Optimization of polymer/ruthenium complex optical oxygen sensor

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OPTIMIZATION OF POLYMER/RUTHENIUM COMPLEX OPTICAL OXYGEN SENSOR

by

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Bachelor of Science
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2001

A thesis submitted in partial fulfillment of the requirements for the

Master of Science Degree in Chemistry
Department of Chemistry
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The Thesis prepared by
Sujanie V.S.V. Gamage

Entitled
Optimization of Polymer/Ruthenium Complex Optical Oxygen Sensor

is approved in partial fulfillment of the requirements for the degree of
Master of Science

Examination Committee Chair

Dean of the Graduate College
ABSTRACT

Optimization of Polymer/Ruthenium Complex Optical Oxygen Sensor

by

Sujanie V.S.V. Gamage

Dr. David W. Hatchett, Examination Committee Chair
Associate Professor of Chemistry
University of Nevada, Las Vegas

This thesis is focused on developing an optical oxygen sensor, to detect oxygen content in sealed packages. The oxygen sensor material was developed using tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) dichloride, a well known oxygen sensitive dye. The [Ru(Ph₂Phen)₃](Cl)₂ dye was incorporated into a polyacrylate polymer in the first step. A plasticizer (dioctylphthalate) was then added to the polymer/ruthenium mixture to improve the oxygen permeability of the sensor material. Optimum composition films were identified by the analysis of fluorescence lifetime decay curves using the OxySense 101 Analyzer. After optimizing each component in the order of polymer, ruthenium and plasticizer, the solution mixture was cured for a minimum of 24 hrs. at 60 °C to produce the final cured polymer/ruthenium/plasticizer material. The optimized sensor material was reconstituted and cast onto suitable substrates before testing. The final optimized, cured sensor material contained 0.005 g Ru per 1 g polymer and 1 g dioctylphthalate per 1 g of polymer.
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CHAPTER 1

INTRODUCTION

1.1 Introduction and Background to Oxygen Sensors

Monitoring oxygen levels is of great importance in environmental and biomedical analysis as well as industrial processes\(^1\). The amperometric method using an oxygen electrode has been the most popular technique in the past decade\(^1\). However amperometric methods are limited by the materials used, including the stability of the electrode surface and instabilities in the oxygen diffusion barrier. In addition, the response time of electrochemical sensors are limited by gas permeability through semi-permeable membranes.

In the past decade there has been considerable interest in luminescence based optical oxygen sensors\(^1\). One significant advantage of photoluminescent sensors over electrochemical sensors is their ability to work in the presence of electromagnetic disturbances. In contrast, the response of photoluminescent sensors is much faster because it does not necessarily require gas permeable separation membranes. However oxygen permeable membranes are typically used to exclude unwanted species in photoluminescent sensors. Therefore, the inherent permeability of oxygen through optical sensing membrane is important in monitoring oxygen quenching using membranes. Another advantage of the photoluminescent sensor is that the optical fibers can be used in the device fabrication, which enables micro dimensions to be achieved\(^6\).

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This thesis focuses on the development of an optical oxygen sensing platform which utilizes polymer/ruthenium complex composites as the sensing transducer. The detection method utilizes fluorescence of the ruthenium complex embedded in a polymeric membrane which is permeable to oxygen. The target sensor for these studies is an optical oxygen sensing device which can be used in food industry. Therefore, when designing the device, cost, fabrication technique and the environmental concerns play a major role and must be evaluated independently.

Most optical sensors utilize the luminescence quenching of an indicator dye in the presence of the target analyte (oxygen, hydrogen, carbon dioxide, etc...)\textsuperscript{1,3,11,14}. Dyes that have been used in optical sensors include luminescent and oxygen quenchable organic dyes, such as polycyclic aromatic hydrocarbons (pyrene derivatives, quinoline and phenanthroline)\textsuperscript{6-9}, transition metal complexes of ruthenium\textsuperscript{1-5}, osmium or rhenium-polypyridyl and metallloporphyrines\textsuperscript{10}. In most optical oxygen sensors these indicators are dispersed in oxygen permeable polymer or sol-gel matrices which can be tailored to enhance or inhibit interactions with different species. Polymers offer advantages for sensor technologies because they are relatively low cost, their fabrication techniques are simple and they can be deposited on various types of substrates. The sensors produced using polymer materials are typically operable and stable at room temperature.\textsuperscript{11} There is a growing literature on the development of an optical sensors on a variety of materials including silicon, polystyrene, nafion, polyacrylate, zeolites etc.\textsuperscript{1-5} Interactions between the luminescent complexes and the polymer are often complex and they can affect the ultimate performance of the sensor.
In this study each individual component used in the synthesis of the sensing membrane is independently optimized to provide the final sensor system. For example the influence of polymer concentration in the casting solution, dye concentration, and plasticizer concentration were monitored and optimized individually. In this thesis the development of an optical oxygen sensor where a luminescent ruthenium(II) polypyridyl complex is immobilized in organic polymers such as nafion, polystyrene and polyacrylate will be discussed. The role of plasticizers in the membrane will be presented providing a systematic study of the composition and influence on the sensor response.

Optical sensing methods which utilize the fluorescence of dye molecules can measure the quenching of a chromophore using two different parameters. The most common method of measurement to date involves monitoring the luminescence intensity quenching. In addition the fluorescence lifetime can be utilized for quenching phenomena. However, this technique typically requires specialized instrumentation and algorithms for fitting the fluorescence decay of the chromophore. The ruthenium(II) polypyridyl complexes used in this study provide strong emission signal with sufficiently long life times which can be measured. The relationship between the emission intensity or the lifetime and the oxygen concentration can be explained using the Stern-Volmer equation which will be explained in section 1.4.12 This equation is the basis for the treatment of oxygen quenchable fluorescent chromophores that have been used in oxygen sensors and a wide variety of sensing applications.1-5
1.2 Introduction to Ru (II) Dyes

Ru(bpy)$_3^{2+}$ has been one of the most extensively studied chromophores in past decade. A unique combination of stability, measurable redox properties, excited state reactivity, luminescence emission and excited state lifetime resulted in a large volume of research on this molecule and many of the derivatives have been produced from this initial molecule.\textsuperscript{13} Ruthenium(II) polypyridyl complexes have played and continue to play a key role in the development of photochemistry, photophysics, photocatalysis, electrochemistry, photo electrochemistry, electrochemical luminescence and electron and energy transfer.\textsuperscript{1-10}

Ruthenium(II) is a d$^6$ transition metal, which forms octahedral complexes with a bidentate ligand polypyridine. Polypyridyl complexes of ruthenium(II) are colored due to an intense metal-to-ligand charge transfer band (MLCT) at $\sim$440 nm and frequently displays photoluminescent band at $\sim$610 nm upon excitation into this MLCT band.\textsuperscript{14} Two well known oxygen sensitive ruthenium(II) polypyridyl complexes were explored in this study. Tris(1,10-phenanthroline) ruthenium(II) dichloride complex \textit{(rac)-[Ru(Phen)$_3^{2+}$](Cl$_2$)) as shown in Figure 1.1\textsuperscript{15} and tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) dichloride complex \textit{(rac)-[Ru(Ph$_2$Phen)$_3^{2+}$](Cl$_2$)) as shown in Figure 1.2\textsuperscript{16}. The two ruthenium polypyridyl complexes were synthesized in the laboratory. The product obtained was a racemic mixture of $\Delta$ (delta) and $\lambda$ (lambda) enantiomers. The dye was incorporated into the polymer matrix without isolating the two enantiomers.
One of the most important advantages of using the ruthenium dye for the optical oxygen sensor for this study is, dye does not interact with nitrogen or carbon dioxide gases. To quench the fluorescence of the ruthenium dye, the target analyte should be of equal energy of the excited Ru(II) molecule. Where energy level of oxygen is comparable with excited ruthenium dye neither nitrogen nor carbon dioxide.

1.3 Introduction to Polymer Matrices

Polymer materials have been used by analytical chemists to construct a wide variety of sensors for oxygen, sulfur dioxide, ethanol and water vapor. Polymer films containing luminescent dyes are widely used in oxygen sensors. The polymer matrix serves to bind the dye and as a medium for oxygen transport from the surrounding environment. The polymer can also act as an impermeable barrier preventing the uptake of water or other unwanted species. To maximize the effectiveness of the sensor, the polymer should have a high oxygen permeability and the polymer-dye combination must be miscible. Although it is often assumed that the transition metal complex is homogenously distributed throughout the polymer matrix, heterogeneous regions can be
encountered. In some cases plasticizers can be added to the polymer to prevent dye aggregation, increase oxygen permeability and increase the sensitivity of the sensor. Furthermore the solvent used to dissolve the polymer and the dye has to be carefully selected because the dye molecules and the polymer should miscible with each other. A solvent that dissolves all three components of the sensor, the ruthenium (II) polypyridyl complex, polymer and the plasticizer, is preferred.

In this thesis four different polymers; nafion, polystyrene, poly(sodium-4-styrene sulfonate) and newly synthesized polyacrylate polymer were doped with tris(4,7-diphenyl-1,10-phenanthroline) complex which is a well known oxygen sensing dye.\textsuperscript{2} Nafion as shown in Figure 1.3\textsuperscript{23} is a perfluorinated polymer which has attracted attention because of it’s thermal stability (up to 200°C), mechanical strength, ease of handling and it’s chemical and biological inertness.\textsuperscript{20} In addition the polymer is conductive and can be used in both optical and electrochemical sensing regimes.

![Figure 1.3](image-url)
Polystyrene as shown in Figure 1.4 is a well known neutral polymer matrix which has been used for variety of sensor applications. Poly(sodium-4-styrene) sulfonate in Figure 1.5 is an anionic polymer. The advantage of using the anionic polymer is, the positively charged ruthenium (II) polypyridyl complexes are electrostatically attached to the polymer and prevent leaching of the complex from the sensor film. Anionic polymers contain chemical functional groups that facilitate the electrostatic immobilization of the dye molecule.

A polyacrylate polymer, which is a heterogeneous polymer containing four different monomer units was also used to develop the oxygen sensors based on the high oxygen permeability of the material. Synthesis of polyacrylate polymer will also be discussed in this thesis.

1.4 Optical Oxygen Sensing Properties of Sensor Films

S.K. Lee and I. Okra’s polymer matrix studies shows that unlike solvents, polymers have inhomogeneous structure influenced by the absolute molecular weight and molecular weight distribution. A homogeneous architecture is the one in which each
element is of the same type. When different structural groups exist, we use the term inhomogeneous. The inhomogeneity can drastically affect the sensitivity, selectivity and limit of detection of the sensor as it applies to Stern-Volmer kinetics.\(^\text{10}\) Stern-Volmer kinetics explains the dynamic quenching behavior of a fluorophore when the target quencher is present in the system. The inhomogeneity of the polymer matrix results in non linear Stern-Volmer plots. Demas, DeGraff and Xu reported a multi-site model and non linear solubility model to explain the results of downward curvature in the Stern-Volmer plots at higher oxygen concentrations. The non-linearity of the Stern-Volmer plots can be found in literature on optical sensor studies\(^\text{1-6}\).

Sensors which utilize Stern-Volmer bimolecular quenching kinetics can be described using the following scheme:\(^\text{12}\)

\[
\begin{align*}
D & + h\nu \quad \longrightarrow \quad D^* & & \quad k_a \quad (1a) \\
D^* & \quad \longrightarrow \quad D & + h\nu \text{ or } \Delta & \quad k_j \quad (1b) \\
D^* & + Q \quad \longrightarrow \quad D & + Q^* & \quad k_2 \quad (2a) \\
D^* & + Q \quad \longrightarrow \quad D & + Q + \Delta & \quad (2b)
\end{align*}
\]

For Stern-Volmer systems D represents the ground state chromophore, Q is the ground state quencher, \(k_a\) is the absorption rate constant, \(k_j\) is the rate constant for the decay of the excited state chromophore when the quencher is absent and \(k_2\) is the quencher rate constant. The possible bimolecular processes involving the quencher Q show in equations 2a and 2b. Equation (2a) shows the deactivation of the excited chromophore by transferring energy to Q and (2b) shows deactivation of D without excitation of Q.
This kinetic scheme gives Stern-Volmer equation, which describes the dynamic quenching of the fluorophore. For optical oxygen sensors, oxygen is the quencher. The Stern-Volmer equation gives the relationship between the intensity or lifetime and the quencher concentration. The derivation of the Stern-Volmer equation can be obtained using the kinetics.

\[
\frac{d[D^*]}{dt} = k_e[D] - k_1[D^*] - k_2[D^*][Q]
\]

At the steady state \( \frac{d[D^*]}{dt} = 0 \)

\[
[D^*] = \frac{k_e[D]}{k_1 + k_2[Q]}
\]

\[
I = k_1[D^*]
\]

\[
I = \frac{k_1k_e[D]}{k_1 + k_2[Q]}
\]

\[
I_0 = k_e[D]
\]

\[
\frac{I_0}{I} = 1 + \frac{k_2}{k_1}[Q]
\]

\[
K_{sv} = \frac{k_2}{k_1}
\]

\[
\frac{I_0}{I} = 1 + K_{sv}[Q]
\]

\[
\tau = \frac{1}{k_{app}}
\]

\[
\tau = \frac{1}{k_1}
\]

\[
\frac{\tau_0}{\tau} = 1 + \frac{k_2}{k_1}[Q]
\]

\[
\frac{\tau_0}{\tau} = 1 + K_{sv}[Q]
\]
\[ I_0 / I = 1 + K_{sv}[O_2] \]  \hspace{1cm} (3a)

\[ \tau_0 / \tau = 1 + K_{sv}[O_2] \]  \hspace{1cm} (3b)

Where \( I \) is the emission intensity in the presence of oxygen, \( I_o \) is the emission intensity in the absence of oxygen, \( \tau \) is the luminescence lifetime in the presence of oxygen, \( \tau_0 \) is the luminescence lifetime in the absence of quencher oxygen and \( K_{sv} \) is the Stern-Volmer quenching constant. The unit of the \( K_{sv} \) is the reciprocal of oxygen concentration (%\(^{-1}\)).

A linear calibration curve results for the plot of \( I_0/I \) versus oxygen concentration and \( \tau_0/\tau \) versus oxygen concentration based on equation (3a).

The luminescence decay curves for the ideal Stern-Volmer relationship are all single exponential curves with a measured quencher-dependent lifetime.\(^{12}\) Most of the sensor studies have been done using luminescence intensity. In this study we are interested in lifetime of the fluorescence. The relationship between the intensity and the lifetime is as follows,

\[ \tau_0 / \tau = I_0 / I \]  \hspace{1cm} (4a)

\[ \tau = \tau_0 / (I_0 / I) \]  \hspace{1cm} (4b)

Figure 1.6 shows a theoretical Stern-Volmer plot, which shows the linear relationship between the relative intensity and oxygen concentration.
Figure 1.6 Theoretical Stern-Volmer plot\(^1\) for Ru(Ph\(_2\)Phen)\(_3\)\(^{2+}\) (●) attached to poly(acrylic acid) films, where \(K_{sv} = 0.3015 \text{ (}\%^{-1}\text{)}\).

Figure 1.7 shows the theoretical non linear Stern-Volmer plot using equation 5(a)\(^2\).

In the equation, \(f_n\) is the fractional contribution to each oxygen accessible site, where there are two sites in the sensor film. \(K_{sv_n}\) is the Stern-Volmer quenching constant for each oxygen accessible site. \(I\) and \(I_0\) represent the luminescence intensity in the presence and absence of oxygen.

\[
\frac{I_0}{I} = \left[ \sum \frac{f_n}{1 + K_{sv_n} [O_2]} \right]^{-1} \quad 5(\text{a})
\]
Figure 1.7. Theoretical non-linear Stern – Volmer plots for \( \text{Ru(Ph}_2\text{Phen)}_3^{2+} \) (O), attached to poly(sodium 4-styrene sulfonate) films and \( \text{Ru(Ph}_2\text{Phen)}_3^{2+} \) (■) attached to poly(acrylic acid) films. \( \text{Ru(Ph}_2\text{Phen)}_3^{2+} \) in poly(sodium-4-styrene sulfonate) \( K_{sv1} = 1.46 \%^{-1}, f_1 = 0.64, K_{sv2} = 0.0019 \%^{-1}, f_2 = 0.361 \). \( \text{Ru(Ph}_2\text{Phen)}_3^{2+} \) in poly(acrylic acid) \( K_{sv1} = 0.300 \%^{-1}, f_1 = 0.55, K_{sv2} = 0.0015 \%^{-1}, f_2 = 0.454 \).

This thesis will discussed the quenching of fluorescence lifetime decay in the form of a time constant (TC). The time constant (TC) is the time required for the fluorescence decay of the chromophores, which is denoted by \( \tau \) in the Stern-Volmer equation. Time constant was measured in nitrogen atmosphere for 0% oxygen and compressed air with 20% oxygen. The difference between TC values (\( \Delta \text{TC} \)) was taken. Oxygen sensor was developed by looking at the \( \Delta \text{TC} \) values, where \( \Delta \text{TC} = 2.0 \) is the targeted value for an optical oxygen sensing device based on the requirements established by our collaborator Oxysense\(^{26} \). The measurements were made using Oxysense 101 non-invasive oxygen analyzer system. It is a novel optical measurement method for determining the amount of
oxygen contaminant within sealed packages. The Stern-Volmer equation is applied by the Oxyesense 101 analyzer software using equation 6(a). Where TC is the time constant at current oxygen concentration in µs (τ), \([O_2]\) is the oxygen concentration, \(A = K_{sv} / \tau_0\) and \(B = 1 / \tau_0\).

\[
\frac{1}{TC} = A [O_2] + B
\]  

(6a)

Figure 1.8 shows a relative fluorescence signals \((I/I_0)\) measured at different oxygen partial pressures using OxySense 101 analyzer. The \([\text{Ru(Ph}_2\text{Phen)}_3]\)(Cl\(_2\)) dye was illuminated at a rate of 1 µs pulses at a frequency of 20 kHz. The fluorescent lifetime lies between 1 µs and 5 µs.

![Figure 1.8](image)

Figure 1.8\(^{26}\). Relative fluorescence signals \((I/I_0)\) in different oxygen pressures at 20 °C.
Most solutions satisfy the ideal linear Stern-Volmer relationship. However, most sensors require that the chromophores are dissolve in a polymer matrix. This is necessary since virtually all luminescent sensors will respond to species other than oxygen (e.g. Proteins, surfactants, solvents, metal ions, oxidants, reductants, etc.) Therefore the sensor must be isolated from these interferences while still providing full access to oxygen. The sensor molecule is isolated from the environments that contain nongaseous solvent born interferences. Therefore, the sensor molecule is typically supported within the gas permeable, solvent impermeable polymer membrane.

The disadvantage of a polymer supported chromophore system is that unlike fluid solutions, virtually all polymer supported sensors exhibit some degree of heterogeneity due to the differences in occupation by the sensor molecules in the membrane. Heterogeneity manifests itself in nonlinear downward-curved Stern-Volmer quenching plots. Two common explanations of the nonlinearity\(^\text{12}\) include multisite binding or the nonlinear solubility properties of the analyte in the sensor\(^\text{12}\). There are two fundamentally different models for quantitation of nonlinear quenching behavior. The first involves the use of a multisite (two-site) model and the second a nonlinear solubility model. In the multisite model, the sensor molecule can exist in two or more sites each with its unique quenching constants. The second model assumes that all nonlinearity in the Stern-Volmer plot arises from the nonlinear solubility of oxygen in the polymer. This is a direct result of the gas permeability issue within the polymer. To minimize the inhomogeneity the polymer and sensing element that is the polymer/chromophore membrane, can be cast, spin coated or chemisorbed onto a surface providing a much more homogenous sensing membrane.

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1.5 Problem Definition

The vast numbers of studies concerning optical oxygen sensors have been focused on diffuse oxygen concentrations in open settings. The purpose of this thesis was to develop an optical oxygen sensing platform for closed container food packages. The same dyes used in previous studies were synthesized and embedded in various polymeric supports. The ruthenium (II) polypyridyl complexes were chosen based on the abundance of studies and successful applications examined previously.¹⁻⁵

This thesis is organized in the following manner: Chapter 2 describes the experimental procedures for synthesis and characterization of ruthenium (II) polypyridyl complexes, which will be used in the oxygen sensor development. Chapter 3 describes the polymers which have been used in several sensor applications, the synthesis of a polyacrylate polymer and the solubility properties of each polymer is discussed. The preparation of oxygen sensing films and optimization of polymer concentration, Ru complex concentration, and plasticizer is also discussed. The best plasticizer for each polymer and the order of addition of the ruthenium(II) polypyridyl complex, polymer and the plasticizer will be the interesting area of this chapter. Chapter 4 describes the oxygen quenching of fluorescence lifetime of the sensor films made in the laboratory using the OxySense 101 Analyzer. In chapter 4 the data will be presented for each sensor system using different polymers and plasticizers. The results obtained for optimization of all three components, dye, polymer and the plasticizer will be discussed along with the data obtained for the deposition of sensor material. Chapter 5 presents the conclusions of this thesis including a discussion of the optimization of the characteristics of sensor film.
1.6 References


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EXPERIMENTAL METHODOLOGY OF DYE SYNTHESIS

2.1 Materials in General

Bathophenanthroline (Alfa Aesar, 98%, 1662-01-7), Ruthenium (III) chloride hydrate (Strem Chemicals, 99.9%, 14898-67-1), N,N-Dimethylformamide (EMD Chemicals, 68-12-2), Acetone (EM Science, 67-64-1), Ethyl ether (VWR International, 60-29-7), Ethyl alcohol (EM Science, 64-17-5), Ammonium hexafluorophosphate (Alfa Aesar, 99.5%, 16941-11-0), 1,10-phenanthroline (Aldrich, 99%, 66-71-7). All materials were used without further purification.

2.2 Synthesis of tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) hexafluorophosphate

Ruthenium(III) chloride hydrate (1.5631 g, 5.97 mmol) and 4,7-diphenyl-1,10-phenanthroline (3.9855 g, 12 mmol) were added to a 100 mL round bottom flask and heated to reflux in dimethylformamide (60 mL) at 170 °C for 6 hrs. with stirring. During this period the reaction mixture becomes dark violet color. After the reaction mixture was cooled to room temperature, 250 mL of HPLC grade acetone was added and the resultant solution and the mixture was cooled at 0 °C overnight. The reaction mixture was filtered using a Buchner funnel and the resultant dark violet-black microcrystalline product was washed three times with 25 ml portions of distilled water followed by three 25 mL
portions of ethyl ether. The dark violet color product was dried by suction. Yield of the product was 3.45 g (4.12 mmol), 69% based on ruthenium(III) chloride hydrate. During this reaction oxidation state of ruthenium changes from +3 to +2, provided the solvent DMF acting as a reducing agent.

Scheme I. Preparation of cis-bis(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) dichloride

\[
\text{RuCl}_3 \cdot 3\text{H}_2\text{O} + \text{"Ph}_2\text{Phen"} \xrightarrow{\text{DMF}} \text{reflux for 6hrs. at 170}^\circ\text{C} \xrightarrow{} [\text{Ru(Ph}_2\text{Phen})_3](\text{Cl}_2)
\]

Bis(4,7-diphenyl-1,10-phenanthroline)ruthenium(II)chloride (1.3514 g, 1.57 mmol) and 4,7-diphenyl-1,10-phenanthroline (0.6561 g, 1.97 mmol) were added to a 250 mL round bottom flask and heated to reflux in 80% ethanol(120 mL) for 8 hrs. with stirring. During this period the reaction mixture becomes red-wine colored. After cooling, the reaction mixture volume was reduced to 1/3 of the original volume by evaporation under reduced pressure using a rotavap. Distilled water (20 mL) was added to the round bottom flask with swirling. The resulting mixture was filtered using a Buchner funnel to remove...
insoluble material. The dark red filtrate was treated with an excess of ammonium hexafluorophosphate in small portions with stirring to precipitate the product. The red orange precipitate was collected using a Buchner funnel and dried. The product was transferred to a small flask and dissolved in minimal amount of acetone with stirring. Insoluble material was removed by suction filtration using a Buchner funnel. Precipitation of the final product was achieved on slow addition of ethyl ether with stirring. The product was filtered and dried under vacuum. Yield of the product was 2.15 g (1.5 mmol), 95% based on the starting bis-ruthenium complex. The product obtained was a racemic mixture of $\Delta$ (delta) and $\lambda$ (lambda) enantiomers. Further studies were not carried out to isolate the two enantiomers.

Scheme II. Preparation of tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) hexafluorophosphate complex

\[
\begin{align*}
[Ru(\text{Ph}_2\text{Phen})_3](\text{Cl}_2) + \text{NH}_4\text{PF}_6\text{excess in solvent} & \quad \rightarrow \quad \text{rac-[Ru(Ph}_2\text{Phen})_3(\text{PF}_6)_2} \\
1) \text{80% EtOH reflux for 8hrs.} & \quad \rightarrow \quad [\text{PF}_6^-]^2
\end{align*}
\]
Single step synthesis of tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) hexafluorophosphate

Single step synthesis was carried out using the same experimental procedure used for the preparation of bis(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) dichloride as discussed before. The yield of the crude product was 2.82 g (2.57 mmol), 43% based on the starting ruthenium trichloride. The crude product was purified by column chromatography on silica gel 60 and eluted with MeOH. The purified ruthenium complex from the column was 6.27% based on starting crude ruthenium complex. The completed synthesis confirmed the two step synthesis is more efficient than the one step synthesis.

Scheme III. Preparation of tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) hexafluorophosphate complex
2.4 Materials Characterization

Tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) hexafluorophosphate, tris(1,10-phenanthroline) ruthenium(II) hexafluorophosphate, bis(1,10-phenanthroline) ruthenium(II) dichloride and bis(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) dichloride were characterized using several conventional techniques. Crude materials were identified using TLC (thin layer chromatography) on silica plates in different solvent combinations. Column chromatography was used to separate the materials using appropriate solvent systems. Melting points of the crude products and recrystallized materials were obtained using Thomas Hoover Capillary Melting point apparatus.

2.4.1 Fluorescence Spectroscopic Characterization

Fluorescence spectroscopy is used to determine the intense metal-to-ligand charge transfer band due to ruthenium (II) polypyridyl complex. Experiments were carried out to determine the emission wavelength of each complex using the Perkin-Elmer LS55 luminescence spectrometer. Both liquid and solid samples were measured. Each sample was scanned at a speed of 1200nm/min and the slit width of excitation and emission was 10nm. All sample measurements were carried out at room temperature. The tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) hexafluorophosphate complex was dissolved in dichloromethane and the sample were excited at 460 nm and the maximum fluorescence intensity was obtained at 600 nm. Literature cited the absorbance at 461 nm and the emission at 610 nm.

2.4.2 UV/VIS Spectroscopy

UV/Vis spectra were obtained for all synthesized ruthenium complexes using a Cary 3BIO UV/Vis spectrophotometer. A quartz cuvette with a 1cm path length was used at
room temperature for all measurements. UV/VIS spectra were taken for tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) hexafluorophosphate complex to determine the wavelength of maximum absorbance. The maximum absorbance wavelength obtained for the [Ru(Ph2Phen)3] (Cl2) in dichloromethane was 462 nm and the [Ru(Ph2Phen)3] (PF6) in dichloromethane was 460 nm under room temperature.

2.4.3 NMR Spectroscopy

Structures of tris and bis ruthenium complexes were confirmed by 1H NMR spectroscopy. All NMR data were obtained by using Bruker AMX 400 NMR spectrophotometer.
2.5 References


CHAPTER 3

EXPERIMENTAL METHODOLOGY OF POLYMER MATRIX PREPARATION

3.1 Introduction to Preparation of Sensor Films

Polymers have been used for a variety of chemical sensors such as oxygen, carbon dioxide, sulfur dioxide, water vapor and ethanol\(^{1-6}\). In this chapter four different polymers: nafion, polystyrene, poly(sodium-4-styrene) sulfonate and a synthesized polyacrylate polymer\(^7\), which used to make sensor films will be discussed. Preparation of polymers and solubility properties of each polymer were examined to determine if the material was applicable.

The introduction of ruthenium (II) polypyridyl complex into the polymer matrix plays an important role in oxygen sensing\(^{2,3,8-13}\). The concentration of the dye relative to the polymer will be examined. Plasticizers will be introduced to optimize oxygen permeation and the oxygen sensing properties of the sensor films. A variety of plasticizers for each polymer matrix will be examined. The method of addition of each component will be examined to determine if the parameters influence the sensing properties. The final goal is to optimize ruthenium concentration, polymer and plasticizer to produce a oxygen sensing material which can be used in the industry.

Two instruments were used to detect the fluorescence of the polymer-ruthenium sensor film. The fluorescence intensity was obtained using the luminescence spectrometer and the lifetime data were obtained using the Oxysense 101 analyzer.\(^{14}\)
3.1.1 Materials used in Studies


3.2 Preparation of Polyacrylate Polymer

A modification of preparation of polyacrylate polymer as described in the patent literature method was used for this study. Acrylonitrile (9.46 g), 2-ethylhexylacrylate (19.71 g), methylmethacrylate (28.56 g), vinyl acetate (12.27 g) and azo-bis-isobutyronitrile (0.07 g) were added to 500 mL round bottom flask. The reaction mixture was stirred using a magnetic stirrer and the flask was capped and saturated with argon.
The oil bath was heated to 60 °C and the reaction mixture was placed on the oil bath and heated for 42 hrs. The mixture of monomers was polymerized to a solid state. The solid polymer was dissolved in ethyl acetate to produce ~10%-20% (w/w) polymer solution.

3.3 Solubility of Polymers

3.3.1 Procedure

The solubility of each solid polymer was determined, by adding about 0.1 mg of polymer into 1 mL of each solvent mentioned in Table 3.1. The polymers and the solvents used to determine the solubility and the results are presented in Table 3.1.

NS -Not Soluble
S –Soluble

Table 3.1 Qualitative Polymer Solubility

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Nafion</th>
<th>Polystyrene</th>
<th>Poly(styrene) sodium salt</th>
<th>Protonated polystyrene sulfonate</th>
<th>Poly(acrylate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>EtOH</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>i-PrOH</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>S</td>
<td>NS</td>
</tr>
<tr>
<td>EtOH:MeOH:i-PrOH: H2O 3:3:3:1</td>
<td>S</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Tris HCl</td>
<td>NS</td>
<td>NS</td>
<td>S</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>DCM</td>
<td>NS</td>
<td>S</td>
<td>NS</td>
<td>NS</td>
<td>S</td>
</tr>
<tr>
<td>CHCl3</td>
<td>NS</td>
<td>S</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>NS</td>
<td>S</td>
<td>NS</td>
<td>NS</td>
<td>S</td>
</tr>
</tbody>
</table>

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3.4 Preparation of Polymer Solutions

3.4.1 Nafion Solution

20 mL of water was added to 5 g of nafion pellets in total 180 mL of ethanol (60 mL), methanol (60 mL), isopropanol (60 mL). The solution mixture was then heated to 40°C and stirred using a magnetic stirrer. After the nafion pellets were fully dissolved in the short-chain alcohol/water mixture, the solution was evaporated until the total volume reached 100 mL. The final solution concentration was 5% (w/w).

3.4.2 Protonated Poly(sodium-4-styrene) sulfonate Solution

Concentrated hydrochloric acid (30 g) was added to the 20 g of poly(sodium-4-styrene) sulfonic acid. The solution was stirred well and isopropyl alcohol (70 g) was transferred to the mixture. The mixture was stirred well and placed under the hood overnight. The solution was filtered and extra 30 g of conc. HCl + i-PrOH solution was added to the filter cake stirred well and allowed it to sit overnight. The mixture was filtered as before and filtrate was added to the first batch. The concentration of the solution was 20% (w/w).

3.4.3 Polystyrene Solution in Chloroform

Polystyrene (10 g) was weighed to a cleaned empty beaker and 50 mL of chloroform was added to the beaker. The solid polymer pellets completely dissolve in chloroform at room temperature. The concentration of the solution was 0.2 g/mL or 20% (w/v).

3.4.4 Polystyrene Solution in Ethyl Acetate

Polystyrene (5 g) was weighed to a cleaned empty beaker and ethyl acetate was added to the same beaker until the total weight of material becomes 50 g. The solid pellets
completely dissolve in ethyl acetate at room temperature. The concentration of the solution was 10% (w/w).

3.4.5 Polyacrylate Solution

Freshly prepared polyacrylate polymer (20 g) was weighed into a clean empty beaker and ethyl acetate (80 g) was added. The solid polymer completely dissolve in ethyl acetate affording a 20% (w/w) polyacrylate solution.

3.5 Preparation of Sensor Films

The target of this research is to prepare a polymer matrix containing oxygen sensitive dye. Oxygen sensing films can be prepared by two methods. First by introducing the dye followed by the plasticizer into the polymer matrix. Second method is by introducing the plasticizer followed by the dye into the polymer. Both of these combinations will be discussed. The composition of the dye, polymer and the plasticizer influence the properties of the polymer films. Four different polymers and plasticizers have been used to make the films with various results. All components of the sensor film was monitored methodically and optimized to determine the best film. In addition the deposition techniques used to make the sensor films were examined. Spin coated, wipe coated and pipetted materials were cured for 24 hours under ambient conditions prior to measurement.

3.5.1 Plasticizers

Several different plasticizers have been examined for the polymer solutions and the best plasticizer will be selected by measuring the optimum oxygen sensitivity for each polymer matrix. In order to improve the oxygen sensitivity of the sensor film the
plasticizer should be soluble in the polymer matrix and the oxygen permeability of the
sensor film should increase with addition of the plasticizer\textsuperscript{8,16}.

3.5.1.1 Procedure for Solubility of Plasticizers

Solubility of plasticizers was determined in polystyrene, protonated-polysodium-4-
styrene sulfonate and newly synthesized polyacrylate solutions and results provided in
table 3.2. Solubility of each plasticizer was examined by adding one drop of each
plasticizer into 1 mL of solvent/polymer mixture.

NS – Not Soluble 

S – Soluble

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>Polystyrene (20% w/w in ethyl acetate)</th>
<th>Protonated polystyrene (20% w/w in i-PrOH)</th>
<th>Polyacrylate (20% w/w in ethyl acetate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dioctyl phthalate</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Diphenyl isophthalate</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>p-Tolune sulfonic acid monohydrate</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Phthalic acid benzyl n-butyl ester</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Diphenyl phthalate</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>p-styrene sulfonic acid</td>
<td>NS</td>
<td>S</td>
<td>NS</td>
</tr>
<tr>
<td>Allylsulfonic acid sodium salt</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Vinylsulfonic acid sodium salt</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>

Table 3.2 Qualitative solubility of plasticizers in polymers.

When the plasticizer was soluble, the mixture was very clear there were no phase
separation in the polymer/plasticizer mixture.
3.5.2 Formulation and Order of Addition

The three main components of the polymer film must be added in a specific form to get the maximum oxygen sensitivity. Experiments were carried out by changing the order of addition of polymer, ruthenium complex and the plasticizer to determine if the order of addition influences the sensor response. The data obtained from the experiments indicated that the order of addition influences the sensor response which will be discussed in chapter 4. In order to get the maximum oxygen sensitivity, ruthenium was dissolved and incorporated into the polymer matrix first and then the plasticizer was introduced to the polymer-ruthenium mixture. The solution mixture was stirred well after addition of each new component.

3.5.3 Optimization of each Component

Experiments were carried out to optimize the relative concentration of each component in the oxygen sensor film. For the measurements one component was adjusted while the other two were kept constant. The optimum concentration of the ruthenium complex, polymer and the plasticizer were obtained independently of the other variables and combined in the end to produce the optimized sensor.

3.5.4 The Preparation of Oxygen Sensing Film

A 20% polyacrylate polymer solution was made by dissolving 20 g of freshly prepared solid polymer in 80 g of ethyl acetate. To this solution [Ru(Ph2Phen)3](Cl2) dissolved in dichloromethane (3 mg/mL wt/v) was added such that the ratio of Ru complex versus polymer was 0.005 g Ru to 1 g of polymer. The solution was stirred mechanically, to incorporate the Ru complex in the polymer solution. Finally,
dioctylphthalate was added to the solution such that the ratio of plasticizer versus polymer was 0.50 g dioctylphthalate per 1.0 g of polymer/Ru/plasticizer.

The sensor material was cured for ~ 24 hrs. at 60 °C in a vacuum oven. The resulting material was transformed from an opaque orange to transluscent orange during the heating. With heating the dye is more fully saturated in the polymer matrix resulting in a higher distribution. Prior to curing the deposition method strongly influenced the sensor response. However the reconstituted material show no dependence on the deposition method.

The freshly prepared sensor solution was either, spin coated, wipe coated, or pipetted as a dot on a glass slide and allowed to dry under ambient conditions overnight. The lifetime measurements were performed on the film after 24 hours of deposition and within 48 hours of preparation using the Oxysense 101 analyzer\textsuperscript{15}. The results of both these studies, curing and without curing will be discussed in chapter 4.

3.6 Characterization of Sensor Films

3.6.1. Fluorescence Spectroscopic Characterization

Fluorescence spectroscopy is used to determine the emission wavelength and intensity of the excited Ru(II) metal-to-ligand transfer band, due to embedded ruthenium (II) polypyridyl complex in the sensor film. The PerkinElmer LS55 Luminescence spectrometer was used to make measurements. Each sensor film was scanned at a speed of 1200 nm/min and the slit width of excitation and emission was 10 nm. All measurements were carried out under room temperature.
Table 3.3 Fluorescence Characterization of sensor films

<table>
<thead>
<tr>
<th>Polymer Film</th>
<th>Excitation Wavelength (nm)</th>
<th>Emission Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td>460</td>
<td>600</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>470</td>
<td>600</td>
</tr>
<tr>
<td>Protonated polystyrene sulfonate</td>
<td>470</td>
<td>620</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>470</td>
<td>610</td>
</tr>
</tbody>
</table>

3.6.2 Fluorescence Quenching Study\(^\text{14}\)

Oxygen quenching of the fluorescence was studied using the OxySense 101 Non-Invasive oxygen Analyzer system. The OxySense 101 Non-Invasive Analyzer System is a novel optical measurement method for determining the oxygen contaminant within sealed packages. It measured oxygen gas within the package headspace or dissolved in the liquid. The oxygen concentration obtained directly, reliably and repeatably without destroying the integrity of the package seal. This instrument has been used to measure oxygen content of a package using the fluorescence lifetime quenching principle. The sensor film can be manually attached to the inside of a package or pre-fabricated into the barrier coating of the package material. The sensor was illuminated by blue LED (470 nm) of 1 \(\mu\)s pulses at a frequency of 20 kHz. During every measurement a single 50 \(\mu\)s pulse of the fluorescent signal was recorded in the computer and 1000 pulses were averaged to calculate the time constant (TC). Figure 3.1 shows a schematic for the OxySense 101 Analyzer.
Figure 3.1 Schematic of the basic components of OxySense 101 analyzer\textsuperscript{15}
3.7 References


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CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter outlines the synthesis and characterization of oxygen sensor films, produced using with four different polymers. Four different polymer matrices including nafion, polystyrene, protonated polystyrene sulfonate and heterogeneous polyacrylate were used to prepare sensor films. These polymers were selected after carefully evaluating literature on oxygen sensing materials. Each sensor film is unique due to differences in the polymer matrix. The polymer matrix serves as a support for the dye and also as a medium for oxygen transport from the atmosphere. To maximize the effectiveness of the oxygen sensor, a variety of approaches were taken, including selecting a dye with long unquenched excited state lifetimes (τ₀), polymers with high oxygen permeabilities and polymer-dye combinations in which the dye dissolves directly into the polymer.

The characteristics of the polymer systems are unique and will be discussed in this section. The data will be presented and compared to show how to obtained the sensor with highest sensitivity to oxygen. Oxygen quenching of fluorescence lifetime data were used to characterize the sensor materials.
When developing oxygen sensing materials, we tried to immobilized the positively charged ruthenium(II) polypyridyl complexes in the polymer matrix when possible. The ruthenium complex exists in +2 oxidation state. Therefore anionic polymers can provide electrostatic binding sites for the dye molecules. Therefore negatively charged polymers were compared to neutral polymers in this study. A variety of approaches were taken to improve the characteristics of the oxygen sensor films. Addition of plasticizers into the polymer/ruthenium mixture improves the oxygen quenching of the fluorescence lifetime by preventing dye aggregation and increases the oxygen permeability in the polymer matrix. An attempt was made to optimize individual components of the sensor film, including polymer composition, ruthenium concentration and plasticizer concentration. A well known oxygen sensing dye, tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) dichloride \(^8\) was used for developing the sensor. The choice of plasticizer used in each polymer matrix was based on the polymer chosen.

Nafion, a perfluorinated, thermally stable, chemically, and biologically inert polymer, was the first polymer to be examined.\(^1,2\) The charge properties make it as an interesting polymer for producing an oxygen sensor because of electrostatic interactions between the polymer and charged ruthenium(II) dye. Polystyrene was also examined because it is a cheap, well studied polymer.\(^4-6\) Polystyrene is a neutral polymer which has been used to prepare variety of sensors.\(^4-6\) Protonated polystyrene sulfonate\(^3\) is an acidic polystyrene derivative which was chosen because of electrostatic interactions with the positively charged ruthenium (II) polypyridyl complex and the negatively charged polymer matrix. These electrostatic interactions were viewed as favorable to prevent leaching of the dye.
from the sensor film. Finally, a heterogeneous polyacrylate polymer\textsuperscript{7}, was synthesized based on high oxygen permeation observed previously for the material.

The typical fluorescent sensor utilizes changes in the fluorescent intensity in the presence of quencher oxygen. Our measurements focus on the change in lifetime decay in the form of the time constant (TC). TC is the term used for the data analysis throughout this chapter, which represents the life time $\tau$ in the Stern-Volmer equation. The relationship between the Stern-Volmer equation and the TC will be given in equation 3(e) and 6(a) in chapter 1. The OxySense\textsuperscript{TM} 101 analyzer was used to measure the lifetimes of the sensor materials. Figure 4.1 shows the picture of the OxySense\textsuperscript{TM} 101 analyzer, and Figure 4.2 shows the fluorescence lifetime signal appears on the main screen of the instrument. The time constant (TC) is the time required for the fluorescence decay of the chromophore. Time constants (TC) were measured using a nitrogen atmosphere for 0% oxygen ($\tau_0$) and compressed air with 20% oxygen ($\tau$). $\Delta TC$ is the difference between time constants ($\tau_0 - \tau$), when measurements were taken in 0% oxygen and 20% oxygen. The goal of this project is to develop an oxygen sensor, which gives a minimum $\Delta TC$ value of 2.0 based on the requirements established by our collaborator, Oxysense.

A one of the advantages of using lifetime over intensity is the measurements do not vary with a shift wavelength of emission of the chromophore commonly associated with quenching of fluorescence intensity. Lifetime measurements are typically more sensitive than intensity with respect to oxygen quenching, is also an advantage of using the fluorescence lifetime. There are several factors that influence the TC and intensity of the fluorescence. The relationship between the TC and intensity will be given in equation 1(a).
\[ TC = \frac{\tau_0}{\left( I_o / I \right)} \]  

Where \( I \) is the emission intensity in the presence of oxygen, \( I_o \) is the emission intensity in the absence of oxygen, \( TC \) is the luminescence lifetime in the presence of oxygen, \( \tau_0 \) is the luminescence lifetime in the absence of quencher oxygen.

Figure 4.1 Oxysense 101 analyzer

Figure 4.2 Fluorescent signal in ambient air as appeared in the main screen of OxySense 101 analyzer, where x axis gives time in \( \mu s \) and y axis gives the relative intensity.
One of the most important factors that influence the fluorescence lifetime and intensity are dye aggregation. When the dye concentration increases the dye molecules aggregate with each other resulting difficulty for the quencher oxygen molecules to penetrate to each dye molecule. As a result the intensity observed will be higher and lifetime is longer than expected. As a result ΔTC value is lower than expected. Therefore optimization of dye concentration plays an important role in developing the oxygen sensor.

![Figure 4.3 Schematic diagram of measuring the oxygen content in sealed package using the Oxysense 101 analyzer reader pen](image)

As shown in Figure 4.3 Oxysense 101 analyzer reader pen get measurements from the oxygen sensing dye from the opposite direction of where oxygen penetrates to the sensing dot. The sensor surface, which absorbs the LED light, is the least oxygen-quenching area. Therefore optical density is also an important factor that influences the TC values of the sensor film. When the polymer concentration is high, it is difficult for the oxygen to quench the fluorescence. When the optical density is high, the fluorescence
intensity and lifetime increases than expected, because oxygen can not quench the fluorescence. As a result ΔTC value is lower than expected. Self quenching of chromophores are also a factor that influence the TC values of the sensor films. When the dye concentration is high, proximity interactions and internal quenching of chromophores can take place. This leads to lower ΔTC values. The oxygen permeability of the sensor film is another factor which influences the TC data. Introducing plasticizer in to the sensor system can improve the oxygen permeability11,12. When the oxygen permeability is high, the fluorescence intensity and lifetime decrease resulting in higher ΔTC values.

4.2 Nafion Polymer Oxygen Sensor

Nafion was the first polymer examined for the sensor because of it's high thermal stability (up to 200°C), mechanical strength and it’s chemical and biological inertness. In addition nafion is a conductive polymer which can be used in both optical and electrochemical sensing regimes if other sensing regimes were needed.

Nafion solutions were made as discussed in section 3.5.1. Two different ruthenium complexes were used for this study; one is the commercially available [Ru(Ph2Phen)3](Cl)2 complex and the second one is the inhouse synthesized [Ru(Ph2Phen)3](PF6)2 complex. The ruthenium complex was synthesized in the laboratory in order to reduce the cost for the oxygen sensor system. Ruthenium solution was made by dissolving each one of these complexes in dichloromethane to obtain the final concentration of 3 mg/mL. 100 μL of each of these solutions were transferred to the 2 mL of nafion solution. The solution mixture was stirred well and aliquots of 3 μL were placed as dots on glass slides and dried overnight.
Four different samples were made. Sample 1 and 2 were prepared with the commercially available \([\text{Ru(Ph}_2\text{Phen)}_3](\text{Cl})_2\) complex. For sample 1, a 3\(\mu\)L aliquot was placed onto a glass slide and dried. Alternatively for sample 2 three 1\(\mu\)L aliquots were added sequentially after each was allowed to dry. In both cases a total of 3\(\mu\)L of material was used for each dot. Sample 3 and 4 were made in the same manner using the synthesized \([\text{Ru(Ph}_2\text{Phen)}_3](\text{PF}_6)_2\) complex from our laboratory. The results are presented in Table 4.1.

Table 4.1 Nafion polymer study of sample 1-4 made up of 0.00015 Ru(g)/Polymer(g) concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\Delta TC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.08</td>
</tr>
<tr>
<td>2</td>
<td>2.08</td>
</tr>
<tr>
<td>3</td>
<td>1.67</td>
</tr>
<tr>
<td>4</td>
<td>1.72</td>
</tr>
</tbody>
</table>

The results show that oxygen sensor films made up of \([\text{Ru(Ph}_2\text{Phen)}_3](\text{Cl})_2\) complex give a \(\Delta TC\) value of 2.08 and \([\text{Ru(Ph}_2\text{Phen)}_3](\text{PF}_6)_2\) complex gives \(\Delta TC\) value of 1.7. These results indicate that the counterion may play a role in oxygen sensitivity or that the inhouse material is not pure. However, the \(\text{PF}_6^-\) is larger than \(\text{Cl}^-\) ion, which could influence the oxygen permeability, reducing the oxygen quenching and lowering \(\Delta TC\). The oxygen quenching lifetime studies proved (\(\Delta TC = 2.08\)) that nafion is an acceptable candidate for the oxygen sensor material.
When developing a sensor for industrial use the cost plays a major role. Nafion is expensive when compared to many other polymers that have been used in sensor applications. For example, 1 g of nafion is $2.00, while 1g of polystyrene is $ 0.10. Therefore the nafion system was considered too costly. We focused on other polymers such as polystyrene, protonated polystyrene sulfonate and heterogeneous polyacrylate polymer, which are much cheaper.

### 4.3 Polystyrene Polymer Oxygen Sensors

Polystyrene is a well known neutral polymer that has been used in variety of sensor applications. As discussed in chapter 3 Table 3.1 polystyrene dissolved in two different solvents, chloroform and ethyl acetate. Experiments were carried out using both solvent systems to find out what system gives better oxygen quenching. The order of addition for each component was the same for each system. First, a 10% polymer solution was added to a vial followed by a 0.01 Ru(g)/Polymer(g) of [Ru(Ph2Phen)3](Cl)2 solution and the plasticizer concentration of 25% plasticizer(g)/Polymer(g). Several plasticizers were added to the polymer-ruthenium matrix. The plasticizer that provided the highest ΔTC value was chosen from the series. The results of the plasticizer study are shown in figure 4.4. In both solvent systems the best plasticizer for the polystyrene was para-toluene sulfonic acid. When we compare both systems, the polymer dissolved in ethyl acetate gave higher ΔTC values than the polymer dissolved in chloroform. So data obtained from polymer dissolved in ethyl acetate system will be discussed in this chapter. The polymer solutions were made as discussed in section 3.5.4 and 3.5.5.
Figure 4.4 Plasticizers incorporated into the ruthenium-polystyrene mixture dissolved in ethyl acetate.

The role of the ruthenium dye concentration in a 10% polymer solution was also studied. The amount of plasticizer used was 25% w/w compared to the polymer. We first started with an average percentage of polymers, dye and plasticizer based on published values in the literature. After that we optimized all three components using individual experiments to examine the influence of each component on ΔTC. If the plasticizer did not dissolve in the ruthenium-polymer mixture we dissolved the plasticizer in an appropriate solvent and added it to the ruthenium-polymer mixture. In the case of polystyrene, the para-toluene sulfonic acid was soluble in the solvent mixture, therefore it was not necessary to dissolve it prior to addition to the polymer-ruthenium mixture. The sensor film mixture was then spin coated on the glass slides at a rate of 1000 rpm for 30
seconds. Spin coated samples were placed under the fume hood to dry overnight and lifetime data was taken after drying.

Figure 4.5 shows the ΔTC data for changing ruthenium concentration in polystyrene. In this study polystyrene was dissolved in ethyl acetate and para-toluene sulfonic acid was used as the plasticizer. The ruthenium concentration study shows that ΔTC values decreases when ruthenium concentration increases from 0.0075 - 0.015 Ru(g)/Polymer(g). After 0.015 Ru(g)/Polymer(g), ΔTC values become constant. These results indicate that at lower ruthenium concentration ΔTC is higher. This observation suggests that lower ΔTC at higher ruthenium concentration may be due to dye aggregation and self quenching of chromophores. When the chromophores are not internally quenched by each other, ΔTC is increases, at higher ruthenium concentrations the ΔTC values become constant due to proximity interactions and quenching of the chromophores. The optimum ruthenium concentration for the polystyrene system is 0.0075 Ru(g)/Polymer(g).
Figure 4.5 Ruthenium concentration study of polystyrene dissolved in ethyl acetate

Figure 4.6 shows the lifetime data obtained for polystyrene-ruthenium system with various plasticizer concentrations. The results obtained from this study shows that ΔTC values increase with increase of plasticizer concentration ranges from 0.2-0.5 plasticizer(g)/polymer(g). After 0.5 plasticizer(g)/polymer(g) concentration, the ΔTC value decreases with increasing plasticizer concentration. The average plasticizer amount for the optimum ΔTC is ~ 0.5 plasticizer(g)/polymer(g) based on the data.
Figure 4.6 Plasticizer study of polystyrene dissolved in ethyl acetate with 0.0025 Ru(g)/Polymer(g) concentration.

Further studies were done to optimize polymer concentration. Figure 4.7 shows the ΔTC data for changing polymer concentration. In this study polymer was dissolved in dichloromethane as well as ethyl acetate. The results were obtained using the optimized conditions, where ruthenium concentration is 0.01 Ru(g)/Polymer(g) and the plasticizer concentration is 0.5 plasticizer(g)/polymer(g).
Figure 4.7 $\Delta TC$ values obtained for the polystyrene polymer concentration studies, polystyrene dissolved in ethyl acetate (□) in spread series, (■) drop series, and dichloromethane spread (○) and drop (●) series.

The polystyrene polymer study shows that Ethyl acetate is a better solvent to prepare sensor material over dichloromethane. In ethyl acetate series the $\Delta TC$ values increases with increase in polymer concentration. Therefore the optimized conditions for polystyrene polymer, where $\Delta TC$ value close to 2.0 is, 30% polymer, 0.5 plasticizer(g)/polymer(g) and 0.01 Ru(g)/Polymer(g) $[\text{Ru(Ph}_2\text{Phen)}_3]\text{Cl}_2$ concentration in ethyl acetate solvent system.
To obtain a reasonable quenching using the Oxysense 101 analyzer, the ΔTC values should be at least 2.0. When using the polystyrene polymer, it gives a ΔTC values less than 2.0. Further studies were conducted using different polymer matrices to find out whether other polymer systems provide ΔTC values of 2.0 or greater.

4.4 Polystyrene Sulfonate Polymer Oxygen Sensor

Protonated polystyrene sulfonate was prepared using polystyrene sulfonic acid sodium salt, which is commercially available as discussed in section 3.5.3. Poly(sodium-4-styrene) sulfonate is an anionic polymer which is interesting because of it's electrostatic interactions with the positively charged ruthenium complexes. These electrostatic interactions can prevent leaching of the dye, which is an advantage.

The order of addition of each component for the protonated polystyrene sulfonate is different than the nafion and polystyrene systems. \([\text{Ru(Ph}_2\text{Phen)}_3\text{]}\text{Cl}_2\) powder was dissolved in isopropanol first. Then polymer dissolved in isopropanol was transferred to the ruthenium solution and mixed well. Para-toluene sulfonic acid was dissolved in isopropanol and added last to the polymer/ruthenium mixture. This plasticizer was chosen using the same protocol used for polystyrene. The solution was stirred well and spin coated at a rate of 1000 rpm for 30 sec. Film samples were dried overnight under the fume hood and measured.

Optimization of all three components was carried out with an initial solution of 20% protonated polystyrene sulfonate acid, 25% plasticizer and the ruthenium concentration was varied from 0.008 – 0.03 Ru(g)/Polymer(g) as shown in Figure 4.8.
Figure 4.8 Ruthenium concentration study of protonated polystyrene sulfonate with 25% (w/w) plasticizer concentration

These films show maximum ΔTC values at the lower ruthenium concentrations. This suggests that the optimum may be at much lower concentration than 0.0008 Ru(g)/Polymer(g). However the values below 0.0008 Ru(g)/Polymer(g) were not acceptable due to low signal. Therefore the optimum concentration used was 0.0008 Ru(g)/Polymer(g). As observed for the polystyrene study discussed previously, ΔTC value decreases with increase of ruthenium concentration. Decreasing ΔTC values as
ruthenium concentration increases, is an indication of dye aggregation, a decrease of optical density, and self quenching of chromophores$^{10}$.

Optimization of the plasticizer was carried out using two different concentrations of ruthenium complex. The amount of plasticizer added to each film was varied from 0 – 0.35 plasticizer(g)/polymer(g) as displayed in Figure 4.9.

Figure 4.9 Plasticizer concentration study of protonated polystyrene sulfonate polymer system using 20% (w/w) polymer concentration, 0.0005 Ru(g)/Polymer(g) (○) and 0.001 Ru(g)/Polymer(g) (●)
Figure 4.9 show that the \( \Delta TC \) values increases with the increase of plasticizer concentration. As discussed for the previous polymer systems, \( \Delta TC \) value increase with the increase of plasticizer concentration. The explanation for this type of relationship is by adding plasticizer to the system, the oxygen permeability of sensor film increases\(^{11,12} \). Oxygen quenches the fluorescence lifetime, and as a result \( \Delta TC \) increases. From the data we find that \( \Delta TC \) has not reached a constant value indicating the optimum concentration of plasticizer is greater than 0.35 plasticizer(g)/polymer(g). The plasticizer concentration couldn’t exceed the 35% limit, because it was not miscible with the polymer matrix and as a result the sensor mixture separates.

In addition, the protonated polystyrene sulfonate polymer system did not provide \( \Delta TC \) values above the threshold of \( \Delta TC = 2.0 \) at any ruthenium or plasticizer concentration. Therefore further experiments were carried out using a heterogeneous polyacrylate polymer.

4.5 Polyacrylate Polymer Oxygen Sensors

The polyacrylate polymer is a heterogeneous material made up of acrylonitrile, 2-ethylhexylacrylate, methylimethacrylate and vinyl acetate monomer units. The heterogeneity of the polymer matrix results in high oxygen permeability\(^7 \) which can provide enhanced oxygen quenching of fluorescence lifetime resulting in higher \( \Delta TC \) values. Polyacrylate solubility studies show that it is soluble in both dichloromethane and ethyl acetate solvents. Therefore sensor films were prepared using both solvent systems to find out which solvent gives higher \( \Delta TC \) values.
Based on our studies the best plasticizer for the polyacrylate system is dioctylphthalate. To prepare the sensor \([\text{Ru(Ph}_2\text{Phen)}_3](\text{Cl})_2\) was dissolved in dichloromethane and added to the polymer solution and mixed. Addition of the plasticizer dioctylphthalate completed the solution preparation. The order of addition of the components followed this procedure regardless of the solvent used in the system.

Plasticizer concentration was studied using two different polymer concentrations. The ruthenium concentration for both 10% and 30% polymer solutions was 0.0015 \(\text{Ru(g)/Polymer(g)}\) (not optimized). In both studies the sensor films were spin coated on glass slides at a rate of 1000 rpm for 30 seconds. Figure 4.10 shows the TC and ATC data for changing plasticizer concentration in 10% polyacrylate.

Figure 4.10. TC in the presence of oxygen (●), in the absence of oxygen (○) and ATC (▲) values for the plasticizer concentration study using 10% polyacrylate polymer concentration that is not optimized for all three components.
When plasticizer concentration increases, there is a very little change in $\Delta$TC between 0-0.2 plasticizer(g)/polymer(g). After 0.2 plasticizer(g)/polymer(g), $\Delta$TC increases rapidly with increase of plasticizer concentration. The $\Delta$TC values do not reached a constant value for the 10% polymer solutions. However, we did not want to exceed 0.5 plasticizer(g)/polymer(g), making the polymer the minor component. Therefore for 10% polymer system the plasticizer concentration is kept at 0.5 plasticizer(g)/polymer(g).

![Figure 4.11 $\Delta$TC values for the Plasticizer study of 30% polyacrylate and 0.0015 Ru(g)/Polymer(g) concentration, not optimized for all three components](image_url)
The plasticizer concentration study using 30% polymer solution is displayed in figure 4.11. When experiments were carried out with 30% polymer concentration, the ΔTC value increases with increase of plasticizer concentration consistent with the 10% polymer. The difference between the two systems is the ΔTC values obtained for the 30% polymer systems are much larger than the 10% polymer system. However neither exceeds the ΔTC = 2.0 threshold at this point.

Figure 4.12 shows the ΔTC data for changing ruthenium concentration in 10% polyacrylate polymer solutions with 0.25 plasticizer(g)/polymer(g).

![ΔTC vs Ru(g)/Polymer(g)](image)

Figure 4.12 ΔTC values for the ruthenium concentration study of 10% polyacrylate polymer films not optimized for all three components

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Polymer films made of 10% polyacrylate shows optimum ΔTC values when the ruthenium concentration ranges from 0.002-0.005 ruthenium(g)/polymer(g). When the ruthenium concentration increases above 0.005 ruthenium(g)/polymer(g), the ΔTC value decreases and the ΔTC values become constant at 0.008 ruthenium(g)/polymer(g). These results indicate that at higher ruthenium concentration dye aggregation takes place and the oxygen quenching of fluorescence lifetime reaches a constant value as ruthenium concentration continuous to increase.

Figure 4.13 ΔTC values for the ruthenium concentration study of 30% polyacrylate not optimized for all three components

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Figure 4.13 shows the ΔTC data for changing ruthenium concentration in 30% polyacrylate polymer solutions. The results obtained for the 30% polyacrylate shows ΔTC increases with increase of ruthenium concentration, but the rate of increase of ΔTC decreases with increase of ruthenium concentration. The optimum concentration of ruthenium is 0.005 ruthenium(g)/polymer(g) when the polyacrylate concentration is 30%. In both studies, when the polymer concentration is 10% or 30% the optimum ruthenium concentration is 0.005 ruthenium(g)/polymer(g).

Polymer concentration studies were performed with freshly prepared films that were spin coated, dip coated and wiped in order to determine the best way to prepare the sensor film. Results were shown in Figure 4.14 – 4.21. Ruthenium concentration used for the polymer concentration study was 0.005 ruthenium(g)/Polymer(g) and the plasticizer concentration was 0.5 plasticizer(g)/polymer(g).

Figure 4.15 and 4.16 shows TC and ΔTC values obtained for 10%, 20% and 30% polymer concentrations, where polymer was dissolved in dichloromethane and series of drops were made. According to figure, ΔTC value decreases with increase of polymer concentration. When the polymer concentration is 10%, the ΔTC values were above 2.0.
Figure 4.14 TC in the presence of oxygen (●) and in the absence of oxygen (○) where polyacrylate dissolved in dichloromethane drop series.
Figure 4.15 ΔTC values for the polymer concentration study of polyacrylate dissolved in dichloromethane drop series

Figure 4.16 and 4.17 shows TC and ΔTC values obtained for 10%, 20% and 30% polymer concentrations, where polymer was dissolved in dichloromethane and series of spread samples were made. According to figure, ΔTC value increases with increase of polymer concentration. When the polymer concentrations are 20% and 30%, the ΔTC value reached above 2.0. However all values are close to the ΔTC = 2.0 value.
Figure 4.16 TC values in the presence of oxygen (●) and in the absence of oxygen (○), polyacrylate dissolved in dichloromethane spread series.
When the polyacrylate polymer dissolved in dichloromethane solvent, the drop series and spread series shows the trend of $\Delta$TC values go in opposite directions. This result suggests that optical density or dye aggregation dominates at higher polymer concentration in that solvent. When the thickness of the film is high oxygen permeability$^{11}$ of the sensor film decreases, as a result $\Delta$TC value decrease with increase of polymer concentration. In both studies; drop and spread series the $\Delta$TC values are

Figure 4.17 $\Delta$TC values for the polymer concentration study of polyacrylate dissolved in dichloromethane spread series
above 2.0, a very good indication that this system can be used to develop the oxygen sensor.

Figure 4.18 and 4.19 show the TC and ΔTC values for the polymer concentration study of polyacrylate polymer dissolved in ethyl acetate where series of samples were placed as drops.

![Figure 4.18 TC values in the presence of oxygen (•) and in the absence of oxygen (○), polyacrylate dissolved in ethyl acetate drop series.](image)

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Figure 4.19 $\Delta$TC values for the polymer concentration study of polyacrylate dissolved in ethyl acetate drop series

Figure 4.20 shows the TC values obtained for polymer concentration study where polyacrylate was dissolved in ethyl acetate and samples were made by spreading the sensor solution. In figure 4.20 the TC values obtained under nitrogen atmosphere, where polyacrylate dissolved in ethyl acetate spread series, at 10% polymer solution the signal was not strong enough to measure.
Polyacrylate dissolved in ethyl acetate spread series shows the same trend as for the dichloromethane spread series. When comparing the drop series with the spread series, the trend of ΔTC values go in opposite directions. In the drop series, ΔTC values decreases with increase of polymer concentration. In the spread series ΔTC values increases with the increase of polymer concentration. These results suggest that dye aggregation\textsuperscript{10} plays a role in developing the sensor. That results suggest that the thickness
of the films and dye solubility are important factors in the sensor response. All the polyacrylate studies show that ΔTC values of 2.0 can be achieved.

Curing of sensor material was tested to find out if it can eliminate the ΔTC dependence on the application method. Previous studies show that ΔTC depend on the application method. When the sensor material was cured for 24hrs. at 60 °C, the material changed from opaque orange to translucent red-orange, indicating the dye interaction with the polymer matrix has changed. Figure 4.21 shows the microscopic images of pre-cured and post-cured sensor films.

![Microscopic images of sensor films](image)

Figure 4.21 Microscopic images of uncured sensor films (a) & (b), cured and reconstituted sensor films (c) & (d).
The microscopic images clearly indicates the number and the size of the ruthenium dye particles in the cured samples were less than uncured samples. The color transition from opaque to translucent and the microscopic images of sensor films indicates the dye molecules solubalized in the sensor platform and the three component system mixing with each other properly and distributing each component evenly. With this treatment the method used to cast the sensor films does not influence the response of the sensor. Prior to curing the deposition method strongly influence the ΔTC values obtained.

The reconstituted sensor materials were prepared by using the optimized concentrations of each component as discussed previously. The ruthenium concentration was based on a dye/polymer ratio of 0.005 and a plasticizer/polymer ratio of 1.0. A 10% polymer solution was used and the three components were mixed in the order of polymer/dye/plasticizer. After mixing the three components, the sensor solution was cured for minimum of 24 hours at 60 °C to produce the final cured material. In the cured material, all solvent was removed under vacuum conditions to facilitate the complete drying of the material. The dried material was reconstituted in using 0.1 g per mL of solvent ethyl acetate and deposited on glass slides using different techniques. TC and ΔTC values were measured for the prepared samples. Figure 4.22 shows the TC and ΔTC values obtained for the reconstituted materials.
Figure 4.22 TC values in the presence of oxygen (●) and in the absence of oxygen (○) and ΔTC (▲) values for the reconstituted polyacrylate dissolved in ethyl acetate, optimized for all three components.

Figure 4.22 proved that all four samples were reached to the goal of ΔTC = 2.0 value. These results suggest that curing removes deviation of ΔTC due to application technique.

When comparing all four polymers, naftion, polystyrene, protonated polystyrene sulfonate and polyacrylate, the best results were obtained with the cured polyacrylate polymer. Batches at this material have produced ΔTC values over 2.0 for well over a year.

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4.6 References


CHAPTER 5

CONCLUSIONS

The goal of this research was to develop an optical oxygen sensing device for the food packaging industry where Oxysense 101 non-invasive oxygen analyzer system can be used to measure the oxygen contaminant within sealed packages. Ruthenium(II) polypyridyl complexes are well known oxygen sensing materials that have been used previously in sensor applications. We chose to focus on these common dyes for our sensor. When developing the sensor, these oxygen sensitive dyes were added to the polymer solution and plasticizer was added to improve the oxygen permeability of the sensor film.

A secondary goal of the research was to synthesize ruthenium complexes for the oxygen sensing. Two different ruthenium complexes were synthesized in the laboratory with an acceptable yield. The tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) hexafluorophosphate complex, which is a well known oxygen sensitive ruthenium complex, can be synthesized in the laboratory with a 95% yield. The tris(1,10-phenanthroline) ruthenium(II) hexafluorophosphate complex can be synthesized with a slightly lower yield of 82%. When synthesizing the tris ruthenium complexes, the two step synthesis procedure was more successful than the single step procedure.

Developing an optical oxygen sensing device was completed successfully using the tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) dichloride complex. A standard
procedure was followed for preparing the sensor material to ensure reproducibility. In this study we utilize fluorescence lifetime quenching parameter to measure the sensitivity to oxygen in the sensor film. The fluorescence lifetime measurements were taken using Oxysense 101 analyzer.

Four different polymer matrices were examined and used to prepare oxygen sensors. Nafion, a perfluorinated polymer was examined and was successful as an oxygen sensor. However the high cost of the polymer precluded it's use. Polystyrene and protonated polystyrene sulfonate polymer were also examined and rejected, because ΔTC values were below the threshold of 2.0. The oxygen sensor made using the heterogeneous polyacrylate polymer gives the ΔTC value of 2.0, which does not change with the method of application and the material was reconstituted.

The best package for the oxygen sensor developed using polyacrylate polymer was with the ruthenium concentration of 0.005 g of \([\text{Ru}(\text{Ph}_2\text{Phen})_3](\text{Cl})_2\) complex per 1.0 g of polymer. The plasticizer dioctylphthalate was in a ratio of 0.5 g plasticizer per 1.0 g of polymer/dye/plasticizer mixture. Ethyl acetate was used as the solvent to dissolve the polymer and the ruthenium complex was dissolved in dichloromethane. The polymer concentration used for the polymer ticket lies between 10%-20%. The order of addition was ruthenium mixed with polymer followed by the addition of the plasticizer. After mixing all three components together, the solution was cured for minimum of 24 hours at 60° C to produce the dried sensor material. This material is reconstituted when required to produce the solutions required for preparing the free standing polymer sensor.
5.1 References


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