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Effects of overoxidation on tris-(5-amino-1,10 phenanthroline) ruthenium (II) electropolymerized thin films

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Abstract

Electropolymerization is a widely used technique to develop polymer thin films, yet research is limited on the effects of deliberate overoxidation of these films. Tris-(5-amino-1,10 phenanthroline)ruthenium (II) was used to produce metallopolymer films on glassy carbon electrodes (GCE). During electropolymerization, the potential window of the cyclic voltammetric (CV) scan was extended beyond 2.00 V to observe the effects of overoxidation on the film. During characterization of the films, when the voltage was extended beyond 2.30 V, significant reduction in the cathodic peak current occurred due to the production of insulating domains within the polymer film and partial delamination of the film from the GCE. When any delamination of the film occurs, the functionality of the electrode is diminished for practical applications. The maximum potential voltage that a film is exposed to is crucial to the stability of the film and should be monitored during the development and testing of sensors.

Keywords: Electropolymerization, overoxidation, cyclic voltammetry, metallopolymer, thin films

Introduction

Polymer thin films have been used in a variety of ways including the detection of cell migration^[1], the detection of lead in water^[2], color displays^[3], medical devices such as pacemakers^[4], and detection of organic molecules⁵. Electropolymerization has proven to be an efficient way to develop chemically modified electrodes that are used in the previously stated applications, along with many others^[6]. Despite the wide array of uses for polymer thin films, little research has been done on the effects of extreme conditions on the integrity of the films, including the effects of an extended potential window.

It is crucial that a film can withstand a variety of intense conditions, especially in medical devices that are not easily removed. These surfaces are responsible for the function and protection of the devices, so they must be resilient to environmental changes. It has been discovered that overoxidation of a polymer film can cause significant delamination of the electrode surface. When delamination occurs, it can cause a serious decline in the intended functionality of the electrode and may lead to decreased efficiency and unreliable data output. Any alterations to the intended polymer film could result in significant changes to the functionality of the film^[7, 8].

Ruthenium itself has proven to be useful in the medical industry. Since ruthenium is more sustainable, less toxic, and more potent than platinum, it has been used in the development of metal anticancer drugs^[4, 9]. Additionally, ruthenium complexes have excellent electrochromic capabilities when a change in the oxidation state of ruthenium occurs^[10]. The ruthenium complex used in this research, tris-(5-amino-1,10 phenanthroline)ruthenium (II), forms covalent bonds with six nitrogen atoms that are part of a 3-ring system (Figure 1). When this ruthenium complex undergoes electropolymerization, it proceeds through chemical steps including radical cation coupling^[11, 12].

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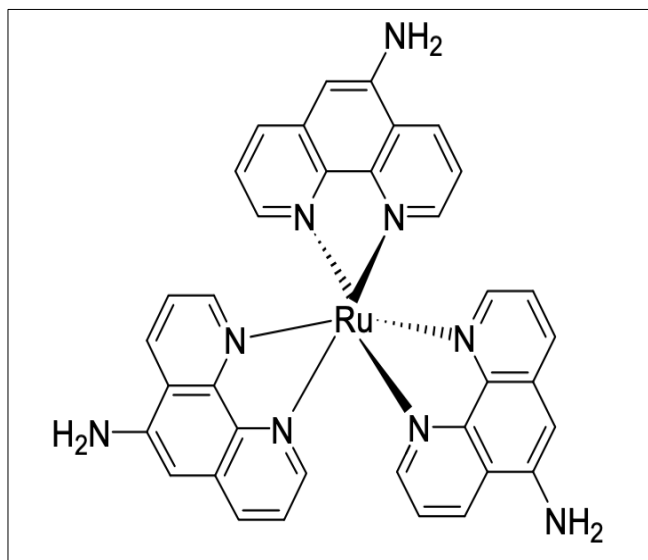


Fig 1: Structure of tris-(5-amino-1,10 phenanthroline) ruthenium (II)

Studies have shown that the area under the cyclic voltametric curve of a characterization cycle is proportional to the amount of material deposited on the electrode [13, 14]. When more of an electroconductive polymer film is deposited onto an electrode, the overall current increases along relative to the amount of voltage applied. Therefore, the area underneath the CV curve can be used to determine the relative amount of film deposited on the electrode surface.

Materials and Methods

Electrode Preparation

The glassy carbon electrodes (GCEs) with surface areas of 0.076 cm² (CH Instruments Inc., Austin, TX) were polished using a 0.05 micron polishing powder (CH Instruments Inc.) on a micro-cloth polishing disk (Buehler, Lake Bluff, IL). The polishing powder was sprinkled onto a wet polishing pad, and the surfaces of the GCEs were polished in circular and figure 8 motions until the surface appeared to be uniformly glossy. To remove any excess polishing powder, the electrodes were sonicated for five minutes in water, rinsed with acetonitrile, and dried thoroughly before use.

Solution Preparation

The tetraethylammonium perchlorate (TEAP) 98% dry weight (Alfa Aesar) was dried prior to using in monomer and characterization solutions, as trace amounts of water compromise the ability to electropolymerize the ruthenium complex. A thin layer was evenly distributed into the bottom of a Buchner funnel and repetitively rinsed with acetone. The acetone was filtered off using a vacuum filtration system, and the TEAP was allowed to dry for several hours before being transferred to a new container. To ensure that the TEAP remained dry, the solid was stored in a desiccator until use. The concentration of the ruthenium complex and TEAP in solution were 1.02 x 10⁻³ mol·L⁻¹ and 0.100 mol·L⁻¹, respectively. The concentration of the characterization solution, TEAP, in acetonitrile was 0.100 mol·L⁻¹. All solutions were stored and utilized at room temperature. The concentration of TEAP was

held in excess relative to the concentration of the ruthenium complex to prevent migration of the complex to the electrode surface. The solutions were not stirred during the cyclic voltametric measurements, hence the primary mode of mass transport of the ruthenium complex to the electrode surface was by diffusion.

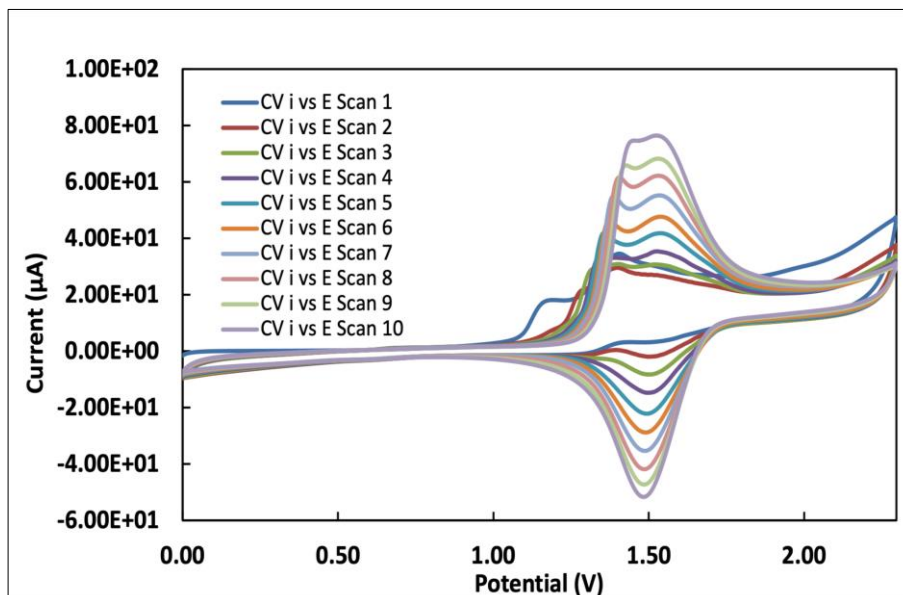
Procedure for Electropolymerization and Characterization

All electrochemical measurements were conducted with the PalmSens 3 potentiostat (Netherlands) and the PSTrace 5.8 software (Netherlands) using a three-electrode cell configuration. The glassy carbon working electrode with a surface area of 0.076 cm² and the platinum auxiliary electrodes were purchased from CH Instruments, Inc. A solid-state Ag/AgCl reference electrode was obtained from Innovative Instruments Corp. (Tampa, FL). The initial potential window used was 0.00 V to 2.30 V for the electropolymerization. The potential window was extended to 2.40 V and 2.50 V to determine the impact of electropolymerization potential window on the properties of the polymer film. A scan rate of 0.10 V/s was used in all ten cycles of electropolymerization. After electropolymerization, the electrodes were rinsed with acetonitrile to remove any excess ruthenium complex solution and placed into the supporting electrolyte solution. The films were characterized using an initial potential window of 0.00 V to 2.30 V. The potential window was extended to 2.40 and 2.50 V to determine the impact of changing the potential window on the properties of the polymer film. A scan rate of 0.05 V/s was used in all characterizations for two cycles.

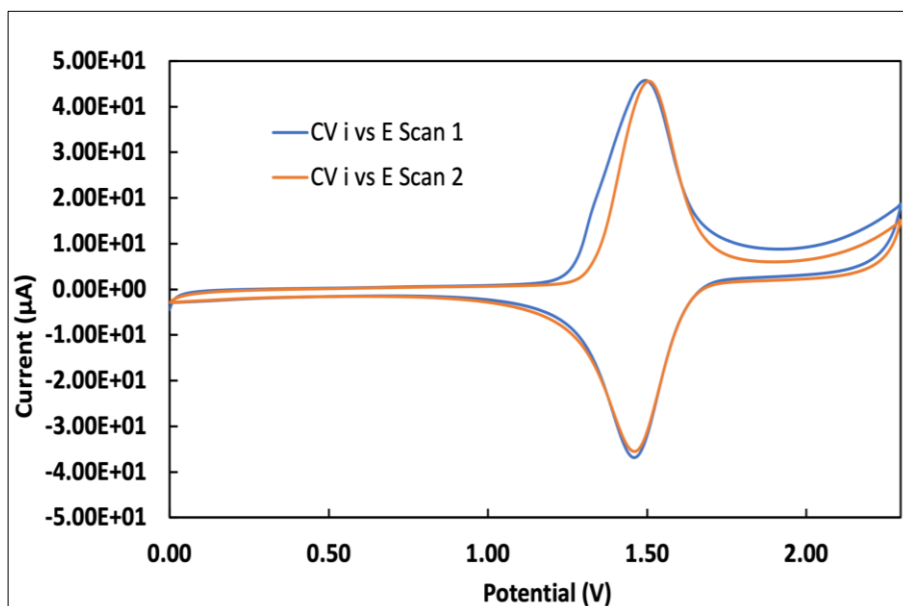
Results and Discussion

Electropolymerization

There are several potential sites for electrochemical reactions of tris-(5-amino-1,10 phenanthroline)ruthenium (II). These include the ruthenium redox center, the -NH₂ groups, and the phenanthroline ligand. When the potential window was set from 0.00 V to 2.30 V, the resulting CV is symmetrical, and the anodic and cathodic peaks have similar peak heights per cycle (Figure 2). The electropolymerization of tris-(5-amino-1,10 phenanthroline) ruthenium (II) follows the same radical cation coupling mechanism as reported for this ligand system with iron as the redox center. In Figure 2A, the initiation step to form the polymer film commences with the oxidation of the -NH₂ group(s) to form radical cations at the electrode surface; this step is shown in the CV as a peak at 1.20 V during the first cycle. On subsequent CV scans, the peak due to the oxidation of the amine group shifts to increased positive potentials and eventually becomes partially overlapped with the peak corresponding to the oxidation of the ruthenium; this is shown on the final CV cycle, which appears as two peaks near 1.50 V. During the CV scans, the peaks corresponding to equations 1 and 2 grow on each subsequent cycle, indicative of the electropolymerization process. Based on the peak currents per cycle corresponding to the Ru^{3+/2+} redox couple, when using the potential window of 0 V to 2.00 V, the polymer film does not grow in regular layers, and hence, multiple CV scans are needed to ensure full surface coverage; complete surface coverage may require several thousand monolayers.



A



B

Fig 2: A CV from 0.00 V to 2.30 V was performed. (A.) A polymer film of the ruthenium complex was formed onto the GCE through electropolymerization using $1.02 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ ruthenium complex solution and (B.) characterized in the $0.100 \text{ mol}\cdot\text{L}^{-1}$ TEAP supporting electrolyte solution.

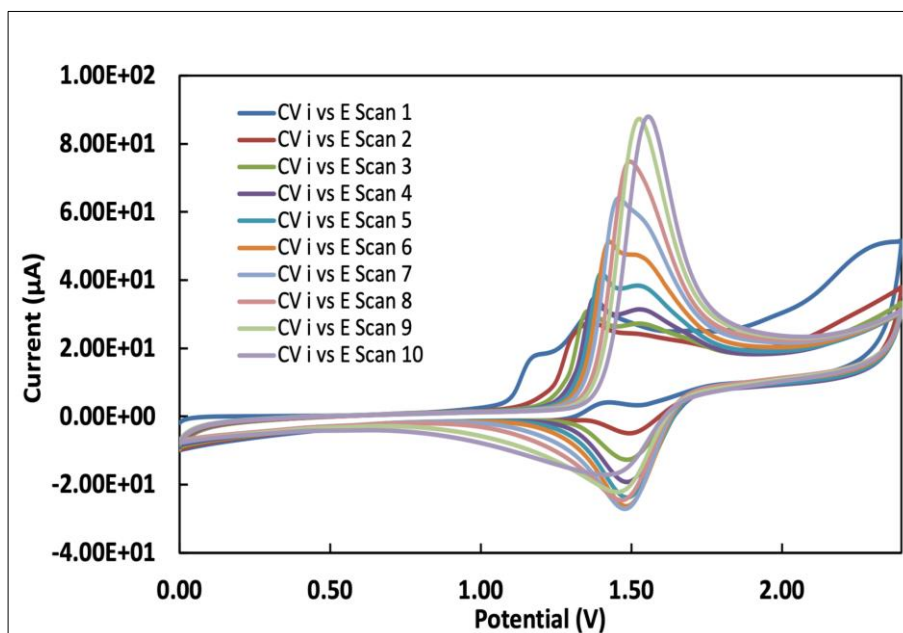
The anodic peak in both the electropolymerization and characterization reactions corresponds to the oxidation of the ruthenium complex (Eq. 1):



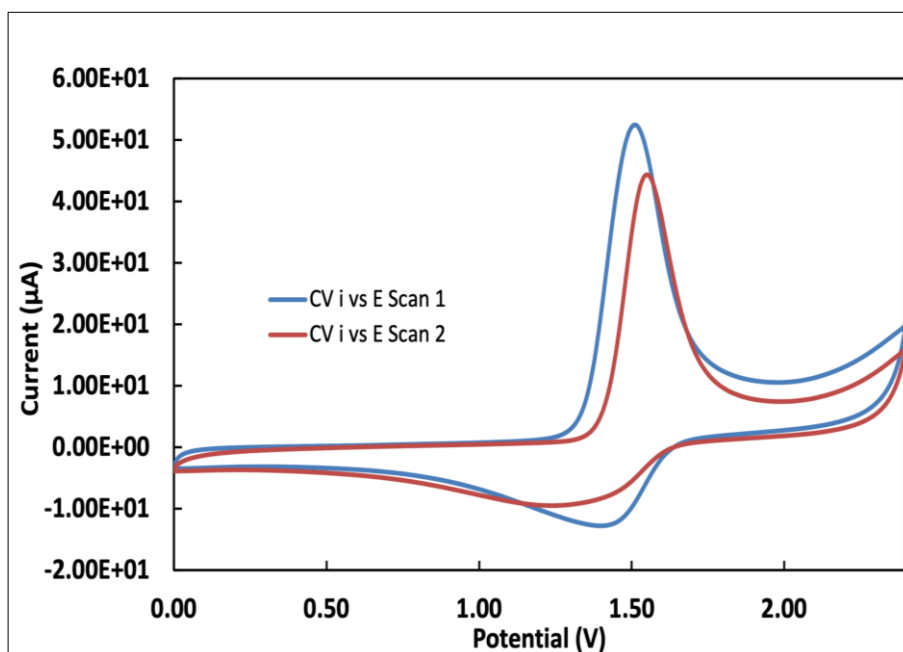
and the cathodic peak represents the reverse reduction reaction (Eq. 2):



When the potential window was increased to 2.40 V, there was a noticeable reduction in the cathodic peak currents that began c.a. cycle eight. The peaks continued to decrease in peak currents for each succeeding scan (Figure 3). The cathodic peaks in the characterization plot showed a significant decrease in area in comparison to the area of the cathodic peaks in the previous condition.



A

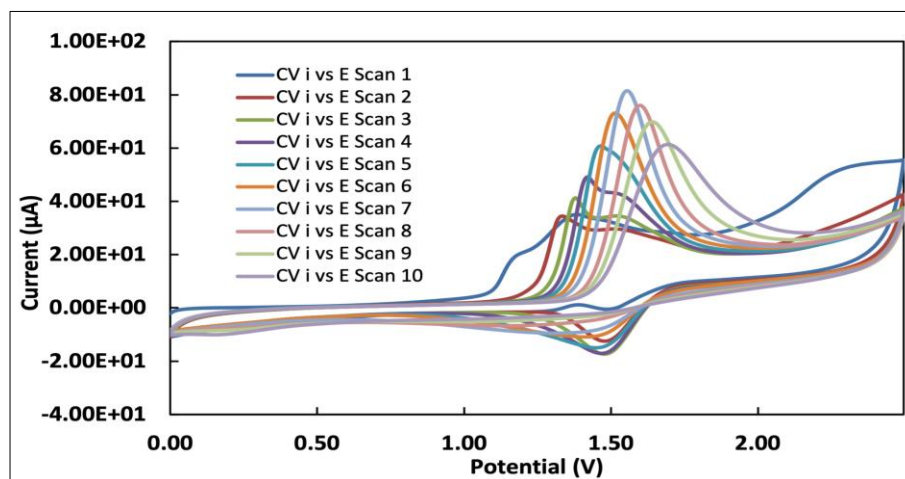


B

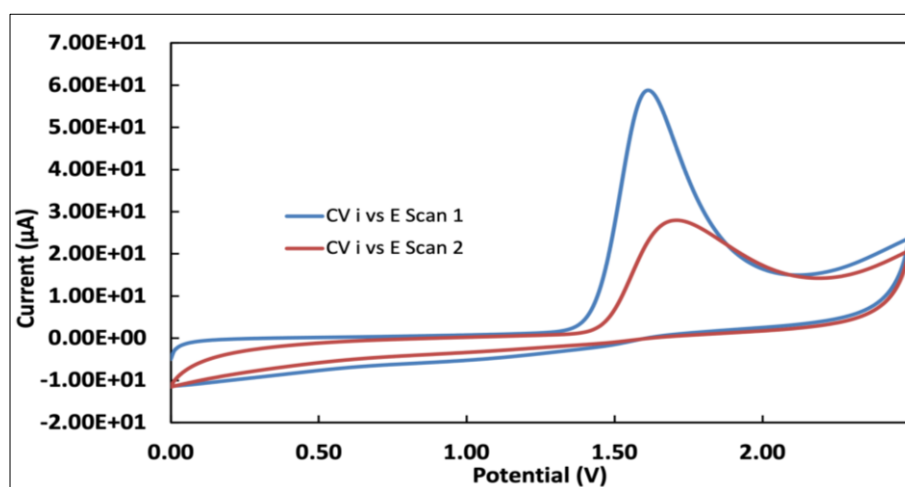
Fig 3: A CV from 0.00 V to 2.40 V was performed. (A.) A polymer film of the ruthenium complex was formed onto the GCE through electropolymerization using $1.02 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ ruthenium complex solution and (B.) characterized in the $0.100 \text{ mol}\cdot\text{L}^{-1}$ TEAP supporting electrolyte solution. A reduction in the cathodic peak current can be noted during cycle eight.

When the potential window was extended to 2.50 V, a reduction in peak current occurred much sooner at cycle four in comparison to cycle eight under the previous condition. In the characterization plot, there were no cathodic peaks observed (Figure 4). Overoxidation of the polymer film causes the system to move toward irreversibility. Even when the scan rate was reduced to 0.01 V/s, the cathodic peak did not appear in the potential window. At much slower scan rates, the system

will approach Nernstian equilibrium (where ΔE_p is ca. 0 mV), with the applied potentials as more time is allowed for the charge transfer process. In cases where the peak separation is near 0 mV, finite diffusion conditions are applicable. However, this does not occur and the system moves far from quasireversibility to irreversibility. In addition, the electrochemical activity of the polymer film is not restored upon returning to the initial potential window.



A



B

Fig 4: A CV from 0.00 V to 2.50 V was performed. A) A polymer film of the ruthenium complex was formed onto the GCE through electropolymerization using $1.02 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ ruthenium complex solution and B) Characterization in the $0.100 \text{ mol}\cdot\text{L}^{-1}$ TEAP supporting electrolyte solution. A reduction in the peak height of the cathodic peak was noted during scan 4

When the maximum cathodic peak currents were compared relative to the potential window, significant decrease in peak heights were noted at any window that extended past 2.30 V. The further the window was extended, the sooner a decrease in peak height occurred (Table 1). When the potential window was set to 2.10 V and 2.20 V, there was no reduction in peak current, which shows that this effect is only present when the complex is overoxidized.

Table 1: Maximum cathodic peak current

	Cathodic Peak Current (μA)		
	2.30 V	2.40 V	2.50 V
Scan 1	-4.48	-4.38	-8.41
Scan 2	-9.35	-11.26	-19.31
Scan 3	-15.71	-18.87	-23.31
Scan 4	-22.65	-25.15	-22.36
Scan 5	-29.89	-29.73	-19.24
Scan 6	-36.88	-32.56	-14.41
Scan 7	-43.82	-33.10	-10.45
Scan 8	-50.14	-29.99	-5.37
Scan 9	-55.45	-26.18	-3.25
Scan 10	-59.83	-19.79	-1.65

The maximum cathodic peak currents obtained from the cyclic voltammograms are compared between the different voltage windows. The window that extends to 2.30 V represents the

typical oxidation/reduction pattern for the ruthenium complex, based on the $\text{Ru}^{3+/2+}$ redox couple. When the voltage window was extended to 2.40 V and 2.50 V, the cathodic peaks did not follow the growth pattern as expected.

To compare the amount of the metallopolymer film that remained on the electrodes, a characterization step was performed. After integrating and analyzing the area under the cathodic peaks, it was evident that there was a significant decrease in area and thus a decrease in deposition of the film (table 2). After exceeding a potential window of 2.40 V, there were no cathodic peaks present in the characterization step indicating that the polymer film had changed properties. It should also be noted that the electrode surface in the 2.30 V potential window appeared orange in color while there was minimal color change when using the 2.50 V electrode.

Table 2: Characterization cathodic peak area

	Peak Area ($\mu\text{A}\cdot\text{V}^{-1}$)		
	2.30 V	2.40 V	2.50 V
Scan 1	-9.68	-7.76	-
Scan 2	-9.67	-6.50	-

The area of the cathodic peak from the characterization was found using the integration software on PStTrace 5.8. There were no cathodic peaks present when the potential window was extended to 2.50 V.

Cyclic voltammetry was used to show the possibility of overoxidation of the ruthenium complex. When the potential window was set from 0.00 V to 2.30 V, both the anodic and cathodic peaks were symmetrical. However, once the potential window was extended out by 0.10 V, there was a significant drop in the height and area of the cathodic peaks. This is due to the overoxidation of the polymer film and the formation of insulating domains within the film. Even during the characterizations of the polymer films, the reduction in peak currents and the change in semiconductive properties of the polymer film become more pronounced as the potential window is extended (Table 2). When the potential window was extended to 2.50 V, there was no cathodic peak present in the characterization CV. This results from overoxidation of the polymer film, which causes the remaining film to become more insulating.

Conclusion

In conclusion, when the polymer film is exposed to an extended potential window during polymerization, the electrode undergoes delamination. The overoxidation causes the free radicals in solution to react with the film and strip it off of the electrode. The more that the potential window is extended, the faster delamination can be observed in the cyclic voltammetry scans. The partial delamination that resulted was not due to the thickness of the film. Due to the versatility of ruthenium and the growing interest in ruthenium complexes, it is crucial that the magnitude of the voltage is carefully monitored during experiments to ensure that overoxidation of the ruthenium complex does not occur. If the maximum potential voltage of the ruthenium complex and its corresponding polymer film is exceeded, the films may become structurally unstable and will produce inaccurate data when used to develop sensors or biosensors. Anyone who is considering using a ruthenium-based sensor should be aware of this. For further research, other transition metals that are commonly used with the ligand system should be analyzed to see if the same effects of overoxidation on the integrity of the film are observed.

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