

Electrochemical behavior of indium tin oxide electrodes spin coated with Nafion-[Ru(bpy)₃]²⁺ thin films

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Indium tin oxide (ITO) electrodes were modified by depositing Nafion-[Ru(bpy)₃]²⁺ thin films on the electrode surface via the spin coating technique. Scanning electron microscopy (SEM) was used to study the surface morphology of the thin films. Cyclic voltammetry (CV) was used to determine the transport mechanism and the diffusion coefficient of the redox mediators within the films. Different film thicknesses were fabricated by varying the speeds with which the spin coater thinned out the films. SEM micrographs showed a trend of increasing smoothness with increasing thinning rate. The resulting film thickness can be manipulated by simply varying the speed at which the deposited film is thinned out. CV results show successful incorporation of [Ru(bpy)₃]²⁺ within the films. The order of the magnitude of the diffusion coefficients confirmed that the redox mediators were immobilized within the Nafion thin film.

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1. Introduction

Mercury has been widely used for many years as a working electrode material in electrochemical sensors due to its high reproducibility and sensitivity. However, mercury is toxic and has a limited anodic potential. Thus, chemically modified electrodes have been developed and utilized as an alternative to mercury electrodes. A chemically modified electrode is a conducting or semiconducting material that has its surface modified to alter the electrochemical characteristics of the bare surface [1]. One of the common approaches of modifying electrodes is coating the surface with a thin film of an appropriate polymer such as Nafion.

Nafion modified electrodes are currently being utilized in sensors such as heavy metal sensors [2-15] and biosensors [16-22]. The working electrode of the said sensors is modified by coating it with Nafion doped with a redox mediator (e.g. Ru(NH₃)₆]³⁺ and [Ru(bpy)₃]²⁺) or a nanomaterial (e.g. graphene and carbon nanotubes) which enhances the sensor's sensitivity by accelerating the transfer of electrons which would proceed slowly with bare electrodes. The Nafion coating also prevents fouling of the electrode surface thereby making the electrode more damage resistant and more lasting.

This study focuses on the fabrication of Nafion-[Ru(bpy)₃]²⁺ modified indium tin oxide (ITO) electrodes. The thickness of the films was varied by controlling the speed at which the films were thinned out using the spin coating technique. Scanning electron microscopy (SEM) was used to study the surface morphology of the thin films. Cyclic voltammetry (CV) was used to determine the transport mechanism and the diffusion coefficient of the redox mediators within the films.

2. Experimental

The concentration of the coating solution used in this study is based on the one step procedure of Bertoncello et al. [23]. 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

7.5 cm x 1.0 cm substrates were cut using a diamond tip glass cutter from ITO coated glass substrates (sheet resistance 15-25 Ω/sq. slide) to obtain 2.5 cm x 1.0 cm strips for electrode fabrication and 1.25 cm x 1.0 cm strips for SEM characterization. The cut substrates were sonicated in acetone and isopropanol for 5 minutes, respectively.

2.2 Preparation of Nafion-[Ru(bpy)₃]²⁺ Stock Solutions

The one-step procedure of Bertonello et al. [23] was adapted in this research to incorporate the [Ru(bpy)₃]²⁺ mediator within the Nafion film. Stock solutions of Nafion-[Ru(bpy)₃]²⁺ were prepared by dissolving 1 mg of the redox mediator in 20 mL of methanol and subsequently adding 200 μL of 5% Nafion solution using a Transferpette® micropipette. The amount of Tris(bipyridyl)ruthenium(II) dichloride was carefully weighed using a BOSCH SAE200 electronic balance by differential weighing. The stock solution was sonicated to make sure that the ruthenium complex was completely dissolved.

2.3 Fabrication of Spin Coated Modified Electrodes

The Nafion-[Ru(bpy)₃]²⁺ solution was deposited on the previously cut ITO coated glass substrates using the spin coating technique. The SPINCOAT G3P-8 spin coating unit coating unit was purged with nitrogen gas to minimize the airborne contaminants and avoid the change in 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 subsequently baked in a Thermolyne model 48000 furnace at approximately 80°C for 30 minutes to evaporate the excess methanol and ensure successful film depositions on the substrates.

The modified electrodes with dimensions of 2.5 cm × 1.0 cm were used as the working electrode of the three-electrode setup for the voltammetric analyses while those with ~1.25 cm × 1 cm dimensions were used for SEM characterization.

2.4 SEM characterization

The ~1.25 cm x 1 cm substrates were analyzed in the surface physics laboratory using the Scanning Electron Microscopy (Model Jeol 5310). The substrates were first 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.

2.5 Cyclic voltammetry

Cyclic voltammetry measurements were performed using a BST8-Stat Potentiostat/Galvanostat using a standard three-electrode setup. The working electrode was the 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 that was dipped in the electrolyte was kept constant at ~1.0 cm² for all measurements. From the voltammograms obtained, the diffusion coefficients were determined.

3. Results and discussions

3.1 Surface morphology and film thickness

Even films were deposited on the substrates for all three thinning rates. The spin coating technique was able to successfully cover the whole surface of the electrode with the coating solution. This proved that the method employed was successful in depositing Nafion-[Ru(bpy)₃]²⁺ films on the ITO electrodes. The thin films deposited on the electrodes only had minimal irregularities and/or contamination. To check for the smoothness of the films, samples were investigated at high SEM magnification (Fig. 1). Only at high magnification (20,000x) was the roughness of the film seen. The texture of the film can be attributed to the roughness of the ruthenium complex. It can be observed from the SEM micrographs that smoothness increased with increasing thinning rate. Summarized in the table below are the average thicknesses obtained from Figs. 2 to 4. It is observed that the resulting thickness can be controlled by varying the rate with which the films are thinned out.

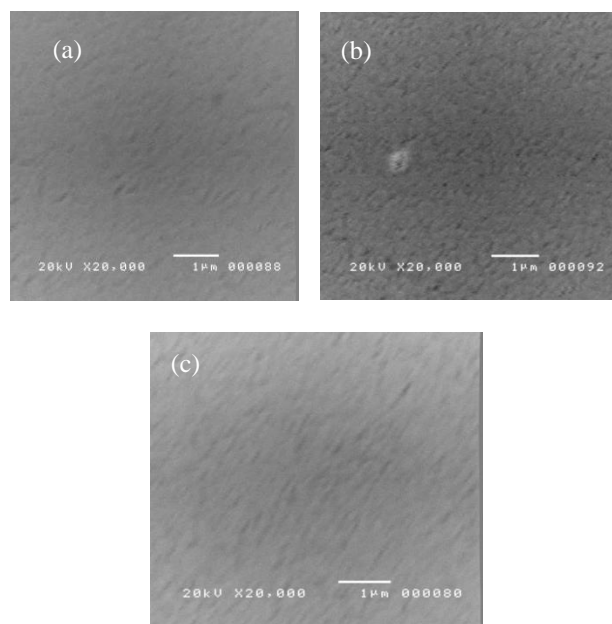


Fig. 1. SEM micrographs of the Nafion-[Ru(bpy)₃]²⁺ thin films spun at (a) 1500 rpm, (b) 2000 rpm, and (c) 2500 rpm

Table 1. Average Thickness of films from different thinning rates

Thinning Stage	1500rpm	2000rpm	2500rpm
Average thickness	252.00 nm	233.75 nm	184.50 nm

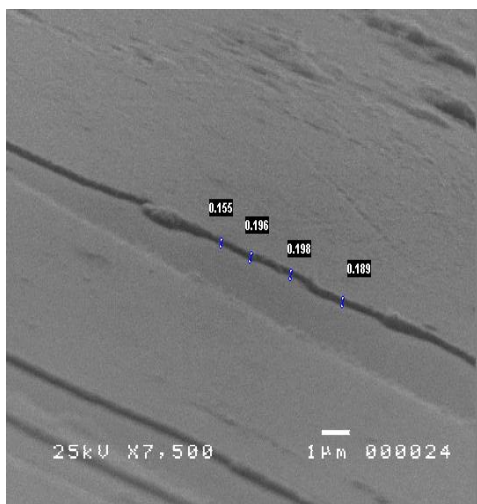


Fig. 2. Thickness of 1500 rpm thin films at 7500x magnification

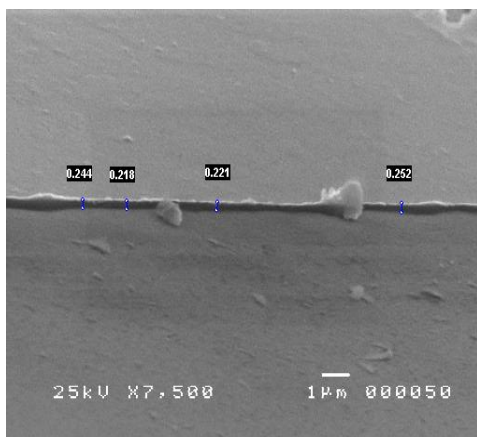


Fig. 3. Thickness of 2000 rpm thin films at 7500x magnification

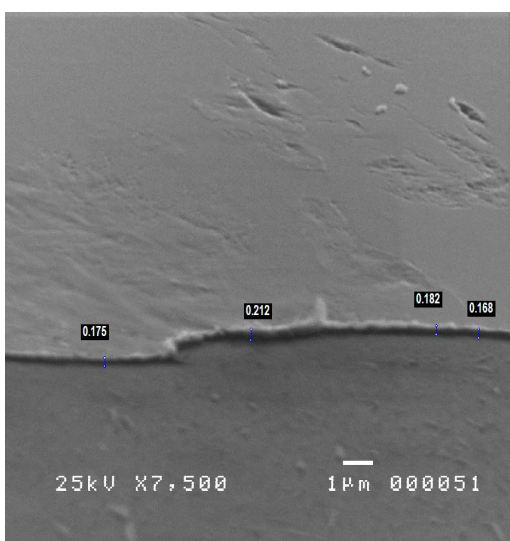
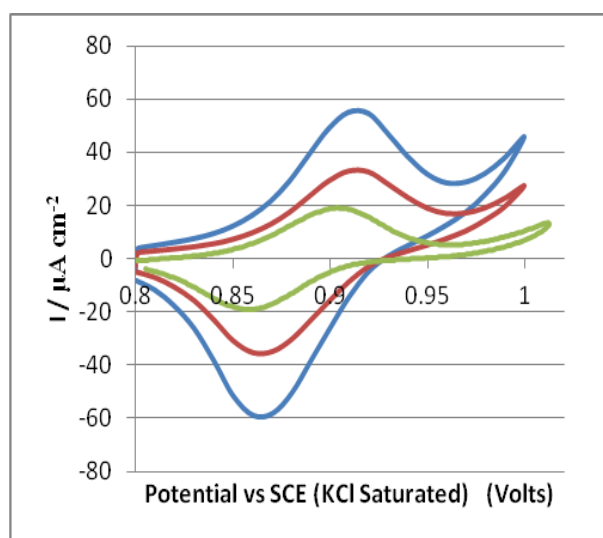


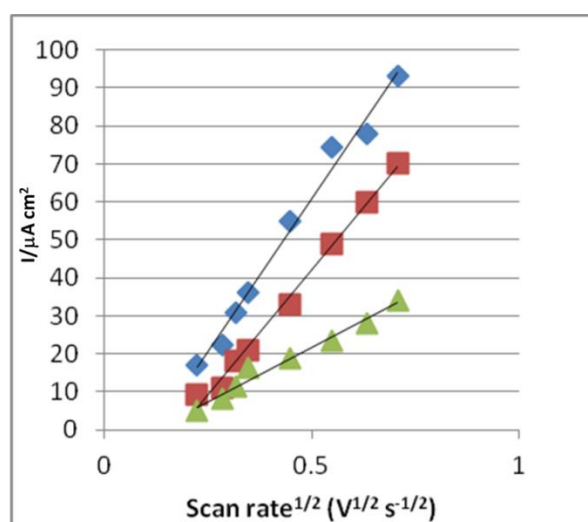
Fig. 4. Thickness of 2500 rpm thin films at 7500x magnification

3.2 Cyclic Voltammetry

The symmetry of the voltammograms (Fig. 5) shows that the reaction is reversible. The increase in peak current at increasing scan rates imply that the diffusion layer is prevented from moving too far from the electrode surface which results in a larger current flux [24]. The peak current densities increase monotonically with the square root of the scan rate indicating that the reaction of the system is diffusion-controlled. In such a case, the reaction happens so quickly that the rate of the reaction is controlled by the diffusion rate [25].



(a)



(b)

Fig 5. (a) 200mV/s CVs of 10mg/ml; (b) peak current density plotted against the square root of scan rate – for films fabricated at 1500 rpm (blue), 2000 rpm (red), 2500 rpm (green).

In Fig. 5, 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 value for total charge obtained was used to estimate the surface coverage values, Γ , 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, Γ , were computed using:

$$\Gamma = \frac{Q}{nFA} \quad (\text{eq. 3.1})$$

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 C / mol) and A is the geometric area of the electrode (1cm² 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.

$$I_p = k n^{\frac{3}{2}} A C D^{\frac{1}{2}} v^{\frac{1}{2}} \quad (\text{eq. 3.2})$$

The Randles-Sevcik [26] (eq. 5.2) was used to calculate for the diffusion coefficient, D (cm² 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 2.686×10^5 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 cm² s⁻¹ in contrast with diffusional mediators which are in the range of 10⁻⁷ to 10⁻⁵ cm² s⁻¹ [26].

The values computed in the table below are within the typical range of diffusion coefficients of immobilized mediators which is 10⁻¹¹ to 10⁻⁸ cm²s⁻¹. Immobilization keeps the redox active material near the electrode surface and prevents the loss of mediator.

Table 2. Average of parameters extracted using cyclic voltammetry on different thicknesses of Nafion-[Ru(bpy)₃]²⁺ films

Thinning (rpm)	D _{app} (cm ² /s)
1500	3.19292E-09
2000	2.71616E-09
2500	2.06813E-09

4. Conclusions

SEM results show that the thickness of the films was controlled by varying the thinning rate of spin coating. Roughness of the films can be observed at high SEM magnification (20000x) and is attributed to the ruthenium complex. From the electrochemical measurements, the mechanism for charge transport of the system is diffusion-controlled. Based on the obtained diffusion coefficients, it can be concluded that the redox mediator is immobilized within the Nafion film.

References

- [1] R. Durst, A. Baumner, R. Murray, R. Buck, C. Andrieux, *Pure & App. Chem.*, **69**, 1317 (1997).
- [2] S. Anandhakumar, J. Mathiyarasu, K. Lakshmi, N. Phani, V. Yegnaraman, *Am. J. Anal. Chem.*, **2**, 470 (2011).
- [3] F. Torma, M. Kadar, K. Toth, E. Tatar, *Anal. Chim. Acta*, **619**, 173 (2008).
- [4] H. Xu, L. Zeng, D. Huang, Y. Xian, L. Jin, *Food Chem.*, **109**, 834 (2008).
- [5] G. Hwang, W. Han, S. Hong, S. Hong, J. Park, S. Kang, *Talanta*, **77**, 1432 (2008).
- [6] D. Li, J. Jia, J. Wang, *Talanta*, **83**, 332 (2010).
- [7] J. Lia, S. Guoa, Y. Zhaia, E. Wang, *Electrochem. Commun.*, **109**, 834 (2008).
- [8] V. Rehaceka I. Hotovya, M. Vojasa, T. Kupsb, L. Spiessb, **63**, 192 (2012).
- [9] Li Chen, Zhaohong Su, Xiuhui He, Ying Liu, Cong Qin, Yaping Zhou, Zou Li, Lihua Wang, Qingji Xie, Shouzhuo Yao, *Electrochem. Commun.*, **15**, 34 (2012).
- [10] K. Keawkima, S. Chuanuwatanakula, O. Chailapakula, S. Motomizuc, *Food control*, **31**, 14 (2013).
- [11] Z. Lia, L. Chena, F. Hea, L. Bua, X. Qina, Q. Xiea, S. Yaoa, X. Tub, X. Luob, S. Luob, *Talanta*, **122**, 285 (2014).
- [12] S. Palisoc, M. Natividad, P. DeVera, B. Tuason, *Phil. Sci. Lett.*, **7**, 372 (2014).
- [13] S. Palisoc, M. Natividad, P. DeVera, B. Tuason, *J. New Mat. Electr. Sys.*, **17**, 205 (2014).
- [14] S. Palisoc, M. Natividad, F. Co, K. Kaw, *Optoelectron. Adv. Mat.*, **9**, 1010 (2015).
- [15] H. Kim, S. Yoon, H. N. Choi, Y.-K. Lyu, W.-Y. Lee. *Korean Chem. Soc.*, **27**, 65 (2006).
- [16] Y. Nia, P. Wang, H. Song, X. Lina, S. Kokotc, *Anal. Chim. Acta*, **821**, 34 (2014).
- [17] E. Canbay, E. Akyilmaz, *Anal. Biochem.*, **444**, 8 (2014).
- [18] L. Yang, G. Wang, Y. Liu, M. Wang, *Talanta*, **113**, 135 (2013).
- [19] L. Yang, G. Wang, Y. Liu, *Anal. Biochem.*, **237**, 144 (2013).
- [20] Y. Xina, X. Fu-bing, L. Hong-wei, W.Feng, C. Di-zhao, W. Zhao-yang, *Electrochim. Acta*, **109**, 750 (2013).

- [21] B. Gill Choia, J. Imb, H. Sik Kimb, H. Park, *Electrochim. Acta*, **56**, 9721 (2011).
- [22] C. Guoa, H. Sun, *Sensor. Actuat B-Chem.*, **164**, 82 (2012).
- [23] P. Bertocello, N. R. Wilson, P. R. Unwin. *Soft Matter*, 2007(3) (2007).
- [24] University of Cambridge. Linear Sweep. Retrieved December 9, 2012, from <http://www.cheng.cam.ac.uk/research/groups/electrochem/JAVA/electrochemistry/ELEC/14html/cv.html>
- [25] Univeristy of Athens. Diffusion Controlled Electrode Processes. Retrieved December 10, 2012, from <http://www.chem.uoa.gr/applets/AppletDiffus/AppletDiffus2.html>
- [26] University of Adelaide. Department of Chemistry. Retrieved December 4, 2012, from <http://www.chemistry.adelaide.edu.au/external/soc-rel/content/cv.htm>

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