Determination of Resonance Parameters of The PANI Thin Film Fabricated using Spin Coating Method

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Abstract. This study aims to determine the resonance parameters of polyaniline thin films to better understand the viscoelasticity properties of polyaniline films. The spin coating method was used with varying solvent concentrations and rotating speed of spin coater during the deposition Polyani(line (PANI) thin film on a quartz crystal microbalance (QCM). To determine the resonance parameters of the PANI thin film, the impedance and QCM frequency measurements were first carried out before and after coated with PANI. The modelling used is a modified BVD model, and the determined resonance parameters are C₀, C₁, L₁, R₁, L₂ and R₂. From the results of the analysis using the GRG Nonlinear solver program, it was found that solution concentration and rotational speed in the spin coating process has a significant effect on resonator parameters of PANI thin film. The best solution concentration from this study was 2% DMF with a rotational speed of 2,000 rpm. This is because in these conditions it provides a minimal damping effect on QCM.

1. Introduction

Quartz Crystal Microbalance or commonly known as QCM is a resonator that has piezoelectric properties. When a potential difference is operated on a quartz crystal, the quartz oscillates at certain frequency. The change in mass that occurs on the quartz surface is directly correlated with the change in the crystal oscillation frequency. The effect of adding mass on the QCM surface is in accordance with the following Saubrey equation

\[ \Delta m = \frac{A\sqrt{\rho_q\mu_q}}{2f_0^2} \cdot \Delta f \]  

(1)

With \( \Delta f \) is frequency changes (Hz), \( f_0 \) is the fundamental resonant frequency of QCM, \( A \) is the area of the deposited quartz (m²), \( \rho_q \) is quartz density (2,684 g/cm³) and \( \mu_q \) is quartz modulus (2,947 x 10¹¹ g/cm s²) [1].

To better understand the resonance behaviour of QCM, several mathematical models have been proposed, one of which is the Butterworth Van Dyke (BVD) model [2]. Based on the physical properties of QCM, the BVD design uses four parameters, namely two capacitors, one inductor and one resistor (Figure 1a), which are divided into two branch circuits. One of the branches consists of only one capacitor, \( C_0 \), which is known as the electrical branch. The other branch, the acoustic branch, consists of a capacitor \( C_1 \), an inductor \( L_1 \) and a resistor \( R_1 \) connected in series. A capacitor \( C_0 \) is the electrical capacitance across the electrodes, an inductor \( L_1 \) is the motional inductance proportional to the mass,
and a capacitor $C_1$ is the motional capacitance inversely proportional to the stiffness. A resistor $R_1$ is the motional resistance that quantifies dissipative losses. QCM that has been coated can be modelled with a modified BVD design (Figure 1. b). There is an additional resistor $R_2$ and an inductor $L_2$ connected in series on the branch of the motional arm. $R_2$ and $L_2$ can be described as the damping parameter of the QCM caused by the layer [3].

![Diagram](image)

**Figure 1.** (a) BVD design for QCM without coating and (b) modified BVD design for QCM + PANI thin film

In order to function as a chemical sensor or biosensor, the QCM must be given an appropriate, sensitive coating. Polyaniline (PANI) is a conductive polymer with many applications, one of which is an active sensor material. Polyaniline coated on the QCM surface has been reported to detect Volatile Organic Compounds (VOCs), especially alcohol, ether, carbon tetrachloride, chloroform and ethyl acetate [4-6]. Several methods can carry out the deposition of a PANI thin layer on the QCM surface. The simplest deposition method is spin coating [7]. The spin coating method requires a sample in a solution, so the PANI powder must be dissolved first using the suitable solvent. There are several parameters of spin coating deposition that can affect both the quality of the thin film and the viscoelasticity of the PANI thin film. These parameters include the concentration of the solution and the rotational speed of the spin coater [8].

The results of a thin film of PANI deposition on the QCM surface using the spin coating method were mentioned in the previous article [9]. In this study, the discussion will be devoted to the effect of PANI solution concentration and spin coater rotational speed on changes in the resonance parameters of the deposited PANI thin film. The resonance parameter's determination is determined by inputting the impedance measurement data using the impedance analyzer in the Microsoft Excel program with the Nonlinear Generalized Reduced Gradient (GRG) method.

### 2. Method

The oxidation method was used in the synthesis of PANI powder, as demonstrated in a preceding study [10]. The synthesized PANI powder was then dissolved in Dimethyl Formamide (DMF) solvent with a 2 and 4% solution concentration. The solution is then stirred with a magnetic stirrer to obtain a homogeneous solution. The PANI solution was dripped on the QCM surface and rotated with a spin coater with a 2,000 and 4,000 rpm rotational speed. After that, the QCM was dried at 100˚ for 10 minutes.

The QCM used in this study was the AT-cut quartz crystal in a standard package obtained from Great Microtama Surabaya Industry. It has a fundamental resonance frequency of 10MHz. Omicron Bode 100 Impedance Analyser was used to measure the impedance on the QCM before and after coating with PANI. Impedance measurements were carried out in the frequency range 9,960,000 to 10,070,000 Hz. Figure 2 shows the impedance spectrum of the QCM without coating. The impedance data is then input into the Microsoft Excel program using the nonlinear GRG method to obtain the resonance parameters of QCM and PANI thin film according to the modified BVD design.
3. Results and Discussion

Determination of the value of the resonance parameter of the PANI thin film begins with inputting impedance data from the Omicron Bode 100 Impedance Analyser into the Microsoft Excel program with the .xlsm file type. The input data is the impedance data from the QCM before and after being coated. According to the BVD circuit model, impedance data from uncoated QCM is used to determine the parameter values $C_0$, $C_1$, $R_1$ and $L_1$. At the same time, the QCM impedance data after being coated is used to determine the parameter values of $R_2$ and $L_2$ according to the modified BVD model. Determination of resonance parameters using the Non Linear GRG method has been successfully carried out by several previous studies [1, 2, 12]. The resonance parameter values for variations in solution concentration and rotational speed can be seen in Table 1. It can be seen that the values of $C_0$, $C_1$, $R_1$ and $L_1$ for each sample are varied because the QCM used is different.

| Sample        | Resonance Frequency (Hz) | $C_0$ (pF) | $C_1$ (pF) | $R_1$ (Ω) | $L_1$ (mH) | $R_2$ (Ω) | $L_2$ (mH) |
|---------------|--------------------------|------------|------------|-----------|------------|-----------|------------|
| dmf1_2000     | 10009020                 | 4.71370    | 0.02219    | 9.48530   | 11.39336   | 79.01295  | 0.00144    |
| dmf1_4000     | 9994879                  | 4.69667    | 0.02227    | 7.28714   | 11.34756   | 45.45017  | 0.03891    |
| dmf2_2000     | 10007311                 | 4.82962    | 0.02309    | 6.62864   | 10.94940   | 25.9253    | 0.00662    |
| dmf2_4000     | 10007304                 | 4.84101    | 0.02210    | 10.26251  | 11.43310   | 18.10632  | 0.00961    |
| dmf3_2000     | 10009145                 | 4.79960    | 0.02220    | 6.98080   | 11.38926   | 105.92203  | 0.00076    |
| dmf3_4000     | 10009042                 | 4.83777    | 0.02264    | 6.82825   | 11.16738   | 58.19544  | 0.00106    |
| dmf4_2000     | 10009124                 | 4.80761    | 0.02264    | 7.52692   | 11.16504   | 118.88732 | 0.00278    |
| dmf4_4000     | 10004812                 | 4.81013    | 0.02193    | 11.18735  | 11.53692   | 66.00451  | 0.00970    |

The value of the resonance parameter of the PANI thin film can be seen from the values of $R_2$ and $L_2$. It can be seen that the variation of the solution concentration (1 – 4%) and the variation of the spin coater rotational speed (2,000 and 4,000 rpm) can affect the value of the resonance parameter of the PANI layer deposited above the QCM. The $R_2$ parameter represents the dissipative properties of the BVD circuit, while the $L_2$ parameter represents the inertial mass which gives a loading effect on the QCM [3]. The smallest $R_2$ value was obtained in the dmf2_4000 sample, namely the PANI layer...
deposited from a 2% PANI/DMF solution with a spin coater rotational speed of 4000 rpm. On the contrary, the most significant $R_2$ value was obtained from the sample dmf4_2000, namely the PANI layer deposited from a 4% PANI/DMF solution with a spin coater rotational speed of 2,000 rpm. This implies that the energy dissipation process that occurs is not the same in each sample. The most considerable energy dissipation process occurs in the dmf4_2000 sample. It can be interpreted that there is a substantial energy loss in the sample, much more remarkable when compared to other samples.

The $L_2$ parameter values are also different for all samples. The smallest $L_2$ value is obtained in the dmf3_2000 sample, while the most significant $L_2$ value is obtained in the dmf1_4000 sample. As mentioned above, the $L_2$ value represents the inertial mass deposited above QCM, so it can be interpreted that the enormous mass deposited above QCM is in the sample dmf1_4000. This result is supported by calculating the amount of mass deposited using equation (1), and the results are given in Table 2. The deposited mass is calculated from the change in the resonant frequency. The significance of the mass deposited above QCM was found in the dmf1_4000 sample. The lowest mass is in the sample dmf3_2000. This supports the results of determining the value of $L_2$ in Table 1 above. The deposited mass came from PANI powder and DMF solvent. DMF solvent does not evaporate when heated because it is trapped on the surface of the QCM.

![Figure 3](image_url)

**Figure 3.** The impedance graph of QCM coated with PANI thin film at (a) 2000 rpm; and (b) 4000 rpm rotating speed

The table below shows the mass deposited on the QCM surface for different samples.

| Sample     | Resonance Frequency (Hz) Before coating | Resonance Frequency (Hz) After coating | Calculated deposited mass (g) |
|------------|----------------------------------------|----------------------------------------|--------------------------------|
| dmf1_2000  | 10009652                               | 10009020                               | $5.64589 \times 10^{-7}$ |
| dmf1_4000  | 10011980                               | 9994879                                | $1.52699 \times 10^{-5}$ |
| dmf2_2000  | 10010349                               | 10007311                               | $2.71358 \times 10^{-6}$ |
| dmf2_4000  | 10011484                               | 10007304                               | $3.73278 \times 10^{-6}$ |
| dmf3_2000  | 10009478                               | 10009145                               | $2.97492 \times 10^{-7}$ |
| dmf3_4000  | 10009539                               | 10009042                               | $4.43999 \times 10^{-7}$ |
| dmf4_2000  | 10010363                               | 10009124                               | $1.10669 \times 10^{-6}$ |
| dmf4_4000  | 10009019                               | 10004812                               | $3.75875 \times 10^{-6}$ |
spectrum. Figure 3(a) shows that the red phase spectrum (sample dmf2_2000) has a symmetrical shape. The shape of the impedance spectrum is also symmetrical, where the shape of the two peaks is tapered. From the spectrum’s shape, it can be seen that the deposited PANI film has no loading effect on QCM. In Figure 3(b), the red spectrum for the dmf2_4000 sample has almost the same shape as the spectrum for the dmf2_2000 sample. The sharp peak of the impedance spectrum indicates that the PANI film is included in the glassy coating material [12]. When related to the results of determining the value of the \( R_1 \) parameter in Table 1, the two samples have a fairly small \( R_2 \) value compared to other samples. Meanwhile, when viewed from the mass deposited above the QCM, the two samples have a less significant mass. There are several impedance spectrums with peaks that are not sharp. A non-tapered peak indicates that the coating includes rubbery coating and will have a loading effect on QCM. These elastic properties can occur as a result of the interaction between QCM and DMF solvent trapped on QCM’s surface.

From the results of the determination of the resonance parameters of the PANI thin film deposited on the QCM using the spin coating method, it can be seen that the concentration of the solution and the spin coater rotational speed significantly affect the value of the resonance parameter. PANI/DMF solution with a solution concentration of 2% will give the lowest dissipative parameter value (\( R_2 \)). The effect of rotational speed on the amount of mass deposited can be seen in the sample with a solution concentration of 1% (Table 3). The difference in the amount of mass deposited is quite significant. A rotating speed of 2,000 rpm provides significantly less mass amount when compared to 4,000 rpm. The lower rotational speed prevents the DMF solvent from being trapped on the QCM surface, and when heated, the DMF can evaporate [13].

4. Conclusion
From the research that has been done, it can be concluded that the resonance parameters of the PANI thin film prepared by the spin coating method can be determined using a modified BVD model. The solution's concentration and the spin coater's rotational speed have a significant impact on the value of the resonance parameter and the amount of mass deposited. When using DMF solvent, the best parameter values will be obtained with a solution concentration of 2% and a rotational speed of 2000 rpm because it has small \( R_2 \) value and small deposited mass.

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