Morphological, thickness and electrochemical analyses of spin-coated $[Ru(NH_3)_6]^{3+}$/Nafion films

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Nafion thin films were fabricated using the spin coating method. Hexaammineruthenium(III) $[Ru(NH_3)_6]^{3+}$ was used as the redox mediator and was incorporated in the film. The amount of $[Ru(NH_3)_6]^{3+}$ was varied and three different solvents were used. The morphology of the films was investigated and the film thickness was measured using scanning electron microscopy (SEM). The effects of varying the amount of the redox mediator and the solvent type on the viscosity of the coating solution, film thickness and morphology were investigated. The electrochemical properties of the fabricated films were studied using cyclic voltammetry.

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1. Introduction

Electrochemical sensors have recently found extensive applications in many branches of industries. At present, these sensors are used either as a whole or an integral part of many analytical instruments used for environmental monitoring, food safety, in pharmaceutical or clinical laboratories and also in most of the commercial point-of-care devices.

An electrochemical sensor is a device that transforms electrochemical information into an analytically useful signal. The basic components of electrochemical sensors are a working (or sensing) electrode, a reference electrode and a counter electrode. The performance of electrochemical sensors is strongly influenced by the working electrode material. Mercury was very attractive as an electrode material for many years because of its high reproducibility and sensitivity to anodic stripping voltammetry which is a technique used for detecting heavy metals. However, mercury is toxic and has limited anodic potential. Chemically modified electrodes have been developed and utilized as an alternative to mercury electrodes.

Chemically modified electrodes result from a deliberate immobilization of reagents that change the electrochemical characteristics of the bare surface. One of the common approaches for incorporating a modifier onto the electrode surface is coating it with an appropriate polymer film such as Nafion.

Nafion-modified electrodes are currently being utilized in electrochemical sensors for heavy metal detection [1-13] and in biosensors [14-20]. A thin layer of nafion is used to immobilize a redox mediator, such as hexaammineruthenium(III) $[Ru(NH_3)_6]^{3+}$, which facilitates electron transfer to the electrode. Spin coating is a widely used method in coating this film.

In this study, $[Ru(NH_3)_6]^{3+}$ doped Nafion thin films were fabricated using the spin coating method. The thin films were spin coated onto indium tin oxide (ITO) coated glass substrates using different amounts of $[Ru(NH_3)_6]^{3+}$ and three different solvents. The effects of varying the amount of the redox mediator and the solvent type on the viscosity of the coating solution, film thickness and morphology were determined. The electrochemical properties of the fabricated films were studied using cyclic voltammetry.

2. Methodology

A. Fabrication of Nafion Thin Films

Rectangular ITO coated glass substrates were spin coated with $[Ru(NH_3)_6]^{3+}$/Nafion stock solutions. Each stock solution was prepared by dissolving $[Ru(NH_3)_6]^{3+}$ in 6 mL of solvent – methanol, ethanol, or isopropyl alcohol and was mixed with 24 mL 5wt% Nafion. This solution was used for the spin coating of the thin films. The amount of $[Ru(NH_3)_6]^{3+}$ per stock solution for each solvent was varied at 25 mg, 50 mg and 75 mg.

The spin coating of the films underwent two stages: deposition and thinning. In the deposition stage, the substrates were spun at 750 rpm for 10 seconds. In the thinning stage, the substrates were spun at a higher speed (2500 rpm) for 30 seconds. The coated substrates were then baked for 3 hours in a furnace at 100°C to eliminate excess moisture.

B. Viscosity measurement

The viscosity of the $[Ru(NH_3)_6]^{3+}$/Nafion stock solution was measured using an Ostwald viscometer. The viscometer was filled with 10mL of the prepared coating solution and placed in a 2000mL beaker filled with water.

The water temperature was regulated and maintained at 25.0°C. The time it took for the liquid to travel between two points (marked regions of the viscometer) was measured 30 times and were averaged.

C. Scanning Electron Microscopy (SEM)

The morphology of the fabricated films was characterized using scanning electron microscopy. A small portion of the fabricated sample was cut using a diamond cutter and was placed on a sample holder. The portion of the sample was then coated with gold for 40 seconds on each side using JEOL Model JFC-1200 gold fine coater. The thickness of the films was measured using the SemAfore imaging program.

D. Cyclic Voltammetry

Cyclic voltammetry measurements were performed using a BST8-Stat Potentiostat/Galvanostat. A standard three electrode setup was utilized. The fabricated $[Ru(NH_3)^6]^{3+}$/Nafion coated ITO glass electrode was used as the working electrode, a platinum coil as the counter electrode and a saturated calomel electrode (KCl saturated) as the reference electrode.

100 mL of 0.1 M NaCl served as the supporting electrolyte for the electroanalysis. The supporting electrolyte was spurged 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.

3. Results and discussions

Viscosity

Fig. 1 shows the plot of the time for the coating solution to travel between two points versus the amount of $[Ru(NH_3)^6]^{3+}$ for methanol, ethanol and isopropanol. It can be noted from the plot that the viscosities of the coating solution with 25mg and 50mg $[Ru(NH_3)^6]^{3+}$ are almost the same and smaller as compared to that of the solution with 75mg $[Ru(NH_3)^6]^{3+}$. The viscosity for 75mg was affected by the solvent type: the most viscous was the solution with ethanol and the least viscous was the solution with methanol. For 25mg and 50mg $[Ru(NH_3)^6]^{3+}$, the solvent type has little effect on the viscosity of the solution.

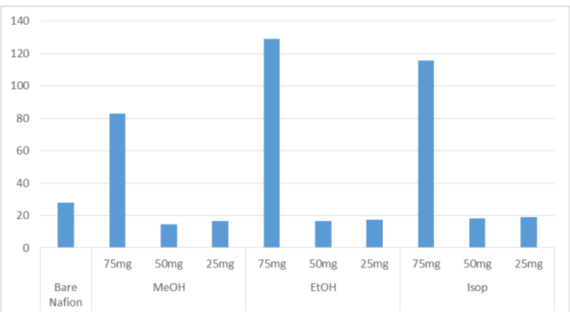

Fig. 1. Viscosity of the coating solutions.

Morphology

Fig. 2 shows the SEM micrographs of the fabricated films with different amounts of $[Ru(NH_3)^6]^{3+}$ and alcohol type. It can be observed from the micrographs that the films with 50mg and 25mg $[Ru(NH_3)^6]^{3+}$ for all alcohols have similar morphology. The surfaces of the films appear to be smooth with less cracks as compared to the films with 75 mg $[Ru(NH_3)^6]^{3+}$. This result is expected since the viscosities of the coating solution with 25mg and 50mg $[Ru(NH_3)^6]^{3+}$ are almost the same and smaller than that of the solution with 75mg $[Ru(NH_3)^6]^{3+}$. The coating solution was less viscous, thus an even and smoother surface was obtained for the films with 50mg and 25mg $[Ru(NH_3)^6]^{3+}$. On the other hand, a coarser surface was obtained for 75 mg due to the high viscosity of the coating solution.

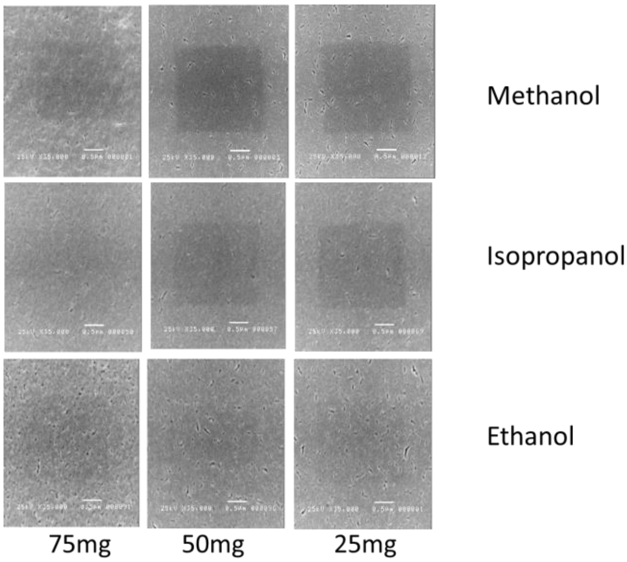

Fig. 2. SEM micrographs of the fabricated films.

Thickness

Table 1 shows the film thicknesses of the fabricated samples. It can be noted that the film thickness increased as the amount of redox mediator $[Ru(NH_3)^6]^{3+}$ increased for all solvents. The thickest film per solvent was obtained from the coating solution with 75 mg $[Ru(NH_3)^6]^{3+}$. This can be attributed to the high viscosity of the coating solution.

Table 1. Thicknesses of the fabricated films.

		Thickness (um)
MeOH	25mg	0.333841667
	50mg	0.4459375
	75mg	0.627848333
Isop	25mg	0.19725
	50mg	0.284016667
	75mg	0.341468975
EtOH	25mg	0.162287879
	50mg	0.277229762
	75mg	0.401197222

Cyclic voltammetry

Figs. 3-5 show the voltammograms of the fabricated films. It can be seen from the voltammograms that as the amount of $[Ru(NH_3)^6]^{3+}$ was increased, the peak current also increased for all the solvents used. The increase in the peak current corresponds to an increase in the total charge (area under the curve) 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. Thus, the higher the amount of redox mediator in the film the more conducting it is. The highest peak current was obtained from the sample with 75 mg $[Ru(NH_3)^6]^{3+}$ and isopropanol as the solvent.

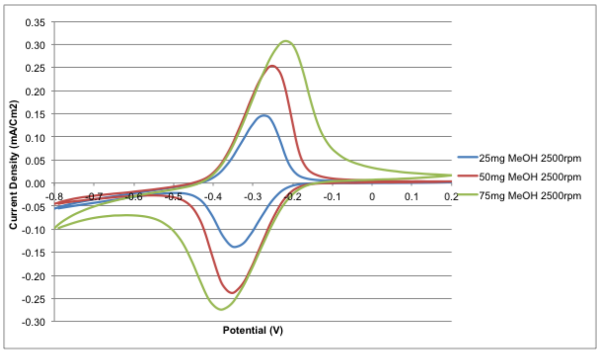

Fig. 3. Cyclic voltammograms of the fabricated films with different amounts of $[Ru(NH_3)^6]^{3+}$ and methanol as solvent.

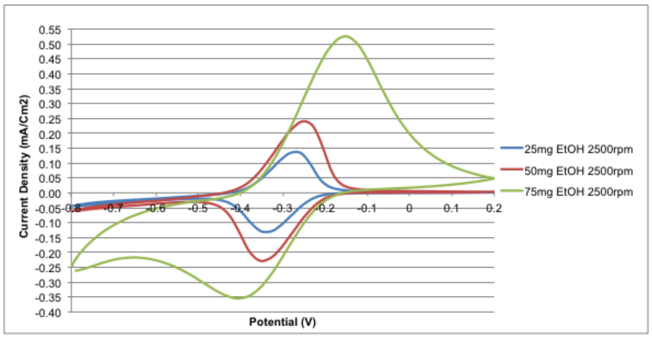

Fig. 4. Cyclic voltammograms of the fabricated films with different amounts of $[Ru(NH_3)^6]^{3+}$ and ethanol as solvent.

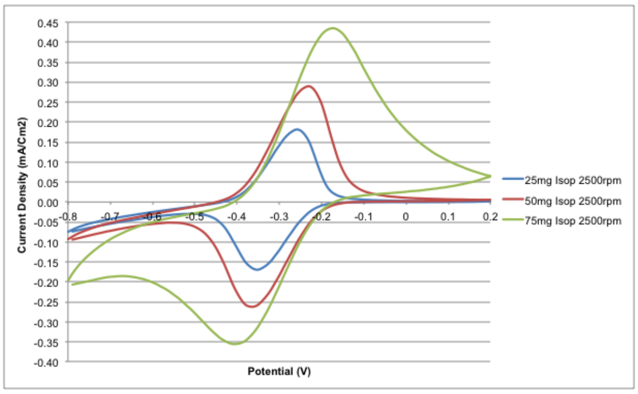

Fig. 5.Cyclic voltammograms of the fabricated films with different amounts of $[Ru(NH_3)^6]^{3+}$ and isopropanol as solvent.

4. Conclusions

$[Ru(NH_3)_6]^{3+}$/Nafion films were fabricated using the spin coating method. Results show that the viscosities of the coating solution with 25 mg and 50 mg $[Ru(NH_3)^6]^{3+}$ are almost the same and smaller as compared to that of the solution with 75 mg $[Ru(NH_3)^6]^{3+}$. Thus, the surfaces of the fabricated films with 25 mg and 50 mg $[Ru(NH_3)^6]^{3+}$ were relatively smooth while the films with 75 mg $[Ru(NH_3)^6]^{3+}$ had coarse surfaces. The film thickness and the peak current increased as the amount of redox mediator increased for all solvents.

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