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by Mira Setiana

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Abstract. Crown ether is a form of ethylene oxide cyclo-oligomer. Crown ether has a strong ability to form a complex with cations. The crown ether has been used as part of the electrochemical sensor and optical sensor because of its selectivity to several cations. There was no report on the use of the 18-crown-6-ether as a single coating layer on the QCM sensor. This work investigates the loading effect of the 18-crown-6-ether as a selective coating for QCM sensors as a pre-requirement for a selective coating layer. The impedance spectrum of the QCM sensor coated with 18-crown-6-ether at different concentrations solved in three different solvents was measured. The effects of solvents and 18-crown-6-ether concentrations to the calculated thickness and the effect of the QCM sensor impedance was investigated. The solvents used are Toluene, Tetrahydrofuran (THF), and Chloroform. The results show that the film behaves like a rubber material, which is shown by the impedance value of the sensor at the series resonance frequency. It can be concluded that the thickness of the 18-crown-6-ether layer must be maintained less than one μm to avoid damping on the QCM sensor.

1. Introduction

The coating layer is an important part of the Quartz Crystal Microbalance (QCM) sensor for these chemical sensors and biosensors. The coating material functions as a selective material or immobilization matrix. The mechanical [1] and functional properties of the material used must be considered so as not to disturb the working frequency of the QCM sensor. In many applications, a combination of mechanical and functional properties can be obtained in the form of a monolayer layer, a thin film layer, and also a thick film layer. In most applications, especially in the sensor field, the monolayer layer and thin-film layer are used [2–4]. However, thick film coatings are also used [5–8]

Thin films in nanometer thickness or monolayer films are used based on the basic assumptions of rigid layer behavior. Therefore, the effect of the mechanical properties of the coating layer on sensor performance is neglected, and the Sauerbrey equation can be used [9]. The mass deposited on the sensor surface can then be calculated using a linear relationship between changes in frequency and deposited mass. Several non-Sauerbrey approaches have been reported in the use of QCM sensors for chemical sensors. Among other things, the mechanical effect of the damping of the coating material to the electrical impedance of the QCM sensor needs to be controlled to minimize the unexpected behavior of the QCM sensor. The solvent effect to the microstructure of the film [10] of the

The 18-Crown-6-Ether (crown ether) is known as a selective material. The crown ether is used in the form of polymer or attached to other supporting materials [11–13]. The use of crown ethers solely as a coating material was not reported. A study has been conducted on the effect of the thickness of the crown ether coating on the electrical impedance of the QCM sensor. The research was carried out to investigate the thickness of the crown ether layer to the electrical impedance of the QCM sensor.

2. Experimental Method

2.1. Material

The QCM sensor used is one that has a silver electrode, which is made of AT-cut with a fundamental resonant frequency of 10 MHz. The crown ether used was 18-crown-6-ether purchased from Sigma-Aldrich (India). The solvents used are toluene, THF, and chloroform from the same factory.

2.2. Methods

The crown ether solution was made from 18-crown-6-ether dissolved in 1 mL of each solvent. The solvent was toluene, chloroform, and tetrahydrofuran (THF). The solution concentration was 1%, 2%, 3%, 4% and 5% mass for each solvent. Furthermore, 50µL of this solution was deposited on the QCM electrode sensor using the spin coating method at a rotation speed of 300 rpm. The solvent in the coating film was left evaporated at room temperature.

Before the coating process, the electrical impedance spectrum of the QCM sensor was measured using the Bode 100 Vector Network Analyzer from OmicronLab. The impedance spectrum of the coated sensor with the crown ether was taken after the evaporation process of the film material solvent took more than 24 h. The resonance frequency and the minimum impedance of the sensor before and after the coating were taken from the impedance spectrum. The film thickness was calculated based on the resonance frequency shift using the Sauerbrey equation [14]. The calculation was done by assuming that the crown ether behaves as a glassy material. Therefore the film thickness (h) can be calculated using the following equation:

$$h = -\frac{\Delta f \, A\sqrt{\rho_Q \mu_Q}}{2f_0^2 \rho_c} \quad (1)$$

where Δf is frequency shift of the series resonance frequency of the QCM sensor, A is the cross-section area of the QCM electrodes, μ_Q is shear modulus of quartz crystal (2.947 x 1011 $gcm^{-2}s^{-2}$), ρ_Q is mass density of quartz crystal (2.648 g/cm^3), f_0 is initial frequency prior to the existence of mass adsorbed, and ρ_c is the mass density of crown ether. The impedance measurement was done in ambient air condition at room temperature. Room humidity varied around 50% to 60%.

3. Result and Discussion

3.1. Impedance Spectrum and Value

The impedance spectrum of the Quartz Crystal Microbalance before coating showed the initial condition of the sensor. The minimum impedance of the sensor was found at 8.4±1.7Ω , and the series resonance frequency of 10.005.000±2000 Hz. The frequency at the series resonance frequency, where phase was zero and the frequency at the minimum impedance was equal. Figure 1 shows the impedance spectrum of the sensor before coating and after coated with crown ether.

The impedance spectrum of the coated sensor shows an increase in the minimum impedance and a decrease in the maximum impedance at series resonance. The impedance curve shifts to the left and formed similar curves, except the lost in a sharp phase change around the series resonance and parallel resonance frequency.

The impedance spectrum of the sensor after coating shows a change in the curve behavior with the increasing crown ether concentration being deposited using a spin coating. Figure 2 shows the minimum impedance of the sensor coated with crown ether at different concentrations and different solvents. The minimum impedance value of the sensor increases with the increasing concentration of the crown ether. The impedance value at a concentration of less than 3% has the same value, although the solvent was different. However, for the higher concentration, the minimum impedance was varied and affected by the solvent. It seems that the evaporation rate which affects the microstructure of the film [10] leads to an impedance change of the sensor. The microstructure effect becomes noticeable as the film thickness increased.

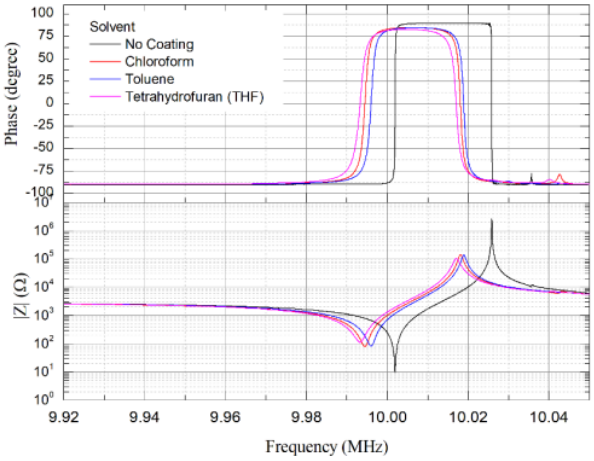

Figure 1. Impedance spectrum of the sensor before coating and after coating with crown ether at 6% concentration.

Although the minimum impedance of the sensor with crown ether coating increases with the crown ether concentration up to the concentration of 6%, the conditions that indicate a glassy characteristic are observed. The impedance and phase curves shifted to the left. The phase shift where the minimum impedance of the sensor exists is equaled to zero. It means that the frequency of the minimum impedance is at the series resonance frequency. There is no different in the frequency at the minimum impedance and zero phases.

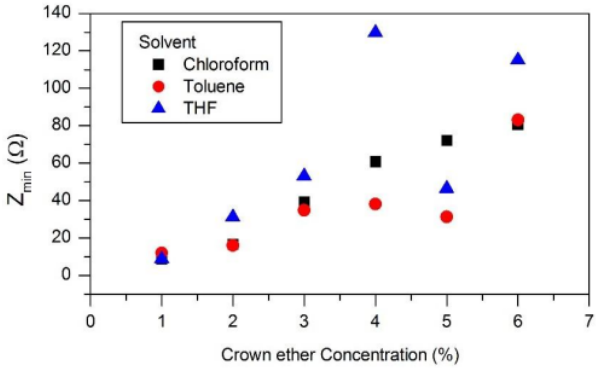

Figure 2. Sensor minimum impedance coated with crown ether using the spin coating.

3.2. Coating thickness

Based on the impedance analyses that showed a glassy property of the coating layer, we can apply the Sauerbrey equation to calculate the coating thickness. It was known that when using a spin coating method, the concentration and rotation speed determined the film thickness. At constant speed, the bigger concentration of crown ether should result in a thicker film. Based on the Sauerbrey equation, the film thickness was calculated using the calculated deposited crown ether mass, sensor electrode diameter, and crown ether mass density.

The effect of crown ether concentration on film thickness is shown in Figure 3. The behavior of the calculated thickness of the crown ether depends on the solvent. The thickness of the crown ether film

solved in chloroform shows a linear increase up to a concentration of 5%. The coating thickness reaches its maximum at around 300 nm. While the calculated film thickness originated from the crown ether solved in toluene reaches its saturation at a concentration of 3%. The calculated thickness is less than 300 nm. Higher crown ether concentration in toluene does not change the film thickness. The highest thickness is obtained using the Tetrahydrofuran (THF) solvent. The film thickness reaches 780 nm at crown ether concentration of 4%

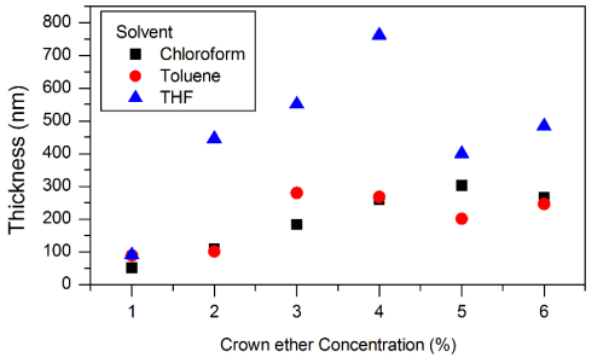

Figure 3. The calculated thickness of the crown ether film based on the Sauerbrey equation.

3.3. Coating thickness and impedance

The effect of thickness on the impedance of the QCM sensor after being coated with Crown ether is shown in Figure 4. The minimum impedance of the sensor is related to the crown ether thickness. As the thickness of the crown ether layer increases, the minimum impedance of the sensor rises. The minimum impedance value of the sensor was significantly affected by the crown ether thickness. Pearson correlation between the film thickness and minimum impedance is 0.7681. It indicated a strong correlation between the minimum impedance and the film thickness.

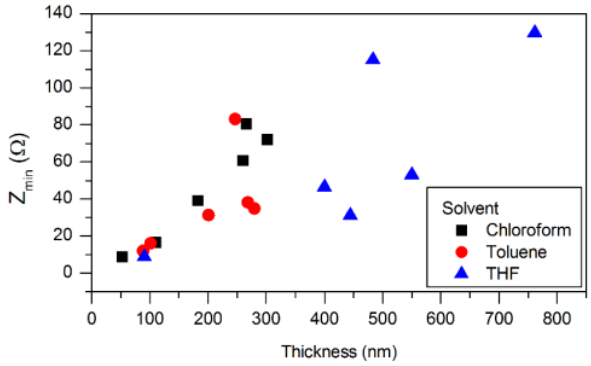

Figure 4. The impedance value of the sensor coated with crown ether with different thicknesses.

Compare to the effect of the film thickness on the QCM sensor minimum impedance which was coated using polystyrene, the increase of minimum impedance caused by crown ether film is much bigger. Using polystyrene coating with similar order of thickness [14], the change of minimum impedance was negligible. The polystyrene film is known as a rigid film [15]; therefore, the effect of the film thickness to the minimum impedance is very small. The change of the minimum impedance of the sensor coated using crown ether tends to mimic a rubbery film.

Conclusion

The impedance spectrum of the QCM sensor coated with an 18-crown-6-ether layer deposited using a spin coating method shows high electrical damping caused by a thin layer of 18-crown-6-ether film. Increasing crown ether concentration in solvent results in thicker film calculated using the Sauerbrey equation, but there is a maximum film thickness that can be achieved. The maximum film thickness depends on the solvent. The crown ether solved in tetrahydrofuran results in the thickest film comparing to the film formed by solved crown ether in chloroform and toluene. The minimum impedance value relates to the film thickness, in which higher film thickness results in bigger minimum impedance value. At the film thickness close to 1μm, the minimum impedance of the sensor coated with 18-crown-6-ether goes up more than 100Ω.

Acknowledgments

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