# The response of QCM sensor coated with polystyrene in contact with potassium chloride solution

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# The response of QCM sensor coated with polystyrene in contact with potassium chloride solution

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ABSTRACT

Quartz Crystals Microbalance responds to the coating film physical property change which is affected by the contacting liquid on the film surface. One of the liquid effects of the film is the film swelling effect. The swelling of the film changes the density of the film and could also be the modulus elasticity. Potassium chloride in water has ionic strength which makes the polystyrene swell. This work shows the effect of the potassium chloride (KCl) solved in distilled water to the polystyrene film which results in a frequency change of the QCM sensor coated with polystyrene. KCl solution with varying concentrations is used to observe the effect of ionic strength on the resonance frequency and minimum impedance of the QCM sensor coated with polystyrene. The resonance frequency of the QCM sensor in contact with the KCl solution changes continuously. It shows a continuous additional mass to the sensor surface. The frequency change was much higher than calculated frequency change caused by the deposition of the KCl on the sensor surface. The effect of the swelling is also indicated by the significant change of the minimum impedance of the sensor in contact with the KCl solution. The minimum impedance is than the minimum impedance in contact with water. It shows that the modulus elasticity of the film changed caused by swelling effect.



## 1. Introduction

Quartz Crystal Microbalance (QCM) is a sensor that works based on piezoelectric principle, which is widely used not only for mass change detection [1] but also the viscosity and density of contacting liquid on its surface [2–5], even those containing a heavy metal ion [6]. A linear relationship between the frequency change of the sensor to the square root of the viscosity and density of the liquid was described by the Kanazawa and Gordon [7]. In liquid applications, the QCM sensor converts the viscosity and density of the liquid into an electrical signal. These signals are measured as a shift in the resonant frequency by the oscillator containing the QCM as the element which determined the frequency of the oscillator. To avoid deterioration in the quality factor (Q) in the liquid, which causes instability and even stopping the oscillation, QCM is operated with one side in contact with the liquid [8]. When one side of the QCM sensor electrode interacts with a solution, the sensor's parallel resonant frequency is affected by the solution's conductivity and dielectric constant [9]. The QCM sensor was immersed on one side in a solution with ionic content. The sensor surface with Polystyrene (Ps) coating film was placed in contact with the liquid.

The application of Ps as a matrix layer has been described in previous studies [10]. Besides protecting the surface of the electrodes from contaminants, this layer can also be used as a functional layer to detect certain fluids through the swelling effect [11,12]. The selection of coating method, treatment after coating, can be used to control the level of surface roughness of the sensor so that the surface area of the active layer of the sensor can also be controlled [2,13–15].

In this paper, we use a QCM sensor coated with Ps immersed with the KCl solution as an ionic monovalent solution. The response in the form of changes in frequency and impedance is observed, to get an analysis of the QCM sensor response to KCl solutions with varying concentrations.

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## 2. Experimental method

### 2.1. Materials

The QCM sensor used has a gold electrode, which is made of AT-cut with a fundamental resonant frequency of 10 MHz. Ps with a molecular weight of 192 kDa was purchased from Sigma-Aldrich. The solvent used is toluene from the same factory. An analytical grade potassium chloride was used. The potassium chloride solution was prepared at a concentration of 1.5 M, 2.5 M, and 3.5 M.

### 2.2. Preparation of thin layers Ps

The polystyrene coating solution was prepared with a mass fraction of 1% in toluene. The film was made by using a spin coating method by depositing a 50 µL of Ps on top of the sensor QCM surface while spun at 3000 rpm for one minute. The coated QCM sensor was annealed at 200 °C for 1 h at atmospheric conditions.

### 2.3. Measurement of frequency and impedance

The electrical impedance of the sensor before and after coating as well as when the sensor was in contact with the potassium chloride solution, was measured using Vector Network Analyzer Bode 100 from Omicronlab. The resonance frequency of the sensor in contact with the potassium chloride solution was measured using an in-house frequency counter system, which has been calibrated to a rubidium oscillator. The response of the QCM sensor with a polystyrene coating to three different potassium chloride solution was observed.

## 3. Result and discussion

The frequency change of QCM with Ps coating was 950 Hz. Based on the Sauerbrey equation those change is equivalent to a polystyrene thickness of 40 nm. With such thickness, it is expected that there is no viscoelastic effect of the polystyrene film. Therefore there should be no additional damping of the sensor after Ps coating. The physical parameter of the KCl solution which affects the QCM sensor resonance according to the Kanazawa-Gordon equation is the density and viscosity [7]. The density and viscosity of the KCl solution with a concentration of 1.5 M, 2.5 M, and 3.5 M at room temperature around 25 °C is depicted in Table 1 was taken from Grimes et al [16]. The initial resonance frequency was 10 MHz. The frequency change and the electrical damping was the calculated value using Kanazawa-Gordon equation [7] based on the assumption of a smooth surface and no other interaction between the liquid and the sensor surface.

The frequency change of the QCM sensor in contact with a distilled water and potassium chloride solution is presented in Fig. 1. The resonance frequency of the sensor was quickly decreased as the sensor surface in contact with the water and potassium chloride. In contact with water, the resonance frequency of the sensor decreased by around 5 KHz. Whilst in contact with potassium chloride solution, the resonance frequency decreased further.

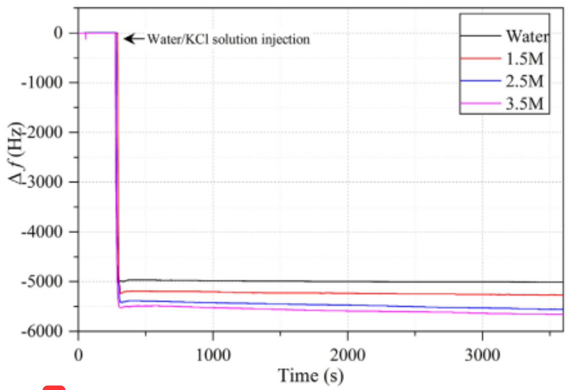


**Fig. 1.** Frequency change of the sensor in contact with water and KCl solution with a concentration of 1.5 M, 2.5 M, and 3.5 M. The frequency when the sensor in contact with air, was taken as initial frequency, therefore the $\Delta f = 0$.

The frequency change of the sensor in contact with water and KCl solution is more significant than predicted by the Kanazawa-Gordon equation as presented in Table 1. The frequency change is also significantly higher compare to the frequency change of the QCM sensor with gold electrode without coating in contact with electrolyte [3]. The bigger change in the resonance frequency could be caused by the surface roughness of the polystyrene coating as well as the hydrophobicity of the polystyrene coating. Higher potassium chloride concentration resulted in a bigger frequency change of the resonance frequency. It could be attributed to the increasing solution density of the KCL solution, as predicted by Kanazawa-Gordon equation that increasing liquid density results in bigger resonance frequency decrease. The bigger frequency change caused by film and ionic liquid interaction was also reported [17].

Fig. 2 shows the detail resonance frequency of the sensor in contact with water and KCl solution up to 60 min. After the resonance frequency reaches the new condition in contact with the water, the resonance frequency of the sensor remained constant. However, the resonance frequency of the sensor in contact with the KCl solution was decreased with time. It indicates that there was an interaction between the KCl solution and the polystyrene. The possibilities are the absorption of the KCl to the polystyrene surface as a pure mass absorption or the change of the polystyrene coating modulus elasticity caused by the contact with the KCl solution together with the solution absorption. Further investigation is required.

The impedance measurement of the sensor in contact with air and water is presented in Fig. 3. The impedance curve of the sensor in contact with air shows no additional damping caused by the Ps coating. The impedance curve of the sensor in contact with water was shifted to the left to the impedance curve in contact with air. The minimum impedance of the sensor increased by 264 Ω. There was 58 Ω higher than the calculated impedance in Table 1. The impedance curve remains after 20 min water contact.

Fig. 4 shows the impedance value around the minimum impedance. The frequency of the minimum impedance after 20 in con-

**Table 1**
Density and viscosity of the KCl solution [16], calculated frequency change and electrical damping of the 10 MHz QCM sensor using Kanazawa-Gordon equation [7].

| KCl (M) | Density (gr/cm3) | Viscosity ($g.cm^{-1}.s^{-1}$) | $\Delta f$ (Hz) | ΔR (Ω) |
|---|---|---|---|---|
| 0 (water) | 0.9972 | 0.891 | –1899 | 206 |
| 1.5 | 1.1118 | 0.885 | –1998 | 217 |
| 2.5 | 1.1863 | 0.910 | –2093 | 227 |
| 3.5 | 1.2608 | 0.935 | –2187 | 238 |

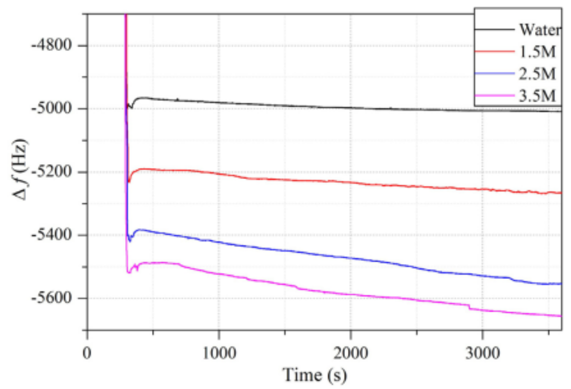


**Fig. 2.** Stability of the resonance frequency in contact with water and KCl solution with a concentration of 1.5 M, 2.5 M, and 3.5 M.

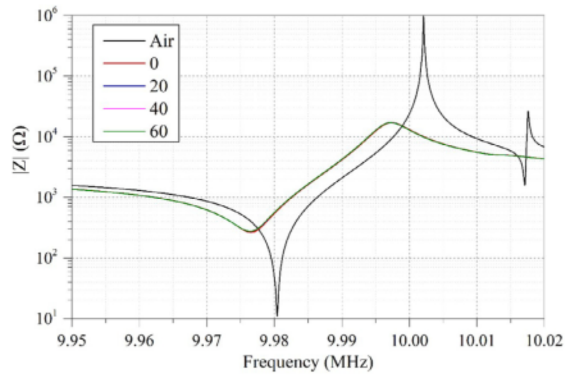


**Fig. 3.** Impedance spectrum of the sensor in contact with air and with distilled water.

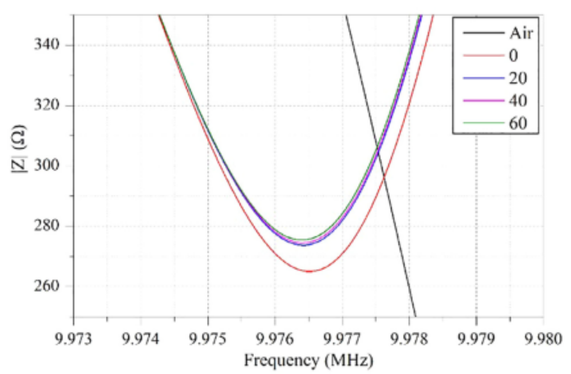


**Fig. 4.** Impedance spectrum at a minimum impedance of the sensor in contact with water.

tact with water decreased by –95 Hz. The impedance values increased by 8 Ω. The resonance frequency and the impedance remained indicated by the same values of the resonance frequency and impedance at 40 and 60 min. The difference between the 0 s and 20 min could be caused by the wetting process of the polystyrene surface with the water.

The impedance curve of the sensor in contact with a KCl solution is presented in Figs. 5 and 6. The change of impedance spectrum in contact with KCl solution is not much different from the impedance spectrum in contact with water. The minimum impedance increased around 280 Ω from its value in contact with air. The value is higher than the predicted value in Table 1 by 42 Ω. The impedance value is bigger than the impedance of 10 MHz sensor (gold electrode without coating) in contact with NaCl [18].

The impedance curve immediately after contact with KCl solution and after 20 min shift slighly. Fig. 6 shows the impedance spectrum of the sensor around the frequency where the minimum impedance occurred. The resonance frequency change after 20 min in contact with KCl solution from the value at initial contact with KCl solution is –126 Hz, and the minimum impedance increased 7 Ω. The resonance frequency and the minimum impedance remained afterward. The fact that the impedance value in contact with water and KCl solution didn't significantly different shows that the modulus elasticity of the polystyrene in contact with KCl does not change due to the KCl ionic strength.

The fact that the modulus elasticity remained, indicated by constant minimum impedance value (Fig. 6), and continuous decreased of the resonance frequency (Fig. 2) suggest that there is a continuous mass absorption into the polystyrene film. There is no modulus elasticity change of the polystyrene film. In contrast to the water which doesn't show continuous water absorption by the polystyrene film, increasing KCl solution concentration which

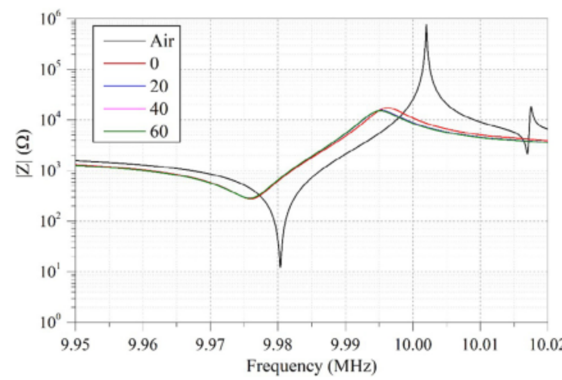


**Fig. 5.** Impedance spectrum of the sensor in contact with air and with KCl solution of 3.5 M.

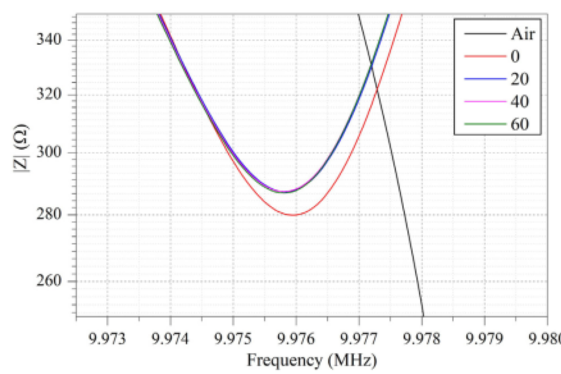


**Fig. 6.** Impedance spectrum at the minimum impedance of the sensor in contact with KCl solution of 3.5 M.

related to the increasing ionic strength of the solution could play a role in KCl solution absorption by the polystyrene film.

## 4. Conclusion

This work presents the respond of the QCM sensor coated with polystyrene in contact with the potassium chloride solution. The different of minimum impedance of the sensor compared to the Kanazawa-Gordon model in contact with KCl solution is not significant diferent from the minimum impedance in contact with water. It means that the modulus elasticity of the polystyrene film doesn't change becaused of the KCl solution ionic strength. Whilst the resonance frequency of the sensor in contact with water still, the resonance frequency of the sensor in contact with KCl solution decreased continously during the measurement up to 60 min. It shows that there is more and more KCl solution absorbed by the polystyrene film.

## CRediT authorship contribution statement

**Mira Setiana:** Conceptualization, Investigation, Methodology, Validation. **Tyas N. Zafirah:** Data curation, Formal analysis, Investigation. **Setyawan P. Sakti:** Conceptualization, Visualization, Writing - review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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