Morphological and voltammetric characterization of different concentrations of spin coated Nafion-Ru(bpy)$_3^{2+}$ thin films

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Abstract. Different concentrations of Ru(bpy)$_3^{2+}$ were successfully deposited on ITO coated glass substrates employing a simple method using a spin coater. The surface morphology was determined by scanning electron microscopy (SEM). The transport mechanism and the diffusion coefficient of the redox mediators within the films were characterized using cyclic voltammetry (CV). The concentrations were varied by dissolving different amounts of the redox mediator in methanol and 5% Nafion. SEM micrographs showed that the roughness of the surface increased with concentration of redox mediator. CV showed successful incorporation of Ru(bpy)$_3^{2+}$. The order of the magnitude of the diffusion coefficients confirmed that the redox mediators were immobilized within the Nafion thin film. The resulting amount of redox mediator immobilized can be manipulated by simply varying the concentration of the casting solution.

1. Introduction

Nafion has received a considerable interest in technological and scientific researches due to its stability in a wide range of applications. Nafion is biologically inert and is mechanically, chemically and electrochemically stable [1]. These properties make Nafion to be the primary material in numerous applications such as fuel cells, water electrolyzers, chloralkali cells, chemically modified electrodes, ion-selective electrodes and especially, sensors.

In sensor applications, electrodes are coated with mediator doped Nafion films since the electrode surface is prone to fouling effect which is caused by the organic components’ adsorption[2]. Redox mediators are often used in reactions of organic compounds which react very slowly with the bare electrode surface. It functions as an intermediate oxidizing/reducing agent, which facilitates the transport of electrons between the organic species in the bulk solution and the electrode. Nafion, as the cation exchange polymer is a suitable coating because it prevents anionic compounds from scavenging the cationic mediators as it would if the mediators are situated in the bulk solution as well.

In electroanalytical studies, Nafion coated modified electrodes are commonly used for determining trace concentrations of electroactive cations[3]. Voltammetric signals relevant to the preconcentrated analytes are dependent on the physical feature of the Nafion film. This is due to the fact that the ionic conductivity of Nafion is strongly dependent on the morphological characteristics of the film [3]. It is

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this reason why exploring different methods of depositing Nafion films and studying the resulting electrochemical behavior is relevant.

Nafion, when doped with the redox mediator, ruthenium(II) bipyridylRu(bpy)$_3^{2+}$, allows the flow of electrons to the ITO coated electrode surface. This conducting material is widely used because of its high transmittance and low electrical resistivity.

This study focuses on the variation of the concentration of the thin films of Nafion integrated with Ru(bpy)$_3^{2+}$ using the spin coating technique. The surface morphology was determined by scanning electron microscopy. The transport mechanism, and the diffusion coefficient of the redox mediators within the films were characterized using cyclic voltammetry.

2. Experimental

Modified electrodes were fabricated from different concentrations of casting solutions using the spin coating technique. The concentrations were based on those used in the one step procedure by Bertoncello et al. [4]. Films with different thicknesses were produced by varying the speed at which the films were thinned out. The spin coated substrates were baked in a furnace at around 70-80°C for 30 minutes.

2.1. Preparation of substrates

Indium tin oxide (ITO) coated glass substrates (sheet resistance 15-25 Ω/sq. slide) with dimensions of 7.5 cm x 1.0 cm were cut using a diamond tip glass cutter on the uncoated part the glass. The substrates were cut into 2.5 cm x 1.0 cm strips for use in fabricating the electrodes and ~1.25 cm x 1.0 cm for the SEM and characterization. The substrates were sonicated in acetone and isopropanol for 5 minutes, respectively. The substrates were then placed in a petri dish until it dried and was immediately used for the film depositions.

2.2. Preparation of Nafion-Ru(bpy)$_3^{2+}$ stock solutions

A protocol based on the one-step procedure of Bertoncello et al. [4] was used to incorporate the cationic redox-active Ru(bpy)$_3^{2+}$ in the Nafion film. Casting solutions of Nafion-Ru(bpy)$_3^{2+}$ were prepared by dissolving 2 mg, 1 mg and 0.2 mg of the redox mediator in 20 mL of reagent grade methanol. 0.2 mL of 5% Nafion solution was subsequently added using a Transferpette® micropipette. For simplicity, concentrations of redox mediator dissolved in the casting solution is expressed in terms of the ratio of mass(mg) of Ru(bpy)$_3^{2+}$ to amount(mL) of 5% Nafion. Thus, the three casting solutions will be referred to as 10mg/mL, 5mg/mL and 1mg/mL respectively.

The amount of Tris(bipyridyl)ruthenium(II) dichloride was carefully weighed using a BOSCH SAE200 electronic balance by differential weighing, using a laboratory grade wax paper as container. The stock solutions were sonicated to ensure that the ruthenium complex was fully dissolved. The concentrations of tris(bipyridyl)ruthenium(II) dichloride were chosen to be less than or equal to that used by Bertoncello et al. [4]. Greater concentrations of the mediator resulted in saturation and precipitation of the ruthenium complex in agreement with Bertoncello et al. [4].

2.3. Fabrication of spin coated modified electrodes

The Nafion - redox mediator solution was casted onto the previously cut ITO coated glass substrates using the spin coating technique. The SPINCOAT G3P-8 spin coating unit requires a constant supply of nitrogen gas to purge the coating chamber to minimize the effects of factors such as airborne contaminants and varying humidity.

The substrates underwent two stages of coating— the deposition and the thinning stages. During the deposition stage, the substrates were spun at 750 rpm for about 6 seconds during which, the casting solutions were sprayed onto the substrates. The substrates were then accelerated until it reached the thinning stage where it was thinned out at 1500rpm for 30 seconds.
The coated substrates were baked in a Thermolyne model 48000 furnace between 70-80°C for 30 minutes to evaporate the excess methanol solvent and make sure that the film was deposited on the substrate surface.

2.4. SEM characterization
The ~1.25 cm x 1 cm substrates were brought to the surface physics laboratory for morphological characterization. Since glass is non-metallic, the substrates were coated with gold to be able to see clear SEM images and avoid it from charging up. The samples were coated for 40 seconds on each side using JEOL Model JFC-1200 gold fine coater. The samples were then analyzed for their surface morphology and thickness using the Scanning Electron Microscopy (Model Jeol 5310).

2.5. Cyclic voltammetric analysis
Cyclic voltammetry measurements were performed using a BST8-Stat Potentiostat/Galvanostat. A standard three electrode setup was utilized. The working electrode was an ITO coated glass electrode on which the Nafion-Ru(bpy)$_3^{2+}$ films were deposited. A platinum coil was used as the counter electrode and a saturated calomel electrode (KCl saturated) was used as the reference electrode.

100 mL of 0.1 M NaCl served as the supporting electrolyte for the electroanalysis. The supporting electrolyte was purged with nitrogen for about 5 minutes before performing voltammetry measurements to remove dissolved oxygen which may react and interfere with or mask the data for the redox reaction of interest.

The area of the working electrode dipped was kept constant at ~1.0 cm$^2$ for all measurements. From the voltammograms obtained, the diffusion coefficients were determined.

3. Results and discussion
The discussion is based on the physical and electrochemical data obtained from the procedure stated. The tests were conducted promptly after the fabrication of modified electrodes to avoid the degradation.

3.1. Fabrication of spin coated modified electrodes
Films of Nafion-Ru(bpy)$_3^{2+}$ were fabricated from 10 mg/mL, 5 mg/mL, and 1 mg/mL casting solutions. The presence of the thin film, with a very faint yellow color, could not be easily seen visually. It must be duly noted that the thin films could be mechanically removed or damaged, thus, extra care was required in handling the electrodes.

3.2. Surface morphology (SEM micrographs)
Even films were deposited on the substrates for all three concentrations of the casting solutions. Aside from the edges of the substrates where there were voids, the spin coating technique was able to successfully cover the whole surface of the electrode with the Nafion solutions. This proved that the method employed was successful in depositing films on modified electrodes. The thin films deposited on the glass electrodes only had minimal irregularities and/or contamination. To check for the smoothness of the films, samples were investigated at high SEM magnification. Only at much higher magnification (7500x and 20,000x) was the roughness of the film clearly seen.
Figure 1. Surface morphology of 10mg/mL thin films at 7500x magnification.

Figure 2. Surface morphology of 10mg/mL thin films at 20000x magnification.

Figure 3. Surface morphology of 5mg/mL thin films at 7500x magnification.

Figure 4. Surface morphology of 5mg/mL thin films at 20000x magnification.
From the surface SEM micrographs obtained, qualitative analysis suggested a trend of decreasing roughness with increasing concentration of the casting solution.

3.3. Film thicknesses
The samples were viewed at an angle allowing the SEM machine to measure the thickness of the films. The technique yields measurements which were used to calculate the volume of the film which was important in determining the electrochemical properties of the thin films such as the diffusion coefficient.

| Concentration | Thickness (nm) |
|---------------|----------------|
| 10mg/mL       | 294.00         |
| 5mg/ml        | 252.00         |
| 1mg/ml        | 248.25         |

Obtained thickness measurements confirmed that the spin coating technique is capable of fabricating thin films with a few hundred nanometers of thickness. Increasing the concentration of the redox mediator in the casting solution increases the thickness of the film. This may be attributed to the increase in the viscosity and density of the solution as these two are factors which affect the thickness dynamics of the spin coating technique.

3.4. Electrochemical measurements
As a control sample, a voltammogram at 100mV/s scan rate of a bare electrode is given in the figure 7. After numerous attempts at getting voltammetric signals relevant to the immobilized redox mediator, it is concluded that the signals from electrodes fabricated with 1mg/mL Nafion–Ru(bpy)$_3^{2+}$ were too weak to be detected. Discussion, comparisons and computations will focus on two concentrations of casting solutions of the Nafion-redox mediator (10 mg/mL and 5 mg/mL) which yielded positive results. The symmetry of the voltammogram, shows that the reaction is reversible.
The increase in peak current at increasing scan rates confirms that the diffusion layer is prevented from moving too far from the electrode surface which results in a larger current flux [5]. Also, the graph of the peak current vs. potential shows the mechanism at which the reaction proceeds. The increase in peak current with thickness corresponds to an increase in the total charge which reacted. The amount of electrons which participated in the redox reaction within the specific potential window can be accounted to the ruthenium complex incorporated within the film. This can be computed through the total charge.

The peak current densities increase monotonically with the square root of the scan rate indicating that for both 10mg/mL and 5mg/mL films, the reaction of the system is diffusion-controlled. This mechanism is operative when the thickness of the diffusion layer is thinner than the polymeric thickness [4]. Diffusion controlled reactions happen when the reaction between the electrode and species of interest occur so quickly that rate of diffusion controls the rate of the chemical reaction [6].
Figure 9. (a) 200mV/s CVs of 5mg/ml films; (b) peak current density plotted against the square root of scan rate.

Figure 10. Total charge at varying scan rates of 10mg/mL (red), and 5mg/mL (blue) films.

The total charge \( (Q) \) was computed and it can be seen from the figure 10 that the total charge, which is proportional to the amount of redox mediator in the film, approximately remains constant even at varying scan rates. In the spin coating method, the amount of redox mediator immobilized within the Nafion film is controlled by varying the concentration of redox mediator in the casting solution.

The value for total charge obtained was used to estimate the surface coverage values, \( \Gamma \), since the amount of electrons correspond to the amount of mediator which reacted during the voltammetric scan. The concentration of mediator within the film, \( C_p \), was also computed and consequently the diffusion coefficients for the mediator within the films casted from 10mg/mL and 5mg/mL.

From the total charge \( Q \) on the cathodic (or anodic) region, the surface coverage values, \( \Gamma \), were computed using:

\[
\Gamma = \frac{Q}{nFA}
\]  

(3.1)

where \( n \) is the moles electrons involved in the reaction (equal to 1 in all cases of this study), \( F \) is the Faraday constant \((96486 \text{ C/mol})\) and \( A \) is the geometric area of the electrode\((1\text{cm}^2\) in all measurements as discussed in the methodology). Dividing the surface coverage by the film thickness obtained from the SEM measurements gives the concentrations, \( C_p \), of the redox mediators incorporated within the Nafion thin films.

\[
I_p = k n^{3/2} A C D^{1/2} \nu^{1/2}
\]  

(3.2)
The Randles-Sevcik[7] (eq. 3.2) was used to calculate for the diffusion coefficient, $D$ (cm$^2$s$^{-1}$), of the immobilized redox mediators within the films. $I_p$ is the peak current (in amperes), and $v$ is the scan rate. The $2.686 \times 10^5$ constant has units of C mol$^{-1}$V$^{-1/2}$. The values computed are within the typical range of values for diffusion coefficients of immobilized mediators which is around $10^{-11}$ to $10^{-8}$ cm$^2$s$^{-1}$ in contrast with diffusional mediators which are in the range of $10^{-7}$ to $10^{-5}$ cm$^2$s$^{-1}$ [8].

Table 2 summarizes the average values for the parameters which are relevant in characterizing the deposited films. The values computed at different scan rates were averaged to come up with one average value of diffusion coefficient per sample. The scan rate does not affect the total charge, corresponding to the amount of species which reacted, as well as the diffusion coefficient which should remain constant as it is an intrinsic property of the fabricated film.

Table 2. Average of parameters extracted using cyclic voltammetry on different thicknesses of 10mg/mL and 5mg/mL Nafion–Ru(bpy)$_3^{2+}$ films.

| Concentration | Thickness(cm) | $\Gamma$ (mol/cm$^2$) | $C_p$ (mol/cm$^3$) | $D_{app}$ (cm$^2$/s) |
|---------------|--------------|------------------------|--------------------|------------------------|
| 10mg/mL       | 0.0000294    | 4.052E-10              | 1.378E-05          | 4.32783E-09           |
| 5mg/mL        | 0.0000252    | 1.899E-10              | 7.536E-06          | 3.19292E-09           |

Finally, to investigate if the modified electrodes are capable of retaining the redox mediators within the film, a 5 mg/mL electrode was subjected to continuous cycling and the total current for each cycle was measured. The results evidenced an approximate 11.2% loss in mediator after 50 cycles. The efficiency of spin coated films in retaining the mediators immobilized within the film is similar to the LS films fabricated by Bertoncello et al. [4] which evidenced a 10% loss of mediators after 50 cycles.

![Figure 11. Total charge through continuous cycling(50 cycles) of 5mg/mL Nafion-Ru(bpy)$_3^{2+}$ electrodes.](https://example.com/figure11.png)

4. Conclusions
The spin coating method was used to successfully produce redox-active thin films of Nafion. The redox mediator Ru(bpy)$_3^{2+}$ used in the study was effectively incorporated and immobilized within the Nafion modified electrodes. As seen from the results, the casting solution concentration could be manipulated to control the properties of the fabricated thin films such as the film thickness and concentration of redox mediator immobilized within the films. Thickness measurements showed that the thickness was proportional to the concentration of the casting solution, the density and/or viscosity were also factors which affected the film thickness.
SEM micrographs showed that the surface of the deposited thin films was generally smooth. However, roughness was observed for the highest concentration (10mg/mL) and reviewed further at higher magnification.

Voltammetric analyses showed that the redox-active thin film was successfully fabricated by modifying and employing the one-step method in spin coating technique. The order of the magnitude of the diffusion coefficients confirmed that the redox mediators were immobilized within the Nafion film.

5. References
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