# Fabrication and morphological characterization of Nafion thin films spin coated on silica

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Nafion thin films (~1 μm) were fabricated via the spin coating technique. Angular velocity and concentration of Nafion solution were chosen as parameters and were varied in order to determine thickness relationships. Energy-Dispersive Spectroscopy (EDS) and Scanning Electron Microscopy (SEM) characterizations were performed in order to determine elemental composition and surface morphology of the films respectively.

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*Keywords*: Nafion, Spin coating, Thin film

## 1. Introduction

Attention to sensors has dramatically increased in the past decade and is continuously growing in the present day [1]. Sensors are devices that detect a physical quantity and convert it to related output [2]. To develop certain electrochemical sensors, a thin film electrode is sometimes fabricated [3-6].

Producing a complete thin film electrode requires for the materials used to be durable and conducting at the very least. Mercury is one of the popular choices due to its sensitivity and high reproducibility to anodic stripping voltammetry (ASV) [6], which is a method used to detect heavy metals, but due to the hazards it imposes to the environment, other materials such as indium tin oxide [7] (ITO) and bismuth films [6] are being studied as alternatives.

While environmentally safer than mercury, the alternative electrodes face a problem worth noting: they experience fouling in direct ASV measurements [6]. This fouling can be addressed by the addition of another film that acts as a protective or permselective layer.

Nafion is a permselective layer [6], chemically composed of a copolymer of tetrafluoroethylene and perfluorosulfonated groups [8]. As a solution, it can be coated onto surfaces via the Langmuir Blodgett [9], Langmuir Schaeffer [10], and spin coating methods [11-14].

Due to the relatively cheaper cost compared to the other equipment, this paper is focused on the fabrication and characterization of Nafion thin films using a spin coater. In this study, three solutions of varying Nafion to ethanol concentration were coated on silica substrate at varying angular velocities.

## 2. Experimental

### 2.1 Material preparation

Nafion in ethanol solution obtained from Sigma Aldrich with 5%, 10%, and 15% Nafion concentration were used in the form they were bought without additional preparation.

Substrates of silica were previously cut into 25 mm x 25 mm dimensions and washed with deionized water, soapy water, and another wash of deionized water. These were then placed in a petri dish containing isopropanol, methanol and acetone to be sonicated for 5 min. per alcohol. To evaporate the remaining water, the substrates were heated in a furnace at 80◦C for 30 min.

### 2.2. Spin coating

A Spincoat G3P-8 spin coater was used in the experiment. The prepared substrates were loaded onto the equipment and coated with Nafion solution in a process consisting of two stages: a deposition stage, where the solution is sprayed on the substrate surface and which lasted for 10s; and a thinning stage, which lasted for 30s. The coated substrates were baked inside a furnace at 70-79◦C for 30min. to evaporate the ethanol.

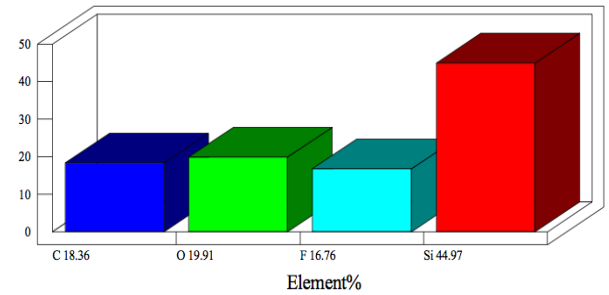
### 2.3 Characterization

Elemental data, surface morphology and thickness analyses of the Nafion thin films were conducted using a JEOL 5310 scanning electron microscope (SEM).

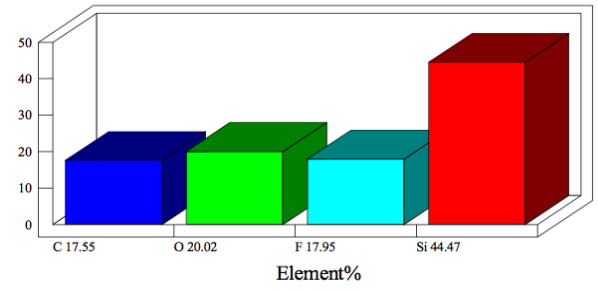
## 3. Results and discussion

### 3.1 EDS Results

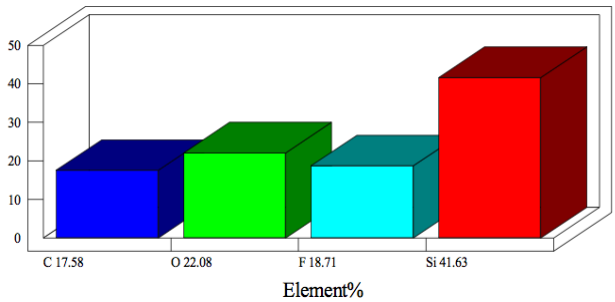
Fig. 1 shows energy-dispersive X-ray spectroscopy (EDS) graphs of thin films respectively spin coated at (a) 1500 rpm, (b) 2000 rpm, and (c) 2500 rpm using 5% Nafion solution. These graphs were made to determine whether or not Nafion was deposited on the substrates. Nafion is elementally composed of carbon, oxygen, fluorine, and sulfur. These graphs show that the aforementioned elements are chemically present in thin films fabricated with 5% Nafion solution except for sulfur, and that varying the angular velocity does not significantly alter the distribution and value of the elements. The absence of sulfur observed here is attributed to the low concentration of Nafion.




(a)




(b)




(c)

*Fig. 1. EDS graphs of Nafion thin films respectively spin coated at (a) 150 0 rpm, (b) 2000 rpm and (c) 2500 rpm using 5% Nafion solution.*

Fig. 2 shows the EDS graphs of Nafion thin films spin coated using 10% Nafion solution.

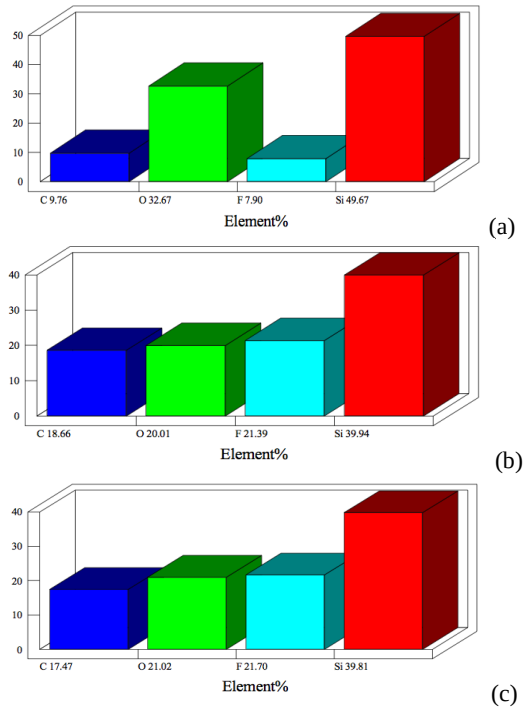



*Fig. 2. EDS graphs of Nafion thin films respectively spin coated at (a) 1500 rpm, (b) 2000rpm and (c) 2500rpm using 10% Nafion solution.*

Fig. 3 shows EDS graphs of Nafion thin films spin coated using 15% Nafion solution.

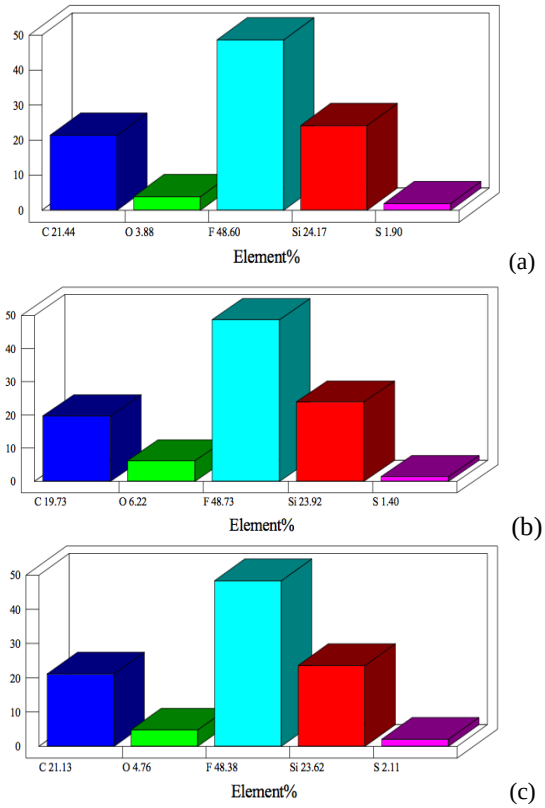



*Fig. 3. EDS graphs of Nafion thin films respectively spin coated at (a) 1500 rpm, (b) 2000 rpm and (c) 2500 rpm using 15% Nafion solution.*

Comparing Figs. 1, 2 and 3 it can be observed that it was only in 15% Nafion concentration that sulfur was detected. The amount of this element is relatively low even at this concentration that it probably goes to show that thin films fabricated using 5% and 10% Nafion concentration have sulfur contents below detection limits. Moreover, the detection of sulfur by EDS does not depend on the spin angular velocity.

### 3.2 SEM Results

Figs. 4 to 6 are SEM micrographs of Nafion thin films fabricated using 5% Nafion solution. It shows that the surface of the films is smooth and free from accumulations at x200 magnification and shows that crack-like features exist at higher magnification (x35000). The smoothness of the films indicates that Nafion thin films follow the contour and shape of the substrates to which they are deposited.

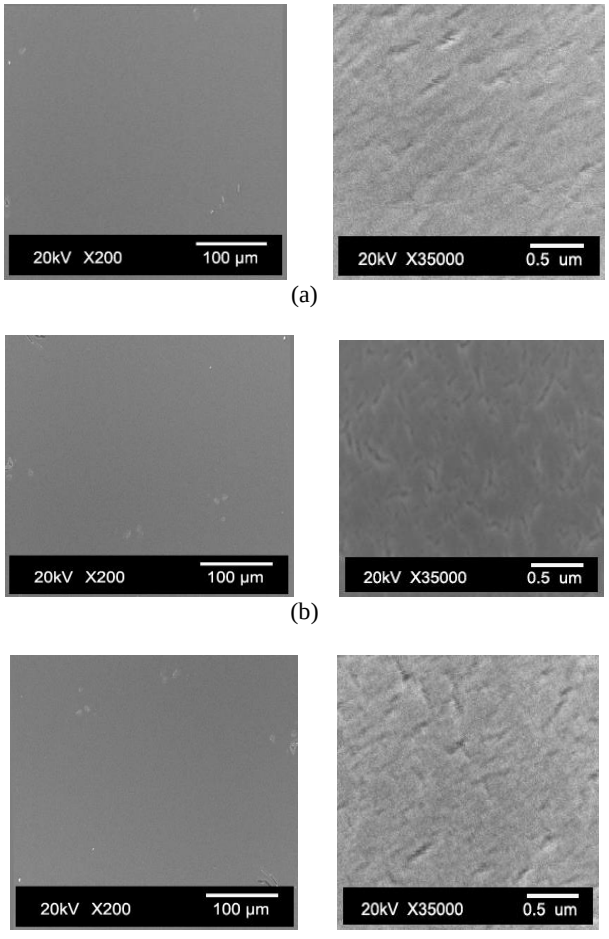



*Fig. 4. SEM micrographs of Nafion thin films spin coated at (a) 1500 rpm, (b) 2000 rpm, and (c) 2500 rpm using 5% Nafion solution.*

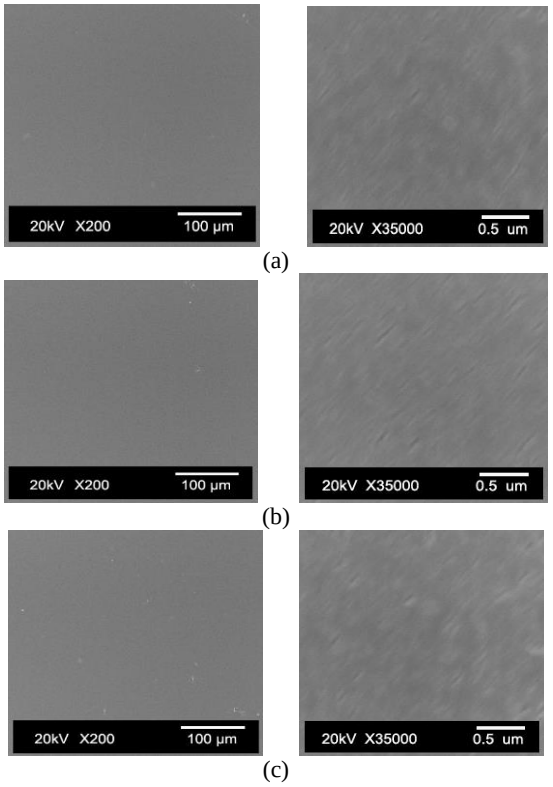



*Fig. 5. SEM micrographs of Nafion thin films spin coated at (a) 1500 rpm, (b) 2000 rpm, and (c) 2500 rpm using 10% Nafion solution.*

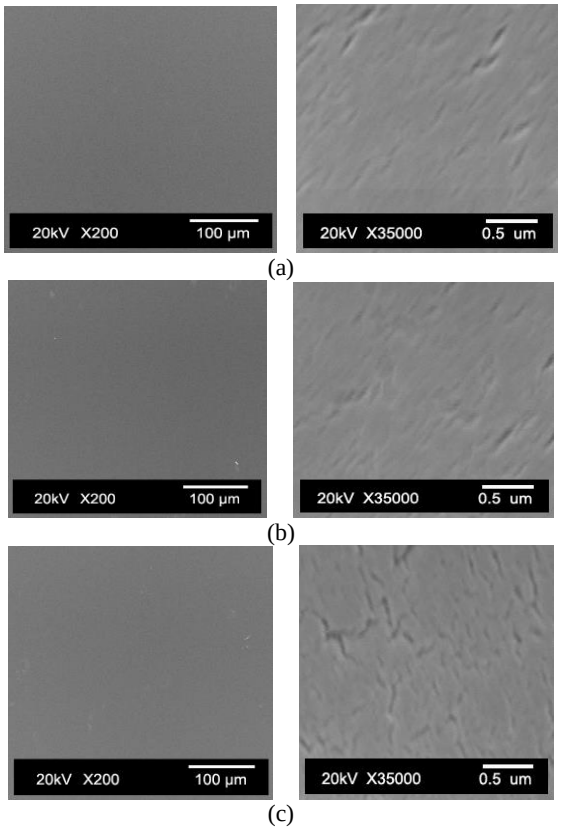



*Fig. 6. SEM micrographs of Nafion thin films spin coated at (a) 1500 rpm, (b) 2000 rpm, and (c) 2500 rpm using 15% Nafion solution.*

### 3.3 Thickness results

Three thickness measurements were taken at the centerline of each Nafion thin film and were averaged as listed on Table 1. As can be seen, increasing the spin coating angular velocity results in decreasing the film thickness, and increasing the Nafion concentration results in increasing the film thickness. The average thickness of the films is ~1 μm, which is the suitable thickness for sensor fabrication.

*Table 1. Nafion thin film thicknesses.*

| Nafion Concentration | Angular Velocity (rpm) | Measured Thickness (μm) | | | Average Thickness (μm) |
|---|---|---|---|---|---|
| 15% | 1500 | 1.23 | 1.23 | 1.23 | 1.23 |
| | 2000 | 1.03 | 1.03 | 1.03 | 1.03 |
| | 2500 | 0.935 | 0.935 | 0.935 | 0.935 |
| | | | | | |
| 10% | 1500 | 0.471 | 0.47 | 0.47 | 0.4703 |
| | 2000 | 0.314 | 0.311 | 0.327 | 0.3173 |
| | 2500 | 0.214 | 0.211 | 0.216 | 0.214 |
| | | | | | |
| 5% | 1500 | 0.346 | 0.338 | 0.335 | 0.3397 |
| | 2000 | 0.239 | 0.248 | 0.239 | 0.242 |
| | 2500 | 0.116 | 0.119 | 0.114 | 0.116 |

Fig. 7 shows a graph of thickness vs. angular velocity. In this figure, data points were plotted into a power function. The relationship of thickness with angular velocity is generally expressed as $h \propto \omega^{-b}$ [15]; where h is thickness, ω is angular velocity, and b is a constant. From the graph, it can be observed that Nafion thin films follow the general relationship.

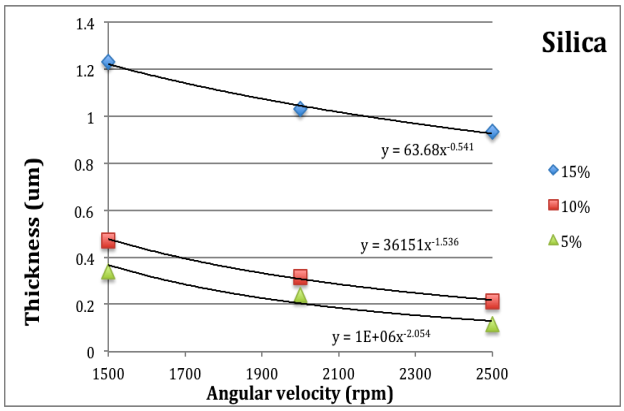



*Fig. 7. Thickness vs. angular velocity graph.*

Below are the equations obtained from the graph above. These equations reveal that the constant b

$$h = 1E+06\omega^{-2.054} \quad (5\%) \qquad (1)$$

$$h = 36151\omega^{-1.536} \quad (10\%) \qquad (2)$$

$$h = 63.68\omega^{-0.541} \quad (15\%) \qquad (3)$$

## 4. Conclusions

### EDS

EDS graphs revealed that Nafion was successfully deposited onto silica substrates via the spin coating method. Furthermore, it showed that sulfur is absent, or possibly present only below detection limits, in Nafion thin films fabricated using 5% and 10% Nafion solutions. Conversely, it shows that thin films spin coated with 15% Nafion solution yielded positive for sulfur.

### SEM

SEM micrographs reveal the surface morphology of the Nafion thin films to be absent of solution formation in one specific area, and reveal it to be smooth and even. It also shows that crack-like deformations are present at higher magnifications.

### Thickness measurements

Thickness measurements show that as angular velocity increases, thickness decreases and that as concentration increases, thickness increases. Furthermore, because each thickness is more or less around 1 μm, the thin films are suitable for sensor use.

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