Morphological and Thickness Characterization of Spin Coated Nafion Thin Films on Glass Substrate

Shirley Tiong-Palisoc, Stephen Tadios, and Michelle Natividad
De La Salle University,
2401 Taft Avenue, Manila, Philippines

Nafion thin films (<2μm) were fabricated using the spin coating technique. The effects of varying the Nafion concentration (5%, 10%, and 15%) and spin coating angular velocity (1500rpm, 2000rpm, and 2500rpm) on the thickness and morphology of the films were investigated. The deposition of the films onto the substrates was verified using energy dispersive x-ray (EDX) and the surface morphology was characterized by scanning electron microscopy (SEM). Surface morphological results show that the films followed the contour of the substrate onto which they are deposited and nanometer scratch-like features appear at high magnification (x35000). Thickness measurements were graphed against the different parameters and results show that thickness of Nafion films decrease with increasing angular velocity and increase with increasing concentration.

Keywords: Nafion, spin coating, thin films, elemental analysis, surface morphology

INTRODUCTION

Research in the field of sensors gained momentum in the early years of this century and has grown rapily since then [1]. A sensor is a device designed to respond and detect a physical quantity and convert it to an observable output [2]. Sensors that deal with components chemical in nature and that are subjected to an electrical set-up are called electrochemical sensors. This type

of sensor requires for an electrical conductor, and may sometimes be made by producing a thin film electrode [3-6]. Electrochemical sensors are currently being used for trace heavy metal detection and as biosensors.

To achieve a quality, fully working thin film electrode, the materials used must be conducting and durable at the very minimum. Mercury is one example and the most commonly used for such, because in addition to being resilient and very conductive, it is also highly sensitive and reproducible to the heavy metal detection method of anodic stripping voltammetry (ASV) [6].

Due to the toxic nature of mercury, however, other materials including indium tin oxide (ITO) [7] and bismuth films [6] are being sought as alternatives. These alternatives are friendlier to the environment, but produce electrodes with films that are more susceptible to fouling under direct ASV measurements [6]. To solve this problem, another layer with a permselectivity feature such as Nafion is added to the thin film electrode so that it becomes more robust.

Nafion, a copolymer of tetrafluoroethylene and perfluorosulfonated groups [8], is a permselective layer [6]. In solution form, coating of this solution using Langmuir Blodgett [9], Langmuir Schaeffer [10], and spin coating methods [11-14] is made possible. Because of its low cost compared to the other deposition techniques mentioned, spin coating was chosen as the method of fabricating Nafion thin films in this study.

EXPERIMENTAL

Material Preparation

Nafion in 5wt%, 10wt%, and 15wt% concentrations in an ethanol solution were obtained from Sigma Aldrich and used without further preparations. Substrates of glass cut into 25 mm x 25 mm were washed with deionized water, soapy water, and again with deionized water, and placed in petri dishes to be washed in isopropanol, methanol, and acetone under a sonicator for 5 min per alcohol. The materials were then heated in a furnace at 80°C for 30 minutes to eliminate any remaining water after the last wash.

Spin coating

To fabricate the thin films, a spin coater of model Spincoat G3P-8 was used. Fabrication consisted of two stages: deposition and thinning. In the deposition stage, a solution of Nafion was sprayed onto the substrate after it has reached

750 rpm. This lasted for 10 seconds until it reached the programmed angular velocity, after which the spinning continues through the thinning stage. In the thinning stage, the solution of Nafion was spread homogenously along the substrate surface for 30 seconds. Through evaporation, the coated substrates were eliminated of excess ethanol by placing them inside a furnace at 70-79˚C for 30 min.

The substrate (silicon, silica, and glass), Nafion concentration (5 wt%, 10 wt%, and 15 wt%), and spin coating angular velocity in the thinning stage (1500rpm, 2000rpm, and 2500rpm) were chosen as parameters. The effects of varying these parameters on the thickness and morphology of the film were investigated.

Characterization

A scanning electron microscope (SEM) of model JEOL 5310 was utilized to conduct elemental, surface morphology and thickness analyses on the fabricated Nafion thin films. The samples were placed inside a coater (JEOL JFC-1200) where each was coated with gold. Coating was done on both sides of the samples (both coated and non-coated in the case of the spin coated thin films). After the gold coating, the samples were held onto a sample holder using a piece of carbon tape and placed inside the SEM (JEOL 5310) chamber. The first to be analyzed were the blank samples. Blank samples were analyzed for comparison purposes. The samples were scanned at x50 (lowest magnification) using EDX. When elements of Nafion were present in the sample, the resulting elemental analysis report was copied to an MS Word file and SEM pictures were captured at x200 and x35000. The platform was then tilted at 75° and an image of the cross section (thickness) was taken at the center of each sample.

RESULTS AND DISCUSSION

Energy-Dispersive X-ray (EDX) Results

A blank substrate was scanned using EDX to provide basis for differentiating Nafion coated and non-coated substrates, followed by the scanning of the samples themselves. The samples were scanned to determine whether they have been coated with Nafion or not. Figure 1 shows the EDX graph

of the blank glass substrate. It can be observed from the graph that the glass substrate is composed of a combination of silicon, oxygen, sodium, magnesium, potassium and calcium.

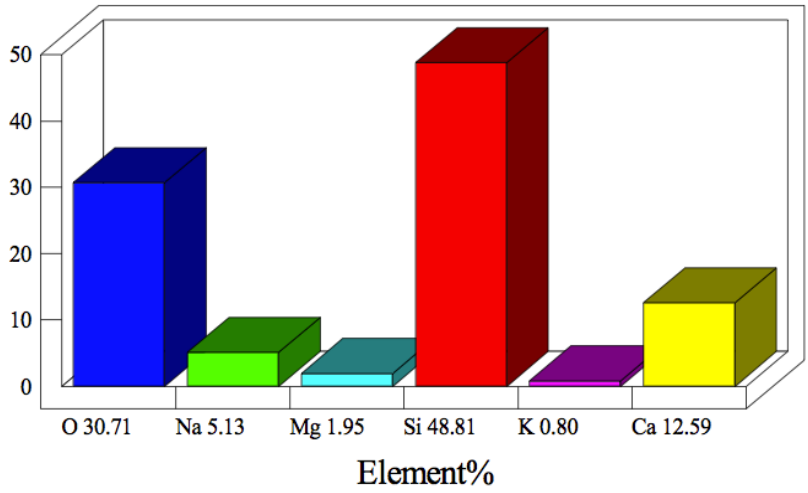


Fig. 1 Detected elements of the blank glass substrate.

Figures 2-4 are the EDX graphs of the sample films. It can be seen that additional elements, which are not in the blank substrate, are found in the samples. These elements, especially fluorine, are taken to be a positive sign that Nafion has been deposited on the substrates. Sulfur in the sample films consistently did not appear by automatic identification at lower concentrations (5 wt% and 10 wt%), and appeared at 15 wt% Nafion concentration (as seen in Figure 4). This absence of sulfur at lower concentrations could be attributed to the small quantity of sulfur in Nafion, which probably was only at trace amounts. It is possible that it might have gone undetected due to its quantity being too small to be quantified. Also shown in the graphs is the near consistent elemental make-up of each Nafion thin film with respect to angular speed, such that angular speed is shown not to have a significant effect on the elemental percentages of the thin films.

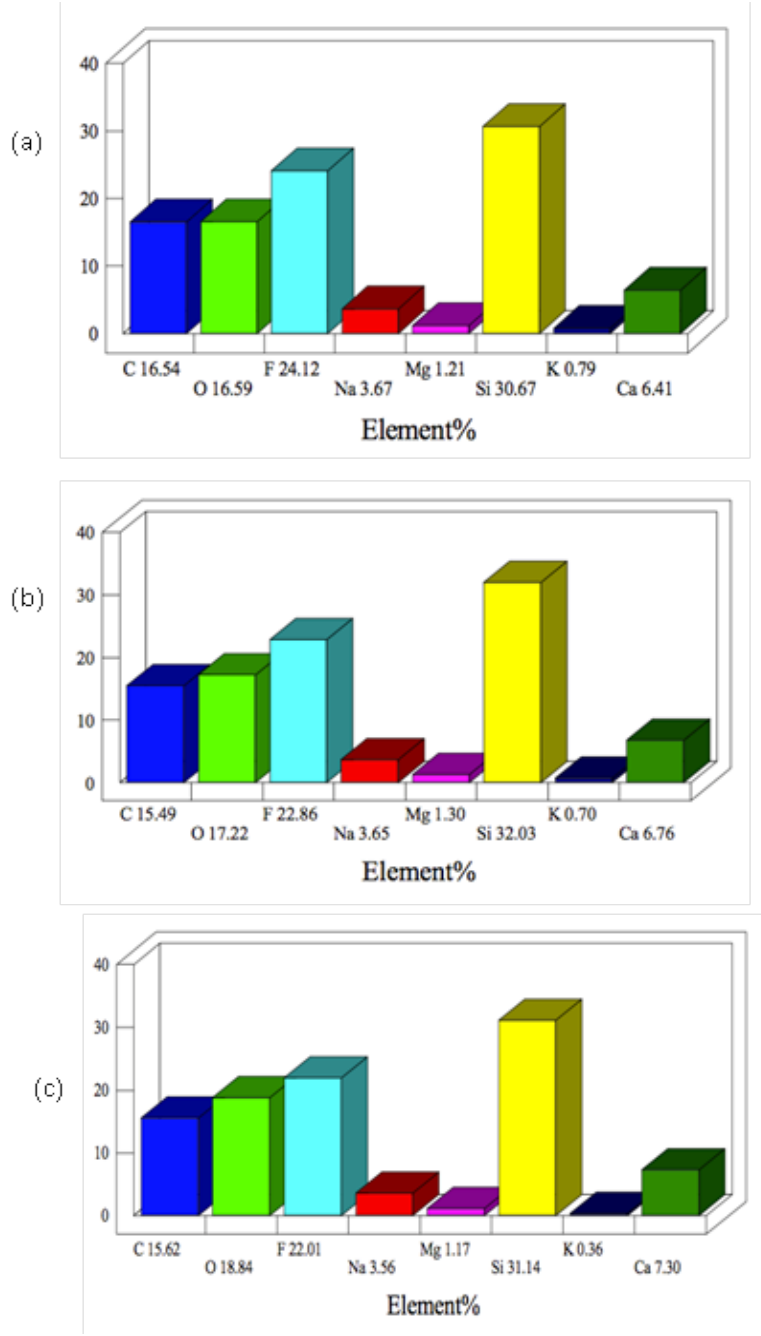


Fig. 2 EDX graphs of Nafion thin films spin coated at (a) 1500 rpm, (b) 2000rpm and (c) 2500rpm using 5 wt% Nafion solution.

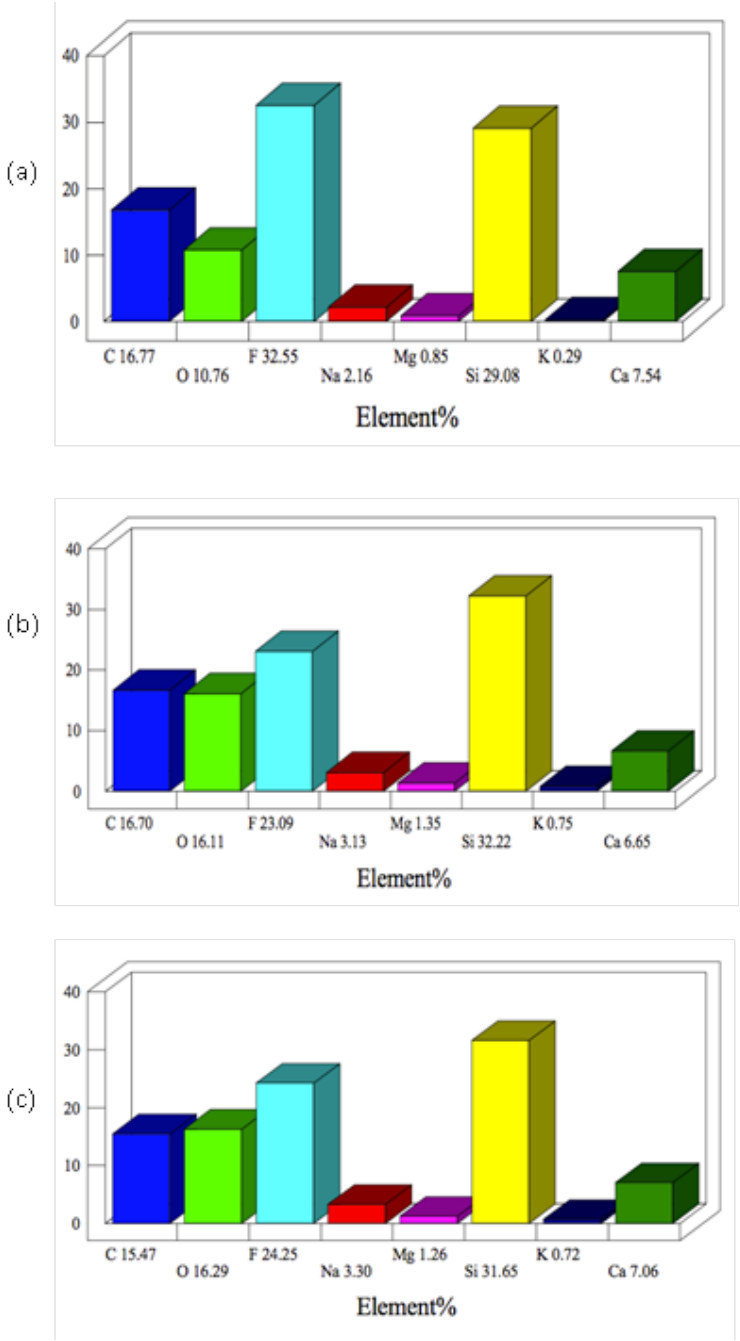


Fig. 3 EDX graphs of Nafion thin films spin coated at (a) 1500 rpm, (b) 2000rpm and (c) 2500rpm using 10 wt% Nafion solution.

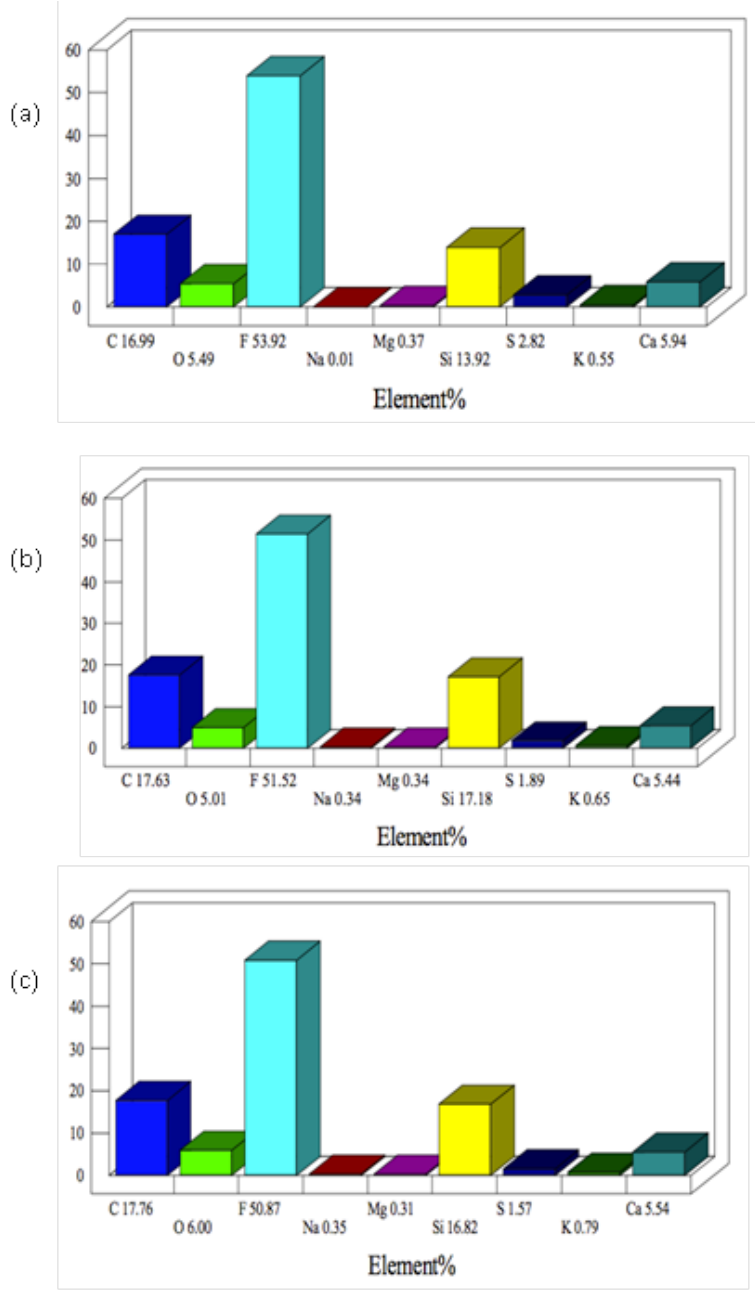


Fig. 4 EDX graphs of Nafion thin films spin coated at (a) 1500 rpm, (b) 2000rpm and (c) 2500rpm using 15wt% Nafion solution.

SEM Results

Figures 5-7 are SEM images of Nafion thin films deposited with 5% Nafion solution. The images at x200 magnification show a relatively smooth surface that is free of lumps or solution accumulation. Magnified at x35000, crack-like features on the thin films appear and become more prominent at a higher concentration. An investigation for the reason behind these was made after Schneider [8] reported damage of Nafion membranes via SEM, and results have shown that SEM does create damage to the films. The reason as to why the cracks are relatively more affected has so far not yet been studied, however.

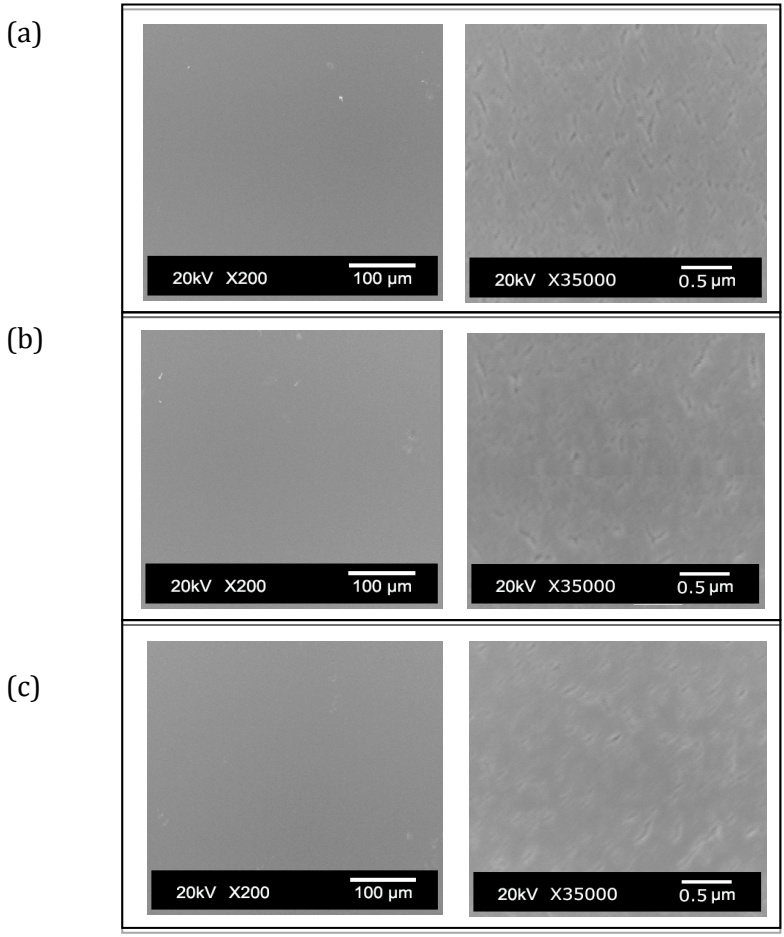


Fig. 5 SEM images of Nafion thin films spin coated at (a) 1500 rpm, (b) 2000 rpm, and (c) 2500 rpm using 5wt% Nafion solution.

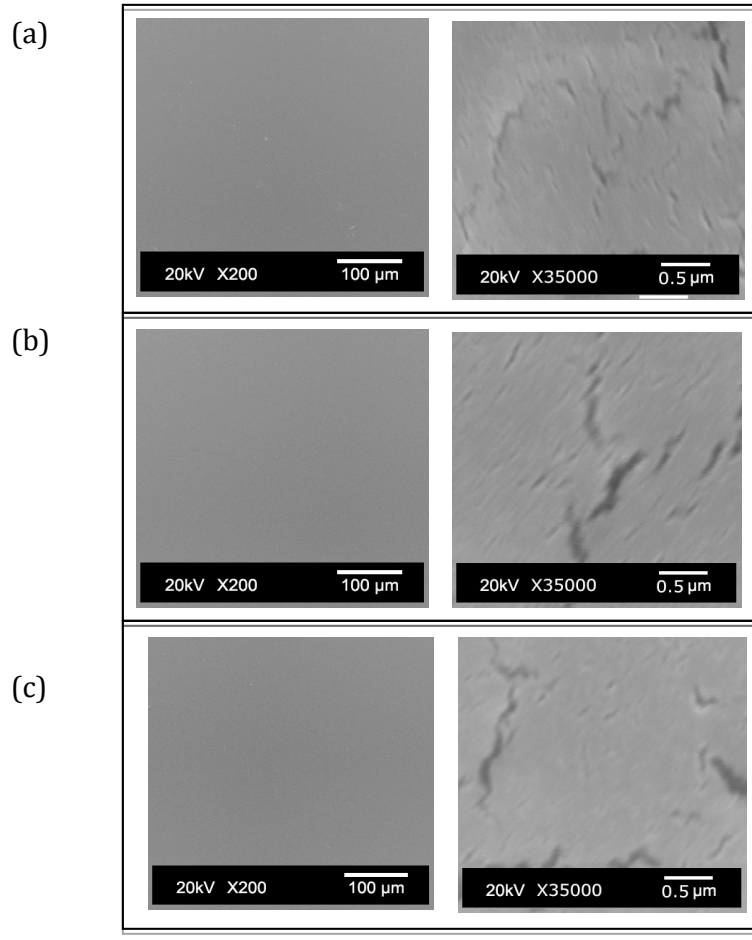
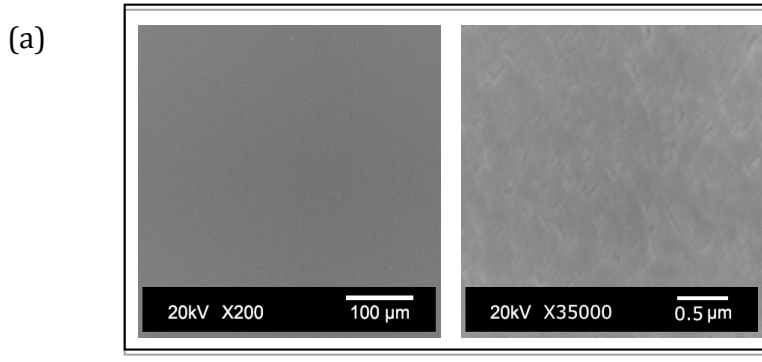


Fig. 6 SEM images of Nafion thin films spin coated at (a) 1500 rpm, (b) 2000 rpm, and (c) 2500 rpm using 10 wt% Nafion solution.



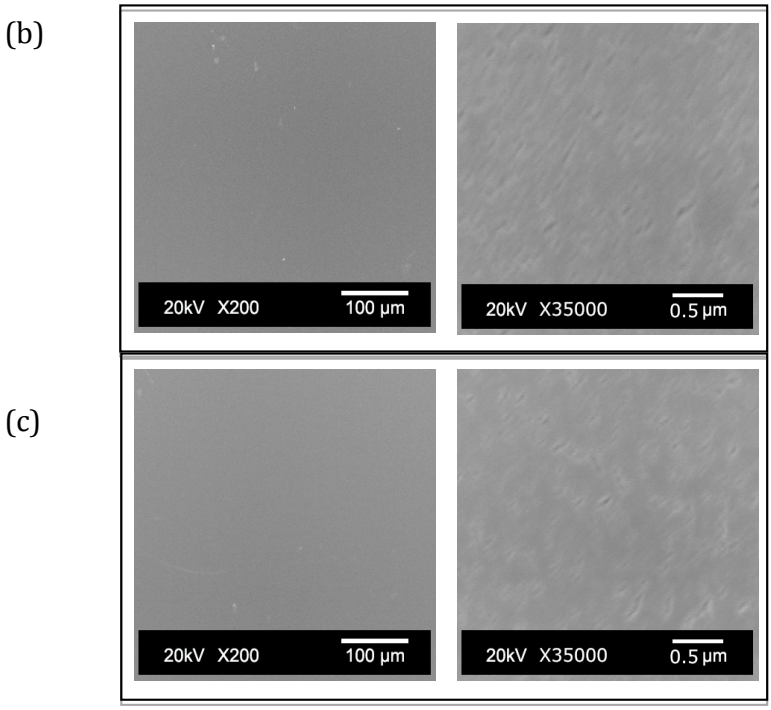


Fig. 7 SEM images of Nafion thin films spin coated at (a) 1500 rpm, (b) 2000 rpm, and (c) 2500 rpm using 15wt% Nafion solution.

Thickness Results

The thicknesses of the thin films were measured using the micrographs obtained from the scanning electron microscope through a program called SemAfore. The lengths of the thin films were measured from the top to the bottom of each layer, taken at an angle perpendicular to the surface of the substrate. One image was taken for each sample and three measurements were done per image (Fig. 8). The three thicknesses per sample were averaged and the approximate thickness was obtained. The data gathered for each were averaged and are listed in Table 1. It can be seen from the data that the relationship of thickness with angular velocity is inverse proportionality and that on the other hand, the relationship of thickness with concentration is direct proportionality. As angular velocity increases, the film thickness decreases; and as the concentration of Nafion increases, the film thickness also increases. Furthermore, it can also be seen that with regard to thickness, the thin films are compatible for sensor applications since they are ~1µm [16].

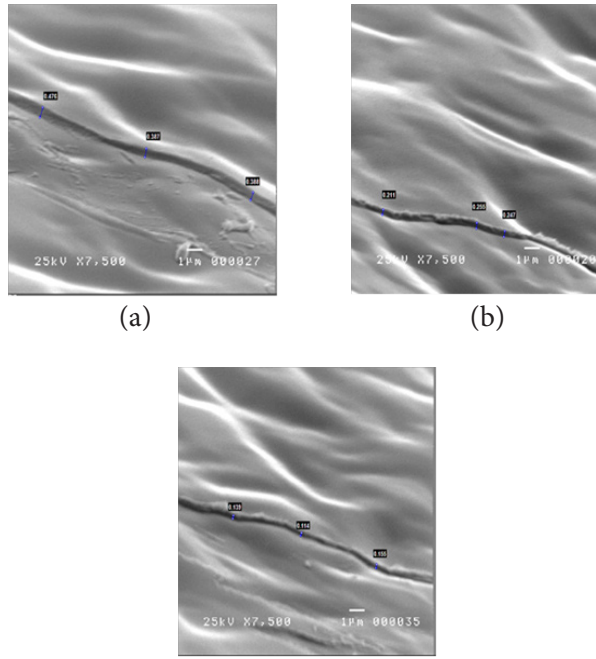


Fig. 8 SEM images showing the three measured thicknesses of film fabricated using 5 wt% Nafion concentration and spun at (a) 1500rpm, (b) 2000rpm, and (c) 2500rpm.

Table 1 Nafion thin film thicknesses.

wt% Nafion	Angular velocity (rpm)	Measured Thickness (μm)			Average thickness (μm)
15	1500	1.94	1.98	1.97	1.97
	2000	1.49	1.47	1.49	1.48
	2500	1.23	1.27	1.25	1.25
10	1500	0.668	0.674	0.676	0.673
	2000	0.363	0.360	0.366	0.363
	2500	0.215	0.215	0.215	0.215
5	1500	0.508	0.495	0.479	0.494
	2000	0.231	0.231	0.231	0.231
	2500	0.140	0.152	0.152	0.148

The graph of thickness with respect to angular velocity is shown in Fig.8, where the data points can be seen in a power function plot. Thickness vs. angular velocity is generally in the form h α ω-b [15]; where h is thickness, ω is angular velocity, and b is a constant. Based on the graph, Nafion thin films are shown to follow this form.

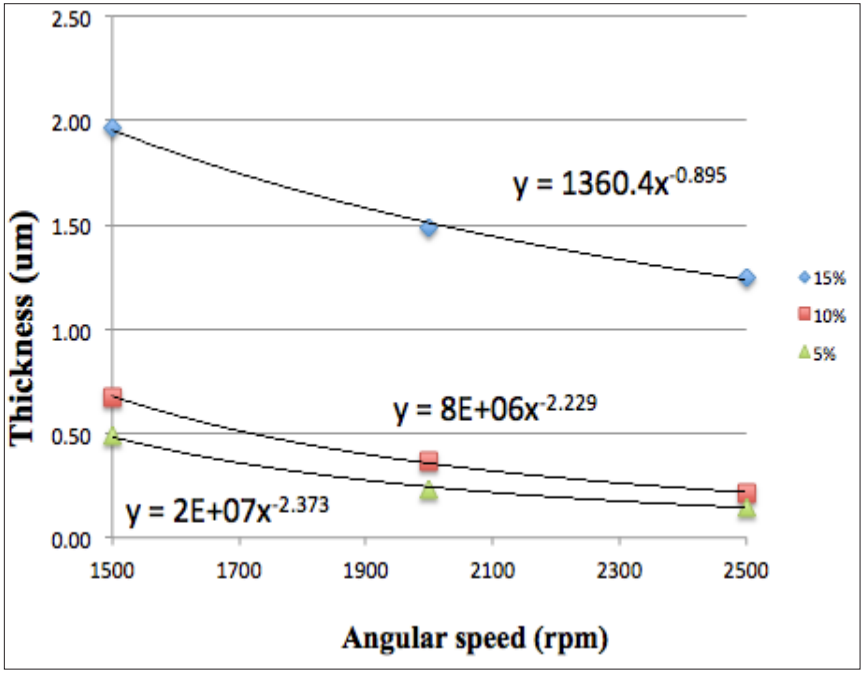


Fig. 8 Thickness vs. angular velocity graph.

The line equations from the graphs are shown below. As the concentration increases, the exponent b decreases.

h = 2E+07ω-2.373	(5%)	(Eq. 1)
h = 8E+06ω-2.229	(10%)	(Eq. 2)
h = 1360.4ω-0.895	(15%)	(Eq. 3)

CONCLUSION

EDX

The EDX graphs of the elemental compositions of the fabricated thin films show spin coating to have successfully deposited Nafion on the substrates.

The expected elements were detected with the exception of sulfur, which only showed up on thin films coated with 15% Nafion concentration. Varying angular velocity did not yield any significant difference.

SEM

Imaging via SEM revealed the Nafion thin films to have a smooth and relatively even surface morphology at low magnification and crack-like deformations at higher magnification.

Thickness Measurements

Thickness measurements show that as angular velocity increases, thickness decreases while as concentration increases, thickness also increases. Furthermore, the thin films are suitable for sensor use since each thickness is more or less around 1 μm [16].

REFERENCES

[1]Wilson J (2005) Sensor application handbook. Elsevier Inc., USA

[2]Dublin City University (n.d.) What is a Sensor Technology? http://www.dcu.ie/~best/st.htm. Accessed December 10, 2012

[3]Ugo P, Cavalieri F, Rudello D et al (2001) Nafion Coated Electrodes as Voltammetric Sensors for Iron Analysis in Sediments and Pore Waters: an Example from the Lagoon of Venice. Sensors 1:102-113

[4]Bertoncello P, Dennany L, Forster R, Unwin P (2007) Nafion-tris(2-2'-bipyridyl) ruthenium(II) Ultrathin Langmuir-Schaefer films: redox catalysis and electrochemiluminescent properties. Anal. Chem. 79:7549-53

[5]Brett CM, Maria Oliveira Brett A, Matysik FM et al (1996) Nafion-coated mercury thin film electrodes for batch-injection analysis with anodic stripping voltammetry. Talanta 43:2015-22

[6]Xu H, Zeng L, Huang D, Xian Y, Jin L (2008) A Nafion-coated bismuth film electrode for the determination of heavy metals in vegetable using differential pulse anodic stripping voltammetry: An alternative to mercury-based electrodes. Food Chem 104:834-39

[7]Mohamed SH, El-Hossary FM, Gamal GA, Kahlid MM (2008) Properties of Indium tin oxide thin films deposited on polymer substrates. Acta Phys Pol A115:704-08

[8]Schneider R (2008) Scanning Electron Microscopy Studies of Nafion Deformation into Silicon MicroTrenches for Fuel Cell Applications. BSE Thesis, Princeton University

[9]Moretto L, Kohls T, Badocco D, et al (2009) Electrochemi-luminescence of loaded in Nafion Langmuir–Blodgett films: Role of the interfacial ultrathin film. J Electroanal Chem 640: 35-41

[10]Bertoncello P, Notargiacomo A, Nicolini C (2005) Langmuir--Schaefer films of Nafion with incorporated TiO(2) nanoparticles. Langmuir 21:172-77

[11]Bertoncello P, Ugo P (2003) Preparation and voltammetric characterization of electrodes coated with Langmuir-Schaefer ultrathin films of Nafion®. J Braz Chemical Society 14(4): n.p.

[12]Bhargava P (n.d.) Creating a Nafion thin-film with a surface water layer in order to increase the accuracy of Neutron Reflectometry studies of lipid bilayers. http://www.ncnr.nist.gov/programs/CHRNS/pdf/HSI09_Bhargava.pdf. Access-ed 3 April 2012

[13]Li X, Feng F, Zhang K et al (2012) Wettability of Nafion and Nafion/Vulcan Carbon Composite Films. Langmuir 28:6698–6705

[14]Wu Y, Wang C, Yeh T et al (2010) Characteristics of controlled Nafion® coating inside nano structured anode for three-phase zone arrangement in micro DMFC. Presented in NEMS at the 5th IEEE conference, Xiamen, January 2010, p. 700-703

[15]Huang Y, Chou K (2003) Studies on the spin coating process of silica films. Ceram Int 29:485–493

[16]Brett C (2008) Electrochemical Impedance Spectroscopy for Characterization of Electrochemical Sensors and Biosensors, ECS Transactions 13:67-80