

A morphological and cyclic voltammetric investigation of spin-coated hexaammineruthenium (III)-incorporated Nafion® thin films

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Hexaammineruthenium(III)-incorporated Nafion® thin films (<600nm) were fabricated using dynamic dispense spin coating. The concentration of the ruthenium complex and the thinning rates were varied and compared. Scanning electron microscopy was used to investigate the surface morphology of the spin-coated thin films and cyclic voltammetry (CV) for the transport properties. Micrographs showed the presence of lumps on the most concentrated film, but were better smoothed with increased thinning rates and vanished with decreased concentration, and that the surface appeared to be smooth. CV characterizations showed that concentrations played a greater role in the conductivity of the film resulting from the concentration of the redox mediator content which indicated that thinner films, therefore, were either more efficient or more sensitive. The test also indicated that the ruthenium complex was immobilized in the Nafion film.

INTRODUCTION

Nafion® by DuPont, is a perfluorosulfonated ionomer that results from the copolymerization of perfluorosulfonated vinyl ether and tetrafluoroethylene (Abuin et al. 2013, Lin and Chang 2008). Nafion has three distinct groups: (1) a hydrophobic poly-tetrafluoroethylene backbone, (2) side chains that connect the

first group and the third group, and (3) a hydrophilic sulfonate group (Viswanathan and Helen 2007, Ijeri et al. 2010). These groups tend to clump together and form clusters or micelle structures which provide a physical passage for the movement of ions for ionic conductivity making it a polymer electrolyte or an ionomer (Viswanathan and Helen 2007, Neves et al. 2010, Klotzbach et al. 2006). Aside from this, Nafion exhibits good mechanical, chemical, and thermal stability for temperatures up to 80°C which makes it a candidate for electrochemical applications such as in polymer exchange membrane fuel cells (PEMFCs) and chlor-alkali separators where it acts as a proton exchange membrane, and in sensors where it provides electrode protection and increases its sensitivity (Viswanathan and Helen 2007, Ijeri et al. 2010, Neves et al. 2010, Klotzbach et al. 2006, Schwenzer et al. 2011, Jao et al. 2012, Sands et al. 2002, Selamet et al. 2011, Bertonecello and Ugo 2003, Bertonecello et al. 2007, Calufmán et al. 2010, Xu et al. 2008). For sensing applications, redox reagents are immobilized in an acceptable polymer membrane where they act as an electron bridge between the electrode and the surrounding medium (Sands et al. 2002). Nafion, however, is expensive; therefore, the use of thin films that use less material for modified electrode fabrication is utilized in this study.

Spin coating involves the deposition of a material onto the substrate and spinning it at high speed where centrifugal force causes the fluid to flow radially outwards and off the edge of the substrate to leave a uniform thin film (Lawrence and Zhou

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1991). It is a relatively simple, economic, and fast technique for coating surfaces compared to dip coating, Langmuir-Blodgett, drop coating method, capillary immersion force, and electrophoretic deposition (Ogi et al. 2007). It is also widely used in the deposition of photoresists, antireflection coatings, dielectric layers, and passivating layers in manufacturing integrated circuits, magnetic storage drives, and super conducting thin films. Spin coating is essentially a part of the automated production process (Lawrence and Zhou 1991, Le roux and Paul 1992, Liu et al. 2003, Birnie III et al. 2010) which signifies that it yields reproducible results (Ogi et al. 2007). These advantages of spin coating make it an attractive fabrication technique for modified electrodes.

Modified electrodes are electrochemical sensors that have been chemically modified by attaching molecules to the surfaces to improve its sensitivity (Oni et al. 2005). Modification of an electrode is achieved by coating the electrode with a film where a surface-active material or mediator is immobilized that mediates fast electron transfer between the electrode and the bulk solution (Hajjizadeh et al. 2008). Modified electrodes have a wide range of potential applications in electrochemical technology, energy conversion, chemical analysis, information storage, electrochromic devices, displays, catalysis of reactions, and in electron transfers between the electrode and biological molecules (Oni et al. 2005, Hajjizadeh et al. 2008).

In this study, varying concentrations of hexaammineruthenium $[\text{Ru}(\text{NH}_3)_6]^{3+}$ -incorporated Nafion thin films were spin coated at 1500 rpm, 2000 rpm, and 2500 rpm on indium tin oxide (ITO)-coated glass substrates. $[\text{Ru}(\text{NH}_3)_6]^{3+}$ was chosen as the redox mediator because it is an established cation model and because it has fast electron transfer (Lojou and Bianco 2000, Limon-Petersen et al. 2010). Scanning electron microscopy (SEM) characterization was used to determine the surface morphology and thickness of the fabricated films. Cyclic voltammetry (CV) was used to determine the transport properties of the fabricated films.

METHODOLOGY

Materials

Nafion at 5% w solution was obtained from Fuel Cell Earth (Wakefield, Massachusetts, United States). Hexaammineruthenium(III) Chloride (98%)- and ITO-coated glass slides, rectangular, with surface resistivity of $15\text{-}25 \Omega \text{ sq}^{-1}$, were procured from Aldrich (St Louis, Missouri, United States).

Preparation of Substrates

Smaller ITO-coated substrates at $2.5 \text{ cm} \times 1.0 \text{ cm}$ and at $\sim 0.25 \text{ cm}^2$ sizes were prepared from ITO-coated glass slides ($7.5 \text{ cm} \times 1.0 \text{ cm}$) by cutting with a diamond tip glass cutter. The smaller pieces were sonicated in acetone and isopropyl alcohol for 5 minutes each, respectively, to remove surface contami-

nants. These were air dried before spin coating.

Preparation of Casting Solutions

The solutions were prepared with 75 mg, 50 mg, and 25 mg of hexaammineruthenium chloride $[\text{Ru}(\text{NH}_3)_6\text{Cl}_3]$ in 30 mL of 5% Nafion solution to obtain a $8.1 \times 10^{-3} \text{ mol dm}^{-3}$, $5.4 \times 10^{-3} \text{ mol dm}^{-3}$, and $2.7 \times 10^{-3} \text{ mol dm}^{-3}$ Nafion- $[\text{Ru}(\text{NH}_3)_6]^{3+}$ casting solution, respectively, in a "one-step process". The "one-step" method avoids a lengthy redox mediator incorporation process, i.e., the redox mediator was incorporated in the Nafion solution before coating instead of incorporation after coating (Bertoncello et al. 2007).

The prepared $8.1 \times 10^{-3} \text{ mol dm}^{-3}$, $5.4 \times 10^{-3} \text{ mol dm}^{-3}$, and $2.7 \times 10^{-3} \text{ mol dm}^{-3}$ solutions were referred to as 75mg, 50mg, and 25mg Ruhex, respectively. The 75mg Ruhex was the optimum concentration because precipitate formed at higher concentrations (Bertoncello et al. 2007). The various concentrations were chosen to determine how concentration affected film thickness in the cyclic voltammetry tests.

The volume of Nafion used was dependent on the requirement that at least 30 mL be used in order for the modified set-up to spray properly. Set-up modification was necessary because the minimum volume required for the unmodified set-up was 200 mL. The set-up was modified by placing a 50 mL container with the casting solution inside the canister. The 50 mL container raised the liquid level such that the solution could be drawn by the dispensing system.

Fabrication of Spin-coated Modified Electrodes

Spin coating was done using a Spin Coat G3P-8 spin coater (Specialty Coating Systems, Indianapolis, United States). A dynamic dispense spin-coating process that involved two steps was used: the deposition stage and the thinning stage. At the deposition stage, the substrate was spun at a low rate and then deposited with the solution. At the thinning stage, the substrate was spun at a higher rate and excess solution was removed from the substrate leaving behind a thin layer. Dynamic dispense was preferred over static dispense because less solution was needed to coat the entire surface. The centripetal force during the deposition stage allowed the solution to immediately spread throughout the surface unlike in static dispense where, depending on the viscosity, too much or too little solution could be deposited on the substrate (Birnie III et al. 2010).

The substrate was spun at an initial rate of 750 rpm for 6 seconds after the solution was sprayed onto the substrate (deposition stage). It was spun at a higher rate of 1500 rpm, 2000 rpm, or 2500 rpm, for 30 seconds to spread and thin out the solution on the surface (thinning stage). The coated substrates were baked in a THERMOLYNE 4800 furnace (Barnstead Thermolyne Corporation, Iowa, United States) at $70\text{-}80^\circ\text{C}$ for 30 minutes to remove excess moisture content.

Scanning Electron Microscopy

A JEOL 5310 scanning electron microscope was used for morphological characterizations at 10,000X magnification. Because the sample was a polymer and non-conductive, the substrate was gold-coated using JEOL JFC-1200 in order to increase the image quality and to prevent the sample from excessive heating and charging. The conducting side of the substrate was gold-coated for 40 seconds while the non-conducting side was gold-coated for 30 seconds. The non-conducting side was also coated to avoid charge build-up and to provide better image quality.

To measure the thickness of the films, the SEM stage was lowered from 15 mm to 40 mm and rotated to an angle of 75°. In measuring film thickness, a 90° angle was drawn and a measuring line was later drawn and tilted such that it was parallel to the 90° angle. Ten (10) measurements were done to determine the average thickness of the film. Measurements with respect to the scale provided on the micrograph were done using SemAfore5.21 (JEOL, Sollentuna, Sweden).

Cyclic Voltammetry

Cyclic voltammetry measurements were performed using BST8-Stat Potentiostat/Galvanostat (NuVant Systems Inc., Indiana, United States) interfaced to a computer with BST8-Stat v.5.2.12.0730. A standard three (3) electrode setup was used, with the coated substrates as the working electrode, a saturated calomel (Hg₂Cl₂) electrode (KCl-saturated) as the reference electrode, and a coiled platinum electrode as the counter electrode. A 100 mL of 0.1 mol dm⁻³ NaCl was used as the supporting electrolyte.

The tests were performed, with the working electrode dipped to submerge 2 cm² of the electrode area, at three scan rates: 50 mV s⁻¹, 100 mV s⁻¹, and 200 mV s⁻¹, at a potential range of -0.6 V to +0.1 V. The reference potential used was the potential of the standard hydrogen electrode and expected results were shifted with respect to the saturated calomel electrode's potential. Three (3) trials were performed for each electrode and the average was reported.

RESULTS AND DISCUSSION

Scanning Electron Microscopy

The results of surface and tilted micrographs of the 75mg, 50mg, and 25mg Ruhex films spin coated at 1500 rpm, 2000 rpm, and 2500 rpm (Figures 1-3) were taken at 10,000X magnification. Some of the tilted micrographs were taken at 7,500X magnification and some at 10,000X magnification because lesser film thickness was more difficult to measure. The lumps observed with the 75mg Ruhex could be attributed to the surface roughness of the ITO substrate and the ruthenium complex as well as the reported formation of precipitates at higher Ruhex concentrations (Bertoncello et al. 2007). The lumps were not

observed at lower concentrations and decreased with increased thinning rate. The surfaces generally appeared to be smooth at lower Ruhex concentrations.

The averaged thicknesses of the films were found to be 567 nm for the 75mg, 589 nm for the 50mg, and 566 nm for the 25mg Ruhex films. The averaged thicknesses were used in the calculation of the diffusion coefficients.

Cyclic Voltammetry

Figures 4A and 5A show the cyclic voltammograms of electrodes fabricated at the 75 mg and 25 mg Ruhex concentration and spin coated at 1500 rpm, 2000 rpm, and 2500 rpm. The results indicate that there was a relatively small difference in current with increased thinning rate which could be attributed to the presence of less redox mediator, which facilitated charge transfer between two mediums. In Figure 6, the cyclic voltammograms of electrodes fabricated at 75 mg, 50 mg, and 25 mg Ruhex concentrations and spin coated at 1500 rpm (a) and at 2000 rpm (b) show a more significant change in current which suggests that the redox mediator content was less, resulting in lower current measured.

Comparison of Figures 4A, 5A, and 6 shows that concentration was more dominant than the thickness parameter in measuring conductivity. This could be attributed to the presence of a higher concentration of the redox mediator in the film. The results indicate that thinner films did not result in more efficient or more sensitive sensors.

To establish whether diffusion or activation controlled the reaction rate, peak currents vs. the square root of the scan rate were plotted (Figures 4B and 5B). A linear slope depicts a diffusion-controlled system in which the diffusion rate is the rate of reaction of the species; in this system, the rate of reaction of the ruthenium complex is dependent on its mobility. The small diffusion coefficient indicates that the redox-active species can move a small distance to the next nearest redox-active species and pass the charge through reduction or oxidation. The differences in the slope of the lines in Figures 4B and 5B indicate that the effect of film thicknesses is better manifested with increasing scan rates.

The diffusion coefficient was calculated using the Randles-Sevcik equation (eq. 1) where I_p is the peak current in Amps that was obtained from the voltammograms; k is the constant $2.69 \times 10^5 \text{ C mol}^{-1} \text{ v}^{-1/2}$; n was the number of electrons transferred, A was the geometric area of the electrode in cm²; D is the diffusion coefficient in cm² s⁻¹; C_p was the concentration of the mediator in the film in mol cm⁻³; and v was the scan rate in V s⁻¹.

$$I_p = k n^{(3/2)} A D^{(1/2)} C_p v^{(1/2)} \quad (\text{eq. 1})$$

Only one (1) electron was transferred during the half reaction of [Ru(NH₃)₆]³⁺ (eq. 2) thus the value of n is 1.

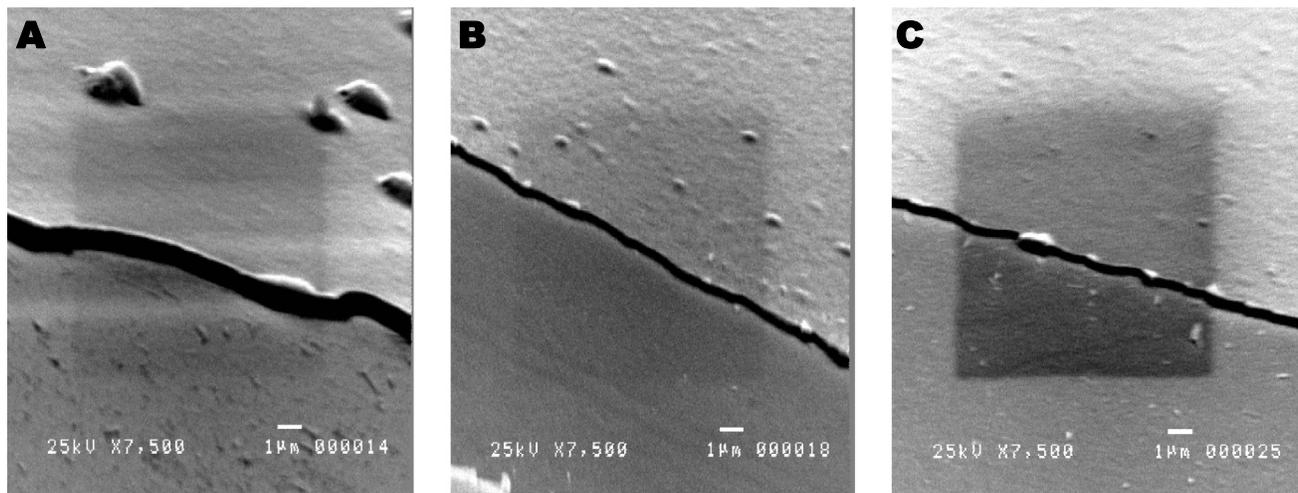


Figure 1. Tilted micrographs of 75mg Ruhex films fabricated at 1500 rpm (A), 2000 rpm (B), and 2500 rpm (C).

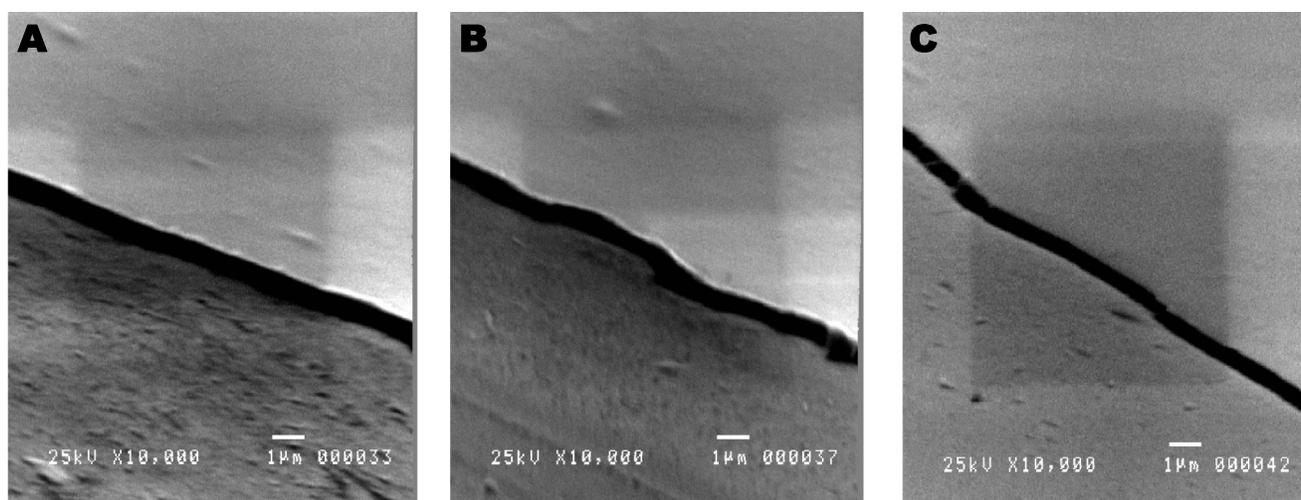


Figure 2. Tilted micrographs of 50mg Ruhex films fabricated at 1500 rpm (A), 2000 rpm (B), and 2500 rpm (C).

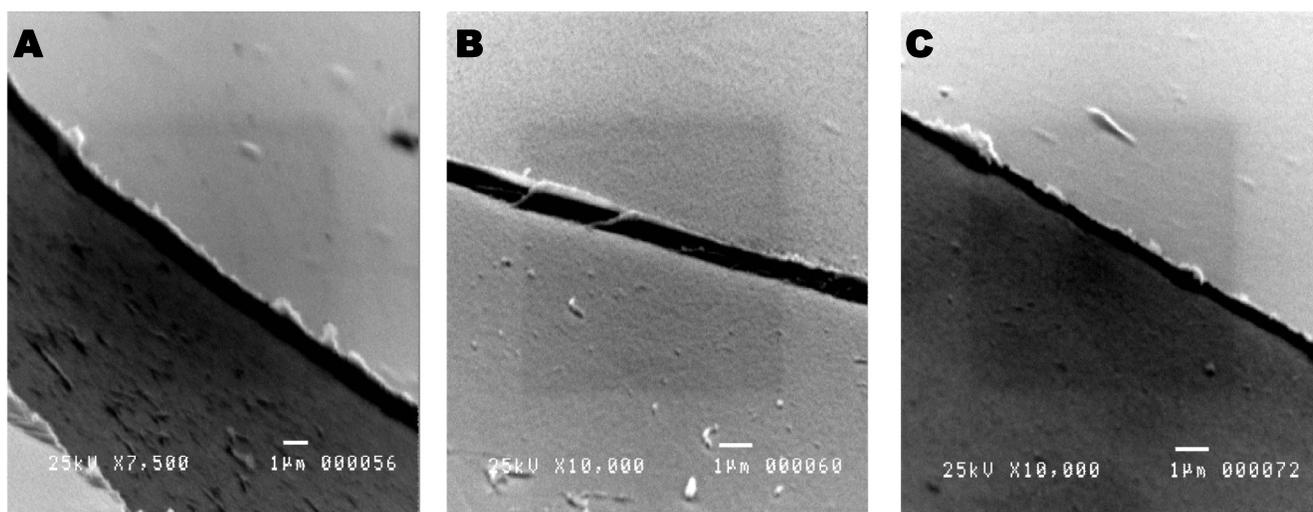


Figure 3. Tilted micrographs of 25mg Ruhex films fabricated at 1500 rpm (A), 2000 rpm (B), and 2500 rpm (C).

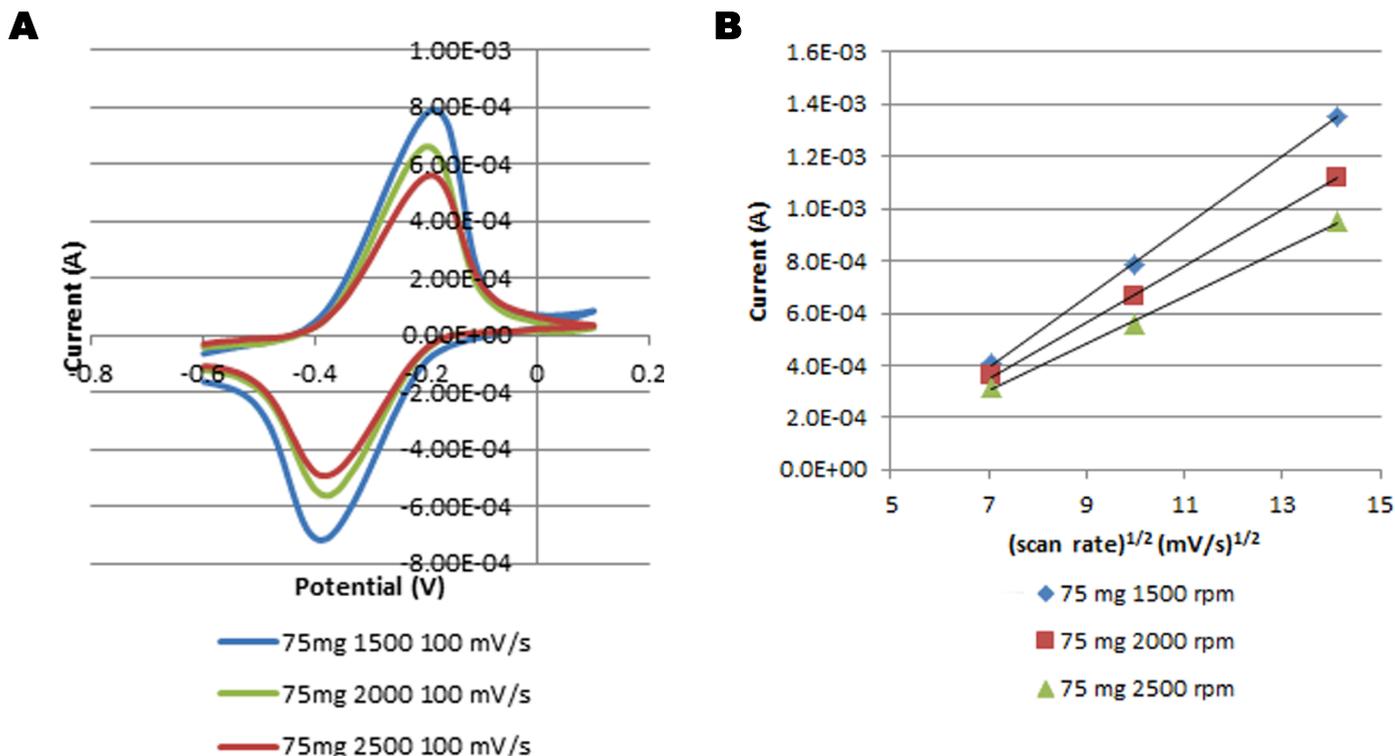


Figure 4. Cyclic voltammograms (A) and plot of the peak currents versus the square root of the scan rates (B) of 75mg films spin coated at 1500 rpm, 2000 rpm, and 2500 rpm.

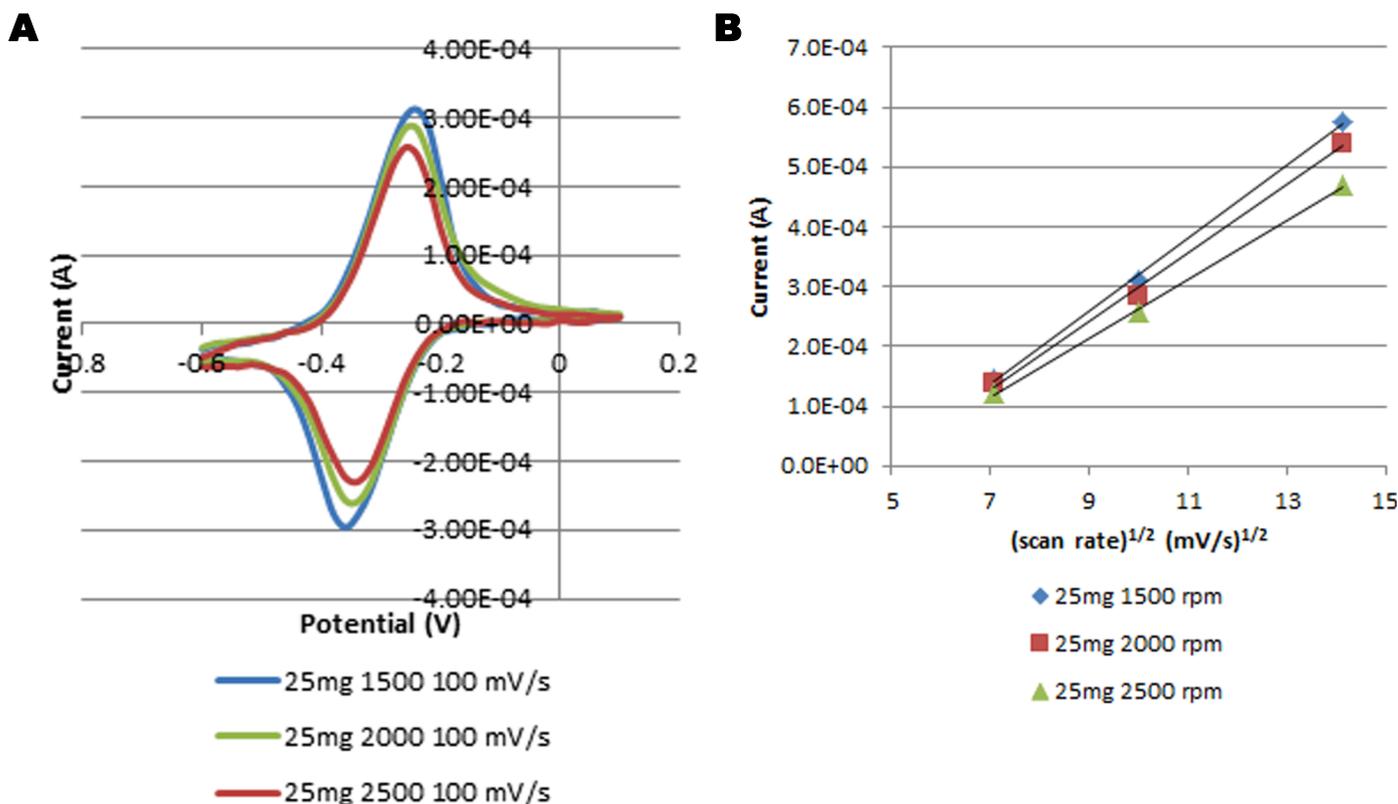


Figure 5. Cyclic voltammograms (A) and plot of the peak currents versus the square root of the scan rates (B) of 25mg films spin coated at 1500 rpm, 2000 rpm, and 2500 rpm.

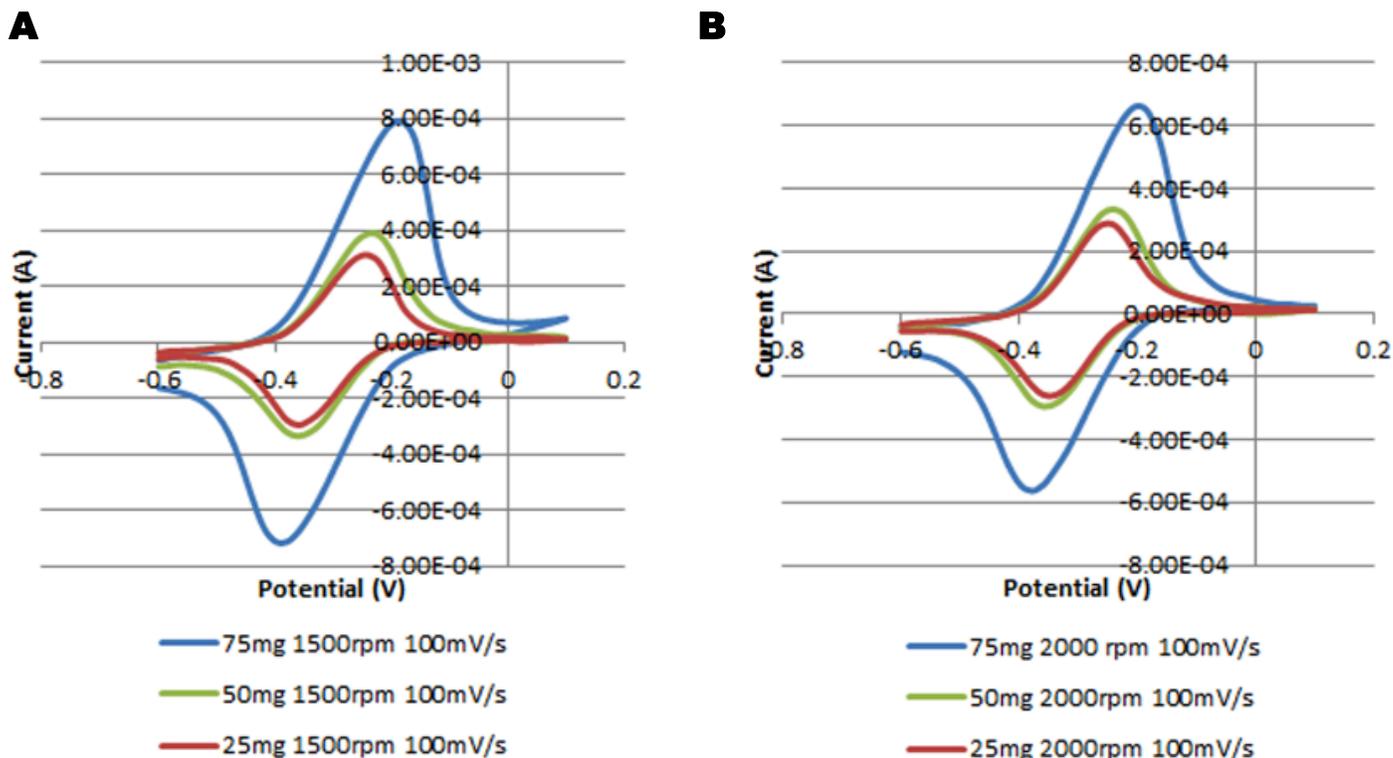
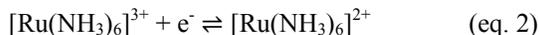


Figure 6. Cyclic voltammograms of 75mg, 50mg, and 25mg films spin coated at 1500 rpm (A) and 2000 rpm (B) comparing concentration with conductivity.



To solve for the concentration of the mediator in the film (C_p), the amount of immobilized redox active material (ΓA) is divided by the volume of the film (V_{film}) in cm^3 (eq. 3).

$$C_p = (\Gamma A) / V_{film} \quad (\text{eq. 3})$$

The surface coverage of the film (Γ) in mol cm^{-2} was calculated by dividing the total charge of the redox mediator (Q) in coulombs (C) by the product of the number of electrons transferred (n), Faraday's constant (F) ($96,486 \text{ C mol}^{-1}$), and the area of the electrode (A) in cm^2 (eq. 4). The total charge (Q) was determined by data analysis using the BST&STAT software which generally measures the area under the curve of the half reaction.

$$\Gamma = Q / (nFA) \quad (\text{eq. 4})$$

The results at calculated values of the films are summarized in Table 1. Average diffusion coefficients (D) are of the order of 10^{-9} and 10^{-10} which correspond to the immobilized redox mediators. Immobilized redox mediators correspond to diffusion coefficients of the order of 10^{-8} to $10^{-11} \text{ cm}^2 \text{ s}^{-1}$; diffusional redox mediators correspond to diffusion coefficients of the order of 10^5 to $10^7 \text{ cm}^2 \text{ s}^{-1}$ (Vielstich et al. 2009). The diffusion coefficients of the ruthenium complex indicate that it was immobilized. Im-

mobilized redox mediators are preferred because they are stationary and conduct electrons by means of electron hopping rather than physically diffusing onto the surface of the electrode. In this study, the immobilization of the ruthenium complex combined with the diffusion-controlled system allowed for a faster response time as the complex diffuses to a short distance almost instantaneously.

CONCLUSIONS

Using a dynamic dispense spin coating technique, varying concentrations and thicknesses of hexaammineruthenium(III) $[\text{Ru}(\text{NH}_3)_6]^{3+}$ -incorporated Nafion[®] thin films were fabricated on ITO-coated glass substrates. SEM characterizations at 10,000X magnification revealed the presence of lumps at the 75mg Ruhex concentration but were better smoothed with increased thinning rates and which vanished with decreased concentration. Tilted micrographs of the surface of the films showed that they generally appear smooth. CV characterizations indicated that thinner and less concentrated films were less conductive compared to thicker and more concentrated films. The spin rate that yielded the highest reduction current for each sample concentration was 1500 rpm. Film thickness played a minor role in conductivity compared with film concentration, and a thinner film did not necessarily correspond to greater sensitivity or greater efficiency. The immobilization of the ruthenium complex was

Table 1. Diffusion coefficient and its corresponding variables.

Concentration (mg)	Thinning rate (rpm)	Thickness (cm)	Peak Current (A)	Total Charge (C)	Γ (mol cm ⁻²)	C _p (mol cm ⁻³)	D (cm ² s ⁻¹)
75	1500	5.666E-05	8.485E-04	1.323E-03	6.858E-09	1.210E-04	1.426E-09
	2000	3.408E-05	7.144E-04	1.176E-03	6.095E-09	1.788E-04	4.850E-10
	2500	3.034E-05	6.072E-04	1.032E-03	1.671E-08	5.509E-04	2.092E-10
50	1500	5.886E-05	4.222E-04	6.608E-04	3.424E-09	5.818E-05	1.599E-09
	2000	3.555E-05	3.821E-04	5.631E-04	2.918E-09	8.208E-05	6.353E-10
	2500	3.236E-05	1.794E-04	3.467E-04	1.797E-09	5.552E-05	3.581E-10
25	1500	5.655E-05	3.419E-04	4.847E-04	2.512E-09	4.442E-05	1.724E-09
	2000	3.711E-05	3.226E-04	4.726E-04	2.449E-09	6.599E-05	6.987E-10
	2500	3.043E-05	2.858E-04	4.031E-04	2.089E-09	6.865E-05	5.131E-10

inferred from the diffusion coefficients, and a linear relation was observed between the peak current and the square root of the scan rate which denoted a fast-response diffusion-controlled system.

CONFLICTS OF INTEREST

None

CONTRIBUTIONS OF INDIVIDUAL AUTHORS

KAYK collected related literature, did the experimental part of the research and took part in the analysis of the data. STP formulated the problem, directed the experiments, analyzed the results, and took charge of the procurement of the materials. MTN took part in the formulation of the problem, devised the experimental procedure, collected related literature, and helped analyze the results.

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