5-2019

Surface Immobilization of Terpyridine Compounds

Elizabeth Hallett
University of Arkansas, Fayetteville

Citation

Hallett, E. (2019). Surface Immobilization of Terpyridine Compounds. *Chemical Engineering Undergraduate Honors Theses* Retrieved from https://scholarworks.uark.edu/cheguht/143

Surface Immobilization of Terpyridine Compounds

Honors Thesis

By

Lily Hallett

Spring 2019

Chemical Engineering

College of Engineering

The University of Arkansas

Acknowledgments

This project was funded through support from the National Science Foundation SURF grant. The author thanks Dr. Stefan Kilyanek for providing mentorship and guidance throughout the project. The members of Kilyanek Lab, including Rajesh Thapa, Joel Baker, Randy Tran, Kayla Denike, Christian Goodnow, Harper Grimsley, Andrew Hodge, Cody Canote, and Sara Spence also provided much support and assistance throughout the author's undergraduate research experiences.

Abstract

The deoxydehydration (DODH) of polyols to alkenes is a promising method of producing high-value chemical feedstocks from biomass-derived materials. Current catalytic systems for DODH require the use of costly reducing agents that generate stoichiometric amounts of chemical waste. Immobilizing catalysts on electrode surfaces using chemical linking groups eliminates the need for sacrificial reductants. In this work, glassy carbon electrodes were modified with 4’-(3,4-dihydroxyphenyl)-2,2’:6’,2’’-terpyridine to investigate *o*-benzoquinone as a potential linking group for DODH, and possibly for other reactions. Previous studies involving electrodes modified with quinone-containing compounds have primarily been focused on catalyzing the oxidation of NADH; the nature or stability of the ligand-electrode bond was not the primary focus of interest. In this work, the long-term chemical stability of the modified electrodes was determined in pHs ranging from 0 to 15. The ability of the ligand-electrode bond to withstand potential cycling, as well as periods of time at constant potentials, was established through cyclic voltammetry and chronoamperometry experiments. The goal of this work is to find the windows of chemical and electrochemical stability in which the bond between the quinone moieties and the electrode surface can survive, and to eventually determine the usefulness of this linking group as a means of catalyst immobilization for DODH reactions. From the stability studies performed, it has been shown that the bond between the electrode surface and 4’-(3,4-Dihydroxyphenyl)-2,2’:6’,2"-terpyridine is robust in chemical environments from pH 3.5 to pH 8, and that it can withstand potential cycling and survive for extended time periods at constant potentials, as long as the potential range is more cathodic than 0.2 V vs. Ag/AgCl sat. KCl.

Introduction

I. Motivation

As global population and energy consumption continue to grow, the search for sustainable and environmentally benign methods of producing fuels and chemicals is becoming increasingly important.[1,2] For governments and researchers alike, there is much incentive to find sustainable methods of generating high-value chemical feedstocks.

Deoxydehydration (DODH) reactions are a promising means of producing alkenes from biomass-derived polyols, thereby eliminating the need to obtain these alkenes from non-renewable resources such as fossil fuels.[3] Figure 1 shows the formation of a mono-oxo metal diolate, which is reduced by an external reductant. An alkene is produced at the end of the cycle. The external reductant can be either chemical or electrochemical.

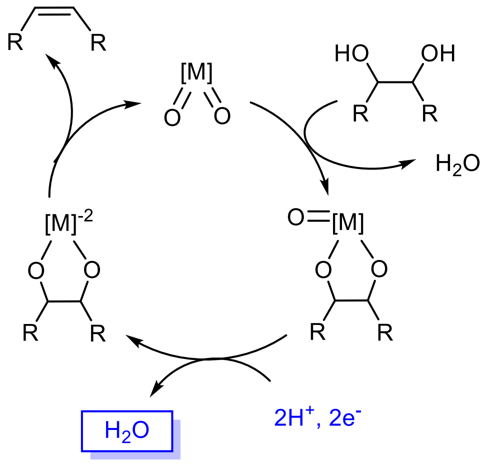


Figure 1. Catalytic DODH cycle generating alkenes from polyols.

Current catalytic systems for DODH require the use of sacrificial chemical reductants.[4] There are several motivations to eliminate the need for these reducing agents. They are costly, they can be challenging to separate from the products of the reaction, and they generate stoichiometric amounts of chemical waste as they are often not recyclable.[2] One such example is shown in Figure 2, where a Mo(VI) catalyst is reduced to Mo (IV) using a sacrificial secondary alcohol as a reducing agent.

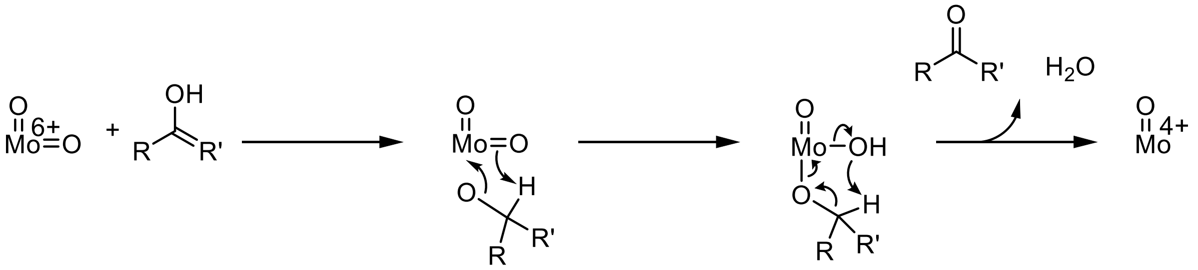


Figure 2. Reduction of Mo(VI) catalyst to M(IV) via sacrificial secondary alcohol.

This work proposes a possible solution to the challenges associated with current catalytic systems used for DODH reactions. This solution is the immobilization of catalysts on electrode surfaces via chemical linking groups, which would provide several advantages over traditional homogeneous catalysis. When a catalyst is tethered to an electrode surface, electrochemical potential can be used as the driving force for the reaction. Species in the reaction can be directly reduced electrochemically, which eliminates the need for chemical reductants and minimizes chemical waste.

Catalyst immobilization also offers greater control of the oxidation state of a species over time. In homogeneous catalysis, a species in solution could interact with a catalyst but diffuse away before becoming fully oxidized or reduced. For an electrochemically driven reaction, the oxidation state of a species at the electrode surface can be observed and controlled by changing the potential at the electrode and observing subsequent changes in current.

Additionally, the tethering of catalytic systems to electrodes could allow for diffusion limited, outer-sphere, multi-electron transfers at the metal center of the catalyst. Surface immobilization opens up new possibilities for control of reactions that require multi-electron transfers and could provide access to reactive intermediates that may be difficult to generate and isolate using traditional redox agents in homogenous solution.

The long-term goal of this project is to establish a library of functional group links and to determine the potential windows and pH ranges in which the bonds between the linking groups and electrodes are stable. With knowledge of the robustness of the ligand-electrode bond in different chemical and electrochemical environments, chemists will have access to information about which linking group can survive a given set of reaction conditions.

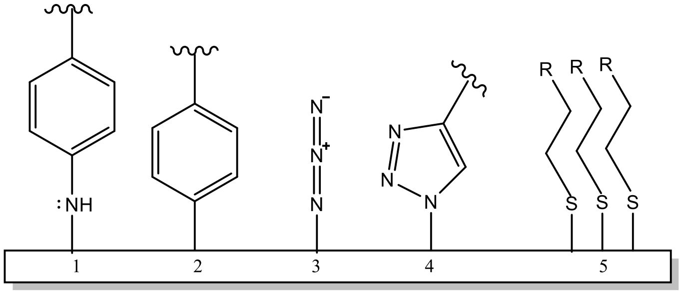


Figure 3. Other possible linking groups for the linking group library.

In this work, a terpyridine compound with an *o*-quinone linking group was examined. The ligand-electrode bond was found to be capable of surviving for extended periods in solutions of various pH values and at electrochemical potentials more cathodic than the quinone/catechol redox couple. There are many other possible linking groups whose bonds to the electrode surface may have different characteristics and might be better suited for other chemical conditions or electrochemical potentials.

Surface immobilization can offer opportunities for electrocatalysis that overcome the limitations of current homogeneous catalysts for DODH reactions. Immobilization of catalysts on electrode surfaces could allow DODH reactions to become industrially feasible, providing an environmentally benign means of generating feedstocks for fuels and high-value chemicals.

II. Background

The linking group investigated in this work is an *o*-quinone linking group. Figure 4 shows the reduced form of the compound, referred to as catechol, undergoing a proton-coupled electron transfer (PCET) reaction in which two protons and two electrons are eliminated from the catechol to produce the oxidized form of the compound, *o*-benzoquinone. This is the redox event that is observed in all of the cyclic voltammograms shown throughout this thesis.

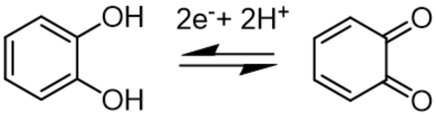


Figure 4. Schematic of PCET between catechol and quinone.

In biochemistry, ubiquinone, also referred to as coenzyme Q or NADH dehydrogenase, is a coenzyme that contains an orthoquinone moiety in addition to a long, hydrophobic carbon tail. The quinone moiety is redox active and participates in electron transfer in mitochondrial transport chains. In the human body, ubiquinone oxidizes NADH to form NAD^+, which is an intermediate in the production of ATP via the citric acid cycle.[5]

Studies involving ubiquinone, or other quinone-containing compounds, are usually focused on catalyzing the oxidation of NADH. Unsubstituted *o*-benzoquinone has previously been electrodeposited onto glassy carbon electrodes in the form of redox-active films that catalyze the oxidation of NADH.[6] A schematic of this reaction is shown in Figure 5, where a quinone group undergoes a two-proton, two-electron reduction, oxidizing NADH and yielding NAD^+.

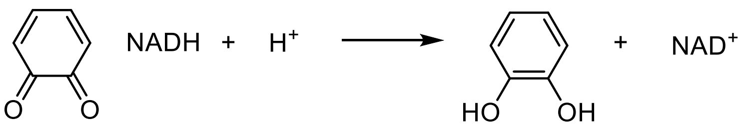


Figure 5. NADH oxidation catalyzed by o-benzoquinone.

Nearly all of the previous work done with immobilized quinones has been for this purpose. Metal complexes with quinone moieties have also been used to modify electrodes for the oxidation of NADH. Several metal-substituted terpyridine compounds have been synthesized as shown in Figure 6, and some of these compounds have been deposited onto platinum and glassy carbon electrode surfaces and have been shown to be active electrocatalysts for NADH oxidation.[8]

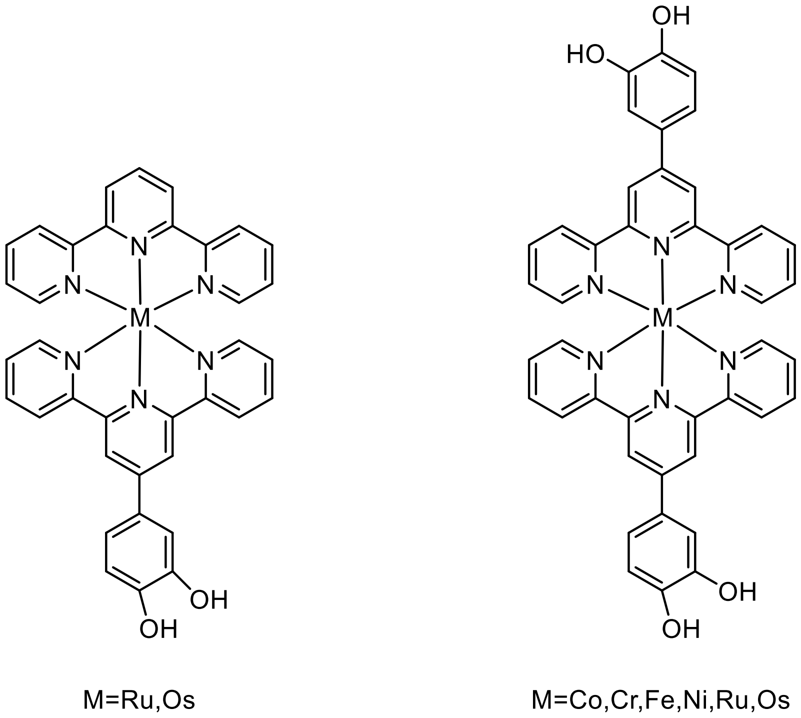


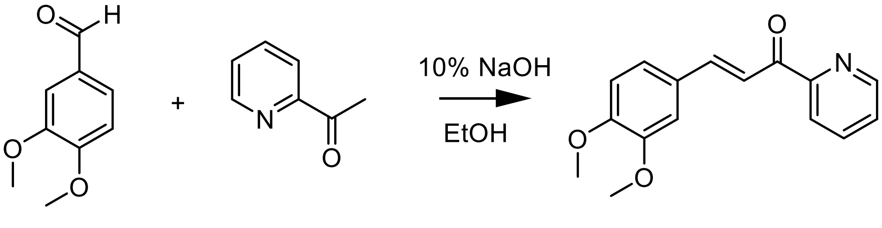
Figure 6.Catechol pendant metal complexes were studied at GCE and Pt surfaces.

No long-term aqueous stability studies have been performed on these linking groups to determine their suitability for industrial scale catalyst immobilization. No rigorous cycling or chronoamperometry studies have been performed to our knowledge. Deposition of substituted quinone compounds has been performed in acetonitrile in previous studies; in this work, it was shown that deposition of a substituted quinone compound is also possible in aqueous media. This work examines the electrodeposition of 4’-(3,4-dihydroxyphenyl)-2,2’:6’,2’’-terpyridine onto glassy carbon electrodes for catalyst immobilization for a reaction other than NADH oxidation and seeks to gain insight into the range of chemical and electrochemical environments in which the ligand-electrode bond is stable. The quinone linking group has the potential to be used in catalyst immobilization with a broader scope than has been previously thought. The stability studies performed in this thesis have shown that this linking group forms remarkably stable bonds with the electrode surface and may one day be implemented as a robust linking group to immobilize catalysts in a variety of reactions.

Experimental

I. Synthesis

Base-Catalyzed Aldol Condensation



1

Figure 7. Base-Catalyzed Aldol Condensation.

The first step in the synthetic process was the production of l-(2-Pyridyl)-3-(3,4-dimethoxyphenyl)propen-l-one, which is labeled as compound 1. 3,4-dimethoxybenzaldehyde and 10% NaOH were combined in ethanol and chilled in an ice bath. Chilled acetylpyridine was added dropwise to the mixture which was allowed to stir for two hours before filtering and washing with ethanol. This reaction yields a light-yellow powder in 60% yield.[7,9]

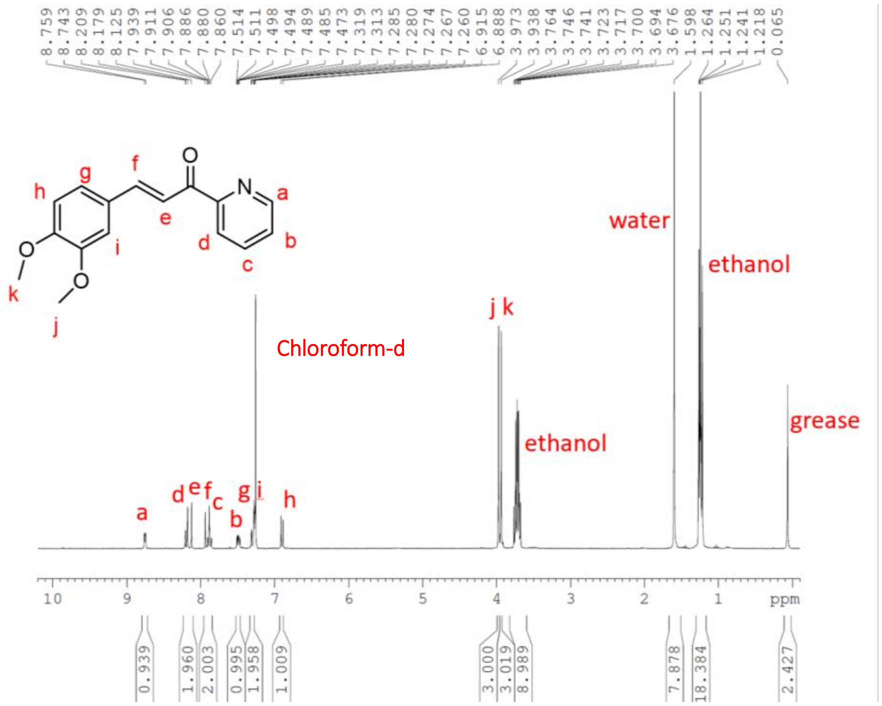
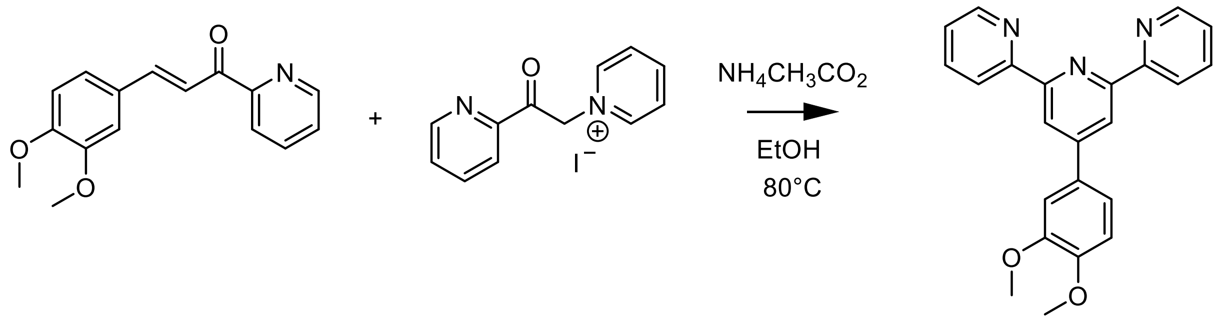


Figure 8. NMR spectra of compound 1 with labeled peaks.

Krönke Pyridine Synthesis



1

2

Figure 9. Krönke pyridine reaction to produce compound 2.

Compound 2, 4'-(3,4-dimethyoxyphenyl)-2,2':6,2"-terpyridine, was synthesized via the Krönke pyridine synthesis. A 1:1:10 ratio of pyridinium iodide, compound 1, and ammonium acetate were combined in ethanol and refluxed for 24 hours. The product was filtered, extracted with chloroform, and recrystallized in methanol to yield a dark teal solid at 30% yield.[7,9]

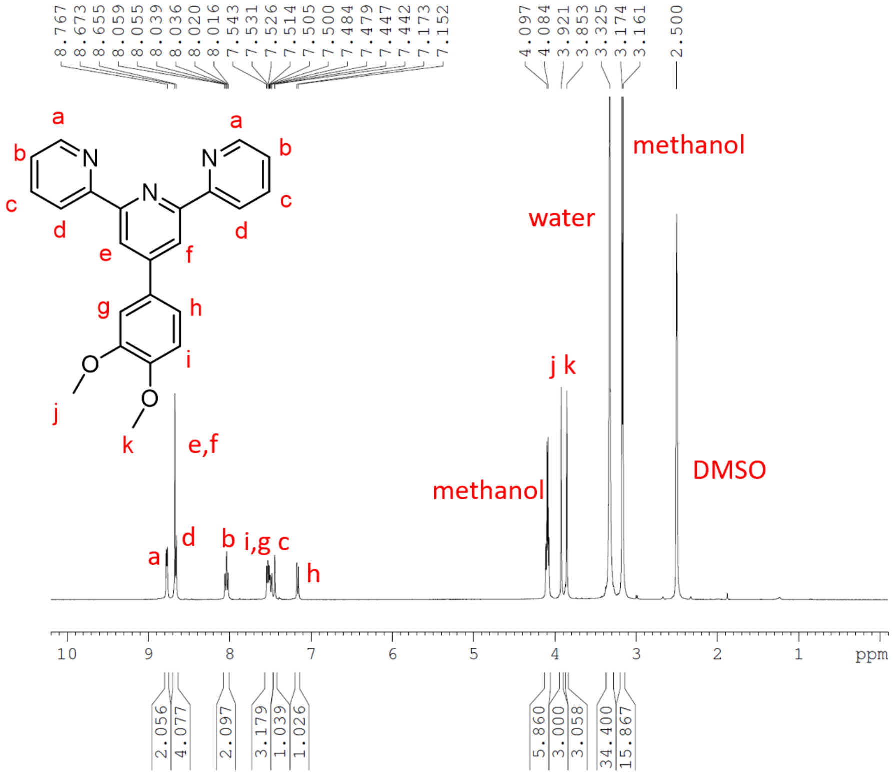
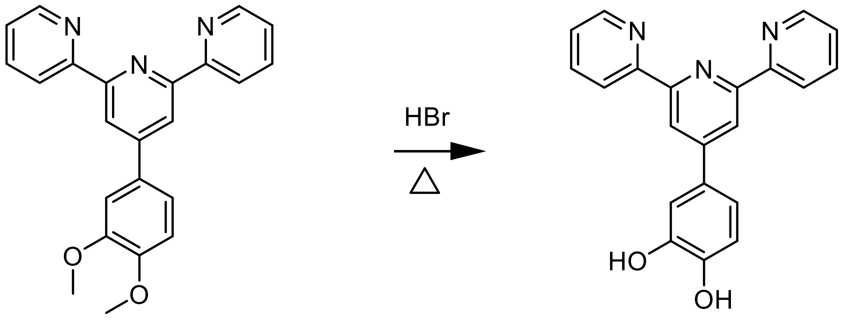


Figure 10. NMR spectra of compound 2 with labeled peaks.

Demethylation



2

3

Figure 11. Demethylation of compound 2 to form compound 3.

The final step was the deprotection of the methoxy groups to form compound 3, 4’-(3,4-dihydroxyphenyl)-2,2':6',2''-terpyridine. Compound 2 was refluxed in 48% HBr for 6 hours. After reflux, the reaction mixture was cooled and neutralized with 10% NaOH. The product was then filtered and washed with water to yield a light brown powder in 90% yield.[7]

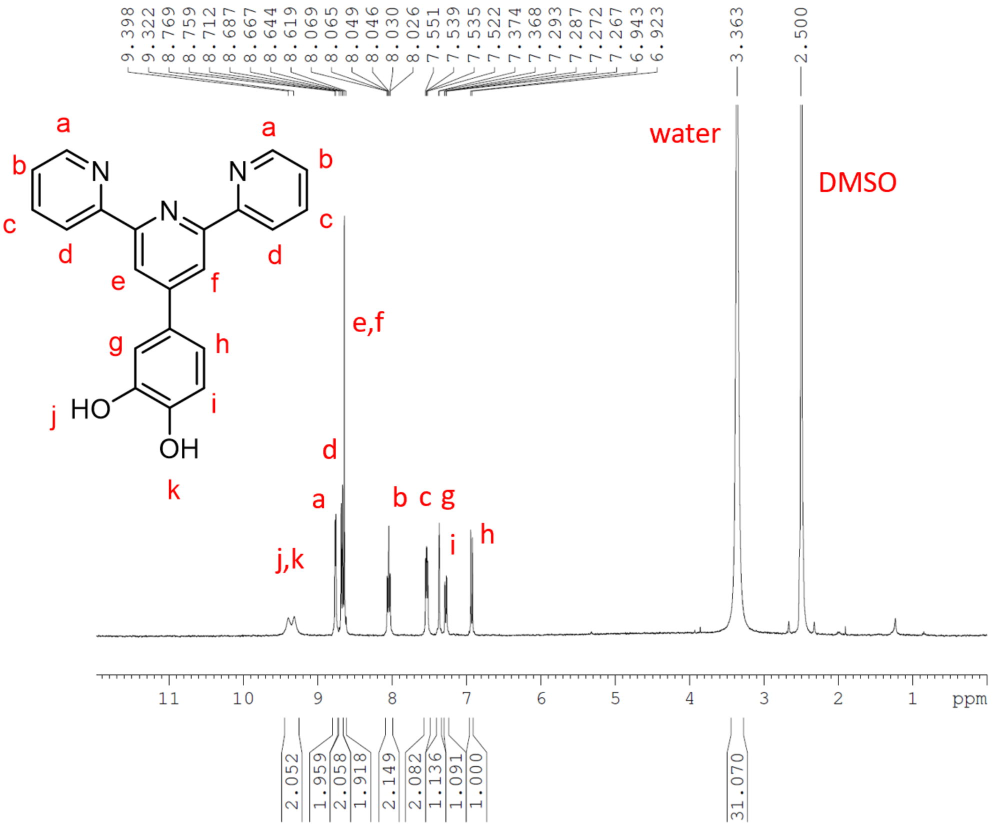


Figure 12. NMR spectra of compound 3 with labeled peaks.

II. Electrochemical Deposition

Preconditioning

For all electrochemical experiments discussed in this work, a 3-electrode cell with a separate counter compartment was used. Glassy carbon working electrodes were polished in alumina slurries of 1, 0.3, and 0.05 microns before each experiment. The counter electrode was platinum mesh, and the reference electrode was Ag/AgCl in saturated KCl.

Oxidative preconditioning was performed in two steps prior to every deposition. In the first step, as shown in Figure 13, the electrode was held at +1.2 V vs. Ag/AgCl for 5 minutes in 1M KOH. Holding the electrode at a highly oxidative potential in a basic chemical environment strips any impurities from the electrode surface. This process also increases the number of oxidative surface groups and improves the reactivity of the electrode surface with the deposited compounds. Oxidative preconditioning is especially crucial with substituted quinone complexes.[6]

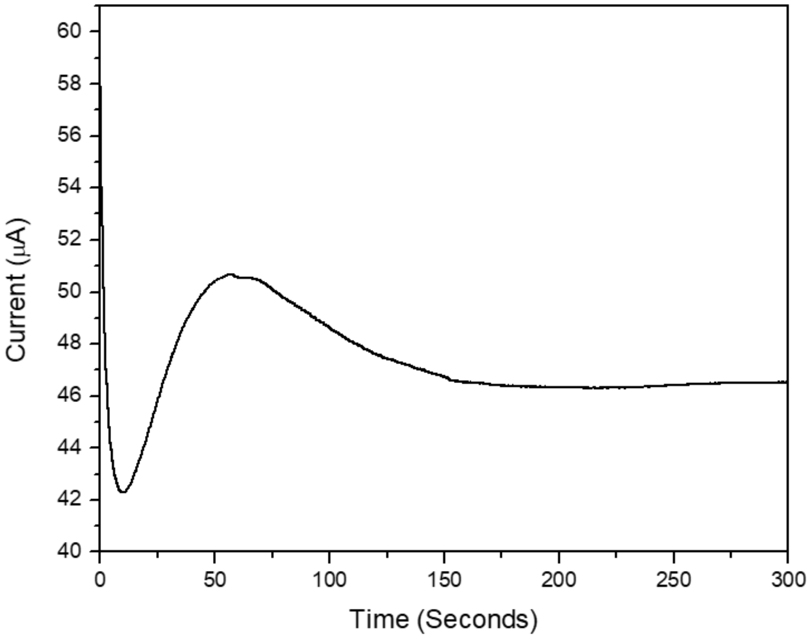


Figure 13. Chronoamperometry of an unmodified electrode held at 1.2 V vs. Ag/AgCl sat. KCl.

The peak that appears in Figure 13 shows that impurities are being oxidized from the electrode surface. Once these impurities are gone, and the oxidation of any surface groups of the electrode is complete, the current decreases.

The second preconditioning step takes place in 0.1 M pH 7.5 phosphate buffer with no other compounds present in the solution. The potential is cycled from -0.2 V to 1 V vs. Ag/AgCl. The cycling is performed for 5 minutes to increase the stability of the electrode surface. It can be seen from the CVs in Figure 14 that with continuous cycling the CVs become more consistent, with less change in current between cycles. With continued cycling, the oxidative current decreases as the electrode surface becomes more uniform.

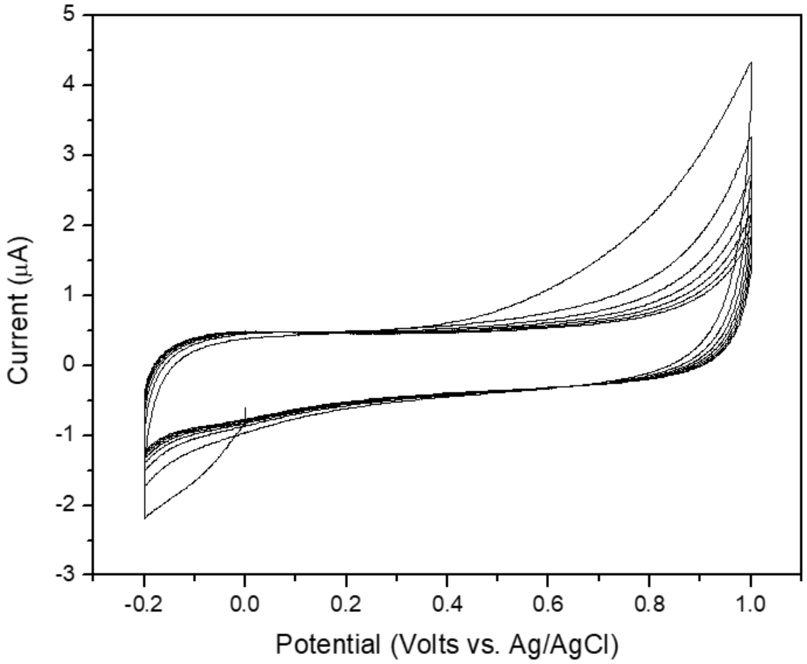


Figure 14. Potential cycling from -0.2 V to 1 V vs. Ag/AgCl sat. KCl.

Once preconditioning is completed, 10 mg of compound 3 is added to the deposition bath, and the electrode undergoes potential cycling, which will be discussed in detail in the following section. It should be noted that the compound is only sparingly soluble in water, but it is soluble enough for the compound to deposit.

Deposition via Potential Cycling

Compound 3 was deposited onto glassy carbon electrodes through potential cycling in a 0.73 mM deposition bath containing aqueous 0.1 M pH 7.5 phosphate buffer. Electrodes were modified by cycling the potential 14 times from -0.2 V to 0.5 V vs. Ag/AgCl sat. KCl. The solution was stirred throughout the deposition to facilitate the transport of the compound to the electrode surface. A total of 26 depositions were performed throughout this work. One deposition is shown below in Figure 15. As the cycle number increases, the peak current also increases, indicating that more material is building up on the electrode surface as the deposition progresses.[6]

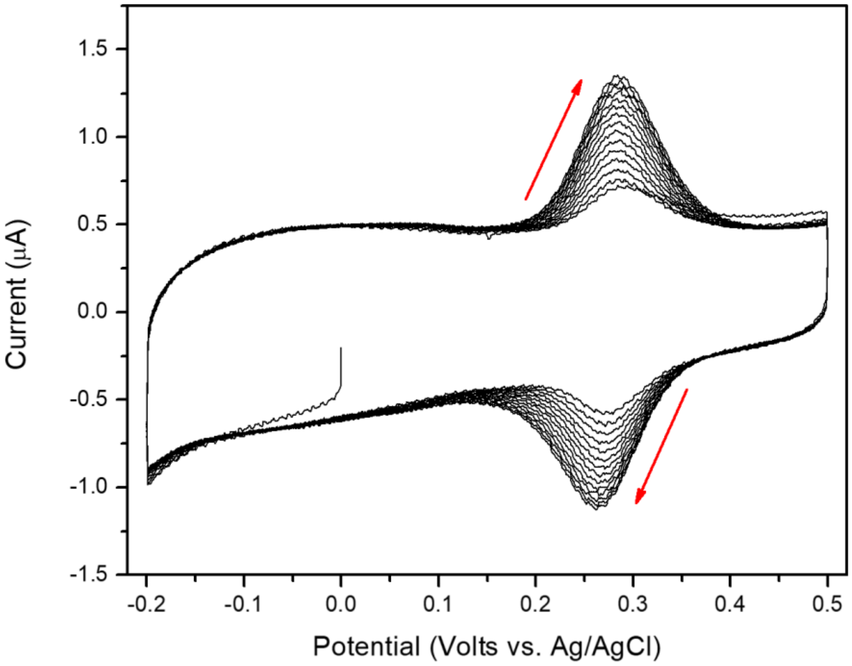


Figure 15. For electrode modification, the potential is cycled 14 times from -0.2 V to 0.5 V.

After potential cycling in the deposition bath, the electrode is removed from the cell and rinsed thoroughly with acetone. The modified electrode is sonicated for 5 minutes in acetone and water, respectively, and rinsed thoroughly with acetone and water between the sonications and with water once the last sonication is completed. This sonication process removes any mechanically adhered material from the electrode.[6]

Figure 16 shows the shift of the anodic and cathodic peak potentials with increasing cycle number during deposition. The cathodic peak shifts negatively throughout the deposition, which indicates that the deposition is happening on the cathodic sweep. This is consistent with quartz crystal microbalance experiments performed in acetonitrile with substituted quinone compounds in the literature.[8] The anodic peak remains relatively unchanged, except for a sharp shift after the first cycle.

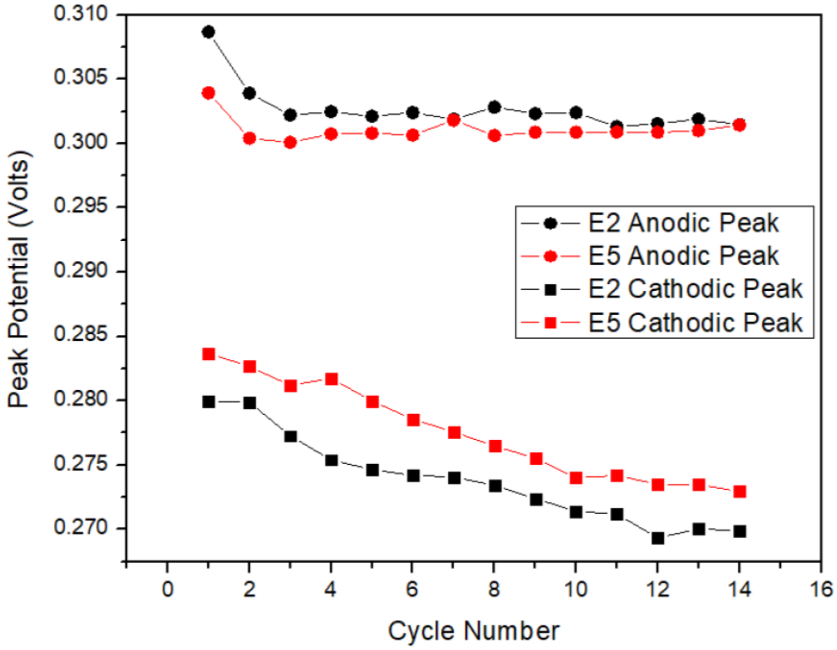


Figure 16. Shift of anodic and cathodic peak potentials throughout depositions.

The shift of the anodic peak potential after the first cycle could be explained in the following way: the deposition process begins at 0 V and sweeps negative to -0.2 V before reversing direction and sweeping anodically to 0.5 V. If the compound is deposited throughout the reductive sweep, no material has been deposited when the first anodic peak is observed. On the first full cathodic sweep, material is deposited on the electrode surface. When the second anodic peak is observed, the newly deposited material is being oxidized, and the deposited material may have a slightly different peak potential that the compound in solution, which is why a sizable shift in anodic peak potential is seen on the second cycle.

Peak separation also showed a notable decrease after the first deposition cycle as a result of the shifting anodic peak potential. After this sharp decrease, peak separation increased slightly with increasing cycle number as the kinetics were changed upon deposition. For the two depositions shown in Figure 17, the increase in peak separation was slightly less than 10 mV from the second to the last cycle. Of the 26 depositions done throughout this work, the total increase in peak separation varied depending on the electrode that was used. For certain depositions, the peak separation remained nearly unchanged, and for others, there was an increase of around 30 mV. In general, peak separation was around 30 mV for newly modified electrodes, corresponding to a reversible two-electron transfer.

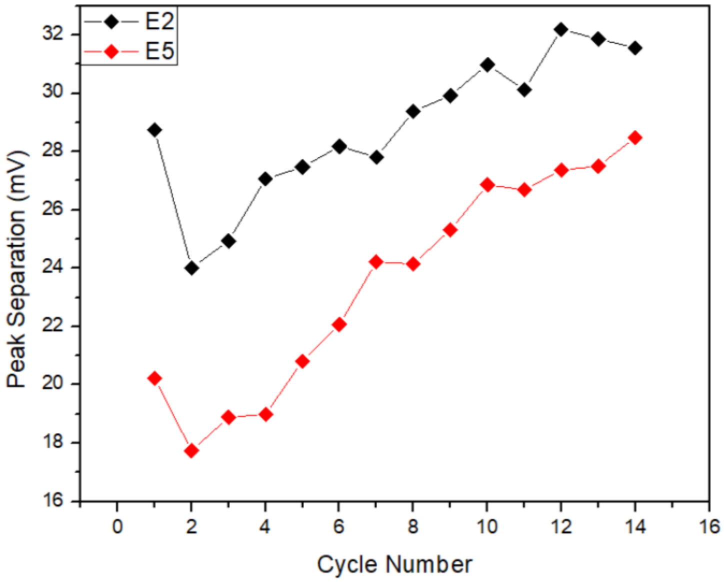


Figure 17. Peak separation vs. cycle number for two different depositions.

Previous literature on the modification of electrode surfaces with quinone compounds does not address the mechanism of deposition or the nature of the bond between the ligand and the electrode surface. While the work in this thesis does not provide unequivocal proof of the mechanism of deposition, observations from the CV data and knowledge about the possible oxidation states of the compound provide insight into what may be happening throughout the deposition.

A square scheme of the catechol and *o*-benzoquinone system is shown in Figure 18. It can be seen that there are a variety of species that can exist at specific pHs and potentials.[10] Within rows of the square scheme, electrons are added moving to the right, and protons are added moving down the columns.

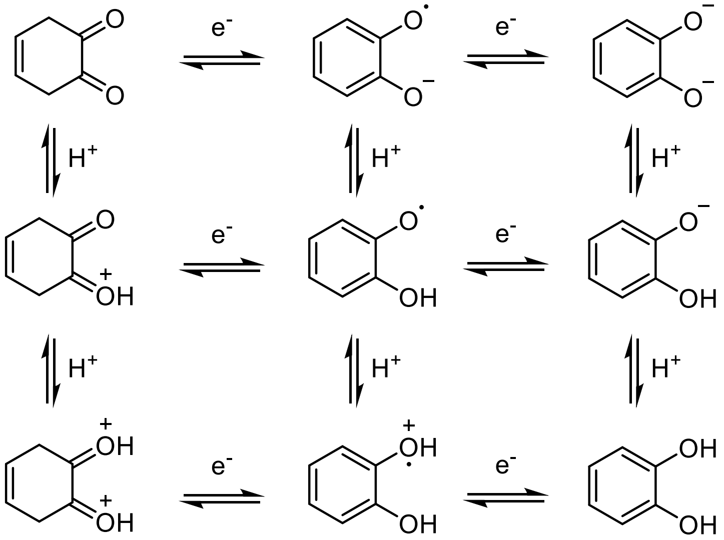


Figure 18. Square scheme of PCET mechanism.

At pH 7.5, the most likely radical intermediate to form is a positive charged hydroxyl radical. Figure 19 shows a possible deposition mechanism that would result in a covalent bond between the ligand and the electrode surface on the reductive sweep. Once the ligand is bound to the electrode, the protons of the hydroxyl radical would no longer be bound to the oxygens but would be present nearby in solution.

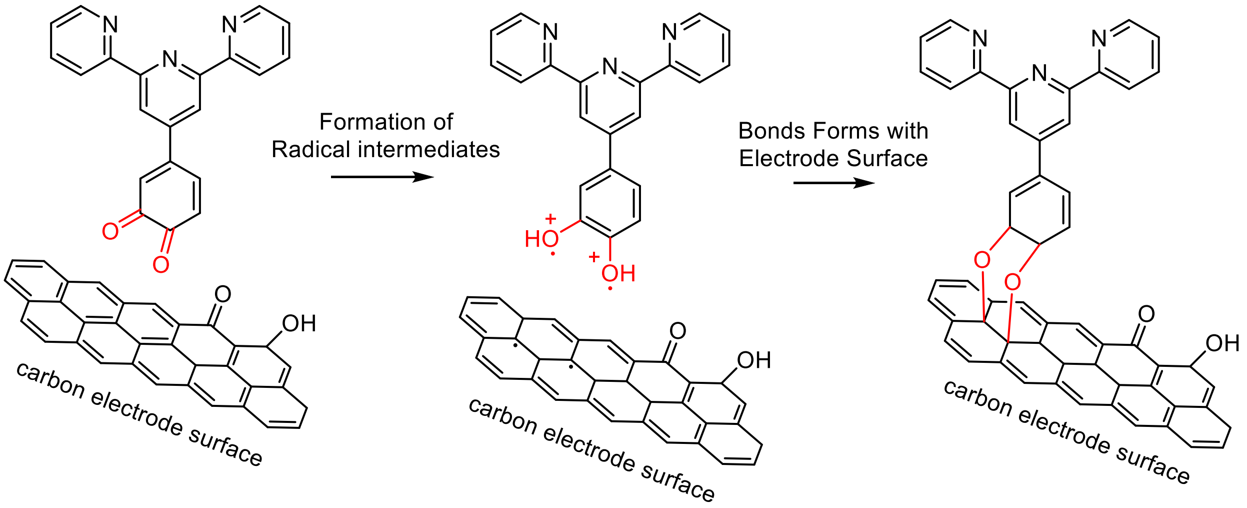


Figure 19. Possible deposition mechanism.

When the modified electrode undergoes potential cycling, the covalent bond would be broken in the anodic sweep, as shown in Figure 20. This could explain why material is stripped from the electrode at oxidative potentials, and why peak height decreases with continuous potential cycling at more positive potentials.

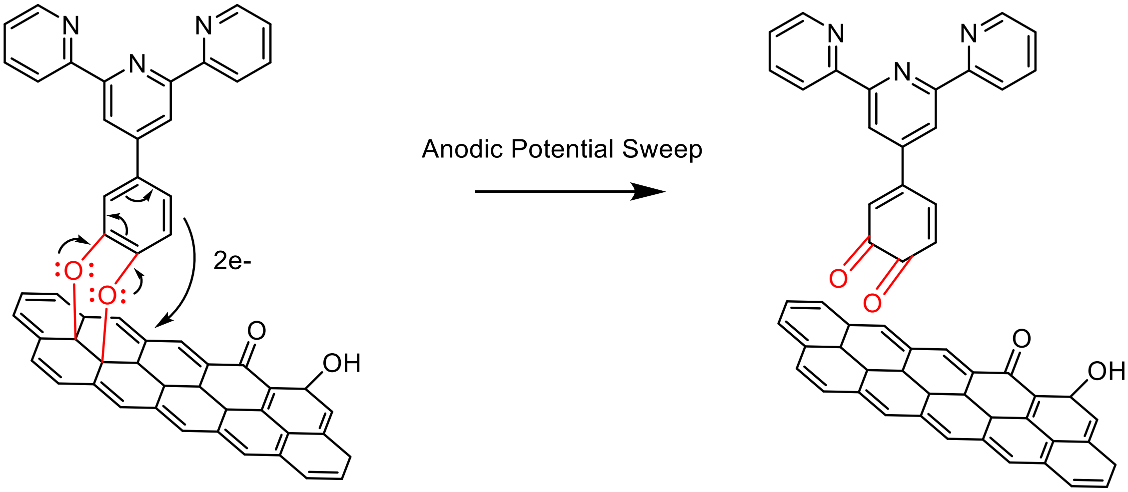


Figure 20. Breaking of the covalent bond upon anodic sweep.

It is also possible that the ligand is very strongly adsorbed to the electrode surface. Figure 21 shows how the ligand may be adsorbed to surface groups on the GCE, as well as the mechanism of the two-proton, two-electron oxidation of the adsorbed species. Peak separations around 30 mV are consistent with expectations of a two-electron transfer. The adsorption is weakened upon oxidation of the modified electrode, which is consistent with the data.

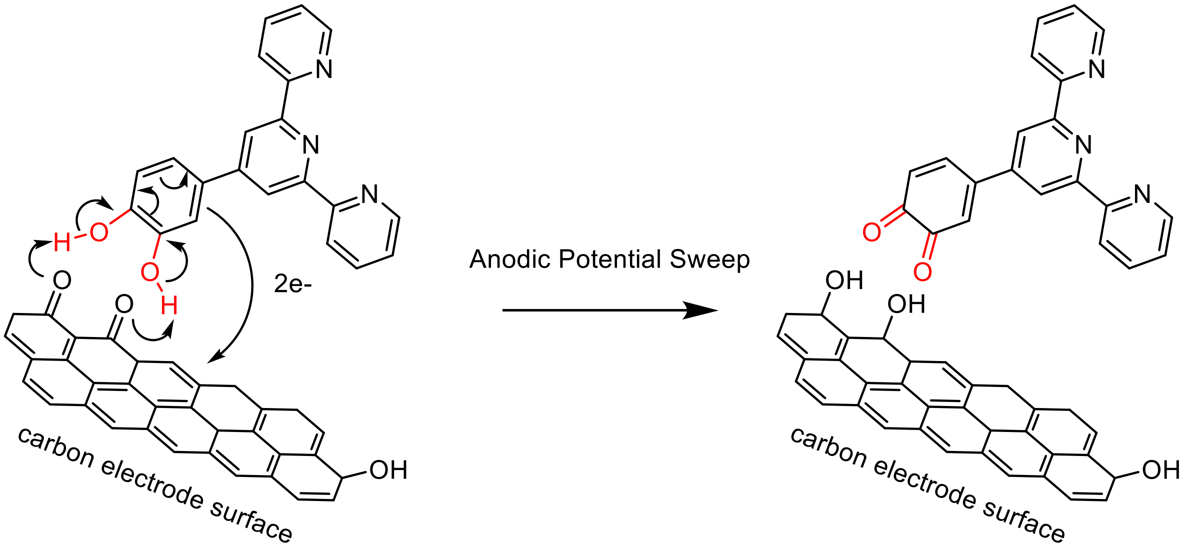


Figure 21. Two-proton, electron oxidation of an adsorbed species.

Whether the ligand is covalently bound to the electrode surface or very strongly adsorbed, the modified electrodes withstand 5 minutes of sonication in acetone, in which the ligand is very soluble, and sonication in water, multiple cycles for scan rate studies, and, as will be discussed in more detail, extended time periods at a variety of pHs and electrochemical potentials.

Scan Rate Studies

Following sonication and rinsing of the newly modified electrodes, a scan rate study is performed in fresh pH 7.5 phosphate buffer. Scan rate studies help to determine the nature of the redox event that is taking place. As shown by the equations in Table 1, for a diffusive event, peak current is proportional to the square root of the scan rate, while for a surface event, the peak current is directly proportional to the scan rate.[11]

Table 1. Equations describing the behavior of peak current for both diffusive and surface events.

Diffusive Event	**Surface Event**
$i_p = (2.69 * 10^5) n^{\frac{3}{2}} A D_o^{\frac{1}{2}} C_o^* \boldsymbol{v}^{\boldsymbol{\frac{1}{2}}}$	$i_p = \frac{n^2 F^2}{4RT} \boldsymbol{v} A \Gamma_o^*$

The buffer solutions used for scan rate studies did not contain compound 3. The redox couples observed in Figure 22 come only from the compound on the modified electrode surface.

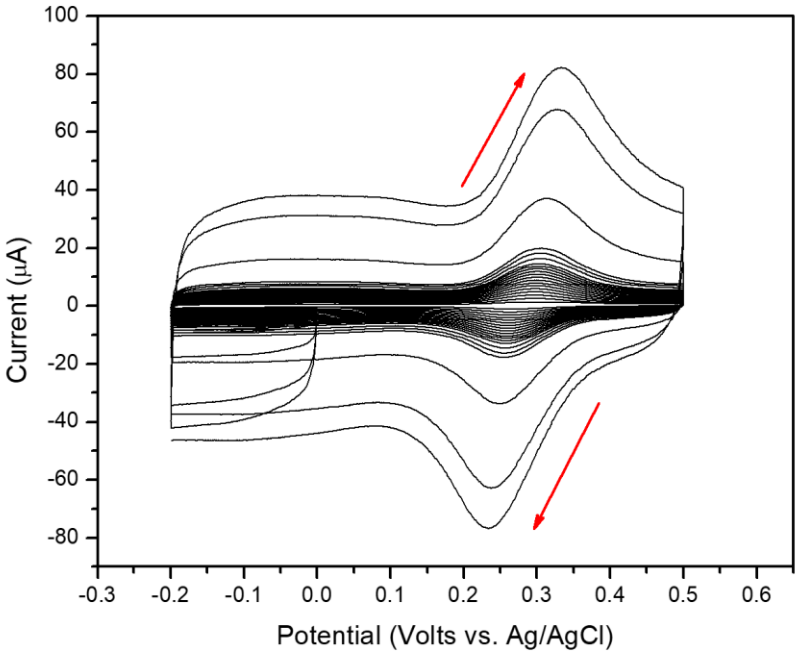


Figure 22. The scan rate was varied from 50 to 5000 mV/s in fresh pH 7.5 phosphate buffer.

From Figure 22, the peak current was obtained and plotted versus the scan rate. A linear relationship results and is shown in Figure 23. For every deposition performed, a linear relationship between peak current and scan rate was found. As demonstrated by the equations in Table 1, this is what is expected for a surface-modified electrode. This result indicates that compound 3 is bound or very strongly adsorbed to the electrode surface. To demonstrate the fact that the increase in peak current is directly proportional to the scan rate, a plot of peak current vs. the square root of the scan rate is shown in Figure 24 for comparison. The relationship is nonlinear, further validating the fact the redox event observed in the CVs is a surface event and that the electrodes have been successfully modified.

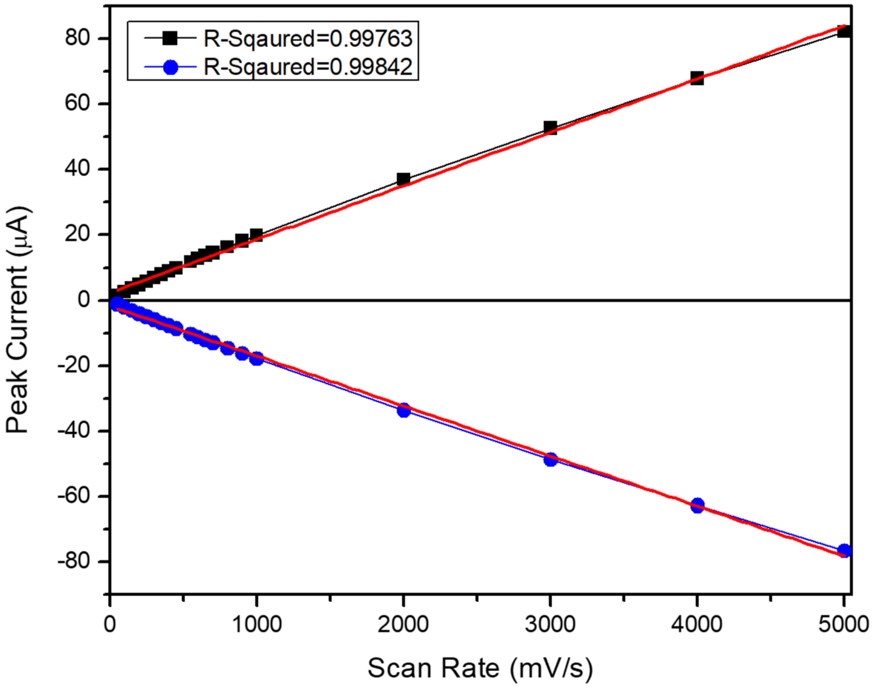


Figure 23. Peak current vs. scan rate displays a linear relationship.

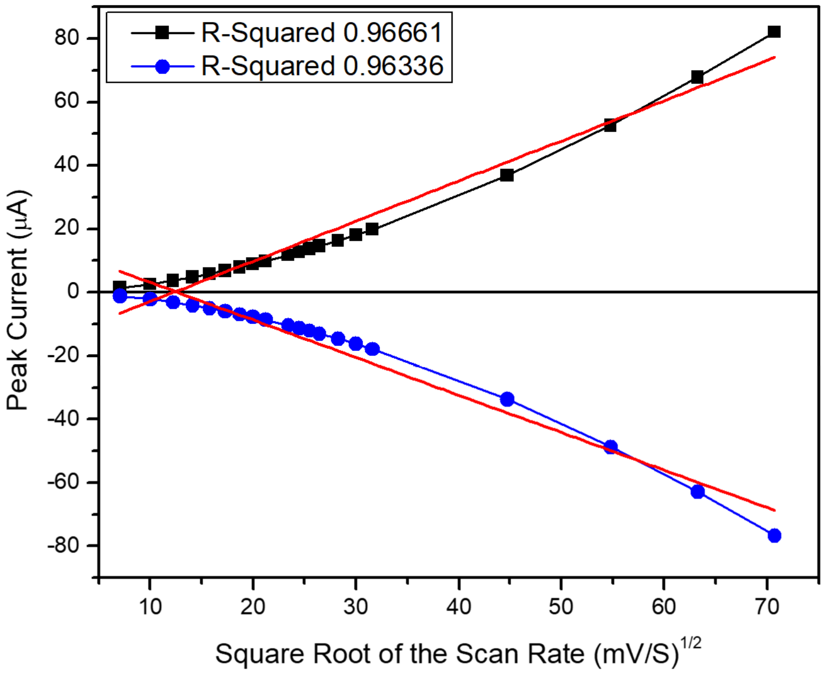


Figure 24. Peak current vs. the square root of the scan rate does not show a linear relationship.

III. Stability Studies

Following deposition, modified electrodes were placed in buffer solutions to test chemical stability over time. Electrodes were placed in 0.1 M solutions of pHs ranging from 0 to 15 with continuous stirring and frequent replacement of buffer solutions. A CV was taken periodically to monitor the presence of the ligand on the electrode surface. For these CVs, the electrodes were removed from their pH solutions, rinsed, and placed in a cell with 0.1 M pH 7.5 phosphate buffer.

Two sets of chemical stability experiments were performed. The first set of experiments was performed with solutions of 11 different pH values ranging from 0 to 15. For intermediate pH values, between pH 4.5 and 7.5, one cycle was taken every five days, on average, until no material remained on the electrode surface. In these studies, the decrease in peak area was more rapid towards the beginning of the study and slowed as time went on. For extreme pH values below 2 and above 11, CVs were taken the day following the start of the study. In most cases, no sign of quinone/catechol redox couple was visible after 24 hours.

An example of a stability study from the first set of experiments is shown in Figure 25. The electrode was placed in a bath of 0.1 M pH 7 phosphate buffer for 47 days, with continuous stirring and frequent replacement of the buffer solution. While this study was useful in showing that material remains on the electrode after an impressive amount of time in buffer solution, it is clear that the most substantial decrease in peak area is seen in the first 7 days. No CVs were taken between days 1 and 7. CVs were not taken to monitor stability at regular time intervals. The second set of experiments was performed to more closely monitor the rate of degradation of the material within the first seven days at regular intervals, with multiple CVs taken every day.

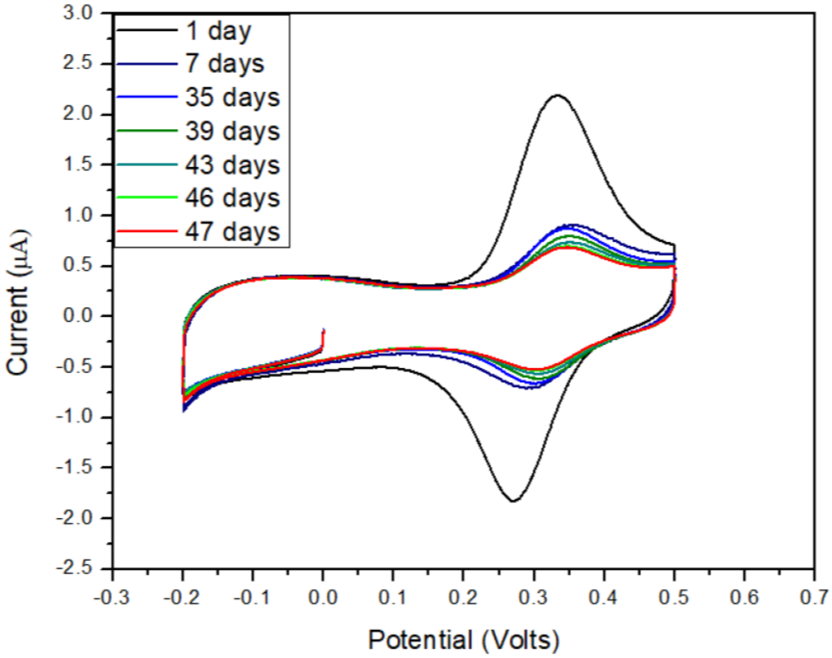


Figure 25. Stability study in pH 7 solution over 47 days with infrequent monitoring.

The second set of experiments was performed at 3 pH levels: 3.5, 7.2, and 8. These pHs were determined from the previous set of experiments to be the lower, middle and upper end of the range in which the modified electrodes were stable. It was desired to observe the rate of degradation of the material in the first days of the study more closely by taking more frequent CVs, both to establish the rate of degradation on shorter time scales and to visually observe this degradation with a greater number of CVs. The electrodes were monitored every day, with several CVs taken a short time apart each day. For clarity, only 8 of these CVs are shown in Figures 26-28.

CVs taken to monitor stability were always taken in fresh phosphate buffer with a pH of 7.5. Percent decrease in peak area per day was calculated as a measure of the relative chemical stability of the ligand-electrode bond in various chemical environments over time. For the second set of experiments, the percent decrease in peak area per day is greater both because the rate of decay is greater within the first week of the study, and also because they were monitored more frequently. The effect of cycling on the peak area will be discussed further in subsequent sections.

Figure 26 shows the CVs taken to monitor the stability of a modified electrode for 6 days in pH 3.5. For the first 24 hours, the peak is still prominent with little change in peak area. After 24 hours, as the peak area decreases, the shape of the CV becomes more resistive, likely due to changes in chemical composition at the electrode surface at this acidic pH. The percent decrease in peak area per day was 21%.

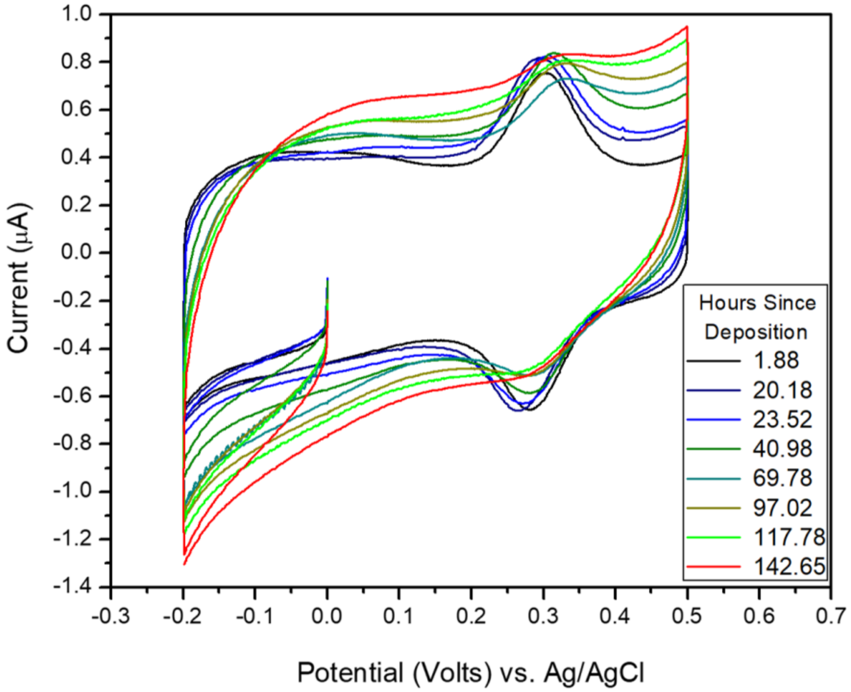


Figure 26. Stability study of a modified electrode in pH 3.5 solution.

Figure 27 shows a similar stability study at pH 7.2 for 8 days. While the peak area decreases over time, the shape of the rest of the CV remains largely unchanged. The percent decrease in peak area per day was found to be 11.6%.

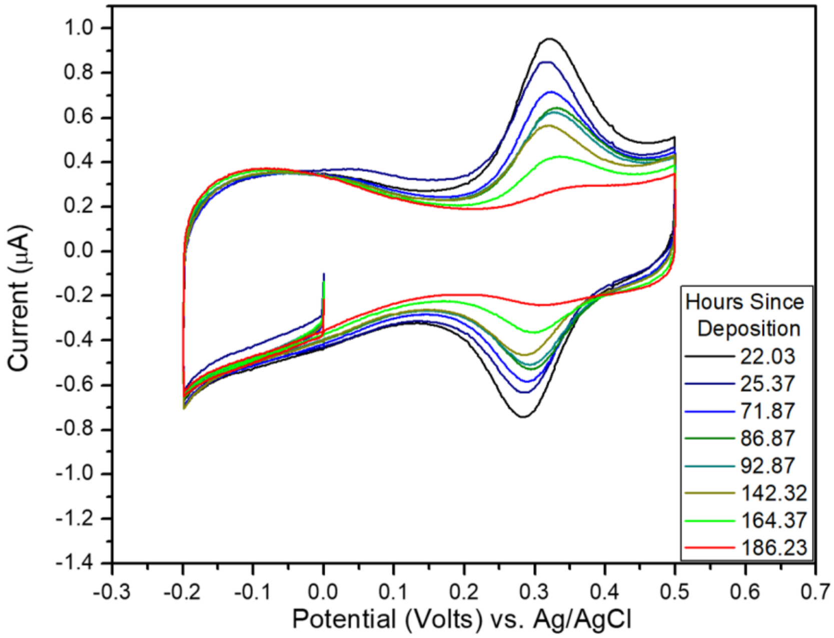


Figure 27. Stability study of a modified electrode in pH 7.2 solution

Figure 28 shows a chemical stability study at pH 8. The results are relatively similar to those at pH 7.2. There was an average of 10% decrease in peak area per day.

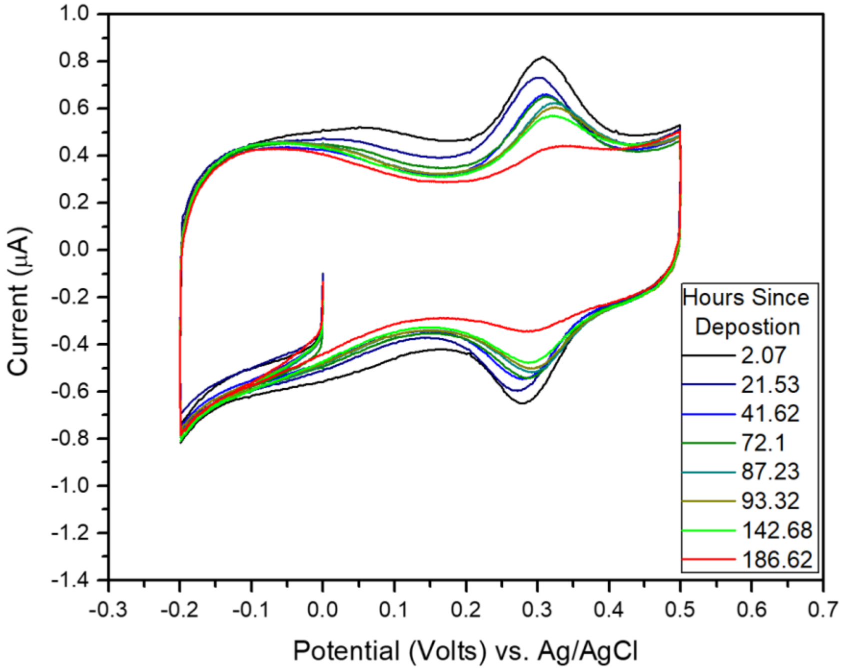


Figure 28. Stability study of a modified electrode in pH 8 solution

In the overlays of CVs from the stability studies, slight changes in peak potential can be seen. These changes in peak potential do not appear to show a consistent trend, such as a peak shifting in one direction due to changes in the surface chemistry over time. These slight shifts are probably due to minor changes in cell configuration. The positioning of the reference electrode may have been slightly different for stability checks performed on different days, despite efforts to note the position of all electrodes and to keep these positions constant throughout the study.

At pHs higher than 9, it is well known that quinones undergo chemical changes. While stability studies were performed at extremely high and low pHs, stability is not expected above pH 9 or below a pH of 2. In basic solutions, oxygen anions can form and react with hydroxyl ions to form 1,2,4-trihydroxy benzene.[10] Quinones are known to be unstable in concentrated acid. Semiquinone radical species can form react with one another to form quinone and catechol in solution.[10]

The stability studies show that the deposited material remains on the electrode surface for extended periods in a range of chemical environments. These studies should be repeated to ensure that results are consistent and reproducible. However, the initial results of these studies suggest that *o*-quinone linking groups could be capable of tethering compounds to the surface of an electrode for extended time periods at pHs within the range of 3.5 to 8.

Results

I. Chemical Stability

All of the chemical stability experiments performed are summarized in Table 2.

Table 2. Summary of all chemical stability studies performed.

pH	Buffer Solution	Duration (Days)	Average % decrease in peak area per day
0	1 M HCl	1	71%
1.75	HCl/KCl	1	65%
2.13	1M Acetic Acid	10	9%
3.5	0.1 M Acetic Acid/Sodium Acetate	4	21%**
4.5	0.1 M Acetic Acid/Sodium Acetate	20	4%
5.5	0.1 M Acetic Acid/Sodium Acetate	19	5%
5.5	0.1 M Acetic Acid/Sodium Acetate	20	4%
6.3	0.1 M Monobasic/Dibasic Potassium Phosphate	34	3%
7	0.1 M Monobasic/Dibasic Potassium Phosphate	47	1.8%
7.2	0.1 M Monobasic/Dibasic Potassium Phosphate	8	11.55%**
7.5	0.1 M Monobasic/Dibasic Potassium Phosphate	60	1.39%
8	0.1 M Monobasic/Dibasic Potassium Phosphate	8	10%**
10.7	0.1 M NaOH/Bicarb	3	32%
14	1M NaOH	3	29%
15	1M KOH	1	100%

*** For these studies, the period of the stability study was shorter, and the frequency of observation by CV was far higher than for the other studies, leading to higher average percent decrease per day.*

The data from Table 2 is represented graphically in Figure 29. By plotting the average percent decrease in peak area per day vs. pH, the range of highest stability can be seen.

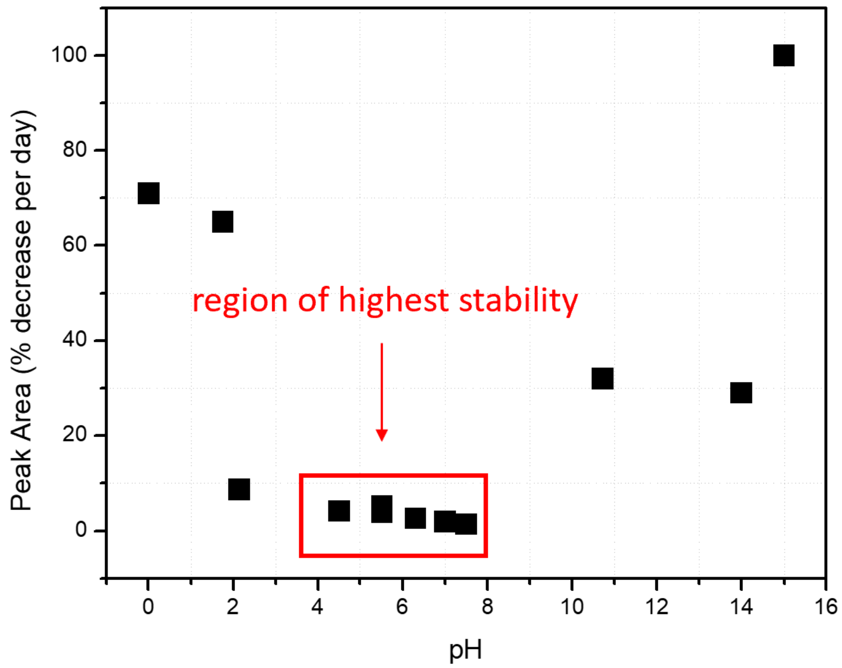


Figure 29. Average percent decrease in peak area per day vs. pH (infrequent observation).

The smallest average percent decrease in peak area per day, indicating the highest stability of the ligand-electrode bond, was observed at pHs between 4.5 and 8 for long-term stability studies. Electrodes were left in solution until no material was observed on the surface by CV. At extreme pHs, such as in 1 M HCl and 1M KOH, the material is stripped off within a day or two. Quinones are known to undergo chemical transformations above pH 9 as well as in acidic solutions, and this is reflected in the more extreme changes in peak area at high and low pH levels.

In Figure 30, results from the long-term studies in Figure 29 are compared with results from the three shorter-term studies previously discussed. The red points on the graph represent the second set of stability experiments where electrodes were monitored every day, with around five cycles per day, taken about an hour apart for a one week.

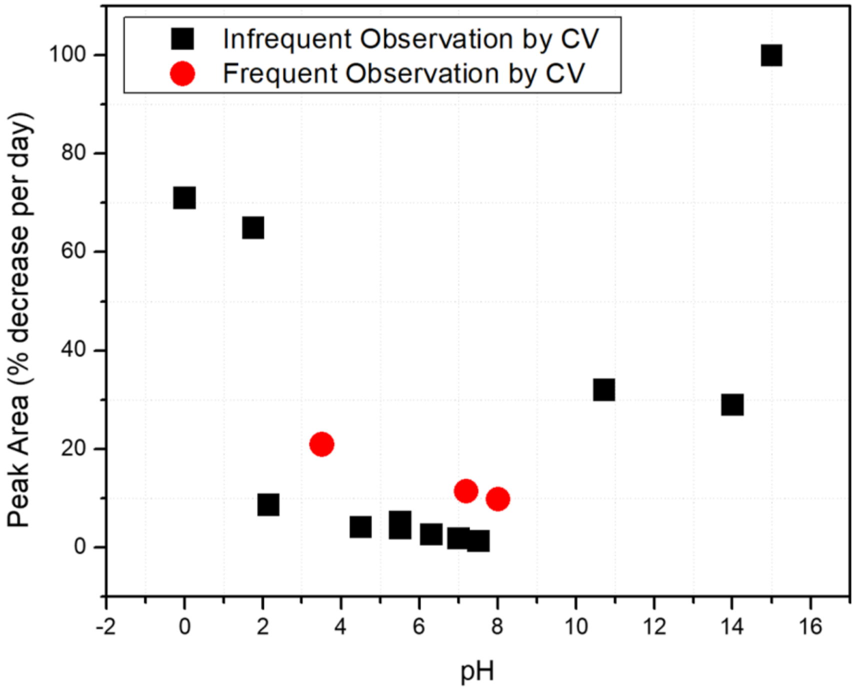


Figure 30. Comparison of electrodes frequently observed for short duration studies (red) and infrequently (black) for extended duration studies.

In addition to having a higher rate of peak area decrease in the first week of the studies, more frequent observation of the electrodes can lead to a higher rate of degradation. The ligand-electrode bond is not stable at oxidative potentials, and therefore material is lost from the electrode surface during the anodic sweep of CVs taken to monitor stability. For this reason, it is desired to have a metal reporter coordinated to the terpyridine compound whose redox potential is more negative of the quinone/catechol redox couple. Using the metal redox couple to monitor stability would leave the quinone/catechol species undisturbed so that observation of the electrode would not affect the ligand-electrode bond.

II. Cycling Stability

Cycling experiments were performed to determine the ability of the ligand-electrode bond to withstand potential cycling. First, a modified electrode was sonicated, scan rate studies were performed, and the electrode was placed in a cell containing 0.1 M pH 7.5 phosphate buffer in the absence of compound 3. The potential was cycled in the deposition window, from -0.2 V to 0.5 V.

On the macro-command line, the potentiostat was programmed to cycle the potential in this range for 34 cycles, then to stop and take a single CV to monitor the change in peak area. This process was repeated 20 times. The single CVs obtained from this experiment are displayed below. It can be seen from Figure 31 that cycling within the deposition window leads to a steady decrease in peak area.

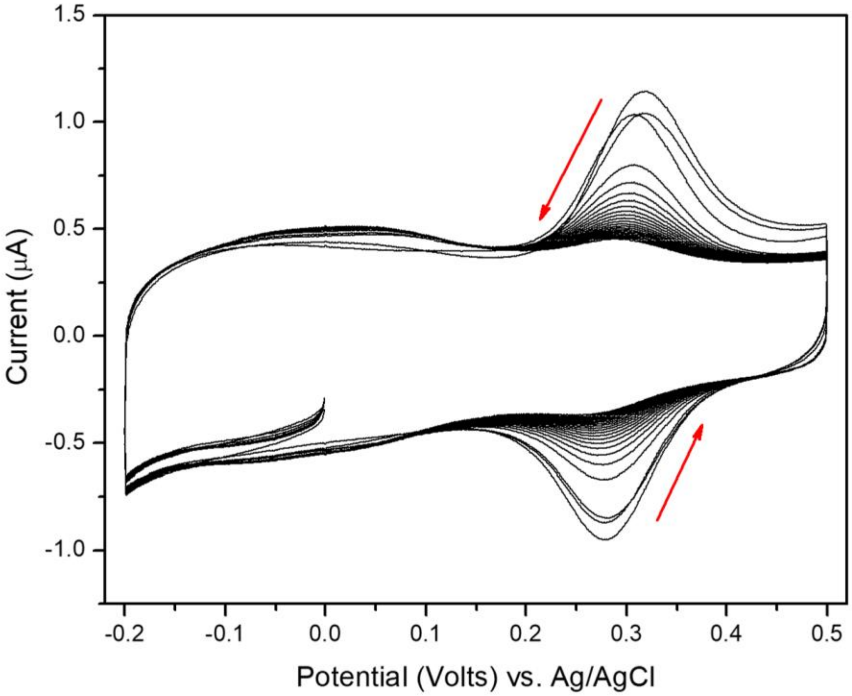


Figure 31. Potential Cycling within the deposition window.

While cycling in the deposition potential window leads to a steady decline in peak area, cycling negatively of the redox couple leads to virtually no change in the peak area. The material that remained on the electrode after the cycling experiment underwent further cycling in a potential range from -0.2 V to 0.2 V, or just negative of the quinone/catechol redox couple. A total of 125 cycles were performed in this potential range. While the continuous cycling took place in the range from -0.2 V to 0.2 V, single CVs were taken in the potential window of -0.2 V to 0.5 V, where the quinone/catechol redox couple is visible, to monitor changes in peak area. These single CVs are shown below in Figure 32. The peak height is nearly unchanged after continuous cycling at potentials more cathodic of the quinone/catechol redox couple.

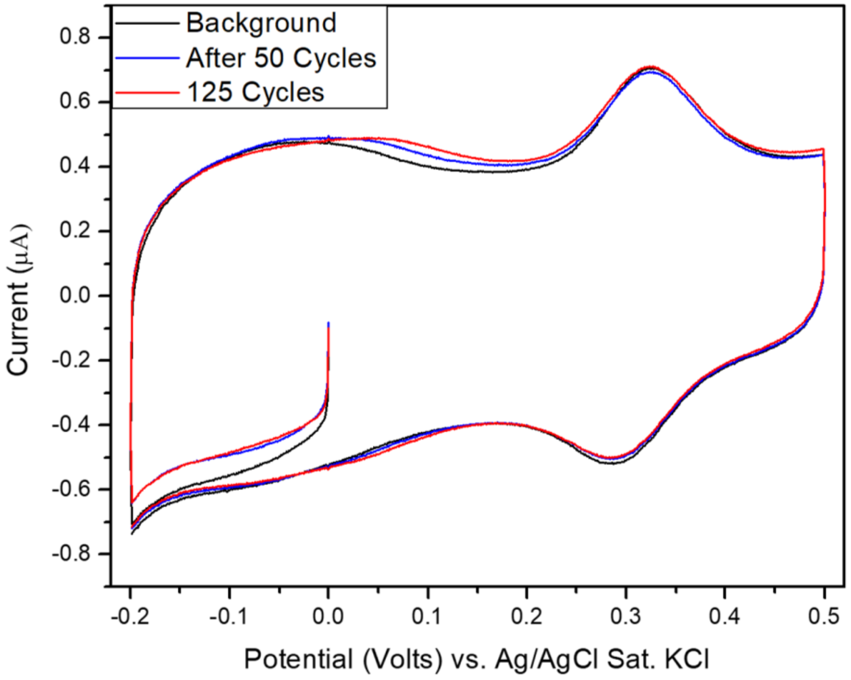


Figure 32. Single CVs taken to monitor peak area after continuous cycling.

The results of this experiment indicate that an electrode modified with a quinone linking group could be used in an electrochemical reaction that takes place at a more cathodic potential than the quinone/catechol redox couple without disrupting the ligand-electrode bond.

Stability at Constant Potentials

As seen from the cycling experiments, when the electrode is at a potential more negative of the catechol/quinone redox couple, material is not stripped from the electrode, and the peak area remains relatively constant. Chronoamperometry experiments were performed to determine if the ligand-electrode bond was stable when the electrode was held at constant potentials more cathodic than the quinone/catechol redox couple. The legend of Figure 33 shows the potential of the CA experiments in volts vs. Ag/AgCl sat. KCl.

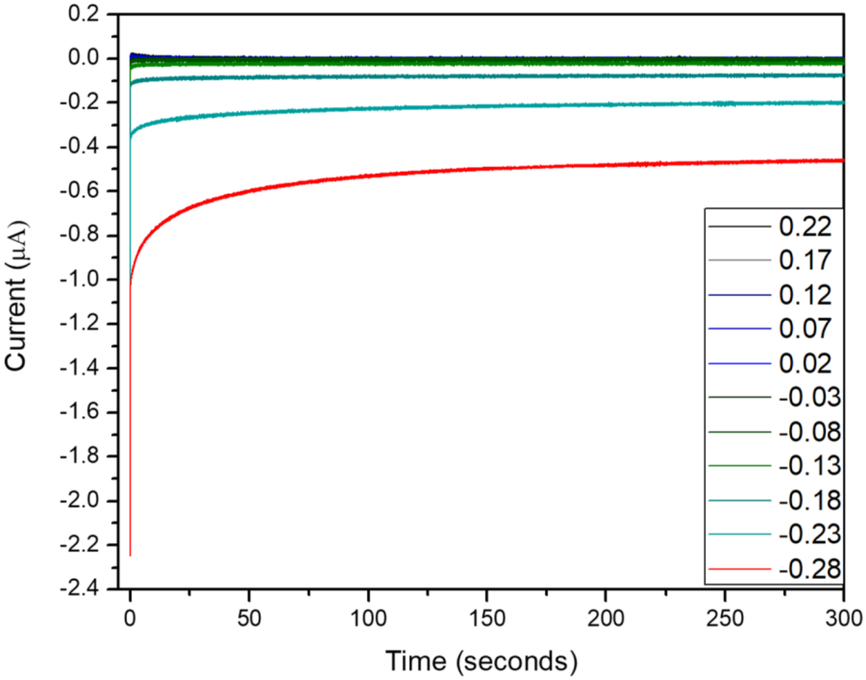


Figure 33. Chronoamperometry experiments at successively more negative potentials.

A modified electrode was placed in a bath of 0.1 M pH 7.5 phosphate buffer. The potential was held at a given value for 5 minutes, and then a CV was taken to monitor changes in peak area. Each chronoamperometry experiment was performed at a successively more negative potential, as shown in Figure 33. The potentials ranged from 0.22 V to -0.28 V vs. Ag/AgCl and were changed in increments of 50 mV. Figure 34 shows the CVs taken in between each CA experiment.

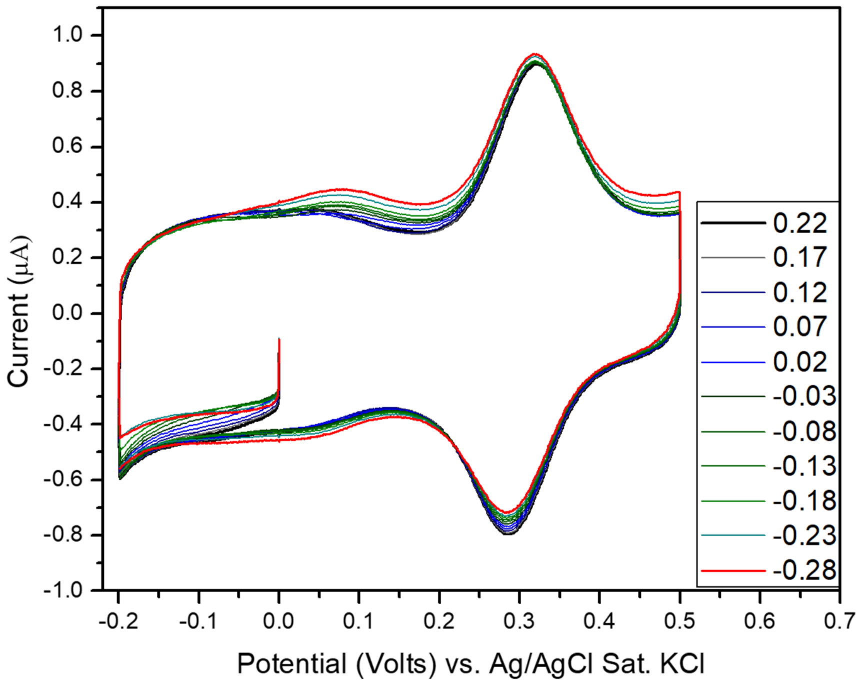


Figure 34. CV checks between CA experiments at successively more negative potentials.

Peak height remained relatively constant, although anodic peak height increased slightly, and the magnitude of the cathodic peak decreased slightly from the first to the last experiment. This is due to the extensive time the electrode was held at negative potentials. After being held at successively more negative potentials for extended periods as the experiment progressed, there was more fully reduced material at the electrode surface, causing the reductive current to decrease and the oxidative current to increase slightly.

In addition to changes in the peak height, the magnitude of the charging current, both anodic and cathodic, increased slightly. An oxidative peak began to appear around 0.08 V, preceding the anodic peak corresponding to catechol oxidation. Long periods at negative potentials could have reduced some species in solution, or at the electrode surface, causing a peak to appear and become more prominent.

Despite slight changes in the CVs throughout the experiment, it is clear that most of the material remains on the electrode. By contrast, a similar experiment was performed with CAs at successively more positive potentials, and the material was rapidly stripped from the electrode. Both cycling and chronoamperometry experiments indicated that at potentials above 0.2 V, peak area steadily decreases, and at potentials more positive of 1V, material is stripped completely from the electrode surface.

Discussion

Deposition of a dihydroxy terpyridine compound has been successfully performed in aqueous media after oxidative pretreatment. Trends in cathodic peak potential throughout the deposition indicate that the modification of the electrodes occurs on the cathodic sweep, which is consistent with previous work.[8] Mechanisms for deposition have been suggested, including the reaction of radical intermediates with carbon radicals on the electrode surface, or adsorption between the quinone moieties and oxygen-containing surface groups on glassy carbon.

The bond or adsorption between the ligand and electrode is stable at potentials more cathodic than 0.2 V vs. Ag/AgCl sat. KCl. For cycling in windows that have an upper limit more positive than 0.2 V, the peak area will steadily decrease with continued cycling or extended time at positive potentials. At potentials more positive than 1V, material is rapidly stripped from the electrode.

The modified electrodes survive sonication as well as extended periods in solutions of various pH values. Long term stability studies with less frequent observation, as well as shorter-term studies with daily observation have been performed to better understand the rate of disappearance of the material from the electrode surface in different chemical environments. The pH range of highest stability is between 3.5 and 8.

For more accurate measurements of the decrease in peak area over time, a metal reporter should be coordinated to the ligand. The redox couple of the metal should be more negative of the quinone/catechol couple. This will allow the stability to be checked without stripping any material from the electrode surface. Stability studies in a wide pH range should be repeated with the metal complex and performed several times to ensure that results are reproducible. Influences of the metal coordination on the ligand-electrode bond stability should be investigated. Depositions and stability studies in non-aqueous media should also be performed.

While further investigation into the stability of the *o*-quinone linking group should be performed, the initial studies discussed in this work indicate that it shows promise as a robust linking group for catalyst immobilization. The windows of chemical and electrochemical stability have been established, though repeated stability experiments with a metal reporter will help to further define and confirm this window of stability. Extensive data on the conditions in which the ligand-electrode bond survives will provide useful information that may allow for the use of this linking group for catalyst immobilization in DODH or other reactions.

References

(1) Sheldon, R. A. Fundamentals of Green Chemistry: Efficiency in Reaction Design. *Chem. Soc. Rev.* **2012**, *41* (4), 1437–1451.

(2) Arends, I.; Sheldon, R.; Hanefeld, U. *Introduction : Green Chemistry and Catalysis*; 2007.

(3) Gallezot, P. Conversion of Biomass to Selected Chemical Products. *Chem. Soc. Rev.* **2012**, *41* (4), 1538–1558.

(4) Shiramizu, M.; Toste, F. D. Expanding the Scope of Biomass-Derived Chemicals through Tandem Reactions Based on Oxorhenium-Catalyzed Deoxydehydration ** Angewandte. **2013**, No. entry 4, 12905–12909.

(5) Tymoczko, J.L, *Biochemistry, A Short Course;* 2015

(6) Maleki, A.; Nematollahi, D.; Clausmeyer, J.; Henig, J.; Plumeré, N.; Schuhmann, W. Electrodeposition of Catechol on Glassy Carbon Electrode and Its Electrocatalytic Activity Toward NADH Oxidation. *Electroanalysis* **2012**, *24* (10), 1932–1936.

(7) Whittle, B.; Everest, N. S.; Howard, C.; Ward, M. D. Synthesis and Electrochemical and Spectroscopic Properties of a Series of Binuclear and Trinuclear Ruthenium and Palladium Complexes Based on a New Bridging Ligand Containing Terpyridyl and Catechol Binding Sites. *Inorg. Chem.* **1995**, *34* (8), 2025–2032.

(8) Storrier, G. D.; Takada, K.; Abruna, H. D. Catechol-Pendant Terpyridine Complexes: Electrodeposition Studies and Electrocatalysis of NADH Oxidation. *Inorg. Chem.* **1999**, *38* (3), 559–565.

(9) Li, Z.; Hou, Z.; Fan, H.; Li, H. Organic-Inorganic Hierarchical Self-Assembly into Robust Luminescent Supramolecular Hydrogel. *Adv. Funct. Mater.* **2017**, *27* (2).

(10) Lin, Q.; Li, Q.; Batchelor-Mcauley, C.; Compton, R. G. Two-Electron, Two-Proton Oxidation of Catechol: Kinetics and Apparent Catalysis. *J. Phys. Chem. C* **2015**, *119* (3), 1489–1495.

(11) Faulkner, A. J. B. and L. R. *Fundamentals and Applications of Electrochemistry*; 1993.