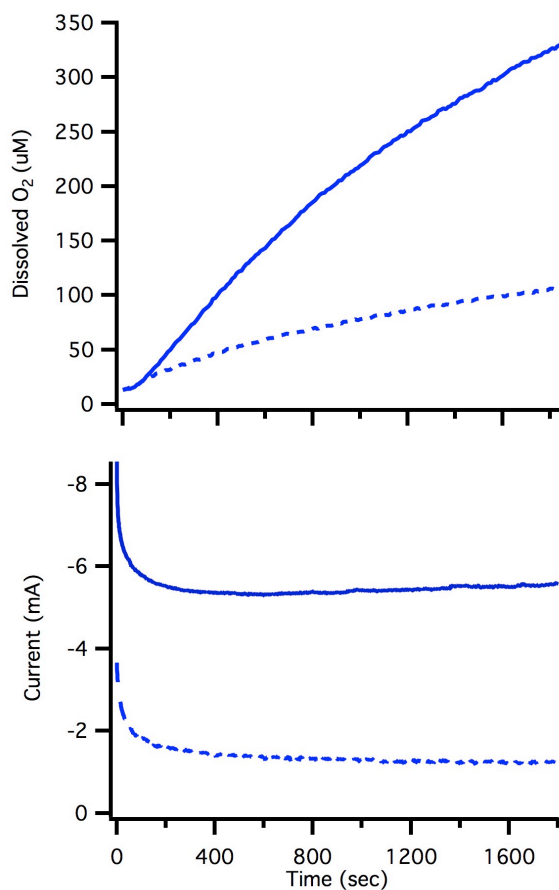


Figure 2.7. CPE at +1.3 V vs. NHE on ITO with (solid) and without (dashed) 0.5 mM $[(bpy)Cu(OH)]_2(OAc)_2$. Performed in 0.1 M electrolyte (NaOAc + NaOH) with a starting pH of 12.5. Electrodes: auxiliary, Pt; reference, Ag/AgCl adjusted to NHE. Reproduced with permission from Nature Publishing Group.

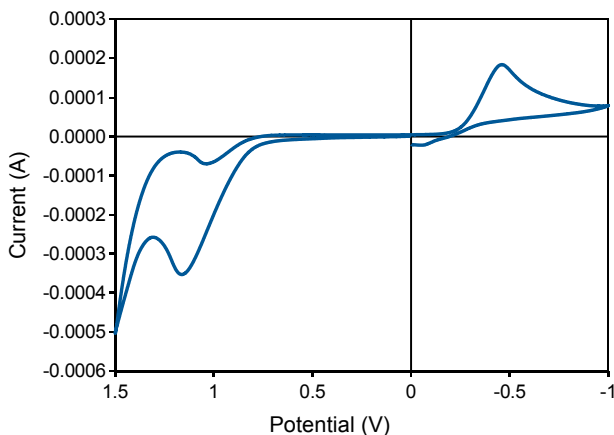


Figure 2.8. CV of 0.5 mM $[(\text{bpy})\text{Cu}(\mu\text{-OH})]_2(\text{OAc})_2$ in 0.1 M electrolyte (NaOAc + NaOH) starting at 0 V vs. Ag/AgCl, scanning through the electrocatalytic wave at 1 V, then scanning back to reducing potentials through the irreversible $\text{O}_2/\text{O}_2^{\bullet-}$ couple at -0.5 V. Electrodes: working, glassy carbon; auxiliary, platinum; reference, Ag/AgCl (not adjusted to NHE).

Thus $[(\text{bpy})_2\text{Cu}_2(\mu\text{-OH})_2]^{2+}$ salts are electrocatalysts for water oxidation to O_2 in water at $\text{pH} > 12$. The onset of the water oxidation wave is at 1.1 V *vs.* NHE and the half-peak potential ($E_{\text{p}/2}$) is at +1.3 V (potentials were recorded versus a Ag/AgCl reference and adjusted to NHE by addition of 0.199 V). High currents are observed, but the catalyst operates at somewhat high overpotentials. At pH 12.5, the thermodynamic potential for water oxidation is +0.493 V. This is 0.6 V below the 1.1 V for onset of catalysis, and ~ 0.8 V below the $E_{\text{p}/2}$. In general, the most efficient water oxidation catalysts perform at overpotentials of 0.4-0.5 V.^{28,29}

2.2.3 Estimation of turnover numbers

Measuring benchmarks for soluble electrocatalysts is more complicated than catalysis with chemical oxidants or heterogeneous electrocatalysts. In homogeneous catalytic reactions, there is full mixing of substrate, catalyst, and oxidant and the

turnover number (TON) and turnover frequency (TOF) can be measured from the rate of appearance of products. In heterogeneous electrocatalysis, the only active material in the system is on the surface of the electrode and (theoretically) active as long as potential is applied. Again, the TON and TOF can be measured directly. Despite its name, however, homogeneous electrocatalysis, is, fundamentally, a *heterogeneous* process because only the catalyst molecules near to the electrode are active. Therefore the ratio of product formed per *total* catalyst in solution is much lower than the ratio of product formed per *active* catalyst. For this reason, TONs for homogeneous electrocatalysts are rarely reported, and often estimated based on reactions with sacrificial oxidants, which may not be an appropriate comparison due to potential differences in reaction conditions and driving force.

Although the rate of product formation will still be slow compared to the actual catalyst turnover frequency, limiting the electrochemical cell volume will facilitate a greater number of turnovers per catalyst in solution. Therefore, to obtain a lower limit for the catalyst TON, water oxidation was performed with $[(\text{bpy})\text{Cu}(\text{OH})]_2(\text{OAc})_2$ in a spectroelectrochemistry cell with a 1 mM path length, thereby minimizing the amount of inactive catalyst (the material distant from the ITO electrode). Electrolysis was performed at +1.3 V vs. NHE with 0.5 mM dimer in 0.1 M electrolyte (NaOAc + NaOH). The pH was started at 12.5. When the pH dropped enough to cause a decrease in current, NaOH solution was added to bring the pH back to 12.5-13. This experiment showed 60 catalyst turnovers (per Cu dimer) over 5.5 hours (Figure 2.9). The amount of generated oxygen was determined from the measured current during electrolysis and the Faradaic efficiency obtained from electrolysis experiments that were followed with the fluorescence O_2 probe.

Optical spectra were collected before and after electrolysis. A 15% decay of the band assigned to the copper-coordinated bpy π - π^* transition was observed (Figure 2.10). However, substantial copper plating onto the auxiliary electrode (a platinum wire) was also observed, since the thin spectroelectrochemistry cell does not allow for a membrane to separate the anode and cathode, as is standard in bulk electrolysis experiments. This Cu reduction at the cathode may account for much of the decay observed, suggesting that the Cu/bpy system may be a quite robust water oxidation electrocatalyst. That conclusion is consistent with the high current densities observed during CPE and CV.

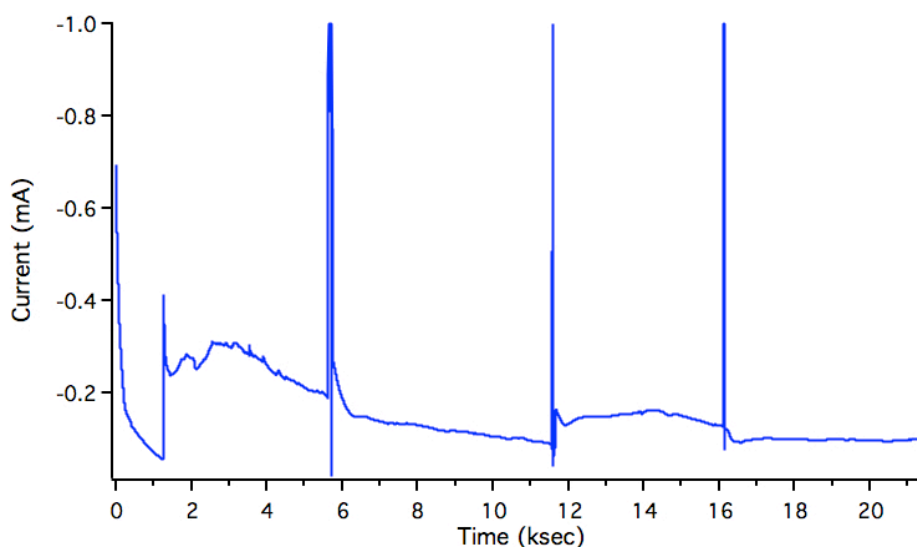


Figure 2.9. Current measured during 5.5 hours of electrolysis at +1.3 V in a low-volume spectroelectrochemistry cell. The cell contained a solution of 0.5 mM $[(\text{bpy})\text{Cu}(\mu\text{-OH})_2(\text{OAc})_2]$ in 0.1 M electrolyte (NaOAc + NaOH) with a starting pH of 12.5. Spikes correspond to added drops of 0.1 M NaOH. Electrodes: working, glassy carbon; auxiliary, platinum; reference, Ag/AgCl.

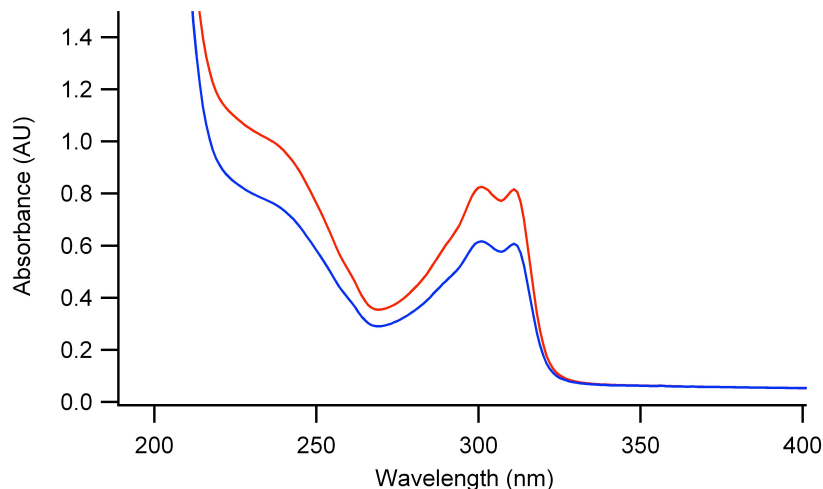


Figure 2.10. UV-vis spectra collected before (red line) and after (blue line) 5.5 hours of electrolysis at +1.3 V with 0.5 mM [(bpy)Cu(μ -OH)]₂(OAc)₂. There is a 15% decrease in absorbance of the π - π^* transition at 300 nm.

2.2.4 Calculation of the Turnover Frequency

The turnover frequency (TOF) of an electrocatalyst can be determined from the current during cyclic voltammetry.^{25,30–32} However, the conditions of the CV are key to the accuracy of this calculation. The CVs must be in the “kinetic regime,” where the rate of catalysis determines the maximum current, not the diffusion of the substrate to the electrode surface. This is analogous to pseudo first-order conditions for determination of homogeneous rates, where it can be assumed that there is a high enough concentration of other reactants that their consumption does not change significantly over the course of the experiment, simplifying the analysis. The kinetic regime in voltammetry is characterized by an S-shaped wave, where the current forms a plateau instead of a peak, and by a lack of current dependence on scan rate (ν).[§]

[§] For standard, diffusion-limited conditions, the current is dependent on $\nu^{1/2}$.

^{**} Speciation of (bpy)Cu²⁺ complexes is discussed further in Chapter 2.

To determine the TOF, or k_{cat} , it is useful to divide the plateau current for the catalytic wave, i_c , by the peak diffusion-limited current for the related non-catalytic redox process in the absence of substrate, i_d (Equation 2.3). The values for i_c and i_d are described by Equations 2.1 and 2.2, respectively. When i_c is divided by i_d , the terms for the catalyst concentration (C_{cat}), the area of the electrode (A), and the diffusion coefficient of the catalyst (D) (Equation 2.3) are eliminated. Elimination of A and D is particularly useful, since they require additional electrochemical measurements to obtain.

$$i_c = n_{\text{cat}} F A C_{\text{cat}} \sqrt{D k_{\text{cat}}} \quad (2.1)$$

$$i_d = 0.4463 F A n_d^{3/2} C_{\text{cat}} \sqrt{F D \nu / RT} \quad (2.2)$$

$$\frac{i_c}{i_d} = \frac{n_{\text{cat}}}{0.4463 n_d} \sqrt{\frac{RT k_{\text{cat}}}{F \nu}} \quad (2.3)$$

Per Equation 2.3, in the kinetic regime, the ratio i_c/i_d is proportional to $(k_{\text{cat}}/\nu)^{1/2}$. In this equation, n_{cat} is the number of electrons passed in each catalytic turnover (4 for water oxidation), n_d is the number of electrons passed in the non-catalytic CV wave (typically 1), and F is the Faraday constant. Unfortunately, for the $\text{Cu}^{2+}/\text{bpy}$ catalyst, it is not possible to observe the non-catalytic CV wave in the absence of substrate, since the substrate is hydroxide and high pH is needed to form the catalyst. When the isolated material is added to an organic solvent, such as an alcohol or acetonitrile, the solvent coordinates to the complex, changing the coordination environment about copper and, therefore, probably the electrochemistry. However, an estimate of i_p can be obtained from the quasi-reversible wave observed in initial cathodic scans of the $\text{Cu}^{2+}/\text{bpy}$ catalyst (Figure 2.3 inset) that was assigned to the one-electron $\text{Cu}^{\text{II/I}}$ couple.

The magnitude of the peak current for this wave (11 μA at 100 mV/s) is close to that of ferricyanide at the same concentration. By assuming that n_{cat} is 4 and n_{d} is 1 for the $\text{Cu}^{2+}/\text{bpy}$ water oxidation system, Equation 2.3 can be further simplified to Equation 2.4. From this equation, the simple relationship between the catalytic current and rate constant is particularly apparent.

$$\frac{i_{\text{c}}}{i_{\text{d}}} = 1.42 \sqrt{\frac{k_{\text{cat}}}{\nu}} \quad (2.4)$$

In Savéant's initial report on the $i_{\text{c}}/i_{\text{d}}$ methodology³³ and in subsequent discussions of the technique,³⁴ Savéant and others strongly emphasize that, in order to apply this treatment, the electrochemical system must be in the kinetic regime. If it is not, then the equations are not a reliable metric, since they only describe electrochemical behavior under those particular conditions. Diffusion-controlled conditions can be shifted to kinetic-controlled conditions by increasing the substrate to catalyst ratio, γ , or by reducing the scan rate.³⁵ At 0.5 mM [(bpy)Cu(OH)]₂(OAc)₂, pH 12.5, and diffusion-limited conditions, the CV waves are peaked ("duck"-shaped) rather than S-shaped, indicating that there is a diffusive contribution to the maximum current. This is most likely due to depletion of hydroxide (one of the substrates) near the electrode surface. Therefore, these catalytic currents are limited, not only by k_{cat} , but also by the diffusion of OH^- . This has been suggested to occur in other water oxidation systems with rapid TOFs.³⁶

The kinetic regime was achieved for this copper system by moving to low catalyst concentrations (≤ 0.1 mM in Cu), low scan rates (≤ 10 mV s⁻¹), and high pH (12.9-13.3). It should be noted that disturbances from outside convection could be a concern at such low scan rates. However, it does not appear to be an issue for this system, as the

CVs displayed clear characteristics of a catalytic system under kinetically controlled conditions (scan rate independence and substrate independence). The CVs displayed large background currents of up to 30% of the maximum current at pH 13.3 and 50 μM catalyst (Figure 2.11). This background is most likely from carbon degradation under the strongly oxidizing conditions. The background was taken into account by a simple baseline subtraction, where the baseline was collected from an identical solution in the absence of catalyst (Figure 2.12). This subtraction may be an overcorrection, based upon the distorted shapes of many of the background-corrected waves, especially the one for pH 13.3 where there was a large amount of background current. It is feasible that electrons that might have contributed to electrode degradation in the absence of catalyst, instead contribute to the water oxidation cycle, thus diminishing the background activity. However, there is no simple way to model this behavior for a more accurate baseline correction.

Values for i_c were collected from the “heel” of the background-subtracted waves and plotted vs. $v^{-1/2}$ (Figure 2.13). The value of k_{cat} calculated from the slope of the linear portion of the curve was 100 s^{-1} . This is a relatively high value. As of this writing, there are only two homogeneous water oxidation catalysts with similar or faster rates, a ruthenium catalyst at 800 s^{-1} and a cobalt catalyst at 80 s^{-1} .^{37,38} Even the fastest of the previously reported homogeneous water oxidation catalysts were generally much slower at 5 s^{-1} or less.³⁹

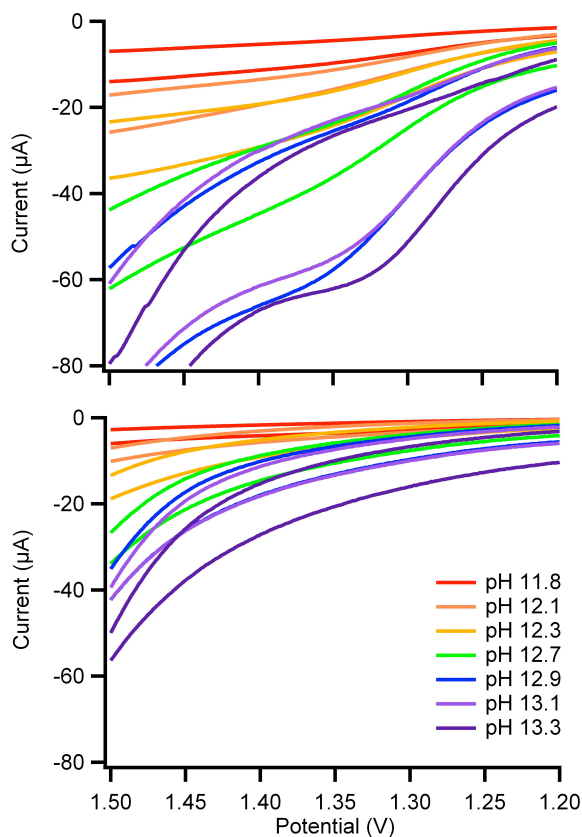


Figure 2.11. Top: CVs of 50 μM $[(\text{bpy})\text{Cu}(\mu\text{-OH})_2(\text{OAc})_2]$ in 0.1 M electrolyte (NaOAc + NaOH) at various pHs. Bottom: CVs of identical solutions in the absence of copper complex. Conditions: Scan rate was 3 mV/s. Electrodes: working, glassy carbon; auxiliary, platinum; reference, Ag/AgCl (adjusted to NHE).

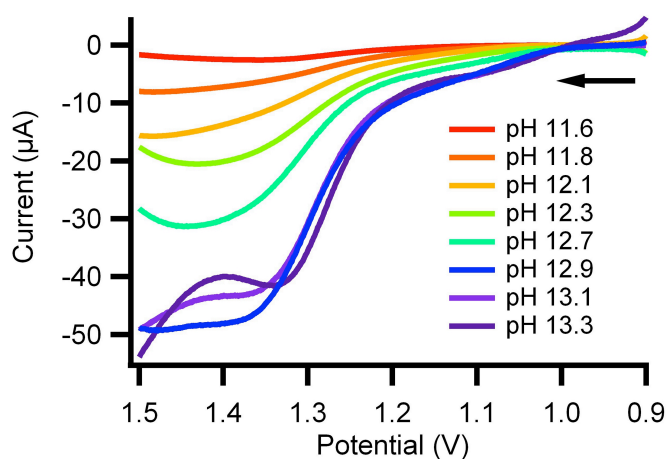


Figure 2.12. CVs shown in Figure 2.11 (top) with background subtracted and the reverse wave removed for clarity. Solutions contained 50 μM $[(\text{bpy})\text{Cu}(\mu\text{-OH})_2(\text{OAc})_2]$ in 0.1 M electrolyte (NaOAc + NaOH) at various pHs. Scan rate was 3 mV/s. Electrodes: working, glassy carbon; auxiliary, platinum; reference, Ag/AgCl (adjusted to NHE). Reproduced with permission from Nature Publishing Group.

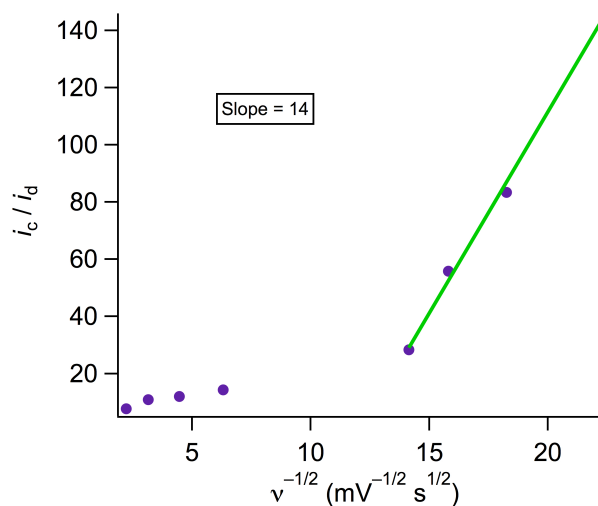


Figure 2.13. Plot of i_c (maximum catalytic current) divided by i_d (maximum one-electron current for $\text{Cu}^{\text{II/I}}$ couple) versus the inverse square root of the scan rate. The curve is linear when scan rates are between 1 and 4 mV/s.

2.2.5 Evidence for a Molecular Catalyst

A continuing concern in molecular catalysis of water oxidation is that the actual catalyst is not molecular, but rather a solid oxide/hydroxide deposit on the electrode or nanoparticle in solution.^{19,20} While the heterogeneous catalyst might be competent at water oxidation, mechanistic study and optimization might become more challenging, especially if the actual identity of the catalyst remains unknown. This concern is of particular importance for Ir and Co molecular catalysts, where the corresponding metal oxides are known to be good water oxidation catalysts.^{19,40–42} Some reports have identified copper oxide as a water oxidation catalyst; however they, have provoked controversy in the literature.^{43–45} A dark brown-black precipitate identified as cupric oxide is sometimes (though not consistently) formed upon standing from solutions of $[(\text{bpy})\text{Cu}(\text{OH})]_2(\text{OAc})_2$ at $\text{pH} \geq 12.5$. Particle formation is sometimes visible within 30

minutes with very dilute solutions (50 μM or less), possibly due to more favorable bpy-copper dissociation at low concentrations. It was rarely observed under “standard” conditions (0.5 mM catalyst, pH 12.5), though decomposition to copper oxide is hastened upon exposure to temperatures of 35° C or higher. Due to this instability, care was taken with catalyst solutions to minimize the catalyst exposure to high pH solutions, particularly before quantitative measurements.

Still, there are several pieces of evidence that copper oxide is not the catalyst in this system. Although the agglomeration of copper oxide particles is time-dependent, there is no induction period before catalysis, both for CV and bulk electrolysis. Furthermore, solutions do not increase in catalytic activity over time, as would be expected for a dispersed particulate catalyst, or with multiple CV scans, as would be expected for an electrolytically formed deposit.

Several other catalyst characteristics provide evidence in favor of a molecular catalyst. As mentioned earlier in this chapter, the catalyst works similarly in three different supporting electrolytes (NaOTf, Na_2SO_4 , and NaOAc) and on two different electrode surfaces (GC and ITO). No discoloration is observed on either GC or ITO. Although discoloration might be difficult to observe on the black GC electrode, ITO is transparent. Optical spectra were collected before and after 5.5 hours of electrolysis, and no new optical bands were observed. An electrochemical test for deposition was also performed. The electrodes were cycled ten times between 0.2 and 1.7 V in a solution containing 0.5 mM $[(\text{bpy})\text{Cu}(\text{OH})_2](\text{OAc})_2$ at pH 12.5. The electrodes were then rinsed (but not polished), immersed in a fresh electrolyte solution at pH 12.5, and a CV was collected. No catalytic wave was present, though the “tail” at 1.7 V increased from 180 μA to 400 μA (Figure 2.14, red trace). This current increase, however, was also observed

when the GC electrode was cycled ten times in the absence of catalyst. Therefore, the increase in current is attributed to decomposition of the glassy carbon electrode, which could increase the electrode surface area and account for the observed change in current.

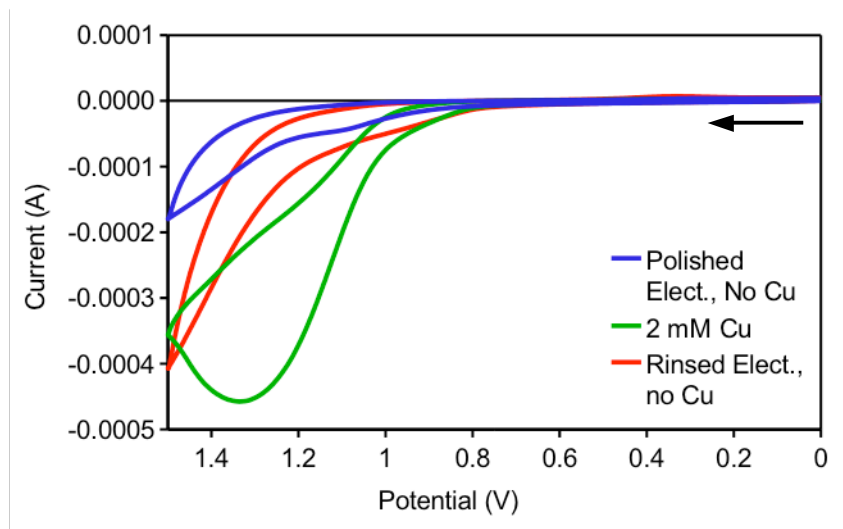


Figure 2.14. Cyclic voltammograms are performed from 0 to +1.5 V (vs. Ag/AgCl). A CV is collected in electrolyte solution without copper on a polished electrode (blue). 10 scans are performed in 1 mM $[(bpy)Cu(OH)]_2(OAc)_2$ + electrolyte (green). The electrodes and cell are thoroughly rinsed, but the working electrode is not polished. The unpolished electrode is used to collect a CV in fresh electrolyte solution (red). The current measured on this electrode does not return to blank current (blue) until it is polished. Electrolyte solution: 0.1 M NaOAc, pH 12.5 (adjusted with 0.1 M NaOH). Electrodes: working, glassy carbon (3 mm dia.); reference, Ag/AgCl, auxiliary, Pt.

Another test for catalyst homogeneity is measurement of the catalytic current vs. catalyst concentration. CVs of $[(bpy)Cu(OH)]_2(OAc)_2$ were collected at pH 12.5 in 0.1 M NaOAc and catalyst concentrations ranging from 10 μ M to 7.35 mM (Figure 2.15). Maximum current values were taken from background-subtracted CVs and plotted vs. catalyst concentration. The data revealed two regimes of concentration dependence. In the low concentration regime ($[cat] < 0.5$ mM), the maximum current has a clear linear

dependence on catalyst concentration. In the high concentration regime ($[\text{cat}] > 0.5$ mM), there is no apparent dependence on catalyst concentration, or possibly a slight inverse dependence. It is possible that the presence of two regimes indicates that the catalyst is heterogeneous, whereby a complete monolayer is not deposited on the electrode until the total copper concentration reaches 1 mM. However, in this scenario, one would also expect to see an induction period before catalysis is possible or reaches full activity. This type of delay is not observed. Furthermore, the process of deposition would probably stem from an equilibrium process, which would likely show a more complicated dependence than a simple linear one.

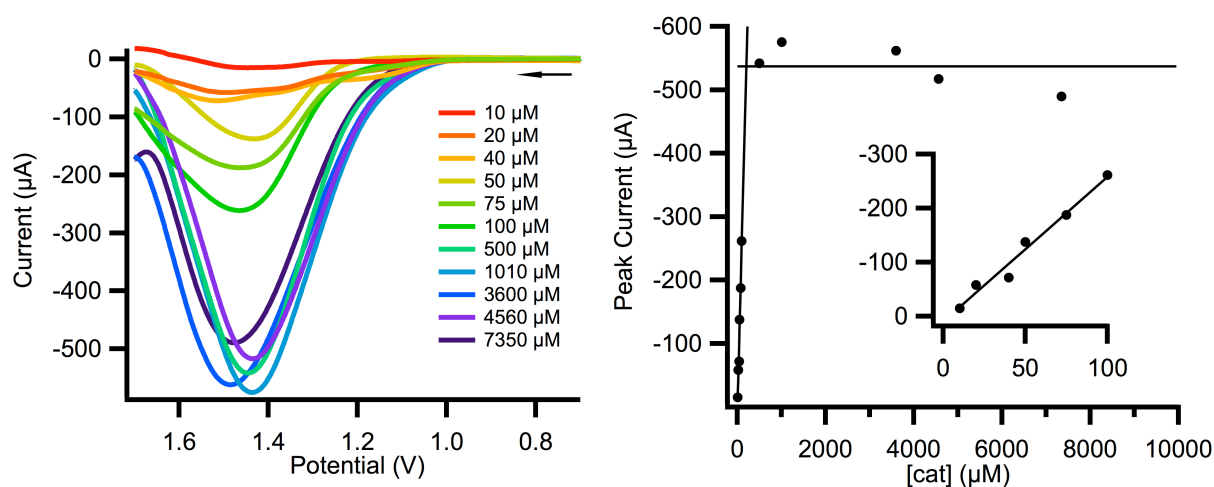


Figure 2.15. Dependence of the catalytic current on copper concentration. Left: CVs of $\text{bpy}/\text{Cu}^{2+}$ at various concentrations. All CVs were collected on GC at 50 mV s^{-1} and pH 12.5 in 0.1 M electrolyte ($\text{NaOAc} + \text{NaOH}$). Returning currents are removed for clarity. Right: At 100 μM and below, the peak current is linear with catalyst concentration. Current increases linearly with catalyst concentration up to 100 μM . At concentrations 500 μM and above, the current stays roughly the same.

It is also possible that the data indicate homogeneous behavior. In the low concentration regime, the system is closer (though not fully within) the kinetic regime described above. In the kinetic regime and close to it, there is a much higher ratio of substrate to catalyst, so the current is largely limited by the catalyst activity and

concentration. At high catalyst concentration, where the system is far from the kinetic regime, the current is largely limited, not by the catalyst activity and concentration, but by the availability of substrate. At a certain point, the substrate is used up so quickly, that more and more catalyst can be added without effect. This scenario has been modeled using the electrochemical modeling software, DigiSim, and is discussed further in Chapter 3.

Finally, there is clear evidence that the bpy ligand is important to this catalytic cycle. Solutions of simple copper salts form the insoluble $\text{Cu}(\text{OH})_2$ complex when exposed to high pH solutions. Suspensions of $\text{Cu}(\text{OH})_2$ are not catalytic for water oxidation. This has been our observation, as well as an observation reported in a recent manuscript by Meyer, describing water oxidation with simple copper(II) salts at lower pH.⁴⁶ Under highly alkaline conditions, starting at pH ~ 12.7 , $(\text{bpy})\text{Cu}^{2+}$ complexes lose the bpy ligand and coordinate additional hydroxide ligands, forming $\text{Cu}(\text{OH})_4^{2-}$.^{47**} A solution of 1 mM $\text{Cu}(\text{OH})_4^{2-}$ was prepared from $\text{Cu}(\text{OAc})_2$ and a 1 M NaOH solution and tested for electrocatalysis. The current measured from a CV of this system was no higher than the current measured from a copper-free solution under the same conditions (Figure 2.16, gray lines). When a single equivalent of bipyridine was dissolved in the solution of $\text{Cu}(\text{OH})_4^{2-}$, a large, electrocatalytic wave was observed in the CV (Figure 2.16, black line). In addition to our observations, there is also a very recent paper on the use of a copper tri-peptide for water oxidation, which presents evidence that the ligand is intact during catalysis.⁴⁸

In sum, there are many pieces of evidence that suggest that the electrocatalysis described above is the result of a molecular, homogeneous species. The lack of

^{**} Speciation of $(\text{bpy})\text{Cu}^{2+}$ complexes is discussed further in Chapter 2.

dependence on electrolyte and substrate would be unusual for a deposit, and the catalytic currents are linear with copper concentrations at low concentrations. It is difficult to see how a nanoscale copper oxide/hydroxide, formed from 10-100 mM $[\text{Cu}^{2+}]$ under equilibrium conditions, would show this simple linear behavior. It is also clear that the bipyridine ligand plays a key role in catalysis. Finally, the “rinse” test for deposition on the electrode is a strong indication that no electroactive species is tightly bound to the surface. Although it is nearly impossible to fully rule out catalysis by a heterogeneous species, these pieces of evidence strongly suggest a molecular, homogeneous catalyst.

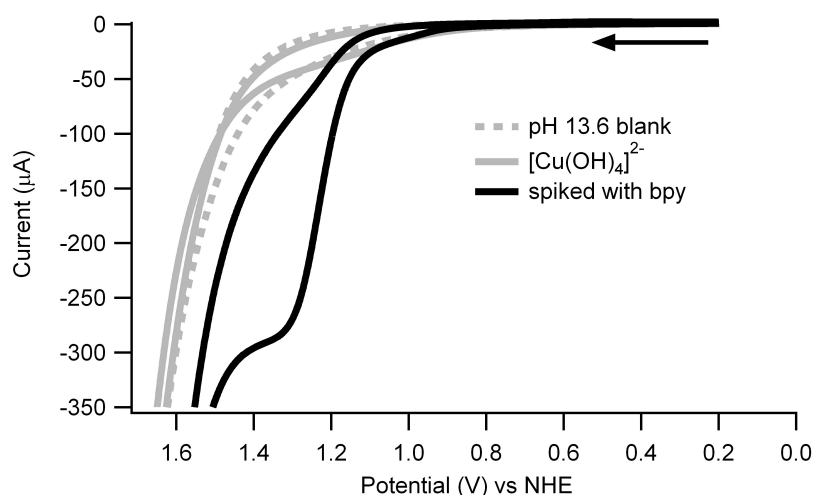


Figure 2.16. CVs at pH 13.6 of: a solution of just electrolyte (grey, dashed) a solution of $\text{Na}_2[\text{Cu}(\text{OH})_4]$ (grey, solid), and the latter solution with 1 equivalent of bpy added (black). The CV of the solution with $\text{Na}_2[\text{Cu}(\text{OH})_4]$ is essentially the same as that of the blank without copper, while addition of bipyridine to form $(\text{bpy})\text{Cu}(\text{OH})_2$ gives a large increase in current at 1.0 V due to catalytic water oxidation. Conditions: 1 mM $\text{Cu}(\text{OAc})_2$, 1 M NaOH, glassy carbon working electrode, platinum auxiliary electrode, Ag/AgCl reference electrode (adjusted to NHE).

2.3 Conclusions

Solutions that are electrocatalytic for water oxidation can be prepared from isolated $[(\text{bpy})\text{Cu}(\text{OH})]_2^{2+}$ salts or formed *in situ* by adding a 1:1 ratio of Cu(II) salt to bipyridine ligand. O_2 was detected both with a fluorescence probe and

electrochemically from the $\text{O}_2/\text{O}_2^{\cdot-}$ couple. Although turnover numbers for homogeneous electrocatalysts are not generally reported, a protocol was developed for monitoring electrolysis in a small volume cell, giving a reasonable lower limit for the catalyst TON. From this experiment, it was determined that the catalyst is relatively robust, with electrolysis performed for 5.5 hours and 60 turnovers with only 15% degradation. The TOF was calculated from CV measurements collected in the kinetic regime. The estimated TOF of 100 s^{-1} is very rapid for a homogeneous water oxidation catalyst, and is currently among the fastest homogeneous water oxidation catalyst. Although it is very difficult to rule out a heterogeneous mechanism, all current evidence suggests that the catalyst operating in the $\text{bpy}/\text{Cu}^{2+}$ system is molecular and homogeneous.

2.4 Experimental Methods

$[(\text{bpy})\text{Cu}(\mu\text{-OH})]_2\text{X}_2$ salts with $\text{X} = \text{acetate}$, triflate , and $\text{X}_2 = \text{sulphate anions}$ were prepared according to literature methods.³⁰ The moderately soluble triflate and sulphate salts were isolated through precipitation by raising the pH to 11. The very soluble acetate salt was isolated by removal of solvent (water) *in vacuo*, followed by recrystallization from water. All three salts were characterized by elemental analysis and UV-vis spectroscopy. The acetate salt was also characterized by ^1H NMR.

$[(\text{bpy})\text{Cu}(\mu\text{-OH})]_2(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$: ^1H NMR (400 MHz, D_2O): δ 12 (s, 1H), 42 (s, 1H), 62 (s, 1H). UV/Vis λ_{max} 617 nm ($109 \text{ M}^{-1}\text{cm}^{-1}$, neutral H_2O). Elemental analysis (calc., found for $\text{C}_{24}\text{H}_{32}\text{Cu}_2\text{N}_4\text{O}_{10}$): C (43.44, 43.40), H (4.86, 4.70), N (8.44, 8.36).

$[(\text{bpy})\text{Cu}(\mu\text{-OH})]_2(\text{OTf})_2$: UV/Vis λ_{max} 617 nm ($105 \text{ M}^{-1}\text{cm}^{-1}$, neutral H_2O).
Elemental analysis (calc., found for $\text{C}_{22}\text{H}_{18}\text{Cu}_2\text{N}_4\text{O}_8\text{S}_2$): C (34.24, 34.10), H (2.35, 2.22), N (7.26, 7.17).

$[(\text{bpy})\text{Cu}(\mu\text{-OH})]_2(\text{SO}_4)$: UV/Vis λ_{max} 617 nm ($110 \text{ M}^{-1}\text{cm}^{-1}$, neutral H_2O).
Elemental analysis (calc., found for $\text{C}_{20}\text{H}_{28}\text{Cu}_2\text{N}_4\text{O}_7\text{S}_1$): C (36.42, 36.63), H (4.28, 4.25), N (8.49, 8.54).

Electrochemistry was performed using a BASi Epsilon potentiostat and a CH Instruments 600D potentiostat. In all cases, a platinum auxiliary electrode and a Vycor-tipped Ag/AgCl (saturated KCl) reference electrode were used. Ag/AgCl reference electrodes were purchased from BASi or prepared from silver wire and solutions of saturated KCl. Electrochemical data were adjusted to NHE by adding 0.2 V to potential measurements. Solutions of 0.1 M electrolyte were prepared by titrating 0.1 M solutions of NaX (where X is the catalyst anion) with 0.1 M NaOH until the desired pH was reached. pH was measured with a Fisher Scientific Accumet pH meter. Cyclic voltammetry was performed using a 0.3 cm glassy carbon disk working electrode (from BASi or CH Instruments) or an ITO electrode (from Delta Technologies) with the surface area restricted with electrical tape. Bulk electrolysis was performed in a custom-designed gas-tight cell using a reticulated vitreous carbon working electrode (from BASi) or a double-coated, unpolished ITO electrode (from Delta Technologies). Solutions used for bulk electrolysis were sparged with nitrogen. The dissolved oxygen concentration during bulk electrolysis was measured with an Ocean Optics FOXY fluorescence probe (<http://www.oceanoptics.com/Products/neofox.asp>).

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Chapter 3

Speciation of (bpy)Cu²⁺ Complexes Under Catalytic Conditions

Abstract

Copper complexes are known to be highly labile. Under alkaline conditions and in the presence of electrolyte (NaX), H₂O, OH⁻, and X⁻ may all act as coordinating ligands. For that reason, there are several possible species present in solutions of (bpy)Cu²⁺ complexes under conditions suitable for electrocatalytic water oxidation. Therefore, the speciation of (bpy)Cu²⁺ complexes was studied, in order to understand which complex is the likely catalytic species for the water oxidation process. Evidence from EPR spectroscopy suggests that this complex is the (bpy)Cu(OH)₂ monomer, which is the dominant species at pH 12.5, where catalysis is most active. Quantitative EPR spectroscopy also suggests an electrolyte effect on the speciation. EPR and UV-vis spectra also indicate that the bipyridine ligand detaches at very high pH, likely forming the Cu(OH)₄²⁻ anion.

3.1 Introduction

There has been significant interest in development of homogeneous water oxidation catalysts, because although they are unlikely to be the ultimate solution to the global energy crisis, homogeneous catalysts are useful for mechanistic study of catalytic water oxidation. From a mechanistic perspective, the most important initial determination is the identity of the catalyst. Once that question is answered, more complex mechanistic questions, such as the catalyst resting state, possible intermediates, and deactivation pathways, can be explored. Unfortunately,

identification of the catalyst can be difficult in aqueous solutions of copper, where several species may be present.

Although water-soluble copper-bipyridine (bpy) complexes have been known since the 1930's,^{1,2} there still disagreements in the literature regarding their composition in solution, particularly in aqueous, alkaline solution.³⁻⁶ There is general agreement that, in acidic solution, the predominant species for bpy/Cu²⁺ solutions in a 1:1 ratio is the monomeric bis(aquo) complex in the absence of a coordinating anion. Several crystals of dimeric bis(μ -hydroxide) complexes have been isolated from equivalent alkaline solutions with a number of different anions, and have been crystallographically defined.⁷⁻¹⁰ However, to our knowledge, no monomeric copper bpy hydroxide complexes have ever been isolated.

Beyond lack of crystallographic evidence, the other major source of uncertainty for the composition of alkaline bpy/Cu²⁺ solutions is a dearth of spectroscopic handles for these complexes. The d-d transition in the visible absorbance spectrum is very broad due and changes only slightly with differing numbers of hydroxides coordinated to the copper center. EPR has been used to good effect in order to determine some structural information.⁵ Finally, although the bis(μ -hydroxide) dimers are antiferromagnetically coupled, they do not have a clear NMR spectrum (Figure 2.2).

This Chapter discusses our effort to overcome these challenges and details our current understanding of the speciation of (bpy)Cu²⁺ species under catalytic conditions. As much as possible, efforts have been taken to study the solutions with the concentrations used for catalysis and in the presence of supporting electrolyte.

3.2 Results and Discussion

3.2.1 UV-vis spectral analysis of the *bpy*/Cu²⁺ system under alkaline conditions

Use of UV-vis spectroscopy was first attempted to understand the speciation of the *bpy*/Cu system. Isolated [(*bpy*)Cu(μ -OH)]₂(OAc)₂ was dissolved in 10 mL of DI water with 0.1 M NaOAc to make a solution that was 2.4 mM in total copper concentration (1.2 mM in dimer). UV-vis spectra were collected between pH 11.6 and 12.9 (Figure 3.1). There were no changes to the *bpy* π - π^* transition and only slight changes to the broad d-d transition at 620 nm and the shoulder at 400 nm. There was no clear isosbestic point, indicating that there is not a clean conversion between starting materials and products. The band at 620 nm blue shifted 10 nm with increasing pH. The λ_{max} of the shoulder did not change with the pH increase. However, the ϵ decreased slightly and then increased again. Although these are clear, observable changes in the absorbance spectrum, the subtleties make it difficult to form any clear conclusion about the speciation of the *bpy*/Cu²⁺ system under these conditions based off of the UV-vis spectra alone. It is clear that there are *some* changes to the coordination environment. However, what these changes are and a way to quantify them are not apparent from these data.

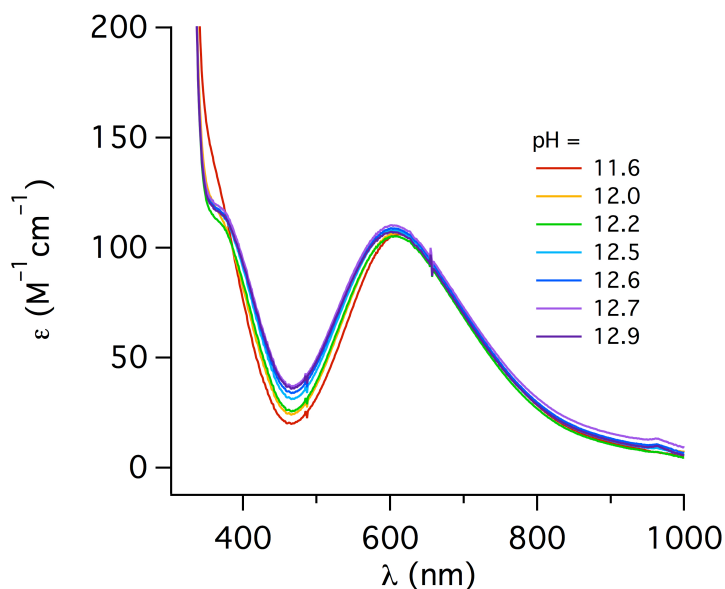


Figure 3.1. Titration of 10 mM [(bpy)Cu(OH)₂](OAc)₂ with aliquots of 1 M NaOH with 0.1 M NaOAc present. The d-d transition at 620 nm shifts to 610 nm as the pH is increased. There are also changes to the shoulder at 400 nm.

3.2.2 Non-quantitative EPR analysis in sodium acetate electrolyte

Based on literature reports, it seemed likely that the predominant species under catalytic conditions was either the dimeric [(bpy)Cu(μ -OH)]₂²⁺ cation⁴ or the neutral, monomeric (bpy)Cu(OH)₂ complex.^{3,5} The dimer is antiferromagnetically coupled, and, therefore, has only a very weak EPR spectrum, which is not observed at room temperature. In contrast, the bis(hydroxide) monomer has a standard 1 e⁻ Cu²⁺ signal.^{11††} Therefore, it is possible to distinguish solutions with a large amount of monomer from ones with a large amount of dimer. Because we preferred to measure the speciation under the specific conditions of catalysis, all EPR measurements were collected at room temperature and in aqueous electrolyte. However, because water absorbs microwaves,

†† EPR spectra of naturally occurring copper have a distinctive pattern of four consecutive signals. This is due to signals from the two stable copper isotopes.

a small volume cell was required for collecting the EPR data. Therefore, EPR spectra were collected in a capillary inside of an empty EPR tube. A stock solution of (bpy)Cu(OAc)₂ was prepared *in situ*.^{‡‡} From this stock solution, solutions of 0.1 M electrolyte (NaOAc + NaOH) and 1 mM copper were prepared at various pH's, and EPR spectra were collected (Figure 3.2).

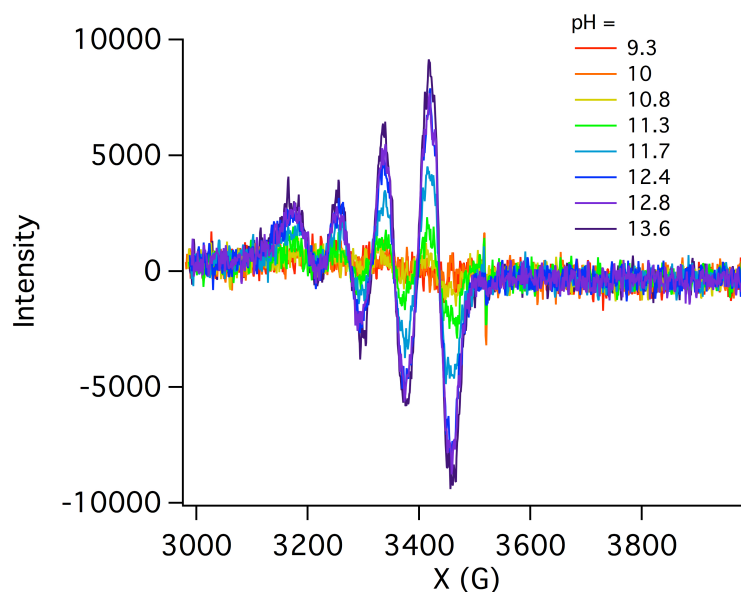


Figure 3.2. EPR spectra of 1 mM (bpy)Cu(OAc)₂ in the presence of 0.1 M electrolyte (NaOAc + NaOH). Spectra were collected at room temperature inside of a glass capillary to minimize water volume. The signal corresponding to a monomeric Cu^{II} species increases as the pH is increased.

At pH 9-10, essentially no EPR signal was observed. As the pH was increased to standard catalytic conditions (pH 12 to 13), there was an increase in an EPR signal associated with a paramagnetic, and therefore, monomeric Cu²⁺ species. The EPR spectrum at pH 12.8 was compared to a spectrum at pH 5.0, where the monomeric (bpy)Cu(H₂O)₂²⁺ complex should be the only species present (Figure 3.3). The EPR

^{‡‡} In this Chapter, (bpy)Cu(OAc)₂ will not refer to an isolated complex, but to a solution of 1:1 bpy:Cu(OAc)₂.

signals were similar in magnitude, indicating that, not only is a monomeric species present under catalytic conditions, but it is also the predominant species. Therefore, these speciation experiments indicate that while a dimeric species is predominant under mildly alkaline conditions, the dimer disproportionates to monomers under catalytic conditions. It is thus reasonable to assume that the active catalyst is a mononuclear copper complex, most likely the (bpy)Cu(OH)₂ species proposed by Fàbian and Garibba.^{3,5}

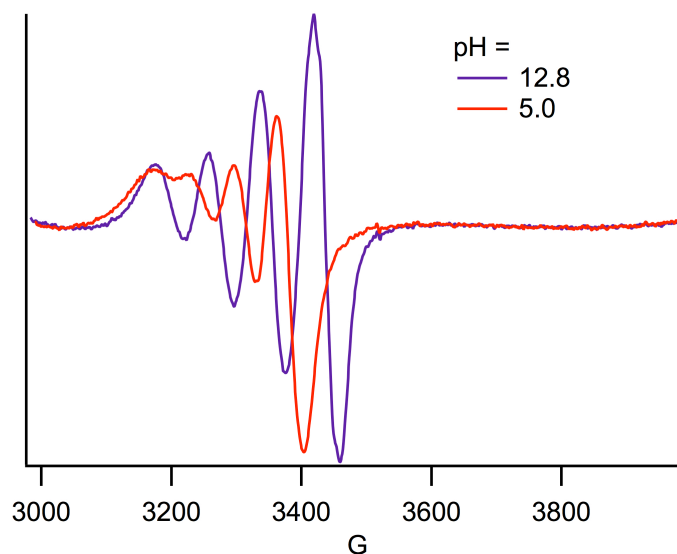


Figure 3.3. EPR spectra of 1 mM (bpy)Cu(OAc)₂ in the presence of 0.1 M electrolyte (NaOAc + NaOH or NaOAc + HOAc). The magnitude of the EPR signal at pH 12.8 is similar to the magnitude of the EPR spectrum at pH 5.0, indicating that monomeric copper is the predominate species under highly alkaline conditions, as it is under acidic conditions.

3.2.3 Quantitative EPR

EPR experiments performed as indicated above, with a capillary inside of an EPR tube, have 10-20% error associated with them. Therefore, a method was designed to perform EPR experiments more quantitatively.¹² Small differences in the environment of

the sample can cause significant changes in the amplitude of the EPR signal. Implementation of a flow cell allows the solution to be changed, without any additional changes to the experimental environment. Since a small volume is required for room temperature EPR, high gauge TeflonTM tubing (20-22g) was threaded through the EPR cavity to serve as the flow cell. Solutions were pushed into the cell by syringe from bottom-to-top, in order to minimize the introduction of air bubbles.

A control experiment with (bpy)CuCl₂ was performed to determine that quantitative experiments could, in fact, be performed with this method. Unlike other (bpy)Cu²⁺ complexes, (bpy)CuCl₂ is relatively stable to changes in pH. A stock solution of (bpy)CuCl₂ was prepared and diluted to concentrations between 10 mM and 0.1 mM. EPR spectra of these solutions were collected with the flow cell in place for the entirety of the experiment (Figure 3.4, left). The spectra were integrated twice, and this total area was plotted vs. copper concentration (Figure 3.4, right). The resulting data formed a straight line that passes through the origin, as expected if the above assumptions were correct (the flow cell controls adequately for environment, the copper complex does not undergo speciation).

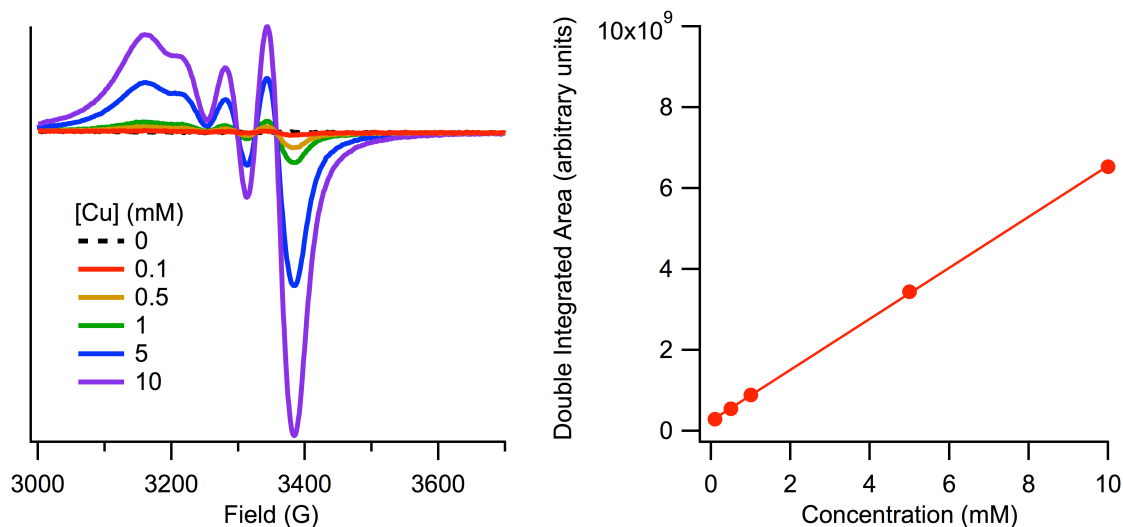


Figure 3.4. Left: EPR spectra of (bpy)CuCl₂ at various concentrations collected in a flow cell (Teflon™ tubing) at room temperature. Spectra have been baseline corrected. Right: The values of doubly-integrating the EPR spectrum are linear with concentration and the line passes through the origin.

Similar experiments were then performed with (bpy)Cu(OAc)₂. Stock solutions of 0.1 to 10 mM (bpy)Cu(OAc)₂ with 0.1 M electrolyte (NaOAc + NaOH) were prepared, with aliquots titrated to a pH between 10 and 12.5. These conditions are identical to those used for electrochemical experiments. An EPR spectrum was collected at each pH level (Figure 3.5). A final spectrum was collected from the same stock solution at pH 5. This spectrum established a relative magnitude for 100% monomer, since, under acidic conditions, there is no dimer present in solution. A baseline EPR spectrum was collected of solution with electrolyte, but no copper or bipyridine. This baseline spectrum was subtracted from all of the spectra that were collected with copper and bpy present.

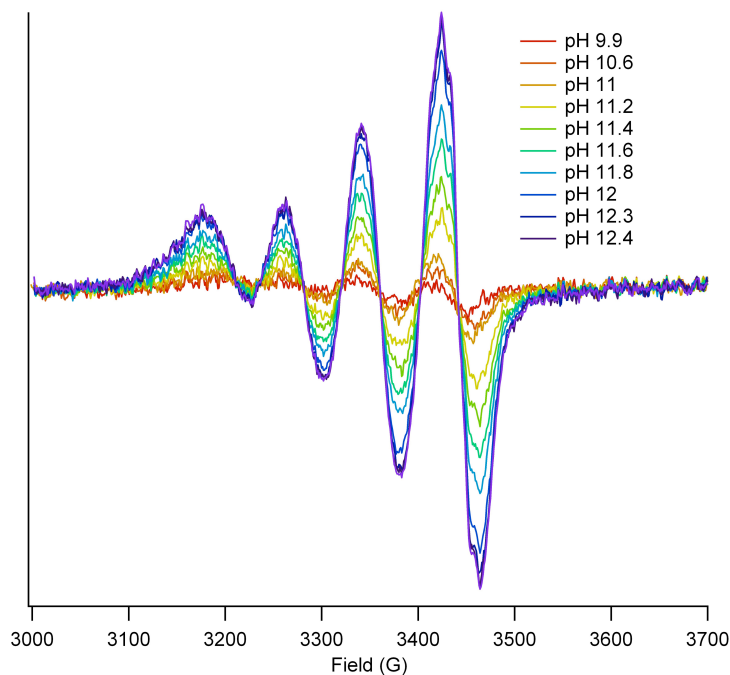
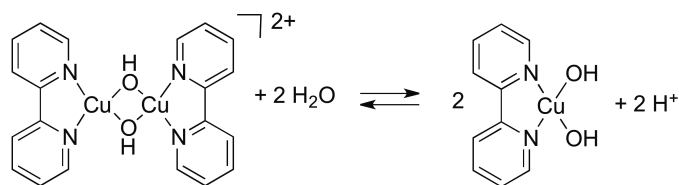


Figure 3.5. Titration of 2 mM (bpy)Cu(OAc)₂ in the presence of 0.1 M electrolyte (NaOAc + NaOH). Spectra have been baseline corrected and were collected at room temperature in a flow cell made of Teflon™ tubing.

Each baseline-corrected spectrum was integrated twice to obtain the total magnitude at that pH. This magnitude was divided by the magnitude of the spectrum collected under acidic conditions, to obtain a percentage of the copper complex that was monomeric. The rest of the copper was assumed to be present as dimer, for complete mass balance. Based upon analysis of isolated [(bpy)Cu(OH)]₂²⁺ salts and the literature, the dimer was assumed to be the bis(μ -OH) dication and the monomer to be the bis(OH) neutral species (Scheme 3.1). If this model is correct, then the equilibrium constant, K , should follow Equation 2.1.

Scheme 3.1



$$K_{eq} = \frac{[\text{monomer}]^2}{[\text{dimer}][\text{OH}^-]^2} \quad (3.1)$$

However, when the data was plotted as $[\text{monomer}]^2[\text{dimer}]^{-1}$ vs. $[\text{OH}^-]^2$, the result was clearly non-linear (Figure 3.6). The model shown in Scheme 3.1 is incorrect for these circumstances. However, a slightly altered model does fit the data. If the term $[\text{monomer}]^2[\text{dimer}]^{-1}$ is plotted vs $[\text{OH}^-]$ (without squaring the hydroxide term), the data is linear (Figure 3.7). This relationship corresponds to the equilibrium expression shown in Equation 3.2 with a calculated equilibrium constant of 0.6 ± 0.05 .

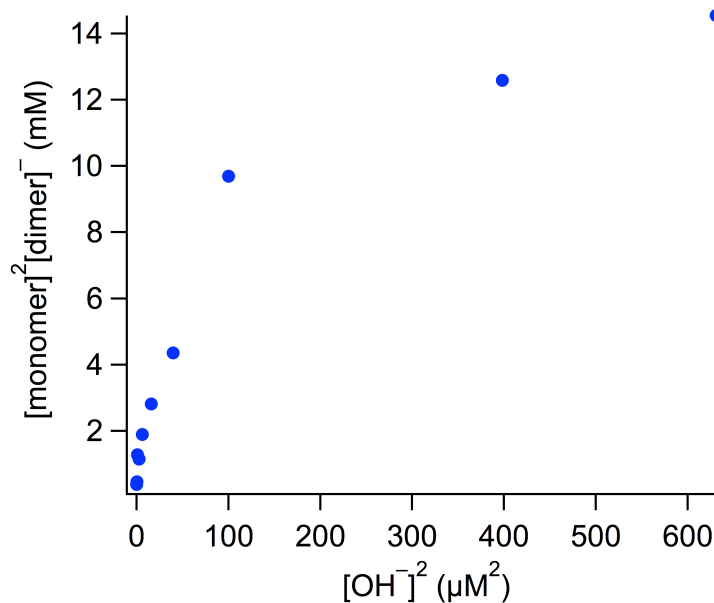


Figure 3.6. Plot of monomer and dimer concentrations according to Equation 3.1, following the equilibrium described in Scheme 3.1. Concentrations of monomer and dimer were calculated from quantitative EPR data from the titration of 2 mM (bpy)Cu(OAc)₂ in the presence of 0.1 M electrolyte (NaOAc + NaOH). For raw data, see Figure 3.5.

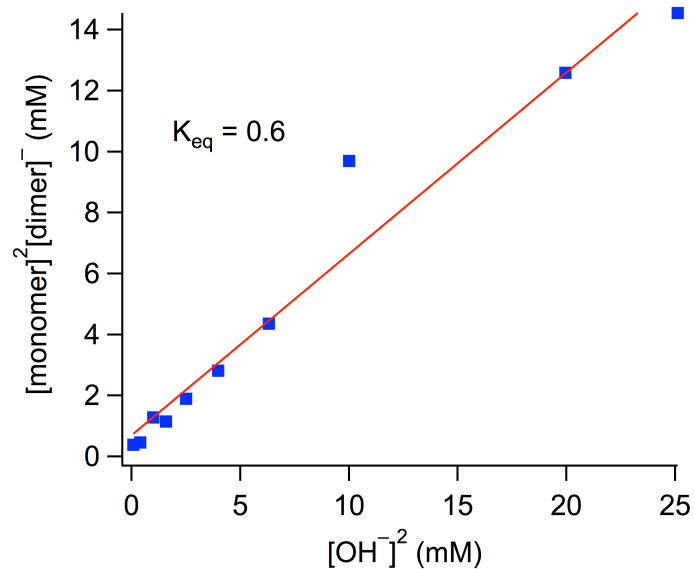


Figure 3.7. Plot of monomer and dimer concentrations according to Equation 3.2. Concentrations of monomer and dimer were calculated from quantitative EPR data from the titration of 2 mM (bpy)Cu(OAc)₂ in the presence of 0.1 M electrolyte (NaOAc + NaOH). For raw data, see Figure 3.5.

$$K_{eq} = \frac{[\text{monomer}]^2}{[\text{dimer}][\text{OH}^-]} \quad (3.2)$$

There are few options for a reaction scheme that would reasonably explain a first order dependence on hydroxide. One possibility is that acetate is somehow involved in the equilibrium, coordinating to both the monomer and dimer, in place of hydroxide. Therefore, a similar experiment was performed with sulfate as the electrolyte, instead of acetate. Although sulfate can and does bind to copper, sulfate does not coordinate as well as acetate, and so the equilibrium behavior would likely be very different if the anion was involved. Due to the insolubility of CuSO_4 , $\text{Cu}(\text{NO}_3)_2$ was used as the starting copper salt. $\text{Cu}(\text{NO}_3)_2$ was allowed to react with one equivalent of bpy to make a stock solution of $(\text{bpy})\text{Cu}(\text{NO}_3)_2$. As in the acetate experiment, this stock solution was used to prepared solutions of $(\text{bpy})\text{Cu}^{2+}$ complex in 0.1 M electrolyte ($\text{Na}_2\text{SO}_4 + \text{NaOH}$). Concentrations of $(\text{bpy})\text{Cu}^{2+}$ were also varied between 0.2 and 2.5 mM. The same analysis methods were used to obtain an equilibrium curve. As with the acetate electrolyte, a linear dependence was not observed for $[\text{monomer}]^2[\text{dimer}]^{-1}$ vs. $[\text{OH}^-]^2$, as fits the original model, but there was linearity for $[\text{monomer}]^2[\text{dimer}]^{-1}$ vs. $[\text{OH}]$ (Figure 3.8). The equilibrium constant calculated from this data was 0.09 ± 0.06 , 7 times lower than the equilibrium constant found in the presence of acetate. This could be indicative of anion binding to one or both of the complexes in equilibrium.

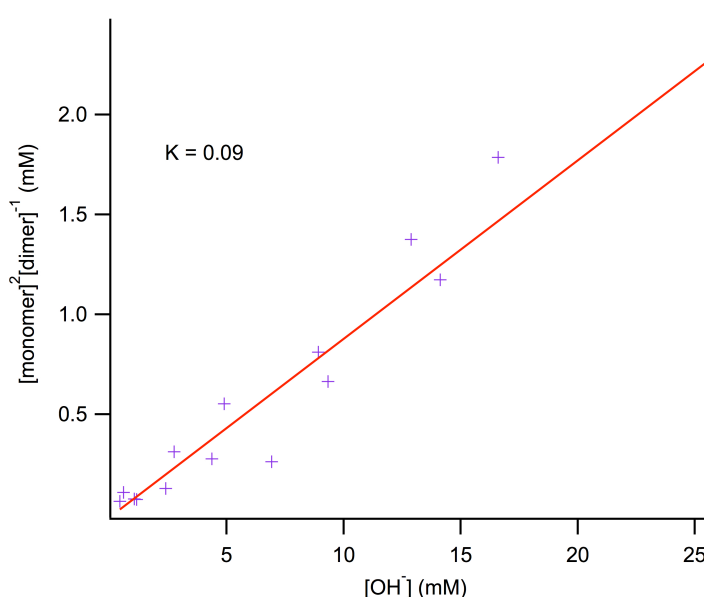


Figure 3.8. Plot of monomer and dimer concentrations according to Equation 3.2, following the equilibrium described in Scheme 3.1. Concentrations of monomer and dimer were calculated from quantitative EPR data from the titration of 2 mM (bpy)Cu(NO₃)₂ in the presence of 0.1 M electrolyte (Na₂SO₄ + NaOH).

The differences in equilibrium constants might explain why there are some differences in maximum current (measured by CV) depending on the supporting electrolyte. Interestingly, there are much slighter differences when the dinitrogen ligand is changed. For instance, for (phen)Cu²⁺ in sodium sulfate, the equilibrium constant was found to be 0.02 ± 0.001 . Although this is still a significant difference between the complexes, it is surprising that it is so much smaller than the difference in equilibrium constants when only the electrolyte is changed.

More investigation is necessary to determine the role of the electrolyte and counter ion in speciation and, therefore, catalysis. Studying the speciation of copper complexes with other bidentate N-donor ligands (or, possibly, different ligands altogether, such as carbenes) and electrolytes could lead to discovery of a complex that

speciates to the catalytically active monomer at lower pH, thereby effectively lowering the overpotential of the system.

3.2.4 Bpy dissociation at $pH > 13$

For solutions of $(bpy)Cu^{2+}$ complex in 0.1 M (NaOAc + NaOH) there are changes to the EPR and UV-vis spectra as the pH is increased from 12.5 to 13.5. The EPR spectrum shifts to a lower field value and decreases in amplitude (Figure 3.9, left). In the UV-vis spectrum, the bands corresponding to the $\pi-\pi^*$ transition of the coordinated bipyridine decreases and a band corresponding to free bipyridine appears (Figure 3.9, right). There is a tight isosbestic point accompanying the transformation, indicating a clean reaction. The process is also reversible, and, upon addition of acetic acid, there is recovery of the band associated with coordinated bipyridine.

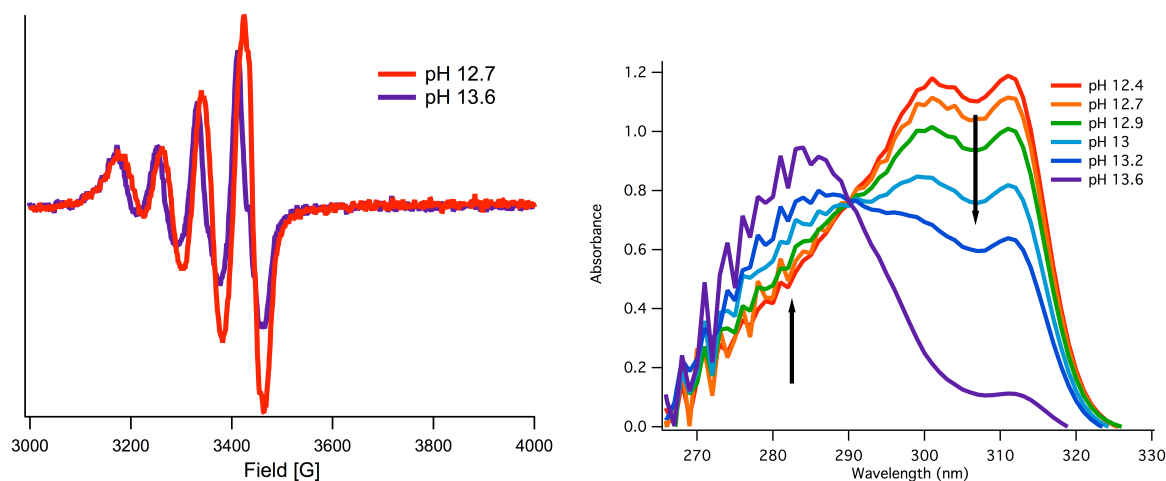


Figure 3.9. Spectra of 2 mM $(bpy)Cu(OAc)_2$ in the presence of 0.1 M electrolyte (NaOAc + NaOH). Left: EPR spectra collected in a Teflon™ flow cell at room temperature. Right: Titration observed by UV-vis spectroscopy.

Solutions of $Cu(OH)_4^{2-}$ can be prepared independently, without the presence of bipyridine or other dinitrogen ligand. Although addition of $Cu(OAc)_2$ or other copper

salts to mildly alkaline water results in immediate precipitation of $\text{Cu}(\text{OH})_2$ (and eventual decomposition to black CuO), $\text{Cu}(\text{OAc})_2$ can be dissolved in pH 13.6 solutions. These solutions are not electrocatalytic for water oxidation, and have CVs similar to glassy carbon in pH 13.6, copper-free solutions (Figure 3.10, grey lines). Upon addition of one equivalent of bipyridine, a wave corresponding to electrocatalytic water oxidation is present in the CV (Figure 3.10, black line). However, this wave has a lower maximum current than the electrocatalytic wave in a CV collected at pH 12.6 (Figure 2.3). The lower current can be explained by an equilibrium between the electrocatalytic $(\text{bpy})\text{Cu}(\text{OH})_2$ and the inactive $\text{Cu}(\text{OH})_4^{2-}$, so at pH 13.6 with 1 mM $\text{Cu}(\text{OAc})_2$ and 1 mM bpy, there is a mixture of $(\text{bpy})\text{Cu}(\text{OH})_2$ and $\text{Cu}(\text{OH})_4^{2-}$. The relatively large current in the presence of less catalytic material is due to the high availability of substrate (hydroxide) under these conditions.

This data proves that a supporting ligand *is* necessary for water oxidation, and electrocatalysis is not possible simply from having copper present in alkaline solutions. The necessity of the bpy ligand makes it even more likely that the catalytic process is molecular, rather than caused by nanoparticulate copper or an electroactive deposit (for further discussion of questions of heterogeneity, see Chapter 2).

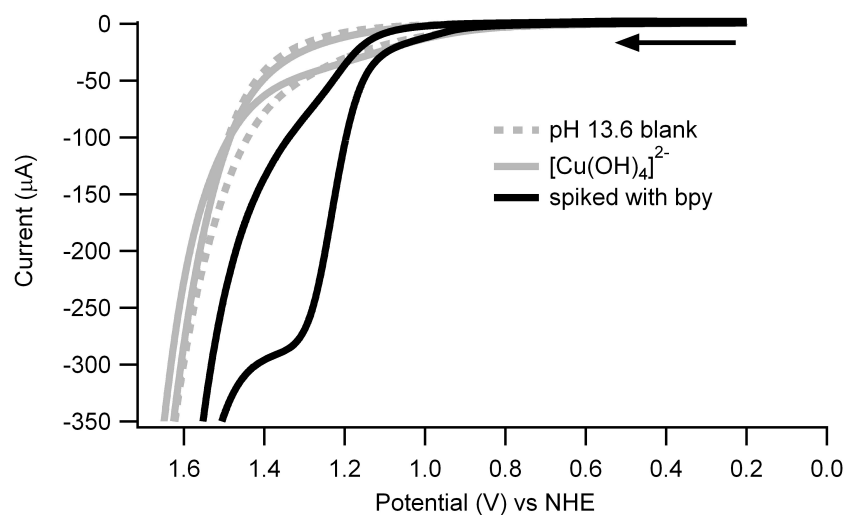


Figure 3.10. CVs of copper-free pH 13.6 solution (grey, dotted line), 2 mM Cu(OAc)₂ dissolved in pH 13.6 solution (grey, solid line), and the same 2 mM Cu(OAc)₂ solution after addition of 1 equivalent of bipyridine (solid, black line). All solutions contained 1 M NaOH in DI H₂O and used the following electrodes: working, glassy carbon; auxiliary, platinum; reference, Ag/AgCl (adjusted to NHE by addition of 0.2 V to the recorded potential).

Although formation of bpy-free $\text{Cu}(\text{OH})_4^{2-}$ provides an explanation for the changes to the UV spectrum and a shift in the EPR signal, it does not explain a decrease in the magnitude of the EPR signal. When $\text{Cu}(\text{OH})_4^{2-}$ is freshly prepared, without the presence of bpy ligand, there is a sharp EPR signal that matches the expected magnitude for the concentration of copper present, based on EPR experiments with bpy and copper at low pH (Figure 3.11). One possibility is that $\text{Cu}(\text{OH})_4^{2-}$ is a precursor to copper hydroxide/oxide oligomers that are not detectable during room temperature EPR experiments. To test for this possibility, EPR spectra were collected with various concentrations of (bpy)Cu(OAc)₂ at pH 13.6 (Figure 3.12). The peak amplitude of the singly integrated spectrum did not show a linear dependence on concentration. Therefore, it is likely that EPR-silent oligomers are being formed, since they would form preferentially at higher copper concentration. This oligomer formation might be an explanation for precipitation of CuO from high pH solutions of (bpy)Cu²⁺ complexes.

Thus, loss of bipyridine to form $\text{Cu}(\text{OH})_4^{2-}$ is likely a pathway for both temporary catalyst deactivation and permanent catalyst decomposition.

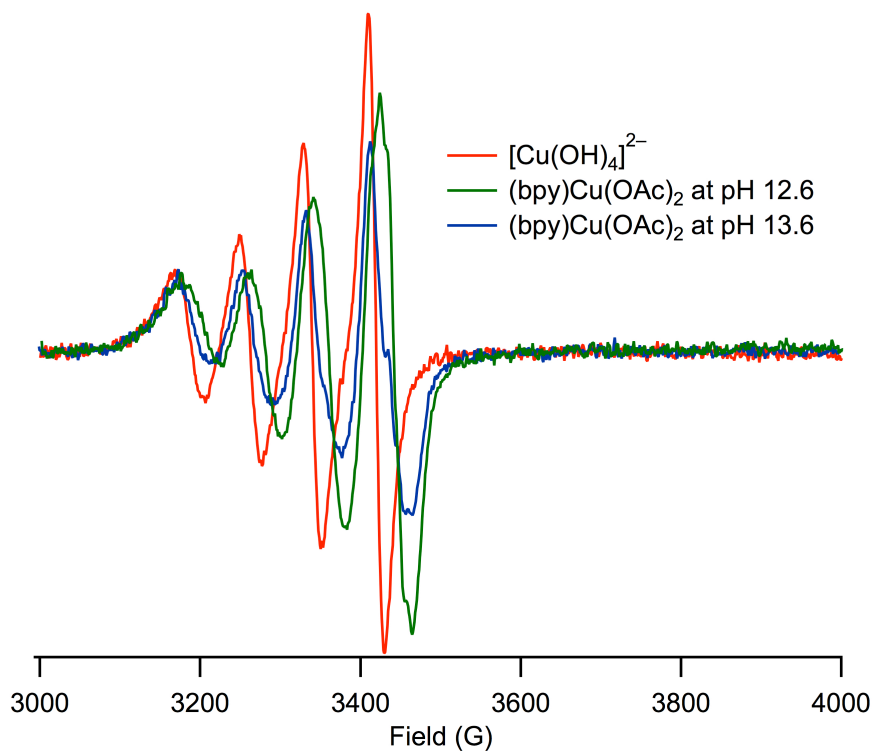


Figure 3.11. EPR spectra of 2 mM copper in aqueous solution in the presence of electrolyte. Spectra were collected at room temperature in a Teflon™ flow cell and are baseline corrected. Red line: $\text{Cu}(\text{OAc})_2$ with no bipyridine added at pH 13.6 (1 M NaOH). Blue line: $(\text{bpy})\text{Cu}(\text{OAc})_2$ at pH 13.6 (1 M NaOH). Green line: $(\text{bpy})\text{Cu}(\text{OAc})_2$ at pH 12.6 in 0.1 M electrolyte (NaOAc + NaOH).

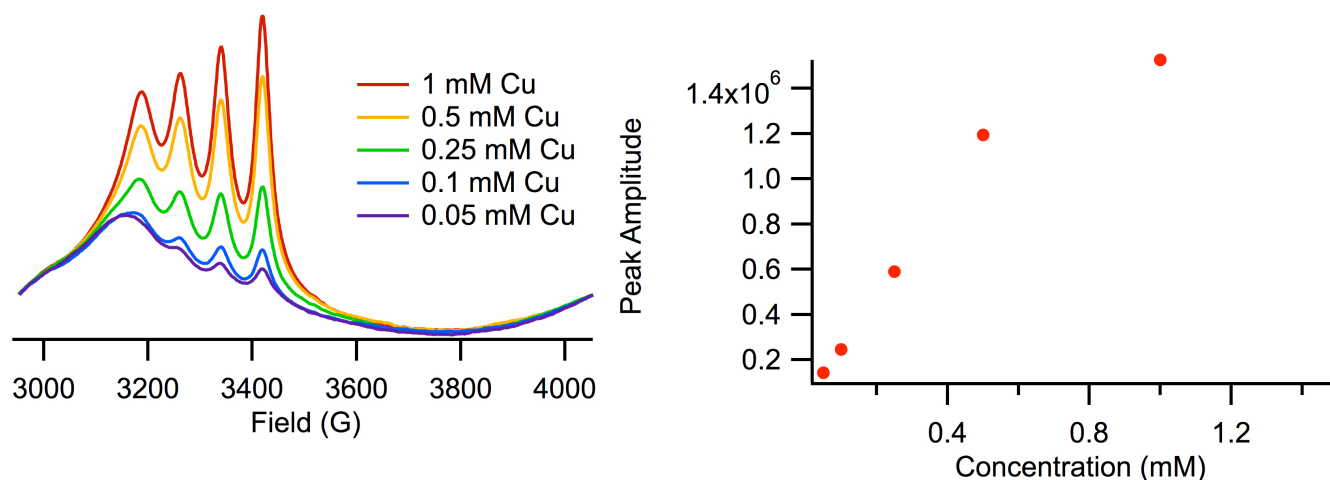


Figure 3.12. Left: Singly integrated EPR spectra of Cu(OAc)₂ at various concentrations in pH 13.6 solution (1 M NaOH). Spectra were collected at room temperature in a Teflon™ flow cell and baseline corrected. Right: A plot of the peak amplitude of the integrated peak at 3425 G vs. copper concentration.

3.3 Conclusions

The results described in this Chapter indicate that the *monomeric* bis(hydroxide) species is the predominant species in solution under the conditions of the electrocatalysis. This is contrary to the original motivation for exploring *dimeric* copper complexes, based upon the chemistry that has been performed with (LCu)₂-O₂ centers.^{13–}
¹⁶ Qualitatively, the magnitude of the electrocatalytic currents seems to parallel the speciation: the electrocatalytic currents increase with increasing pH, as the speciation shifts towards formation of (bpy)Cu(OH)₂, then begin to drop off as speciation shifts towards formation of Cu(OH)₄^{2–}. This result has stimulated investigation into possibilities for a single-site mechanism or a mechanism that originates at a single site (see Chapter 4 for further discussion of mechanism).

Although the rapid interconversion of (bpy)Cu²⁺ complexes makes mechanistic analysis more challenging, it potentially makes the system more valuable. Because all

the copper(II) complexes are in rapid equilibrium in aqueous media, it is not necessary to use synthesized $[(bpy)_2Cu_2(OH)_2]X_2$ complexes to perform electrocatalysis. In all of the cases we have tested, identical results were obtained with isolated $[(bpy)_2Cu_2(\mu-OH)_2]X_2$ and with solutions of $CuX_2 + bpy$ in the same buffer/electrolyte. This is consistent with the very high lability of most Cu^{2+} complexes.

The results of quantitative EPR experiments indicate that the species at moderately basic pH might not be the $[(bpy)Cu(OH)]_2^{2+}$ complex, as suggested in the literature, but possibly a different dimeric species with coordination to the anions. Further investigation is necessary to determine the identity of this species. Observation of a strong anion effect on speciation suggests the possibility of modulating the speciation with anions other than sulfate and acetate. An improved system would allow formation of the bis(OH) monomer at a lower pH.

Finally, observation of a bpy-free, soluble copper species at high pH confirms that bipyridine coordination is important for this catalytic process and argues against a heterogeneous mechanism. The deactivation and decomposition of the catalyst at very high pH gives offers even more reason to work towards lowering the operating pH of this system. Other reasons include higher overpotential at higher pH and instability of the carbon electrode, and general safety and engineering concerns with highly corrosive solutions.

3.4 Experimental Methods

Preparation of solutions for analysis

Solutions of $(bpy)Cu(OAc)_2$ and $(bpy)CuSO_4$ were prepared *in situ* from $Cu(OAc)_2$, $CuSO_4$, or $Cu(NO)_3$; 2,2'-bipyridine; and NaOAc or Na_2SO_4 . Copper salts and

bipyridine were purchased from Sigma-Aldrich, and the sodium salts were purchased from Fisher Scientific. All reagents were used as received without further purification. The pH was adjusted using NaOH, also purchased from Fisher Scientific. Materials were used as received with no further purification. An example preparation procedure went as follows:

A 100 mM solution of (bpy)Cu(OAc)₂ was prepared by first dissolving 181 mg of Cu(OAc)₂ into 10 mL of DI water in a 20 mL scintillation vial. The appropriate amount of water was measured in a graduated cylinder. The solution was a light blue color. 156 mg of 2,2'-bipyridine were weighed and added to solution. The vial was shaken and sonicated in order to dissolve the bipyridine. As the bipyridine dissolved, the color became a darker blue. Sonication was continued for 5 minutes, until all bipyridine was dissolved.

A 0.1 M stock solution of NaOAc and NaOH were prepared in DI water. The NaOAc was titrated to the desired pH through addition of the NaOH solution, maintaining the electrolyte level at 0.1 M. 100 μ L of (bpy)Cu(OAc)₂ solution were then added to 10 mL of the electrolyte solution, diluting it to 1 mM (bpy)Cu(OAc)₂. A color change was observed immediately, from blue to indigo. The pH of this solution was measured before spectra are collected.

Spectroscopy

All EPR spectra were collected on a Bruker EMX X-band spectrometer at room temperature. Non-quantitative EPR spectra were collected inside of a glass capillary that was sealed with paraffin wax on each end and placed inside of a quartz EPR tube. The EPR tube was inserted into the instrument so as to center the solution in the

capillary inside the cavity. Quantitative EPR spectra were collected in a flow cell assembled from an 18 or 22 g piece of TeflonTM tubing with a Luer lock fitting attached to the bottom end and the top portion attached to the inside of a receiving vessel. 3-5 mL of solution was pushed through the cell by syringe, and the visible portion of the tubing was examined for air bubbles before spectra were collected. For non-quantitative experiments, baseline spectra were acquired from spectra of an empty EPR tube. For quantitative experiments, baseline spectra were acquired from spectra of the flow cell filled with neutral electrolyte solution.

All analysis of EPR data was performed in IGOR Pro. For double-integration of quantitative EPR, the baseline spectrum was subtracted from all other spectra. The baseline-corrected derivative spectra were integrated once. The four peaks corresponding to the copper signal were fit to Gaussian curves. The fit spectrum was then integrated once again, to obtain the total signal area.

UV-vis spectra were collected on an Agilent 8453 spectrophotometer. Samples were added to a quartz cuvette with a 1 mM path length. "Blank" spectra were collected from solutions of DI water with no additions.

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Chapter 4

Mechanistic Investigations of the (bpy)Cu Water Oxidation Catalyst

Abstract

Several studies were undertaken to explore the mechanism of the (bpy)Cu water oxidation catalyst. Catalyst concentration dependence studies show two regimes. Below 1 mM (bpy)Cu(OAc)₂, the current is linear with catalyst concentration, and above 1 mM (bpy)Cu(OAc)₂, the catalytic water oxidation current is independent of [cat]. The dependence at low catalyst concentration indicates a first order dependence on catalyst. The current is also linear with hydroxide concentration, which indicates a second order dependence on hydroxide. A ligand study shows limited sensitivity of the (bpy)Cu system to electron donating or withdrawing substituents. Similar onset potentials and currents are also observed with (Me₂-TPA)Cu and (phen)Cu complexes. Addition of hydrogen peroxide results in catalytic disproportionation of H₂O₂ to water and O₂ with an intermediate that absorbs at 380 nm, likely the (bpy)Cu^{II}-OOH complex. Cyclic voltammograms of solutions of (bpy)Cu(OAc)₂ and H₂O₂ at pH 12.5 show electrocatalytic waves that are nearly identical to ones collected before addition of H₂O₂, suggesting that the water oxidation and H₂O₂ disproportionation processes may share intermediates.

4.1 Introduction

Mechanistic understanding is key to optimization of reactions and catalysts. If we know where the bottleneck of a reaction is, we can attempt to widen it, by changing the reaction conditions to facilitate that process or by changing the catalyst itself.

Understanding the water oxidation reaction presents a particularly difficult mechanistic challenge, since the reaction requires the transfer of four protons and four electrons.

As discussed in the General Introduction, our initial inspiration for pursuing copper as a catalyst for water oxidation was based on the prolific study of copper-oxygen chemistry.¹⁻³ We hoped that the existence of this literature would facilitate and inform the mechanistic study for water oxidation catalysis mediated by copper. As discussed in Chapter 1, the majority of copper-oxygen chemistry has been focused on dimers. Coincidentally, there has been more recent interest in exploration of monomeric copper-oxygen species, just as we have discovered that the likely starting catalyst is a *monomeric* bis(hydroxide) complex (see Chapter 3 for further discussion of speciation).

There are several other challenges inherent to the (bpy)Cu²⁺ water oxidation system. First, the system turns over very rapidly. This is advantageous for a catalyst in general, but hinders mechanistic study. As a result, it is difficult to detect intermediate species. For instance, UV-vis spectroelectrochemistry does not show changes during electrolysis. Secondly, operation of the system is limited to very alkaline conditions and requires a strong oxidant. Although chemical oxidation could produce enough of an intermediate to detect spectroscopically, few strong oxidants are stable to basic conditions. Finally, the lability of the copper center presents some benefits and challenges. Because copper readily exchanges ligands, the catalytic copper complexes can be formed quickly *in situ*, allowing for facile screening of various copper complexes. However, this lability results in complex speciation, which can convolute kinetic studies. This Chapter presents the mechanistic studies that have been possible, despite these challenges. Although there is still substantial work that must be done to form a

more complete picture of the catalytic mechanism, these initial studies lay a foundation for that work.

4.2 Results

4.2.1 Concentration dependence

Because the CV experiment is essentially a time-dependent measurement of rate vs. driving force, it is a particularly useful tool for analyzing reaction kinetics. The current for electrocatalytic water oxidation, i_c is described by Equation 4.1, where x is the order of reaction in catalyst and y is the order in base.^{4,5} In this Equation, n is the number of electrons involved in the catalytic process, F is the Faraday constant, A is the area of the electrode, D is the diffusion coefficient of the substrate, and k is the rate constant of the catalytic reaction.

$$i_c = nFA[cat]^x \sqrt{Dk[OH^-]^y} \quad (4.1)$$

To determine the order of reaction in copper complex, cyclic voltammograms were collected with different concentrations of (bpy)Cu(OAc)₂^{§§} and with the pH held constant at 12.5 (Figure 4.1). The electrolyte was held at 0.1 M, and was comprised of NaOAc and NaOH. Especially for the very dilute solutions, there is a significant background current contribution. Therefore, before each CV was collected with (bpy)Cu(OAc)₂, a “background” CV was collected of the polished electrode in pH 12.5 solution with 0.1 M (NaOAc + NaOH) electrolyte. This background was subtracted from each CV, giving the total current strictly from catalytic water oxidation (Figure 4.2, right).

^{§§} A prepared solution of 1:1 bipyridine to Cu(OAc)₂. The (bpy)Cu(OAc)₂ salt is not isolated. More detail can be found in the Experimental Methods section.

The peak current for each CV was plotted versus copper concentration. (Figure 4.2, left). Two regimes are apparent from the data, one at low concentration (below 1 mM) and one at high concentration (above 1 mM). In the low concentration regime, the current is linear with concentration of added copper complex. At high catalyst concentration, there is roughly no dependence on catalyst concentration, or possibly a slight inverse relationship. Although a decrease in current is observed at very high catalyst concentration, it is within the experimental error.

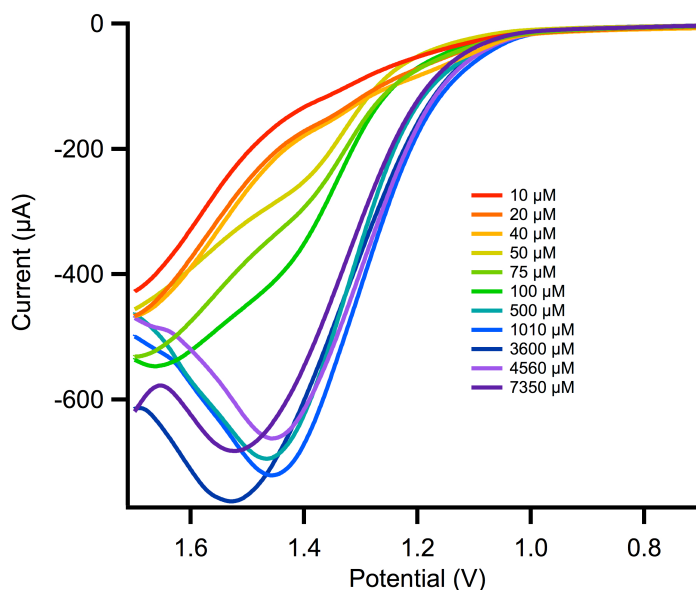


Figure 4.1. CVs of (bpy)Cu(OAc)₂ at various concentrations without background subtraction. The return waves are omitted for clarity. CVs were collected at pH 12.5 and 0.1 M electrolyte (NaOAc + NaOH) at a scan rate of 100 mV/s. Electrodes: working, GC; auxiliary, Pt; reference, Ag/AgCl adjusted to NHE.

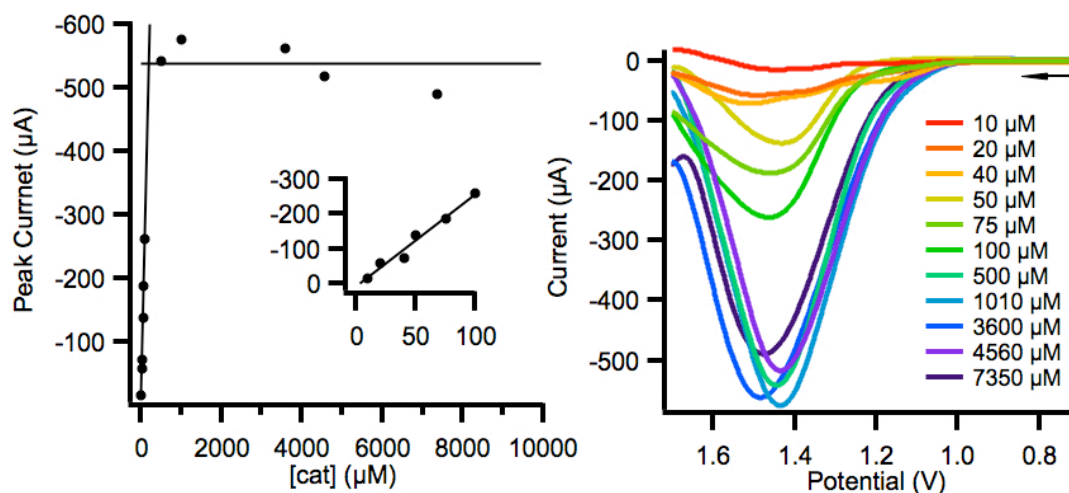


Figure 4.2. Left: a plot of peak current vs. catalyst concentration, taken from background corrected CVs of (bpy)Cu(OAc)₂. The inset shows only the points at low concentration. Right: Background corrected CVs of (bpy)Cu(OAc)₂ at various concentrations. CVs were collected at pH 12.5 and 0.1 M electrolyte (NaOAc + NaOH) at a scan rate of 100 mV/s. Electrodes: working, GC; auxiliary, Pt; reference, Ag/AgCl adjusted to NHE.

The peak current can also be plotted versus concentration of (bpy)Cu(OH)₂, the suspected active catalyst (see Chapter 3 for discussion of catalyst speciation). For (bpy)Cu²⁺ in alkaline, aqueous solution, the conversion between dimer and monomer with added hydroxide follows the equilibrium expression shown in Equation 4.2.

$$K_{eq} = \frac{[\text{monomer}]^2}{[\text{dimer}][\text{OH}^-]} \quad (4.2)$$

The equilibrium constant is dependent on the supporting electrolyte, and has a value of 0.06 for the (bpy)Cu²⁺ system where the total electrolyte concentration (NaOAc + NaOH) is 0.1 M. This equilibrium constant can be used to calculate the concentration of (bpy)Cu(OH)₂ for each CV. The peak current was then plotted vs. concentration of the catalytic species (Figure 4.3). The calculated concentrations show that, in the low concentration regime, the vast majority of (bpy)Cu²⁺ is present as the (bpy)Cu(OH)₂

species, with very little dimer present. As a result, the linearity is maintained, with an identical slope. As the concentration is increased, there is a larger discrepancy between the calculated amount of $(\text{bpy})\text{Cu}(\text{OH})_2$ and the amount of $(\text{bpy})\text{Cu}(\text{OAc})_2$ that was added initially. However, the lack of dependence on catalyst concentration is maintained in the high concentration regime.

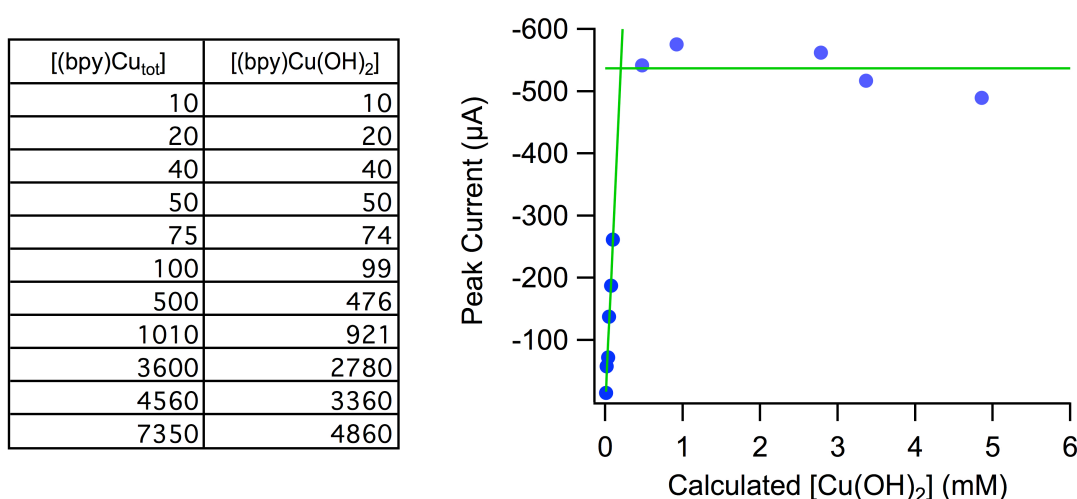


Figure 4.3. Left: a table of total $(\text{bpy})\text{Cu}$ and the corresponding amount of $(\text{bpy})\text{Cu}(\text{OH})_2$ based on calculations with the equilibrium constant. Right: The peak currents from CVs of $(\text{bpy})\text{Cu}(\text{OAc})_2$ at pH 12.5 plotted vs. the calculated amount of $(\text{bpy})\text{Cu}(\text{OH})_2$. CVs were collected at pH 12.5 and 0.1 M electrolyte ($\text{NaOAc} + \text{NaOH}$) at a scan rate of 100 mV/s. Electrodes: working, GC; auxiliary, Pt; reference, Ag/AgCl adjusted to NHE.

4.2.2 pH dependence at high and low concentration

In addition to the rate dependency on catalyst concentration, there is also a relationship between the rate and pH. CVs were collected between pH 11.5 and 13 in both the high (1 mM Cu complex) and low (0.05 mM Cu) concentration regimes. In both cases, the current dramatically increases with pH. This relationship is convoluted by the speciation equilibrium, which causes a different amount of active catalyst to be present at different pH's. As discussed in section 3.1, the amount of $(\text{bpy})\text{Cu}(\text{OH})_2$ present for

each measurement can be calculated from the equilibrium constant. The currents can then be normalized based on the amount of catalyst actually present.

For the CVs collected at 1 mM (bpy)Cu(OAc)₂, both the normalized and raw peak data show a linear dependence of the current with the hydroxide concentration (Figure 4.4). Due to the square rate term in Equation 4.1, this relationship corresponds to a *second* order dependence on hydroxide.

The above conditions for CV (1 mM Cu, 100 mV s⁻¹ scan rate) are within the diffusion-limited regime for electrocatalysis.⁶⁻⁸ The pH dependence was also analyzed under kinetically controlled conditions, where the catalyst concentration was reduced to 50 μM and the scan rate was lowered to 3 mV s⁻¹. CVs were collected from pH 11.6 to 13.3. The CVs at pH 12.9-13.3 have nearly identical currents (Figures 2.11 and 2.12), consistent with conditions in the substrate-independent regime.⁴ These conditions represent the maximal current possible with that particular catalyst concentration and scan rate—essentially, zero-order conditions. These CVs were used to calculate the turnover frequency for catalysis, which is discussed further in Chapter 2. Because the current does not change with increasing pH, the points at 13.1 and 13.3 were not included in the line fits for kinetic analysis.

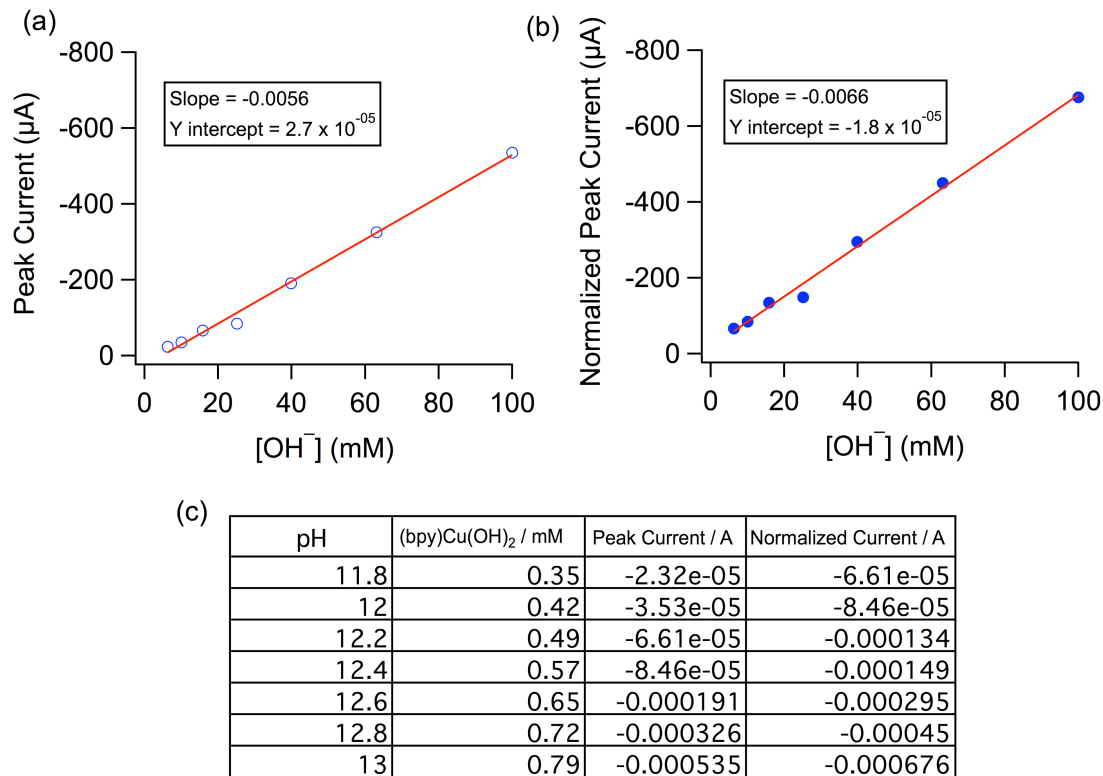


Figure 4.4. (a) A plot of the peak current from CVs of 1 mM (bpy)Cu(OAc)₂ vs. hydroxide concentration without accounting for speciation between the inactive dimer and active (bpy)Cu(OH)₂ monomer. (b) A plot of the normalized peak current from CVs of 1 mM (bpy)Cu(OAc)₂ vs. hydroxide concentration. The peak currents are normalized based on the calculated amount of (bpy)Cu(OH)₂ present at the various pH's. (c) Table of the pH, calculated amount of (bpy)Cu(OH)₂ for that CV, the peak current from the raw data, and the peak current after normalization. CVs were collected at pH 12.5 and 0.1 M electrolyte (NaOAc + NaOH) at a scan rate of 100 mV/s and were baseline corrected. Electrodes: working, GC; auxiliary, Pt; reference, Ag/AgCl adjusted to NHE.

The representative currents were once again taken from the background corrected data. However, due to the very low currents observed at $\text{pH} < 12.3$ with the very low scan rates used and low catalyst concentration, the “peaks” were not well-defined at these lower pH's. Therefore, “peak currents” were taken from the current values at 1.37 V vs. NHE. This potential is where the background-corrected current flattens into an S-shape at pH 12.9 and 13.1. The currents were again normalized based on the equilibrium constant for the (bpy)Cu(OAc)₂ system and plotted versus $[\text{OH}^-]$ and $[\text{OH}^-]^{1/2}$ (Figure 4.5). The fits were forced through the origin. All plots contained more

error than the data collected at higher concentrations. For the normalized data, the standard deviation was 8.8% when the peak currents were plotted vs. $[\text{OH}^-]$ and 6.4% when plotted vs. $[\text{OH}^-]^{1/2}$, though when the data is plotted without normalization, the plot vs. $[\text{OH}^-]$ has a slightly lower error than the plot vs. $[\text{OH}^-]^{1/2}$, 7.1% vs. 7.7%. Because there isn't a large difference between the quality of these fits overall, it is difficult to establish the order of reaction in hydroxide from this data set.

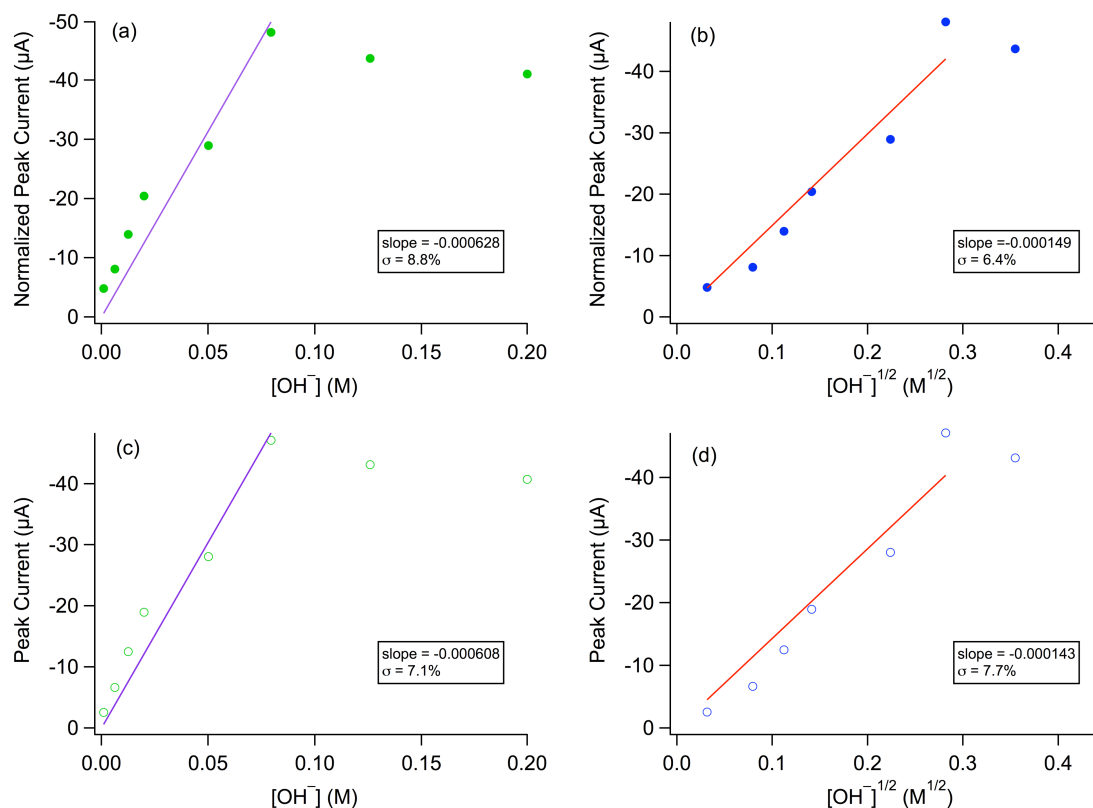


Figure 4.5. Plots of normalized and unnormalized peak currents of CVs taken from solutions of $50 \mu\text{M}$ (bpy) $\text{Cu}(\text{OAc})_2$ vs. $[\text{OH}^-]$ or $[\text{OH}^-]^{1/2}$. CVs were collected at pH 12.5 and 0.1 M electrolyte ($\text{NaOAc} + \text{NaOH}$) at a scan rate of 3 mV/s. Electrodes: working, GC; auxiliary, Pt; reference, Ag/AgCl adjusted to NHE.

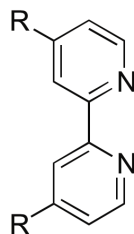
4.2.3 Ligand study

To test the effects of changing the ligand electronics, several 4,4'-disubstituted bipyridine derivatives were treated with copper salts to yield solutions of the (R_2 -bpy) Cu^{2+} complexes, with $R = ^t\text{Bu}$, $-\text{OMe}$, Me , and $-\text{COO}^-$ (Scheme 4.1). Terpyridine (terpy), phenanthroline (phen), and $\text{Me}_2\text{-TPA}^{***}$ analogues were also generated. CVs were performed with 1 and 0.05 mM solutions of the unisolated copper complexes in 0.1 M electrolyte ($\text{NaOAc} + \text{NaOH}$) between pH 11.5 and 12.6 (Figure 4.6). Most of the complexes performed water oxidation catalysis at roughly the same pH, potential, and current density as the unsubstituted bipyridine. Though some differences were observed in a single broad scope experiment (Figure 4.6a), they were not seen upon closer comparison between complexes (Figure 4.6b-d). For instance, the 4,4'-dimethoxy-bpy complex performs water oxidation at the same applied potential as the bpy complex. The 4,4'-dicarboxy-bipyridine complex is one exception to this similarity, displaying catalysis at the same potential as other bpy complexes but consistently with much lower currents. The terpyridine complex is another exception, with no observed catalysis in the potential range that was studied.

There are some subtle differences at the “foot-of-the-wave” in all CVs. Although these differences might have been caused from simple experimental error, further electrochemical analysis might clarify whether these are “real” effects. Experiments with a suitable chemical oxidant may also be helpful in comparing the complexes, since subtle differences tend to be more apparent in chemical oxidation experiments than in CV experiments.

*** $\text{Me}_2\text{-TPA} = \text{Bis}(6\text{-methyl-2-pyridylmethyl})(2\text{-pyridylmethyl})\text{amine}$

Scheme 4.1



R = Me, t-Bu, -OH, -COOH, -OMe

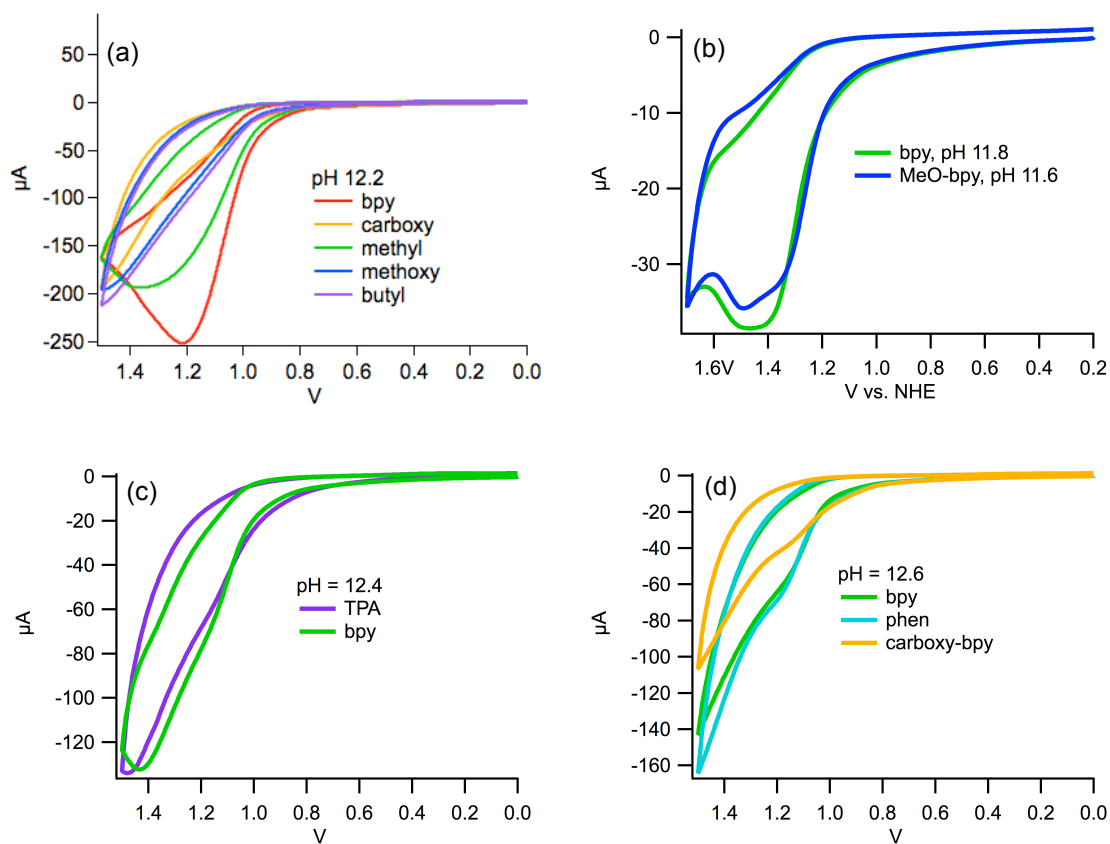


Figure 4.6. CVs of copper complex solutions with various ligands (L) at various pH's. The top CVs were collected with 1 mM (L) $\text{Cu}(\text{OAc})_2$ and the bottom CVs with 50 μM (L) $\text{Cu}(\text{OAc})_2$. CVs were collected with 0.1 M electrolyte (NaOAc + NaOH) at a scan rate of 100 mV/s. Electrodes: working, GC; auxiliary, Pt; reference, Ag/AgCl (not adjusted to NHE).

4.2.4 Reactions with hydrogen peroxide

Initially, hydrogen peroxide (H_2O_2) was added to solutions of $(\text{bpy})\text{Cu}(\text{OAc})_2$ at pH 12.5 in order to probe the possibility of peroxide generation during electrolysis. However, upon addition of ~ 50 equivalents of H_2O_2 to the 2 mM $(\text{bpy})\text{Cu}(\text{OAc})_2$ solution under electrocatalytic conditions, the solution changed color from blue to green and bubbles rapidly evolved (Figure 4.7, left). Bubbles continued to evolve for several minutes after the addition of H_2O_2 and the color eventually returned to blue. This observed reaction is the decomposition of H_2O_2 to form H_2O and O_2 , which can be performed by copper salts with pyridine and bipyridine ligands.⁹ Evolution of O_2 was confirmed by CV measurements. The reaction can be monitored by UV-vis spectroscopy. Upon addition of 100 equivalents of H_2O_2 to a 1 mM solution of $(\text{bpy})\text{Cu}(\text{OAc})_2$ at pH 12.6, a band quickly grows in at 380 nm (Figure 4.7, right). The band slowly dissipates over several minutes; however, a complete return to the original spectrum was not observed. Further study of this reaction under very dilute catalyst conditions indicates that the intermediate is not green, but orange, consistent with the observed spectrum. The green color observed in more concentrated $(\text{bpy})\text{Cu}^{2+}$ solutions is due to a mixture of the blue $(\text{bpy})\text{Cu}(\text{OH})_2$ species and the orange intermediate.

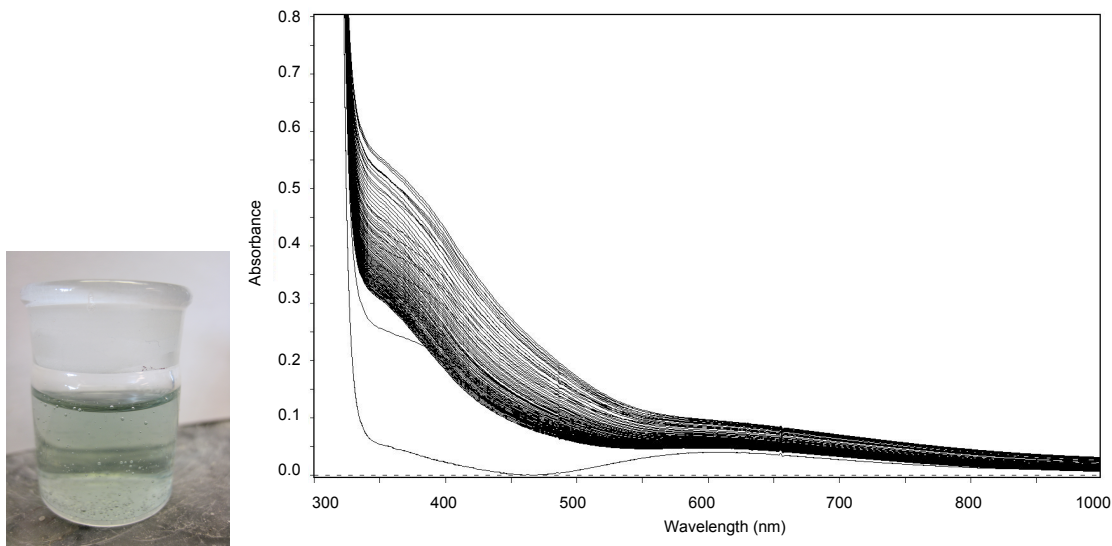


Figure 4.7. Left: Upon addition of H₂O₂, a solution of 1 mM (bpy)Cu(OAc)₂ at pH 12.5 turns green and bubbles evolve. Right: Upon addition of H₂O₂, a band at 380 nm grows in rapidly and then bleaches over several minutes.

CVs were performed following the initiation of catalytic H₂O₂ decomposition by (bpy)Cu(OAc)₂ at pH 12.5 (Figure 4.8). Interestingly, the CVs were nearly identical before and after addition of H₂O₂. There was a slight decrease (~10 mV) in the onset potential of the catalytic wave. However, the peak current was maintained after addition of H₂O₂. After 10 minutes of reaction with H₂O₂, there was a decrease in the peak current of about 20%, but no further change to the potential or shape of the catalytic wave.

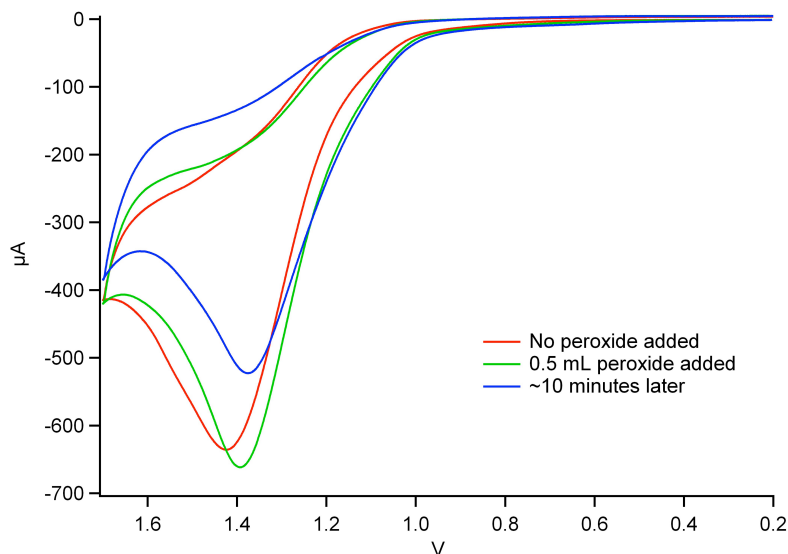


Figure 4.8. CVs of 1 mM (bpy)Cu(OAc)₂ at pH 12.5 before addition of H₂O₂ (red), immediately after addition (green), and 10 minutes after the H₂O₂ reaction was initiated (blue). CVs were collected at pH 12.5 and 0.1 M electrolyte (NaOAc + NaOH) at a scan rate of 100 mV/s. Electrodes: working, GC; auxiliary, Pt; reference, Ag/AgCl adjusted to NHE.

4.3 Discussion

4.3.1 Catalyst and hydroxide dependencies

The catalyst concentration dependency study can be best explained as having two regimes. In the low concentration regime, there is a linear dependence of the current on catalyst concentration, and in the high concentration regime, there is no dependence. These two regimes can be explained through an understanding of the influence of diffusion on electrocatalytic processes. As discussed in Chapter 2, there are two regimes that describe substrate dependence on electrocatalysis.⁶⁻⁸ One is the substrate-limited regime, where the catalytic process is, at least in part, limited by diffusion of substrate to the electrode surface. In this regime, the catalytic wave resembles a peak, rather than having a S-shape. In the kinetic-limited regime, the ratio

between substrate and catalyst (γ) is high enough that the current is not limited by diffusion of substrate at all. Instead, it is entirely dependent on the catalyst activity.

At low catalyst concentration, γ is high. As the catalyst concentration is increased while pH remains constant, the γ decreases. At pH 12.5, for instance, γ is 600 at 50 μM catalyst concentration, and at 3 mM catalyst, γ is only 10. With a fast catalyst, like the (bpy)Cu²⁺ water oxidation, this low amount of substrate is quickly used up. More catalyst can be added, but because the amount of available substrate remains the same, the current does not increase.

Computer simulations of cyclic voltammetry support this analysis. A simple model of a fast catalytic process displays the same two catalyst dependency regimes (Figure 4.9). The model is comprised of two steps, an electrochemical step to oxidize the catalyst and a chemical step whereby the oxidized catalytic species then converts substrate to product and is reduced back to the starting species.

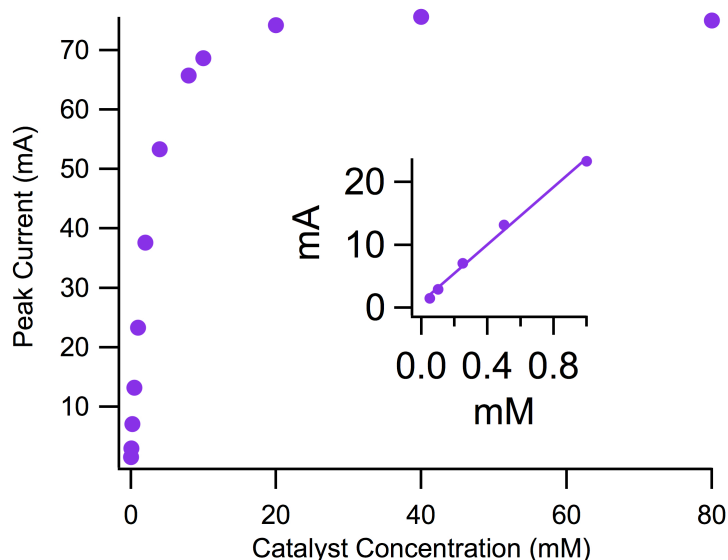


Figure 4.9. A plot of peak current versus catalyst concentration for a simple model catalytic system with a single electrochemical step followed by a single chemical step. See Experimental Methods section for details.

Following the above analysis, the reaction kinetics for this system must be evaluated in the *low concentration regime*. For an electrocatalytic system, the linear dependence on catalyst concentration indicates a reaction that is first order in catalyst. A rate law that is first order in catalyst concentration implicates a mono-copper mechanism, given that the speciation results indicate that $(\text{bpy})\text{Cu}(\text{OH})_2$ is the active complex.

It should be noted that there are other possible interpretations of the two regimes present in the catalyst concentration dependence. Most notably, it could be indicative of deposition onto the electrode surface. At the low concentration regime, the deposit would be less than a monolayer. Then at the high concentration regime, a monolayer is reached and so addition of more catalyst does not increase the current. Although this is a reasonable interpretation, there are many other pieces of evidence that argue against a heterogeneous catalyst for this system (see Chapter 2 for further discussion).

The dependence on hydroxide is more difficult to elucidate. The clear linear dependence of the peak current on hydroxide at 1 mM (bpy)Cu(OAc)₂ indicates a reaction that is second order in hydroxide, due to the relationship shown in Equation 4.1. However, it is possible that, due to being in the diffusion-limited regime, one factor in that second order dependency is from diffusion of hydroxide to the electrode. Analysis under kinetically controlled conditions could address this issue. Unfortunately, the data collected at 50 μ M (bpy)Cu(OAc)₂ is inconclusive. The linear fits of the catalytic peak current vs. [OH⁻] and [OH⁻]^{1/2} both contain significant error. There is not enough of a difference between them to conclude that the reaction is definitely first or second order in hydroxide. Further analysis is necessary here, possibly from collecting a greater number of points at a slightly higher copper concentration, to minimize error.

4.3.2 *Ligand study*

It is surprising that the catalysis has such limited sensitivity to ligand electronics. Although the terpy and (ˆOOC)₂-bpy ligands displayed reduced catalytic activity, both of these are quite different from the original bpy ligand. Terpy is potentially tridentate (though the Me₂-TPA ligand is as well and *does* display catalytic activity) and, under basic conditions, the (ˆOOC)₂-bpy ligand is dianionic. One other copper-based water oxidation catalyst with nitrogen ligands has been published, and it, too, has a similar onset potential.¹⁰

This phenomenon does not appear to be unique to the copper system. For instance, iridium complexes that have different catalytic properties when undergoing water oxidation with a chemical oxidant display very similar electrochemistry.¹¹ This

suggests that further analysis of these complexes by chemical oxidation might be helpful in determining the ligand's role in catalysis.

Although Meyer reported copper-mediated water oxidation with phosphate and carboxylate ligands under neutral conditions, they were unable to observe electrocatalysis under alkaline conditions due to precipitation of the copper salt. Under the alkaline conditions discussed here, the nitrogen ligand does appear to be necessary in order for catalysis to proceed. As discussed in Chapter 3, we have been able to prepare a $\text{Cu}(\text{OH})_4^{2-}$ complex that is soluble under very basic conditions, and it does not undergo water oxidation electrocatalysis. Therefore, while the role of the ligand in catalysis is not clarified by the ligand study, the ligand is clearly essential to the catalytic process.

One possible explanation for the lack of ligand dependence is dissociation of the bpy ligand before the rate limiting step. Further study of the speciation of the substituted bpy complexes, particularly at high pH where such dissociation occurs for Cu^{2+} complexes, might provide some evidence about the viability of this possibility.

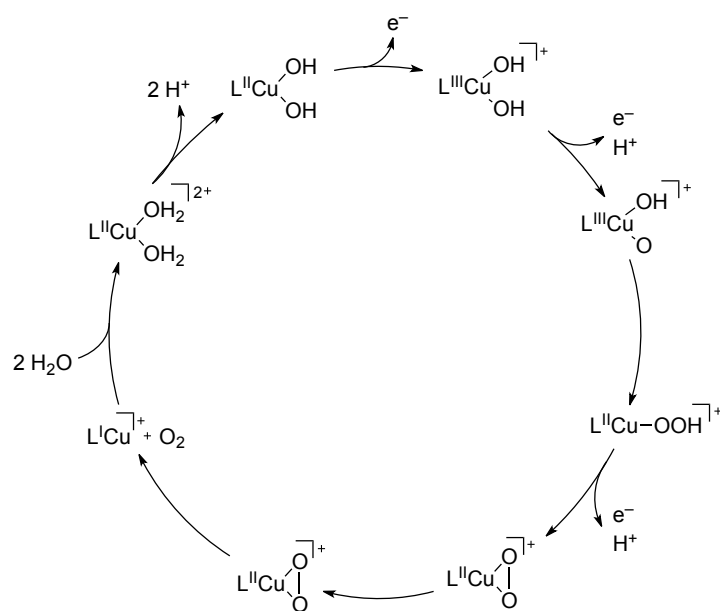
4.3.3 Reactions with hydrogen peroxide

It is quite interesting that the addition of H_2O_2 does little to affect the electrochemical water oxidation process. The observation of an intermediate that absorbs at 380 nm is consistent with other studies of copper-mediated H_2O_2 disproportionation, of which there are many, due to interest in biomimetic catalase-type chemistry.^{9,12,13} The proposed intermediate in these processes is the monomeric copper(II) hydroperoxo complex ($\text{Cu}^{\text{II}}\text{-OOH}$). It is quite possible that this complex is an

intermediate in the catalytic cycle for water oxidation. A possible mechanism involving this complex is shown in Scheme 4.2.

If this is the case, the $\text{Cu}^{\text{II}}\text{-OOH}$ species might be visible by spectroelectrochemical methods, though UV-vis spectroelectrochemistry has already been attempted without success. In other systems, the $\text{Cu}^{\text{II}}\text{-OOH}$ species has been observed in multiple solvents and has been isolated with other ligands.¹⁴ Therefore, it may be possible to observe in the (bpy)Cu water oxidation system in mixed solvent systems at low temperature.

Scheme 4.2



4.4 Conclusions

The data at this point suggests that the (bpy)Cu water oxidation system goes through a monocopper mechanism, possibly involving a $\text{Cu}^{\text{II}}\text{-OOH}$ species. It is first

order in catalyst, and either first or second order in hydroxide. The fast catalytic rate makes kinetic study more challenging. However, appropriate conditions for optimal kinetic study may be found at lower catalyst concentration. Studies at low temperature in mixed solvent systems might also prove advantageous.

The system has limited sensitivity to the supporting ligand. However, it is clear that the ligand is necessary for the electrocatalyst to work. Further analysis with chemical oxidants might be able to show differences between the catalysts that are subtler when the catalysts are studied electrochemically. Speciation studies might also be useful, especially if a dissociative mechanism is suspected.

Although there is no clear mechanism at this point, much progress has been made towards understanding the (bpy)Cu system. Further study will prove important for understanding, not only this system, but also water oxidation and mononuclear copper chemistry in general.

4.5 Experimental Methods

Preparation of solutions for analysis

Solutions of (L)Cu(OAc)₂ (where L = R₂-bpy, phen, terpy, or Me₂-TPA) were prepared *in situ* from Cu(OAc)₂, L, purchased from Sigma-Aldrich and NaOAc purchased from Fisher Scientific in all cases except where L = Me₂-TPA. Me₂-TPA was prepared following literature procedures.¹⁵ The pH was adjusted using NaOH, also purchased from Fisher. Materials were used as received with no further purification. A representative preparation procedure went as follows:

A 100 mM solution of (bpy)Cu(OAc)₂ was prepared by first dissolving 181 mg of Cu(OAc)₂ into 10 mL of DI water in a 20 mL scintillation vial. The appropriate amount of water was measured in a graduated cylinder. The solution was a light blue color. 156 mg of 2,2'-bipyridine were weighed and added to solution. The vial was shaken and sonicated in order to dissolve the bipyridine. As the bipyridine dissolved, the color became a darker blue. Sonication was continued for 5 minutes, until all bipyridine was dissolved.

A 0.1 M stock solution of NaOAc and NaOH were prepared in DI water. The NaOAc was titrated to the desired pH through addition of the NaOH solution, maintaining the electrolyte level at 0.1 M. 100 μ L of (bpy)Cu(OAc)₂ solution were then added to 10 mL of the electrolyte solution, diluting it to 1 mM (bpy)Cu(OAc)₂. A color change is observed immediately, from blue to indigo. The pH of this solution was measured before spectra were collected.

Electrochemical measurements

Electrochemistry was performed using a BASi Epsilon potentiostat and a CH Instruments 600D potentiostat. In all cases, a 0.3 cm glassy carbon working electrode, platinum auxiliary electrode, and a Vycor-tipped Ag/AgCl (saturated KCl) reference electrode were used. Working electrodes were purchased from BASi or CH Instruments, and the Ag/AgCl reference electrodes were purchased from BASi or prepared from silver wire and solutions of saturated KCl. Electrochemical data were adjusted to NHE by adding 0.2 V to potential measurements. Solutions of 0.1 M electrolyte were prepared by titrating 0.1 M solutions of NaOAc with 0.1 M NaOH until the desired pH was reached. pH was measured with a Fisher Scientific Accumet pH meter.

Reactions with H₂O₂

Fresh 30% H₂O₂ purchased from Fisher Scientific was used in all experiments. H₂O₂ was added by syringe to 10 mL samples of (bpy)Cu(OAc)₂ at pH 12.5. Upon addition of H₂O₂, gas evolution was observed and the solutions became green or brown. The reactions were monitored by UV-vis spectroscopy. The spectra were collected on an Agilent 8453 spectrophotometer. Samples were added to a quartz cuvette with a 1 mM path length. “Blank” spectra were collected from solutions of DI water with no additions.

Computer simulations of CVs

Simulations were performed using DigiSim[®], produced by BASi. Two reactions were entered into the simulator, an electrochemical step, Equation 4.3, and a chemical step, Equation 4.4. The E⁰ for the electrochemical step was set at 0 V and the α parameter at 0.5. For the chemical step, the equilibrium constant was set at 100 and the rate constant at 1×10^5 . These were relatively arbitrary selections to represent a chemical step that is fast and quantitative.



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Chapter 5

Surface Attachment of a Copper-Based Water Oxidation Catalyst

Abstract

Copper-phenanthroline complexes were adsorbed to edge-plane pyrolytic graphite electrode surfaces. These modified surfaces are water oxidation electrocatalysts that are stable between pH 11.5 and 12.2, with a calculated turnover frequency of roughly 3 s^{-1} . Electrochemical activity is observed with substituted phenanthrolines, with subtle differences between the systems. The surfaces lose catalytic activity when pH is increased or when agitated, such as during rotating disk voltammetry. This system represents an unusual case where the heterogeneous system has many similarities to its homogeneous $(\text{phen})\text{Cu}^{2+}$ counterparts, including the pH dependence and overpotential.

5.1 Introduction

Because water oxidation is such an important challenge in the field of renewable energy and fuel generation,¹⁻⁴ many types of catalysts have been studied. Metal oxides have been explored as competent and stable water oxidation catalysts, though there are still substantial improvements than can be made, especially in the areas of overpotential, turnover rates, and cost. Homogeneous, molecular water oxidation catalysts have been developed and studied with a number of different metals to try to understand how water oxidation mechanisms can proceed. This understanding can be used to develop industrially viable catalysts, which will likely be supported, heterogeneous materials.⁵ There are several advantages to heterogeneous catalysts, such

as reduced requirements in amount of material and easier separation of catalysts and products. In an electrochemical cell, different heterogeneous catalysts can be used at the anode and cathode.

Attachment of defined, molecular catalysts to electrode surfaces and study of these species bridges the gap between homogeneous, molecular catalysis and heterogeneous catalysis performed by metal oxides. This Chapter describes the surface attachment and characterization of a phenanthroline (phen) analog of the homogeneous (bpy)Cu(OH)₂ water oxidation catalyst described in the previous Chapters.⁶

In general, there are three possible ways to attach a molecular species to surface: covalent attachment, non-covalent attachment through exploitation of physical forces, and trapping the molecule in a matrix or sol-gel such as NafionTM.⁷⁻⁹ Since we had discovered that (phen)Cu²⁺ complexes were active for water oxidation (see Chapter 4), and phenanthroline ligands will easily adsorb to graphite through π - π stacking, physisorption was the logical first step for an attempt to immobilize a molecular copper water oxidation catalyst. Adsorption avoids the necessity of a covalent linker or adhesive gel that might degrade under the highly oxidizing conditions required for water oxidation.

In the 1980's, Anson and co-workers described physisorption of phen-copper species to edge-plane pyrolytic graphite (EPPG) that increased the oxygen reduction activity of ruthenium-modified electrodes.^{10,11} The copper-modified electrodes were then shown to be oxygen reduction catalysts in their own right, and were further studied by Anson and other groups.¹²⁻¹⁶ Chidsey published a report in 2007 that thoroughly investigated oxygen reduction behavior with substituted phen-copper complexes adsorbed to EPPG. We were inspired by this report, as well as a later one

detailing a covalently attached (R-phen)Cu²⁺ oxygen reduction catalyst,¹⁷ to investigate the possibility that similarly-prepared surfaces might also be electrocatalysts for the reverse process, water oxidation. The preparation and analysis detailed in this Chapter roughly follows the methods described in Chidsey's earlier report.

Some key challenges associated with immobilization of molecular catalysts include catalyst stability, maintenance of catalyst activity (which is often reduced after surface-attachment^{18–20}), and establishment of catalyst identity. For water oxidation catalysts, in particular, it can be difficult to distinguish attached molecular catalysts from heterogeneous metal oxide catalysts, which might be formed under the highly oxidizing conditions of the water oxidation reaction. This Chapter presents evidence for a heterogeneous, molecular copper-based water oxidation catalyst and attempts to address the above challenges.

5.2 Results and Discussion

5.2.1 *Electrode preparation*

An EPPG disk electrode purchased from Pine Instruments was roughened on 1200 grit Si-C sandpaper to obtain a high surface area electrode. The electrode was then sonicated in DI water for 30 seconds to remove excess carbon. The electrode as purchased had been polished to a mirror finish. After roughening, the surface appeared matte with some directional striations visible from an acute angle relative to the surface. In the 2007 report by Chidsey, the surface obtained by the same preparative technique is described as having a mica-type macrostructure.¹⁶

Unless noted otherwise, phen was adsorbed to the EPPG by soaking the electrode in a 1 mM H₂O/MeCN solution of ligand for 30 minutes. The phen-modified

electrode was then rinsed and soaked in a 500 mM solution of $\text{Cu}(\text{NO}_3)_2$ for 5 minutes. The electrode was rinsed and used as prepared in electrochemical experiments. Solutions for electrolysis contained no added copper—only 0.1 M electrolyte, generally a mixture of Na_2SO_4 and NaOH . In a few experiments, pre-complexed $(\text{phen})\text{Cu}(\text{NO}_3)_2$ was adsorbed directly to the EPPG electrode. Phen could also be attached to EPPG by drop coating solutions of phenanthroline in acetonitrile, ether, or acetone directly onto the electrode. Copper was complexed to the phenanthroline-modified electrode through soaking in $\text{Cu}(\text{NO}_3)_2$ solution.

5.2.2 Electrochemical characterization

Cyclic voltammograms (CVs) were performed in 0.1 M electrolyte: 0.1 M Na_2SO_4 , with 0.1 M NaOH added until the desired pH was reached. Upon scanning oxidatively, the modified electrodes show a large, irreversible wave, with onset at 1.1 V vs. NHE.^{†††} This wave is pH-dependent, increasing in current as pH is increased, from a peak current of 69 μA at pH 11 to 712 μA at pH 12.5 (Figure 5.1, top). The onset potential for catalysis, however, does not increase. The pH-dependent current increase is most likely caused by a combination of factors, as with the homogeneous system. First, the relationship could be indicative of at least a first order rate dependence in hydroxide, as is seen in the homogeneous system (see Chapter 4 for further discussion of kinetics in the homogeneous system). An increase in the amount of substrate (hydroxide) would cause an increase in rate (current), provided the system is not in the substrate-independent regime, which is unlikely under these conditions.²¹ There is also possible contribution from the speciation of $(\text{phen})\text{Cu}^{2+}$ complexes towards the catalytically

^{†††} CVs were collected with an Ag/AgCl electrode and adjusted to NHE by addition of 0.199 V.

active species, which is the monomeric bis(hydroxide) in the homogeneous systems (see Chapter 3 for more discussion of speciation). Although accounting for speciation to the active monomer does not contribute strongly to the overall hydroxide dependence in the homogeneous system, effects from speciation are likely to be different when the complexes are adsorbed to the surface.

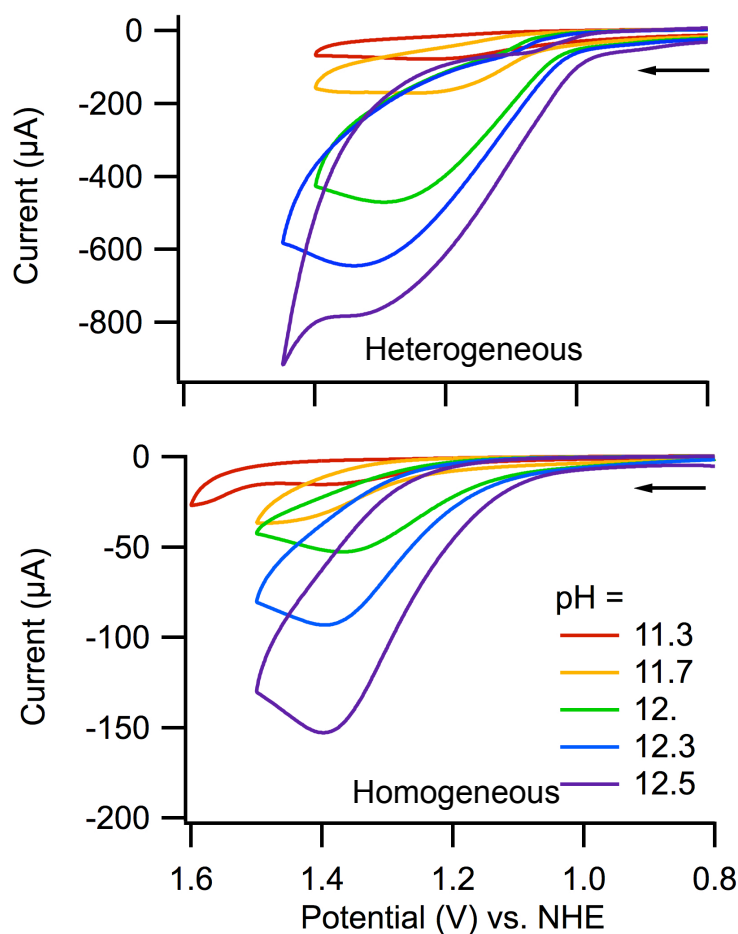


Figure 5.1. CVs collected of the catalytic wave for attached and free $(\text{phen})\text{Cu}^{2+}$ catalysts at various pH levels. Solution contains 0.1 M electrolyte ($\text{Na}_2\text{SO}_4 + \text{NaOH}$). Auxiliary electrode, Pt; reference electrode, Ag/AgCl adjusted to NHE. Top: CVs of the attached catalyst, EPPG soaked in 1 mM phen, then 0.5 M $\text{Cu}(\text{NO}_3)_2$. Bottom: CVs of 1 mM $(\text{phen})\text{Cu}(\text{NO}_3)_2$ on a GC electrode.

Although the non-catalytic $\text{Cu}^{\text{II/III}}$ couple is not observable in aqueous solution, the catalytic wave can be compared to the 1 e^- $\text{Cu}^{\text{II/I}}$ couple at -0.34 V (Figure 5.2). The wave at oxidizing potentials is ~ 48 times greater than the $\text{Cu}^{\text{II/I}}$ couple at pH 12.5, indicating electrocatalysis. Oxygen can be detected by CV by sweeping to reducing potentials.

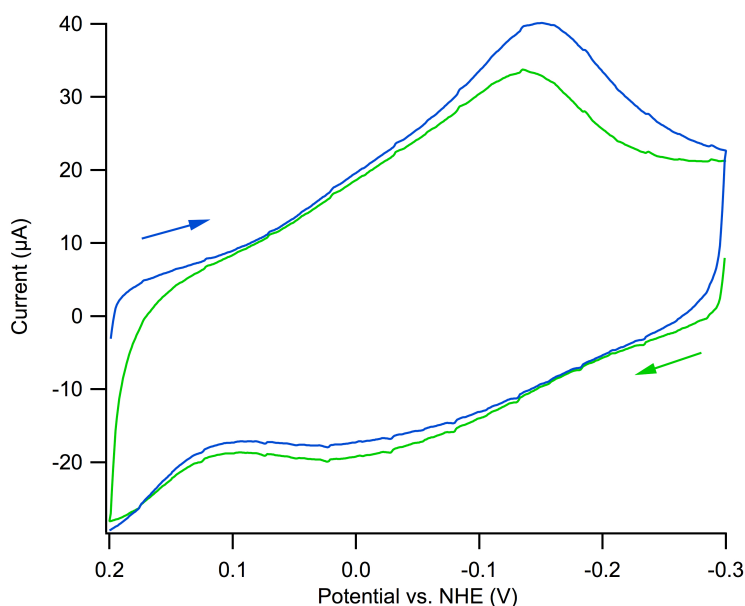


Figure 5.2. Cu^{III} couple of adsorbed catalyst (EPPG soaked in 1 mM phen for 30 min then in 0.5 M $\text{Cu}(\text{NO}_3)_2$ for 5 min) at pH 12.2. Green trace shows sweep starting from more reducing potentials, blue trace shows sweep starting from more oxidizing potentials. Solution contained 0.1 M electrolyte (Na_2SO_4 + NaOH). Auxiliary electrode, Pt; reference electrode, Ag/AgCl adjusted to NHE.

The $\text{Cu}^{\text{II/I}}$ wave is irreversible, deviating from ideal behavior with a diffusive-shaped cathodic peak and a broad, Gaussian anodic peak (for an ideal, surface-attached species, the wave would consist of two overlapping Gaussians^{22,23}). However, the integrations of the anodic and cathodic peaks are roughly equivalent, as would be expected for a standard 1 e^- couple. A plot of the peak current vs. scan rate for both the

anodic and cathodic waves shows that the current follows a linear dependence on scan rate, as expected for a surface-attached species (Figure 5.3).²² The current for the catalytic wave, however, follows a square root of scan rate dependence, indicating that the current is being limited by a diffusive process. This is predicted for a fast catalytic process where catalysis is limited by diffusion of *substrate* instead of the catalytic rate.²⁴ For a catalytic system that is not limited by diffusion of substrate, the current should continue to increase as a function of overpotential, η .²² This phenomenon is observed in a covalently attached oxygen reduction catalyst, where the current reaches a peak when catalyst surface coverage is high, but does not when surface coverage is low and, therefore, has a higher ratio of substrate to catalyst at the electrode.¹⁷

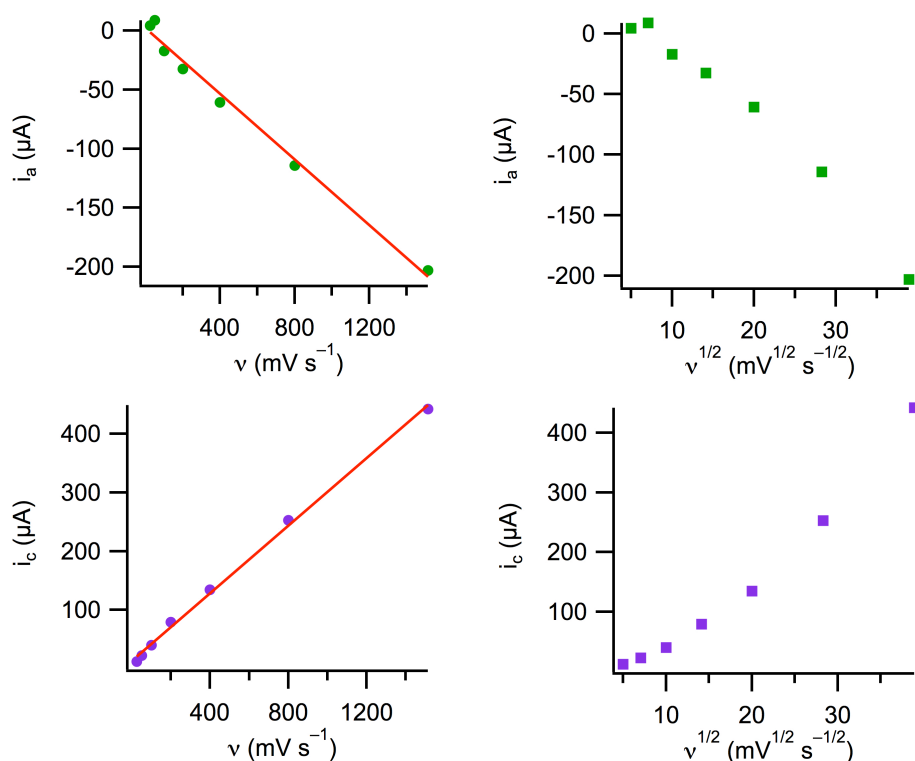


Figure 5.3. The maximum anodic and cathodic currents of the $Cu^{II/I}$ couple plotted vs. scan rate (v) and square root of scan rate ($v^{1/2}$). Homogeneous species show a linear dependence on $v^{1/2}$ and surface bound species show a linear dependence on v . For (phen)Cu on EPPG (pH 12.2), only the plots of current vs. v show a linear dependence, indicating that the copper species is attached to the electrode.

5.2.3 Control experiments

Several controls were performed to determine both the molecular nature of the catalyst and whether it was, in fact, attached to the EPPG surface. NaOTf and NaOAc were tested as electrolytes (in addition to Na_2SO_4), since the electrolyte can have a dramatic effect on metal cluster catalysts.^{3,25} Similar activity was observed with all three electrolytes with identical onset potentials (Figure 5.4). Slightly higher currents were observed in NaOTf, but the slight difference in current is in line with observations of the homogeneous (bpy) Cu^{2+} system.

CVs were also collected on EPPG that had been exposed to phenanthroline, but not copper, and ones that had been exposed to copper, but not phenanthroline. For these experiments, soaking time in phenanthroline was 30 minutes and soaking time in $\text{Cu}(\text{NO}_3)_2$ was 5 minutes. No additional electrochemical activity was observed for electrodes with only adsorbed phenanthroline (no Cu). Some current was observed at pH 11.5 for EPPG electrodes that had been exposed to $\text{Cu}(\text{NO}_3)_2$ solutions, without exposure to phenanthroline (Figure 5.5, middle). Activity was also observed at pH 11.5 on glassy carbon electrodes that had been exposed to the same solutions. However, this activity is not present under optimal catalytic conditions (pH 12.2-12.5).

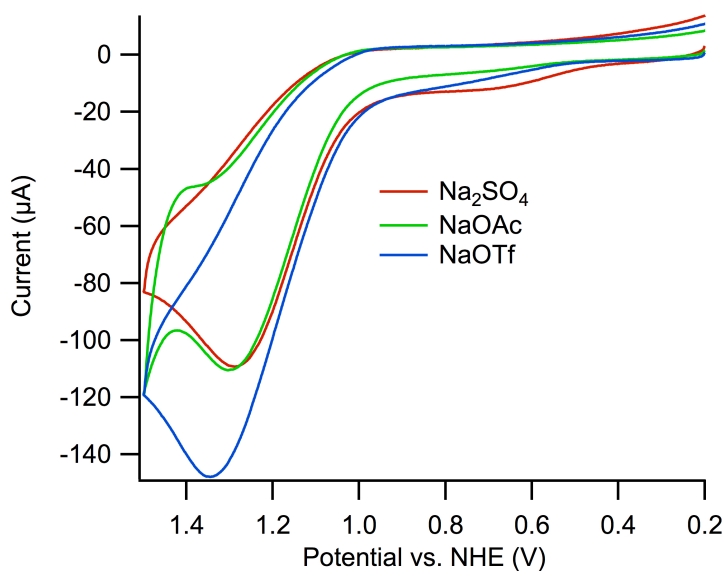


Figure 5.4. CVs of (phen)Cu²⁺ on EPPG (soaked in 1 mM phen for 30 min and 0.5 M Cu(NO₃)₂ for 5 min) at pH 11.5 with various supporting electrolytes (NaX). Solutions contained 0.1 M (NaX + NaOH). Auxiliary electrode, Pt; reference electrode, Ag/AgCl adjusted to NHE.

Electrode exposure to copper also causes passivation of the relatively large background current below +0.8 V. This phenomenon is attributed to copper binding to functional groups on the roughened carbon surface, and is observed with and without the phenanthroline adsorption step (Figure 5.5).

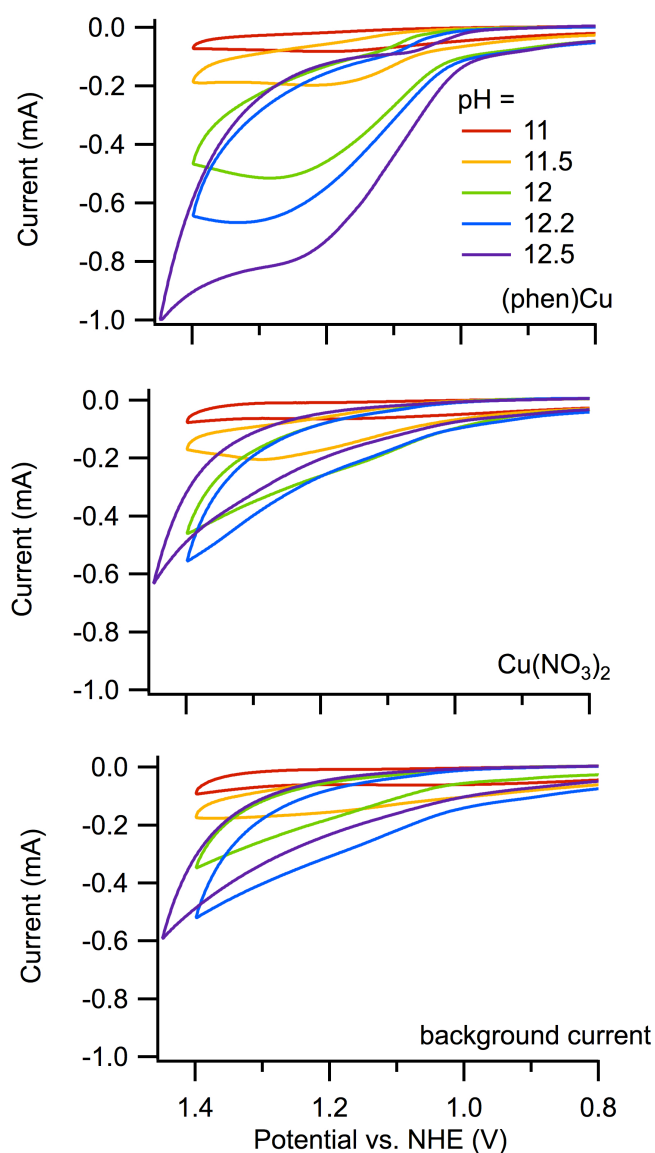


Figure 5.5. CVs at various pH levels of the bare EPPG electrode (bottom), EPPG exposed to $\text{Cu}(\text{NO}_3)_2$ alone (middle, 0.5 M for 5 min, no phen exposure), and EPPG exposed to phen (top, 1 mM for 30 min) followed by $\text{Cu}(\text{NO}_3)_2$ (0.5 M for 5 min). Solutions contained 0.1 M electrolyte ($\text{Na}_2\text{SO}_4 + \text{NaOH}$). Auxiliary electrode, Pt; reference electrode, Ag/AgCl adjusted to NHE.

5.2.4 XPS analysis of the prepared surface

XPS measurements of the modified EPPG surface were collected. A removable EPPG disk was used, so that the disk could be secured in the vacuum chamber of the

instrument. The electrode was prepared following the standard procedure outlined above, but with solutions containing HPLC water instead of water from the DI tap to minimize any possible contamination. The electrode was also rinsed and sonicated with HPLC water. XPS spectra show signals corresponding to carbon, oxygen, nitrogen, and copper, as expected (Figure 5.6). Integration of the copper and nitrogen signals show a 1:6 ratio, indicating two phenanthrolines per $\text{Cu}(\text{NO}_3)_2$. It should be noted that some phenanthrolines might be inaccessible to copper binding due to orientation on the carbon surface, so the 2:1 ratio observed by XPS does not necessarily correspond to a bis(phen) copper complex.

Although further analysis by surface characterization techniques is necessary, the XPS spectra provide evidence for two important characteristics of the modified EPPG surfaces. First, there is both copper and phenanthroline present on the EPPG. It is impossible to obtain the observed Cu:N ratios without contribution from both molecules. Second, there is not likely to be a dramatic amount of uncoordinated copper nitrate or phenanthroline on the surface. There are similar amounts of both copper and phenanthroline present on the surface, which are likely coordinating to form the catalytic species.

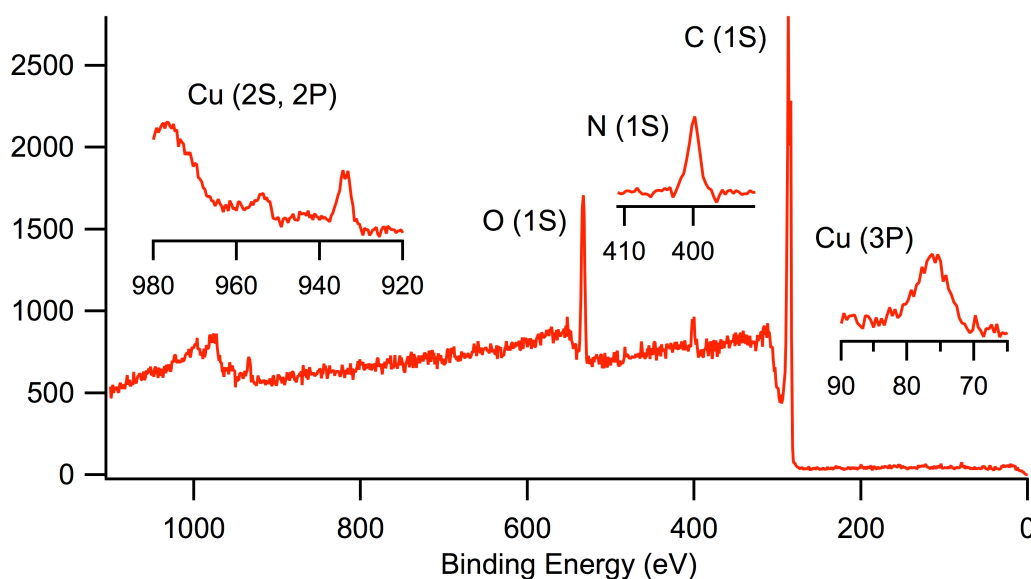


Figure 5.6. XPS spectra of the EPPG electrode after exposure to 1 mM phen for 30 minutes and 0.5 M $\text{Cu}(\text{NO}_3)_2$ for 5 minutes. The electrode was analyzed after preparation and was not exposed to electrolyte or elevated potential. The spectrum contains signals corresponding to copper(II), oxygen, nitrogen, and carbon.

5.2.5 Stability measurements

Electrode stability was tested by collecting several CVs in succession at multiple pH's between 11.5 and 12.5 and by performing controlled potential electrolysis (CPE) at pH 12.2. In successive CVs, there is a pronounced change between the first and second scan at all pH's (Figure 5.7 and 5.8, red and orange lines). There is further suppression of the baseline current at 0.8 to 1 V (beyond the initial quenching after exposure to copper that is mentioned above) and a ~30 mV increase in the onset potential. This is attributed to oxidation of residual functional groups that might be attached to the carbon surface. These functional groups tend to persist on carbon in alkaline solution, but can be removed by cycling the electrode to high potential.^{26,27} The baseline current and onset potential remain relatively constant for the successive scans at all pH's tested.

However, there is a decrease in the maximum current in these successive scans (Figure 5.7 and 5.8). In solutions at pH 12.25 and lower, when the electrode is agitated, the maximum current returns to the levels observed in the second scan (Figure 5.7, bold purple line). Thus, the decrease in current can be explained by bubble formation at the electrode surface or by a local decrease in pH. Due to the high surface area of the EPPG electrode, these effects might be magnified when compared to the homogeneous system studied on GC, and might also require physical agitation to reverse.

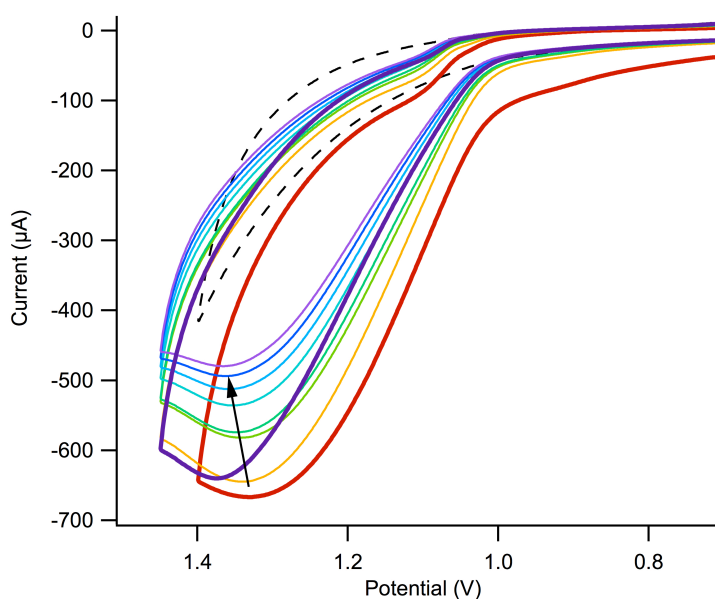


Figure 5.7. Successive CVs of the (phen)Cu modified electrode. The current decreases with subsequent scans (red to dark purple traces). Upon agitation, the current returns to previous levels (dark purple). First and final scans are bolded. Solution was at pH 12.2 and contained 0.1 M electrolyte ($\text{Na}_2\text{SO}_4 + \text{NaOH}$). Reference electrode: Ag/AgCl adjusted to NHE.

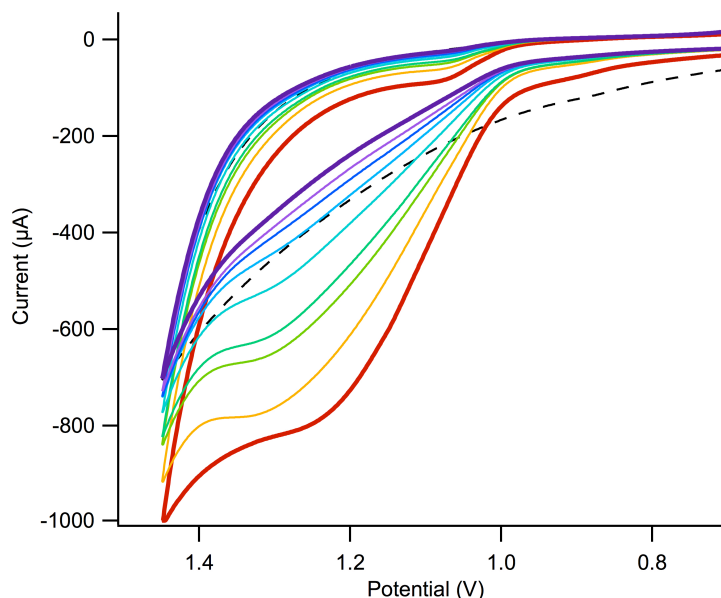


Figure 5.8. Successive CVs of the (phen)Cu modified electrode. The current decreases with subsequent scans (red to dark purple traces). Upon agitation, the current returns to previous levels (dark purple trace). First and final scans are bolded. Solution was at pH 12.5 and contained 0.1 M electrolyte (Na_2SO_4 + NaOH). Reference electrode: Ag/AgCl adjusted to NHE.

At pH 12.5, the current is higher than it is at pH 12.2, 800 μA , versus 650 μA . While this activity increase is desirable, the current decreases *irreversibly* with every scan (Figure 5.8). Even after the electrode is agitated, the current does not return. There are two possible explanations for this irreversible deactivation of the catalytic surface. The first is that the carbon electrode is degraded under the highly oxidative conditions at pH 12.5. There is approximately twice as much hydroxide present at pH 12.5 (32 mM) than at pH 12.2 (16 mM). If the carbon electrode is degraded, this may cause detachment of the catalyst attached to the carbon surface. However, analysis of the background current does not show a significant increase in activity between pH 12.2 and 12.5 that might signal degradation of the carbon electrode (Figure 5.5).

Another possible explanation for the catalyst deactivation at pH 12.5 is based on the speciation of homogeneous (phen)Cu²⁺ complexes.²⁸ Around pH 12.5, the phenanthroline-free Cu(OH)₄²⁻ monomer starts to form in small amounts. This species would not be attached to the electrode and, therefore, free to migrate to the bulk of the solution. As Cu(OH)₄²⁻ is removed from the solution closest to the electrode, the equilibrium would be pushed towards generation of more Cu(OH)₄²⁻, depleting the attached (phen)Cu²⁺ species. Similar speciation is observed in the homogeneous (bpy)Cu²⁺ system, and is a possible pathway for catalyst deactivation in that system (See Chapter 2).

Controlled potential electrolysis was performed at 1.2 V vs. NHE for 25 minutes in a pH 12.2 solution (Figure 5.9). The nominal current density was sustained at 145 $\mu\text{A}/\text{cm}^2$ for the first 600 seconds of electrolysis. At this point, the current began to decrease and more NaOH was added to the solution. The current stabilized once again for an additional 100 seconds, before decreasing again. The decrease continued slowly for the rest of electrolysis. The final current density after 1500 seconds was 119 $\mu\text{A}/\text{cm}^2$, 82% of the initial value. Assuming 4 e⁻ per molecule of O₂, and 100% Faradaic efficiency, the total charge corresponds to 130 turnovers. This initial test for extended electrolysis indicates some robustness of the catalyst. However, more thorough tests should be performed, for longer time periods and with quantitative pH monitoring to track the Faradaic efficiency over time.

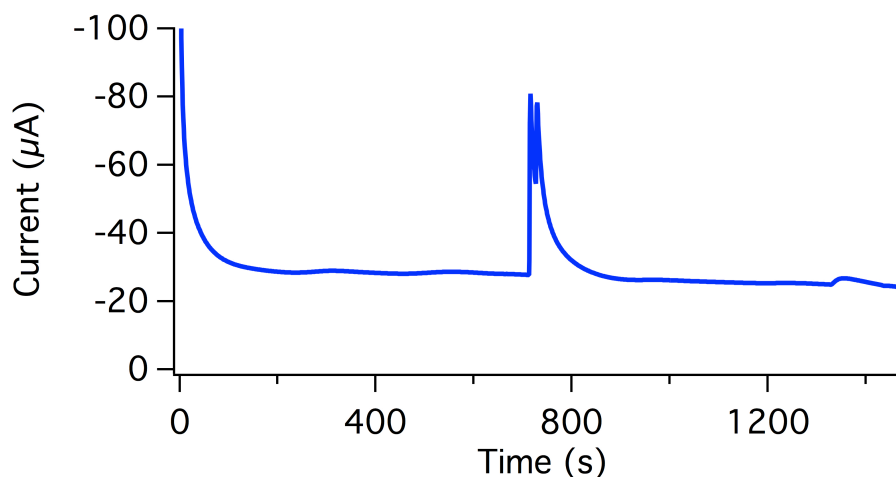


Figure 5.9. CPE at 1.2 V vs. NHE at the (phen)Cu modified EPPG electrode (soaked in 1 mM phen for 30 min and 0.5 M $\text{Cu}(\text{NO}_3)_2$ for 5 min). The spike at 720 seconds is due to addition of NaOH and jostling of the electrodes. The solution started at pH 12.2 and contained 0.1 M electrolyte (Na_2SO_4 + NaOH). Auxiliary electrode, Pt; reference electrode, Ag/AgCl adjusted to NHE.

Although the catalyst is relatively electrochemically robust on a stationary electrode, it does not appear to have the same level of robustness on a rotating disk electrode (RDE). When the electrode is spun, even as low as 60 RPM, only 3-4 scans can be performed before nearly all activity is gone. This instability could be explained by an equilibrium between adsorbed and free (phen) Cu^{2+} complex. At a stationary electrode, the equilibrating species remain close to the electrode, and so the equilibrium is unperturbed and the majority of the copper remains adhered to the electrode. However, once the electrode is spun, convective forces drive away the free (phen) Cu^{2+} complex, driving the equilibrium towards desorption of the complex. Further evidence for this type of equilibrium is observed when a phen-modified electrode (without copper) is soaked in a solution of $\text{Cu}(\text{NO}_3)_2$. Bare electrodes soaked in the $\text{Cu}(\text{NO}_3)_2$ solution that had been exposed to the phen-modified electrode showed catalysis identical to electrodes that have been soaked in both phenanthroline and copper. This result

indicates that some phen ligand and/or (phen)Cu²⁺ complex is detaching from the electrode during the soaking process.

5.2.6 CVs with substituted phenanthrolines

Several substituted phen/Cu²⁺ systems were evaluated for catalysis. The ligands used are shown in Scheme 5.1. For each ligand, the same soaking procedure was followed as is detailed above for phen (soaked for 30 minutes in 1 mM ligand, rinsed, then soaked for 5 minutes in 0.5 M Cu(NO₃)₂). CVs of the oxidative region were collected at pH 12.2, and a catalytic wave was observed for all ligand/Cu systems (Figure 5.10, left). CVs of the Cu^{II/I} couple were also collected for each ligand/Cu system (Figure 5.10, right).

For both the catalytic and non-catalytic wave associated with the substituted phen/Cu²⁺ complexes, the differences in potential were very slight, with a spread of only 70 mV between the cathodic peak of the Br₄phen Cu^{II/I} couple and the cathodic peak of the (MeO)₂phen Cu^{II/I} couple. Ligands that were substituted in the 2 and 9 positions, such as neocuproine and Br₄phen, displayed reduced currents for both waves. It is possible that substitution close to the nitrogen inhibits formation of the catalytic complex. Homogeneous complexes of copper with neocuproine tend to preferentially form the (neocup)₂Cu⁺ complex, regardless of stoichiometry.²⁹ These complexes are particularly interesting because they are bright red—the hindered stoichiometry causes a twist in the conformation of the ligands about the copper, leading to stabilization of a tetrahedral Cu^I center rather than a square planar Cu^{II}. Formation of this sort of complex would also explain the reduced Cu^{II/I} currents for the neocuproine and Br₄phen complexes. Stabilization of the Cu^I oxidation state also makes

them particularly ill suited for water oxidation chemistry, where stabilization of *higher* oxidation states would be more desirable.

Scheme 5.1

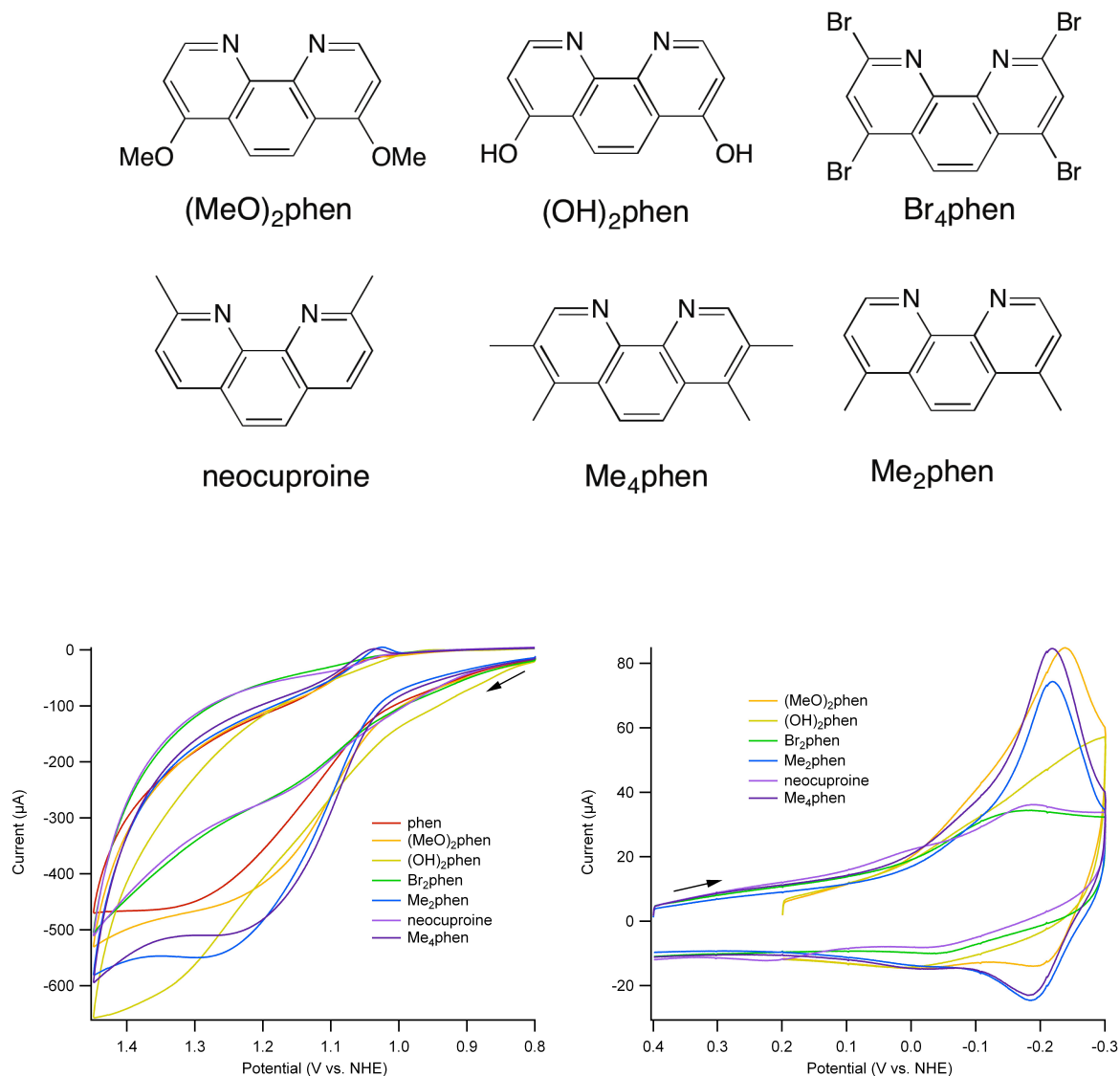


Figure 5.10. CVs of the EPPG electrode modified with substituted phenanthrolines and Cu(NO₃)₂. CVs were collected in 0.1 M electrolyte (Na₂SO₄ + NaOH) at pH 12.2. Auxiliary electrode, Pt; reference electrode, Ag/AgCl adjusted to NHE. Left: CVs of the electrocatalytic wave at oxidizing potentials. Right: CVs of the Cu^{III/II} couple at reducing potentials.

Although all of the substituted phen systems do appear to perform water oxidation chemistry in some capacity at approximately the same potential, there are significant differences in the rise of the catalytic wave, indicating that some catalysts are more efficient. In particular, the (MeO)₂phen, Me₂phen, and Me₄phen systems increase in current much more rapidly than the unsubstituted phen, indicating that placement of electron donating groups in the 3 and 6 positions may be beneficial. The (OH)₂phen system does not have the same improved property, and, in fact, has a slower rise to the catalytic wave than the unsubstituted phenanthroline. However, it is possible that, under the strongly alkaline conditions of catalysis, the HO- group is deprotonated, and, as a result, the deprotonated phenanthroline behaves differently from the others, since it would then be an anionic ligand.

The (MeO)₂phen, Me₄phen, and Me₂phen systems also have similarities in the Cu^{II/I} couple. They are much more reversible in appearance than the phen system (Figure 5.2) or any of the other substituted phen systems that were tested, and display overlapping Gaussian waves associated with a reversible couple from a surface attached species.^{22,23} The improved catalysis in these systems might be related to the good reversibility of these complexes—further study would be useful. These systems might also have an additional advantage for mechanistic study. In the Me₄phen and Me₂phen systems, a small return wave is observed in the CV of the catalytic wave. This return wave indicates persistence of some intermediate species that can be reduced upon sweeping to the appropriate potential. It is possible that this intermediate could be studied by electrochemical or surface spectroscopic techniques.

5.2.7 Comparison with the homogeneous analog

The catalysis observed on these electrodes is remarkably similar to that observed in the homogeneous phen and bipyridine systems (Figure 5.1). They have similar onset potentials that are independent of the supporting electrolyte. The pH dependence for the heterogeneous catalyst also follows the same trends as in the homogeneous systems. This could be due to a first or second order dependence in hydroxide, as discussed further in Chapter 4, or could be caused by pH-dependent formation of the catalytic species. As in the bipyridine system, the homogeneous (phen)Cu²⁺ complex forms the paramagnetic (phen)Cu(OH)₂ species in increasing amounts pH is increased. This process was observed with a 1 mM solution of (phen)Cu(NO₃)₂ (formed *in situ*) with 0.1 M electrolyte (Na₂SO₄ + NaOH). (Figure 5.11).

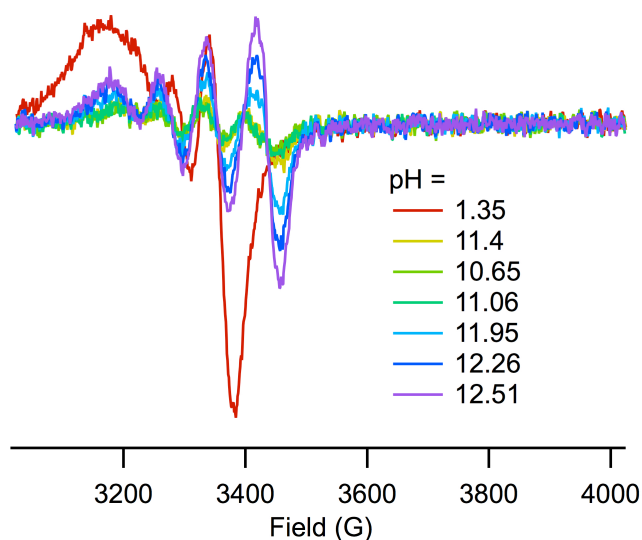


Figure 5.11. EPR spectra of 1 mM (phen)Cu(NO₃)₂ at various pH levels in 0.1 M electrolyte (Na₂SO₄ + NaOH). Spectra were collected at room temperature in a Teflon™ flow cell. As in the (bpy)Cu²⁺ system, there are different pH spectra under acidic and alkaline conditions, corresponding to different species under these conditions. The EPR signal corresponding to (phen)Cu(OH)₂ increases as the pH is increased.

The turnover frequency (TOF) for the attached catalyst can be calculated from CVs of the catalytic waves. An estimate of the electroactive copper surface (ρ_0) concentration can be calculated from double-step chronocoulometry (DSCC). In DSCC, the potential is stepped from a potential where there is little electroactivity to a potential where most of the species has been converted. It is then stepped back to the original potential, which establishes the baseline capacitive current. The data is then charted as an “Anson plot,” which is the charge vs. the square root of time (Figure 5.12). The intercepts from the straight part of the curves are obtained. The intercept of the back step (Figure 5.12, red) is subtracted from the intercept of the forward step (Figure 5.12, blue) to obtain the value of the charge corresponding to only the adsorbed species (Q_{ads}), where Q_{ads} is defined by Equation 4.1 (n = number of electrons transferred during the electrochemical process, F is the Faraday constant, and A is the area of the electrode, with the nominal area used here).^{30,31}

$$Q_{ads} = nFA\rho_0 \quad (4.1)$$

From this data, the surface concentration is approximately 4×10^{-10} mol cm⁻², for a total of 8×10^{-11} mol of electroactive (phen)Cu²⁺ on the surface (note that DSCC will only measure the amount of electroactive material, not the total amount of material on the surface). For this electrode, a maximum current of 480 μ A of current was achieved at 1.13 V vs. NHE at pH 12.2. The current can be converted to a turnover frequency with Equation 5.2, where n is the number of electrons transferred in the catalytic reaction, F is the Faraday constant, ρ_0 is the catalyst surface concentration, and A is the surface area of the electrode. This equation assumes 100% Faradaic efficiency.

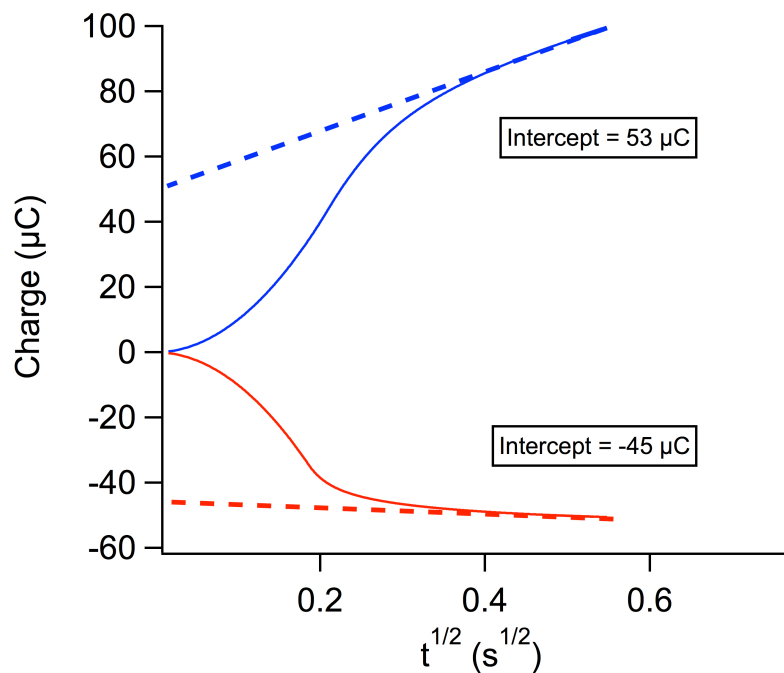


Figure 5.12. An exemplary Anson plot made from DSCC data of (phen)Cu on EPPG (soaked for 30 min in 1 mM phen and 5 min in 0.5 M Cu(NO₃)₂). The initial potential was +0.15 V and the stepped potential was -0.25 V, with a pulse width of 0.3 s. The intercepts were extrapolated from the linear portion of both curves.

$$\text{TOF} = \frac{i_{\text{max}}}{nF\rho_0 A} \quad (5.2)$$

The calculated TOF at pH 12.2 is 3 s⁻¹, based on the maximum current of the catalytic wave. Although this is a fast turnover frequency for a molecular catalyst, it is significantly lower than the TOF calculated for the homogeneous bpy system (100 s⁻¹). There are several possible reasons for the difference. The TOF for the homogeneous bpy system was calculated at pH 12.7-13, where the current is the highest. Although the current does increase with pH for surface attached catalyst, it is unstable above pH 12.2, which is where the TOF is calculated. However, that accounts for only a small

difference in TOF, since the current at pH 12.5 for the heterogeneous catalyst is only 30% more than the current at pH 12.2.

A larger contribution to the difference in calculated TOF likely stems from the diffusion limited state of the CVs collected for the heterogeneous catalyst. For the calculation of the (bpy)Cu²⁺ TOF, several steps were taken to ensure that the catalyst was in the rate-limited regime in order to find the intrinsic turnover rate of the catalyst. The same equations applied under diffusion-limited conditions will give a turnover frequency; however, one that is influenced and limited by the diffusion of substrate (hydroxide, in this case). Although it is more accurately used to calculate a TOF in the kinetically limited regime, Equation 5.3 can be applied to the homogeneous (phen)Cu²⁺ system to obtain a diffusion-limited TOF of ~5 s⁻¹. This TOF is essentially the same, within error, of the diffusion-limited TOF for the surface-attached catalyst. Therefore, this system represents an important example of a catalyst that does not appear to be inhibited by attachment to the electrode surface and, in fact, appears to operate very similarly to its homogeneous analog.

$$\frac{i_c}{i_d} = \frac{n_{\text{cat}}}{0.4463n_d} \sqrt{\frac{RTk_{\text{cat}}}{F\nu}} \quad (5.3)$$

5.2.8 Current dependence on surface concentration

Multiple attempts were made to analyze the dependence of the catalytic current on the surface concentration. As discussed further in Chapter 4, the homogeneous (bpy)Cu²⁺ system has two regimes for concentration dependence: linear dependence at low [cat] and no dependence at high [cat]. To further understand how the surface

attached and homogeneous catalysts are related, it would be useful to study the surface concentration dependence on catalysis.

Several methods were employed to vary the surface concentration of phenanthroline before exposure to the 0.5 M $\text{Cu}(\text{NO}_3)_2$ solution. Solutions between 10 mM and 0.1 mM of phen in ether, acetonitrile, acetone, and isopropanol were drop coated using a micropipette. However, in all cases, the range in concentration of electroactive $(\text{phen})\text{Cu}^{2+}$ on the surface remained between 300 and 700 pmol cm^{-2} . Even within this relatively narrow range, there was no clear trend linking the catalytic current with the surface concentration. There was also an attempt to vary the surface concentration by soaking the electrode in solutions containing various concentrations of phen. Again, there difference in measured electroactive surface concentration was low, and no clear trend was observed between surface concentration and the maximum current of the catalytic wave.

There are two potential explanations for this behavior. First, it is possible that even the lowest concentration phen solutions used in the experiments described above will form close to a monolayer on the surface. The excess phenanthroline then would either not adhere, or intercalate into the bulk of the EPPG electrode (because the phen ligands are not covalently attached, they may be mobile on the surface³²). Evidence for intercalation was observed over the course of several experiments. After months of routine use for adsorption of $(\text{phen})\text{Cu}^{2+}$, primarily using the soaking method detailed above, residual traces of $(\text{phen})\text{Cu}^{2+}$ were still observed after multiple sessions of manually roughening the surface with Si-C sandpaper. The electrochemical waves associated with $(\text{phen})\text{Cu}^{2+}$ were no longer observed after 0.5 mm of the electrode tip

was removed. The mica-like structure of EPPG may be responsible for this intercalation; capillary action has been observed with other carbon nanostructures.^{33–35}

Another explanation is that an increase in catalysis is limited by the diffusion of hydroxide, as is predicted for the homogeneous system in the high catalyst concentration regime (see Chapter 4 for further discussion). And, of course, both of these explanations may be factors simultaneously. It may be possible to reduce those factors by using even more dilute phen solutions to modify the surface concentration and to operate at slower scan rate or on a rotating disk electrode, where diffusion of hydroxide should not limit the catalytic current.

5.3 Conclusions

This system represents immobilization of a molecular catalyst on an electrode surface. There are remarkable parallels between the heterogeneous system and the analogous homogeneous system, particular with the onset potential, pH dependent behavior, and turnover frequency. The evidence so far indicates that the adsorbed (phen)Cu catalyst is, in fact, a molecular analog to the homogeneous (phen)Cu²⁺ system, as originally intended. Although a lack of stability and relatively low current densities clearly prohibit this physisorbed copper complex from becoming an industrially viable catalyst for water oxidation, further comparison between the homogeneous and heterogeneous systems could provide crucial mechanistic insight that would greatly contribute to the field of water oxidation catalysis. In addition, preliminary analysis of substituted phenanthrolines is promising, and should be investigated further. The

catalyst immobilization demonstrated herein represents an essential step in further understanding and manipulation of these important catalyst systems.

5.4 Experimental Methods

Electrode Preparation by soaking

A stock solution of 10 mM phenanthroline was prepared by dissolving 18 mg phen in 10 mL acetonitrile. This stock was diluted to 1 mM phen by addition of 9 mL of DI H₂O to 1 mL of the phen/acetonitrile solution. A stock solution of 0.5 M Cu(NO₃)₂ was prepared by dissolving 60 mg Cu(NO₃)₂ in 50 mL DI H₂O. The EPPG electrode was roughened on Si-C sandpaper by rotating the electrode in figure-8's for 60 seconds in each direction. After roughening, the electrode was sonicated for 10 seconds in DI H₂O to remove excess carbon. A background CV was then collected in 0.1 M electrolyte at pH 12.2 to check for a residual copper signal. If a residue was detected, the roughening procedure was repeated.

If there was no residue, the electrode was rinsed in DI H₂O and soaked for 30 minutes in the 1 mM phen solution. After 30 minutes, the electrode was rinsed and soaked in the Cu(NO₃)₂ solution for 5 minutes. The electrode was rinsed again, and then used for electrochemical or XPS analysis.

Electrode preparation by drop coating

10 mM stock solutions were prepared in ether, acetonitrile, acetone, and isopropanol as indicated above. The solutions were diluted to concentrations between

0.1 and 8 mM through addition of the desired carrier solvent. 5 μ L drops were added with a micropipette in a fume hood. The electrode was held towards the back of the fume hood (to facilitate drying) for 30 seconds. After drying, the electrode was soaked in a 0.5 M $\text{Cu}(\text{NO}_3)_2$ aqueous solution for 5 minutes. The electrode was then rinsed and electrochemical measurements were collected.

Preparation of (phen) $\text{Cu}(\text{NO}_3)_2$ solutions

Solutions of (phen) $\text{Cu}(\text{NO}_3)_2$ were prepared *in situ* from $\text{Cu}(\text{NO}_3)_2$ and 1,10-phenanthroline according to literature procedure,³⁶ with all chemical materials purchased from Sigma-Aldrich. Na_2SO_4 electrolyte was added and the pH was adjusted using NaOH, both purchased from Fisher Scientific. Materials were used as received with no further purification. The preparation procedure went as follows:

A 100 mM solution of (bpy) $\text{Cu}(\text{NO}_3)_2$ was prepared by first dissolving 241 mg of $\text{Cu}(\text{NO}_3)_2$ into 10 mL of DI water in a 20 mL scintillation vial. The appropriate amount of water was measured in a graduated cylinder. The solution was a light blue color. 180 mg of phen were weighed and added to solution. The vial was shaken and sonicated in order to dissolve the phen. As the phen dissolved, the color became a darker blue. Sonication was continued for 10 minutes, until all phen was dissolved.

A 0.1 M stock solution of Na_2SO_4 and NaOH were prepared in DI water. The Na_2SO_4 was titrated to the desired pH through addition of the NaOH solution, maintaining the electrolyte level at 0.1 M. 100 μ L of (bpy) $\text{Cu}(\text{NO}_3)_2$ solution were then added to 10 mL of the electrolyte solution, diluting it to 1 mM (bpy) $\text{Cu}(\text{NO}_3)_2$. A color change was observed immediately, from blue to indigo. The pH of this solution was measured before CVs were collected.

Electrochemistry

All electrochemical measurements were collected on a CH Instruments 600 D potentiostat or a BASi Epsilon bipotentiostat. The EPPG electrode was purchased from Pine Instruments, the GC electrode and Pt auxiliary electrodes were purchased from CH Instruments, and the Ag/AgCl reference electrode was purchased from BASi (Vycor glass tip). All measurements were performed in DI H₂O. All CVs were performed with a 100 mV s⁻¹ sweep rate unless indicated otherwise. Potentials were adjusted to NHE from Ag/AgCl by addition of +0.2 V.

EPR Spectroscopy

EPR spectra were collected on a Bruker EMX X-band spectrometer at room temperature. EPR spectra were collected in a flow cell assembled a 22 g piece of Teflon™ tubing with a Luer lock fitting attached to the bottom end and the top portion attached to the inside of a receiving vessel. 3-5 mL of solution was pushed through the cell by syringe, and the visible portion of the tubing was examined for air bubbles before spectra were collected. Baseline spectra were acquired from spectra of the flow cell filled with neutral electrolyte solution.

XPS Spectroscopy

The soaking electrode preparation procedure was performed with HPLC water for soaking and rinsing the electrode. The electrode used was a removable rotating disk electrode, purchased from Pine Instruments. After soaking in Cu(NO₃)₂, the electrode

was removed from the sheath and placed in ultrahigh vacuum for analysis by XPS. The instrument used for XPS was a Surface Sciences Instruments M-Probe. The spot analyzed by the XPS instrument encompassed the majority of the electrode disk.

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VITA

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