Effect of the polystyrene surface hydrophobicity on QCM sensor resonance frequency in contact with water-glycerol mixture

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Abstract. Quartz Crystal Microbalance sensor responds to the mass change on the sensor surface as well as liquid viscosity and density which is in contact with the sensor surface. When the sensor surface was contacted with a liquid, the resonance frequency will decrease together with an increase of the series impedance of the sensor. Higher viscosity and density resulted in a decreased of the resonance frequency and increased the minimum impedance of the sensor. This paper showed that the surface hydrophobicity of the sensor surface also affected the change of the sensor resonance frequency as well as the sensor impedance. Surface hydrophobicity of the polystyrene coating was altered using UV irradiation. A variation of liquid viscosity was prepared by mixing water and glycerol. By varying the liquid viscosity from 1 to 2.6 cPs, the frequency and impedance change of the sensor was linearly related to the liquid viscosity. It was also observed that frequency and impedance change was also increase caused by a more hydrophilic surface. This result showed that lowering the hydrophobicity of the surface results in a better coupling between the sensor and the liquid. Those resulted in a higher energy transfer from the sensor to the liquid occurred and increased the sensor impedance.

1. Introduction
Quartz Crystal Microbalance (QCM) is known to work well in contact with the liquid. The sensor responds to the liquid viscosity, and density which is expressed into a frequency change and impedance change at its resonance frequency. This behavior extends the use of the QCM sensor not only as a mass sensitive sensor but also to detect a mechanical change of the liquid property in contact with the sensor. The relationship of the QCM sensor resonance frequency to the viscosity and density change of the liquid in contact with the sensor surface was described by Kanazawa and Gordon [1]. The resonance frequency of the QCM sensor changed caused the liquid density and viscosity. A linear relationship between the frequency change of the sensor to the square root of the viscosity and density of the contacting liquid was observed and modeled [2].

Since then the used of QCM to detect the liquid viscosity and density measurement in much different liquid conditions was reported. Lead acid liquid viscosity and density change using QCM sensor were successfully measured during the charging cycle [3] by measuring the frequency change of the sensor. The QCM was used to measure the lubricant liquid density and viscosity up to 220°C[4,5]. The mentioned report was done by using the QCM sensor with gold electrode without coating. Therefore the contact between the sensor and the liquid were established by the gold liquid interaction.
The relationship between the frequency change and the viscosity and density of the liquid described Kanazawa & Gordon did not explain the interface condition between the sensor surface and the liquid. The effect of the interface condition between the sensor surface and the liquid was described by Duncan-Hewitt and Thompson [6]. They present the effect of the surface water contact angle to the impedance spectrum of the QCM sensor with a smooth surface. Another report [7] showed that the interfacial effect of the surface and liquid affected the resonance behavior of the sensor. In a specific condition, the resonance frequency of the sensor did not exist anymore. Another surface condition which affects the sensor impedance curve in contact with liquid was the surface roughness. It was suggested that if the sensor surface was rough, part of the liquid was trapped and acted as a rigid mass [8]. Further analysis using molecular dynamics simulation [9] showed that the Kanazawa-Gordon prediction model had a good agreement with the simulation at a no-slip condition, but the further prediction was required in a slip condition.

Based on those reports, it was necessary to control the surface hydrophobicity and also surface roughness in the order used the QCM sensor to detect a viscosity and density of the contacting liquid. In this experiment, we investigated the resonance frequency and impedance change of the QCM sensor with slight rough polystyrene coating in contact with the water-glycerol mixture. Two difference surface with different contact angle was used.

2. Experimental Methods

2.1. Materials

The QCM sensor was made from an AT-cut commercial crystal resonator HC-49/U with a fundamental resonance frequency of 10MHz. The crystal resonator is commonly used as a quartz crystal resonator in an electronic circuit. The resonator was produced by PT Great Microtama Electronics, Surabaya, Indonesia.

The resonator dimension is disc shape with a diameter of 8.7 mm. The electrode was made from silver with a diameter of 5mm. The resonator has a frequency tolerance of 10ppm at 25°C. The frequency stability is 10ppm. Load capacitance of the resonator is 12pF with the minimum series resonance of 30Ω.

The coating material was polystyrene with a molecular weight of 35KD purchased from Sigma Aldrich. The solvent was toluene from the same manufacturer. The glycerol was purchased EMSURE with product number Z0379294-627 has a mass density of 1.23g/ml.

2.2. Methods

The QCM sensor was prepared by measuring its electrical impedance in contact with air using Vector Network Analyzer Node 100 from Omicronlab. The impedance was measured in the measuring cell to make sure that the same mechanical condition which may affect the sensor impedance during the measurement. Figure 1 shows the measuring cell and the sensor and measuring cell connected to the impedance analyzer port. The sensor was clamped in the center of the cell with two silicone rings on both sides. The clamping force of the measuring cell was made using a pair of magnet and iron pair to ensure a constant force applied to the silicone ring. The impedance was measured from 9.92 MHz to 10.05 MHz with a sweep frequency step of 31.7Hz. This frequency range covered the series resonance frequency and the parallel resonance frequency of the sensor.

Both sides of the resonator surface were coated using polystyrene. Polystyrene with a molecular weight of 35KD was solved in toluene with a concentration of 6% weight for the coating solution. The polystyrene and toluene were purchased from Sigma Aldrich. The coating was done using spin coating at 3000rpm. A 50 μL polystyrene solution was dropped on top of the sensor surface when the sensor was spinning at 3000 rpm. The coating was done on both sides of the sensor. The coated sensor was then put in an oven at 100°C for 1 hour.
The curve of the sensor in contact with air and in contact with water. It can caused a change of the impedance curve. The contribution of the viscoelastic effect of the liquid on top of the sensor surface significantly indicated by viscoelastic effect of the liquid on top of the sensor surface.

After coating and treated using UV, the contact angle of the sensor surface was 84.4 ± 1°. Other measurement was done by swapping the sensor surface in contact with the liquid.

3. Results and Discussion

The thickness of the polystyrene coating was calculated using the Sauerbrey equation based on the fact that the polystyrene behaves as a rigid layer, therefore its fall in the gravimetric regime. Sensor coating affects the acoustic load of the sensor. Based on the transmission line model, the acoustic load of the finite coating layer will be transformed into the electrical impedance of the resonator [11]. Using the BvD model, the acoustic load was expressed in an additional resistance and inductance of the sensor. For the thin glassy film, the resistive contribution to the sensor was very little [12]. The series resonance frequency at zero phase change was equal to the resonance frequency at minimum impedance.

The impedance measurement of the resonator before and after coating with polystyrene and treated using UV irradiation showed that the minimum electrical impedance of the sensor did not change significantly. Minimum impedance of the sensor after coating and UV treatment was 9.56 ± 1.5 Ω, and the minimum impedance before coating was 9.35 ± 2.6 Ω. In another hand, the resonance frequency of the sensor was changed significantly. The resonance frequency at series resonance was decreased by (13000 ± 300) Hz. Using the Sauerbrey equation, the frequency change was equalled to 11.8μg deposited coating layer. With the polystyrene mass density of 1.06 g/cm³ and electrode diameter of 5mm, the coating thickness of the polystyrene film was 567nm. Figure 2a showed the impedance curved of the sensor before and after coating and treated using UV. There was no significant impedance curve change before and after UV irradiation. The contact angle of the polystyrene without UV irradiation was 84.4 ± 2.2 and 66.6 ± 4.4 after UV irradiation.

In contact with water and water-glycerol mixture, the impedance curve of the sensor was changed significantly indicated by a significant change of the minimum impedance and resonance frequency at minimum impedance. The contribution of the viscoelastic effect of the liquid on top of the sensor surface caused a change of the impedance curve. Figure 2b shows the comparison between the impedance curve of the sensor in contact with air and in contact with water. It can be seen that both the resonance frequency and the minimum impedance of the sensor changed significantly. The curve of the sensor in
contact with water was shifted to the left and lifted up. It indicated a decrease in the resonance frequency and increasing minimum impedance of the sensor.

![Graph](image1.png)  
**Figure 2.** (a) Sensor impedance before and after coating, (b) Impedance spectrum of the QCM sensor in contact with air and water

Some essential points of the impedance spectrum of the sensor changed when the surface of the sensor in contact with liquid. The minimum impedance of the sensor was not at 0°. The series resonance frequency was not in the same frequency as the frequency at minimum impedance (see **Figure 3**). Based on **Figure 3**, the minimum impedance, frequency at series resonance and minimum impedance were extracted from the impedance spectrum with phase spectrum. Where $Z_{\text{min}}$ is minimum impedance, $f_{m}$ is the frequency at minimum impedance and $f_{s}$ the resonance frequency at series resonance. The series resonance frequency is higher than the frequency at minimum impedance.

![Graph](image2.png)  
**Figure 3.** Sensor impedance and phase spectrum in contact with liquid (a) wide frequency range (b) frequency around minimum impedance. $f_{m}$: the frequency at minimum impedance, $f_{s}$: series resonance frequency

Impedance measurement of the sensor in contact with the water-glycerol mixture with a different fraction of glycerol to make the viscosity variation from 1 to 2.6 cPs was measured. The sensor still has an impedance spectrum with the observed series resonance frequency. This implied that the sensor could be used in an oscillator circuit to oscillate at its series resonance frequency. **Figure 4** showed the minimum impedance of the sensor in contact with the water-glycerol mixture from 1cPs to 2.6cPs. One can see that the relationship was well approached with linear regression. The change of the minimum impedance of the sensor with a lower contact angle resulted in higher sensitivity.

![Graph](image3.png)  
**Figure 4.** Impedance measurement of the sensor in contact with the water-glycerol mixture from 1cPs to 2.6cPs. One can see that the relationship was well approached with linear regression.
Figure 4. Minimum impedance of the QCM sensor again viscosity change

Figure 5. Frequency change of the QCM sensor again liquid viscosity at (a) minimum impedance (b) series resonance again

Figure 5a depicted the frequency change of the sensor at minimum impedance. The frequency change of the sensor was higher than predicted [1]. This can be the contribution of the trapped liquid as described in [8]. The result showed that the lower the surface contact angle, the higher the frequency change of
the sensor at minimum impedance. It suggests that the frequency change of the sensor was also affected by the surface interaction of the polystyrene and the liquid. A similar result was also observed in the frequency change of the sensor at series resonance as presented in Figure 5b. However, the frequency change of the resonance frequency was smaller compared to the frequency change at the minimum impedance. The slope of the frequency change at minimum impedance was also higher than at the series resonance. Therefore it is suggested to use the frequency change at the minimum impedance to achieve better sensitivity for sensor respond to the liquid viscosity.

4. Conclusions
We can conclude that the minimum impedance, frequency change at minimum impedance and frequency change at series resonance of the QCM sensor with polystyrene surface was affected by the surface contact angle of the polystyrene. Lower contact angle results in a higher change for those three parameters. For a small change of the liquid viscosity, the minimum impedance of the sensor was linearly related to the viscosity. The frequency change of the sensor at minimum impedance was higher than the frequency change of the sensor at series resonance.

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6. References

[1] Keiji Kanazawa K and Gordon J G 1985 The oscillation frequency of a quartz resonator in contact with liquid Anal. Chim. Acta 175 99–105
[2] Talib Z A, Baba Z, Kurosawa Z, Sidek H A A, Kassim A, and Yunus W M M 2006 Frequency Behavior of a Quartz Crystal Microbalance (QCM) in Contact with Selected Solutions Am. J. Appl. Sci. 3 1853–8
[3] Cao-Paz A M, Rodriguez-Pardo L, Fariña J and Marcos-Acevedo J 2012 Resolution in QCM sensors for the viscosity and density of liquids: Application to lead-acid batteries Sensors 12 10604–20
[4] Wang D, Mousavi P, Hauser P J, Oxenham W and Grant C S 2005 Quartz crystal microbalance in elevated temperature viscous liquids: Temperature effect compensation and lubricant degradation monitoring Colloids Surfaces A Physicochem. Eng. Asp. 268 30–9
[5] Acharya B, Sidheswaran M A, Yungk R and Krim J 2017 Quartz crystal microbalance apparatus for study of viscous liquids at high temperatures Rev. Sci. Instrum. 88
[6] Duncan-Hewitt W C and Thompson M 1992 Four-layer theory for the acoustic shear wave sensor in liquids incorporating interfacial slip and liquid structure Anal. Chem. 64 94–105
[7] Ferrante F, Kipling A L and Thompson M 1994 Molecular slip at the solid-liquid interface of an acoustic-wave sensor J. Appl. Phys. 76 3448–62
[8] McHale G and Newton M I 2004 Surface roughness and interfacial slip boundary condition for quartz crystal microbalances J. Appl. Phys. 95 373–80
[9] Huang K and Szlufarska I 2012 Friction and Slip at the Solid/Liquid Interface in Vibrational Systems Langmuir 28 17302–12
[10] Sakti S P, Aji R Y and Amaliya L 2017 Low-Cost Contact Angle Measurement System for QCM Sensor TELKOMNIKA (Telecommunication Comput. Electron. Control. 15 560–9
[11] Lucklum R, Behling C, Cernosek R W and Martin S J 1997 Determination of Complex Shear Modulus with Thickness Shear Mode Resonators J. Phys. D. Appl. Phys. 30 346–56
[12] Lucklum R, Behling C and Hauptmann P 2000 Gravimetric and non-gravimetric chemical quartz crystal resonators Sensors Actuators B Chem. 65 277–83