QCM을 이용한 에탄올의 수분함량 인라인 측정

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In-Line Measurement of Water Content in Ethanol Using Quartz Crystal Microbalance

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1. Introduction

The use of ethanol for automobile application is increased drastically, since the fuel is relatively clean and sustainable. Though chemical synthesis has been a major process of its production, the grain fermentation is a desirable process having sustain ability. The beer produced from the fermentation has low ethanol contents and a lot of suspended particles of solid waste. Due to the suspended particles and the formation of an azeotropic mixture with water, the common separation technique of distillation is not implemented for the dehydration of the fermented ethanol. Zeolites, a known adsorbent for the water removal, are developed for the adsorptive dehydration of the ethanol.

A quartz crystal microbalance (QCM) has a thin quartz crystal plate with two metal electrodes on both sides that establish an alternating electric field across the plate, causing vibration of the plate at its resonant frequency. This frequency is sensitive to mass loading on the electrodes [1]. For example, a 9 MHz resonator detects mass variation with a sensitivity of 1.4 ng/Hz [2].

Instead of the direct measurements of surface loading, a modification of the electrode surface of a quartz crystal resonator has been utilized for the entrapment of target materials inducing a load change. In the determination of organic substances either in gas or liquid phase, organic film has commonly been coated on the surface of one of its electrodes [3,4]. Though polymer film coated sensors improved the stability of coated material and selectivity of the detected material, they have different characteristic with solid adsorbent coated sensors [5,6]. Carbon coated quartz crystal sensors have high stability for wide range of applications.

In this study, an in-line measurement device of water contents in ethanol is developed by applying PVA on the electrode surface of the QCM. For the performance evaluation, the 2 % to 10 % water contents are utilized to determine the frequency drop of the PVA coated QCM.

2. Experimental

2.1 Materials

Polyvinyl alcohol (Mw. 22,000) was from Junsei Chemical, and ethyl alcohol was from Burdick & Jackson. The chemicals were used as received. Quartz crystal resonators (Sunny

Electronics Co., Korea) were purchased from a local store as capped state for electronic circuit use. The cap was removed before coated with PVA. The sealing prevents the erosion of the silver resonator electrode.

2.2 Equipment

An AT-cut quartz crystal resonator having base frequency of 8 MHz was utilized in this experiment. The electrodes of the resonator were silver finished. The PVA was dissolved in water at a concentration of 0.6 %, and the solution was stirred for half an hour. A 1.8 μL of the completely dissolved PVA solution was applied on the one of electrode surfaces of the resonator. After briefly dried in air, the resonator was baked in an oven at a temperature of 120 ℃ for half an hour. The resonator was cooled in a Petri dish containing silica gel for 10 minutes. Figure 1 describes the sensor preparing procedure. The resonator was placed in the measuring cell module shown in Figure 2 for the in-line measurement. The thickness of three polypropylene plates was 5 mm. The left plate has two nipples to make the sample solution flow to the resonator for the electrode surface contacted. To prevent leakage two o-rings are placed either side of the resonator. The sizes of the three plates were the same with a dimension of 24 mm by 27 mm. Four screws tighten the three polypropylene plates as shown in Figure 2.

2.3 Procedures

The PVA coated resonator was mounted in the module, and the resonator was connected with the oscillation circuit. The sample holding flask contains 100 mL solution to provide continuously the solution to the module at a rate of 10 mL/min. While the solution was stirred supplied, the resonant frequency was measured after 10 min. sattlement. The oscillation circuit provides a small amount of oscillating current to the resonator, and the resonant frequency of the resonator is determined by the load and rheological variation on the surface of the resonator electrode. The frequency is counted with a home-made counter connected to a PC. The measured frequency was stored in the PC for later data analysis. When the frequency is stable, water is added to ethanol to increase the water content by 2 % point each time up to 10 %.

3. Results and discussion

The variation of resonant frequency of blank resonator with increased water contents is shown in Figure 3. The variation of water content affects the frequency variation even with a blank resonator due to the change of solution property on the electrode surface. The step-wise decrease of the frequency indicates the elevation of water content by 2 % each. The measurement was conducted for about 4 minutes at each water contents. The drop of frequency was recovered with the reduced water content. The recovery was not complete, but the variation apparently shows the relation between the water content and the resonant frequency. When the PVA coated resonator was used for the water content measurement, the frequency variation is demonstrated in Figure 4. The measurements exclude the blank variation. For the compensation of the frequency variation the results of the blank tests were used with the fitting of the experimental results. The relation shown in Figure 4 indicate that the frequency measurement from the in-line application of the PVA resonator is satisfactory. shows the frequency variation. The frequency variation of bare resonator is deduced from the actual measurement. Also the amount of PVA coating affects the frequency variation. The repeated measurements of water content in ethanol using the resonator illustrate the measurement is persistent. Though there is some deviation, the decrease of the frequency with the increased water content is clearly demonstrated. The measurement of water content using a quartz crystal resonator is relatively simple compared with other measurement technique utilizing analytical instruments.

4. Conclusion

Quartz crystal resonators coated with PVA are utilized to determine water contents in ethanol for in-line application. The PVA is easily dissolved in water, but is insoluble to ethanol. When the PVA coated quartz crystal resonator is dipped in the ethanol containing small amount of water, the water is absorbed in the PVA increasing the load on the PVA coating to result in frequency drop. The determination performance of PVA coated resonator is examined by measuring frequency decreases in 2 % to 10 % water contained ethanol. The measurements indicates that the higher water content is the more the frequency reduction is, though some variation in the measurement is observed. The blank test using the bare QCR yields the insignificant drop of frequency.

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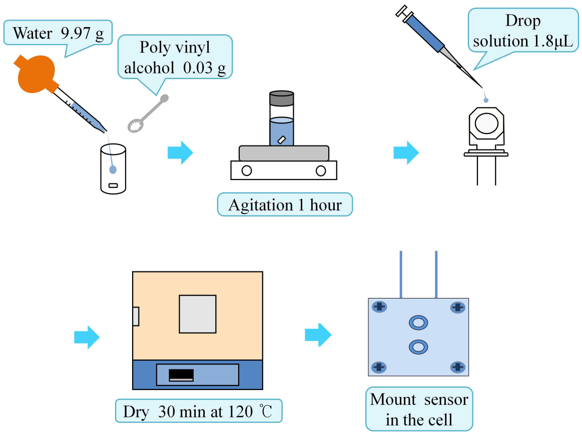

Figure 1. A schematic of QCR preparation procedure.

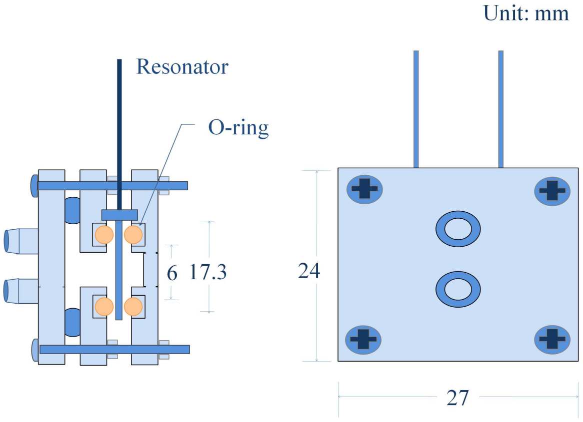

Figure 2. A schematic diagram of resonator cell module

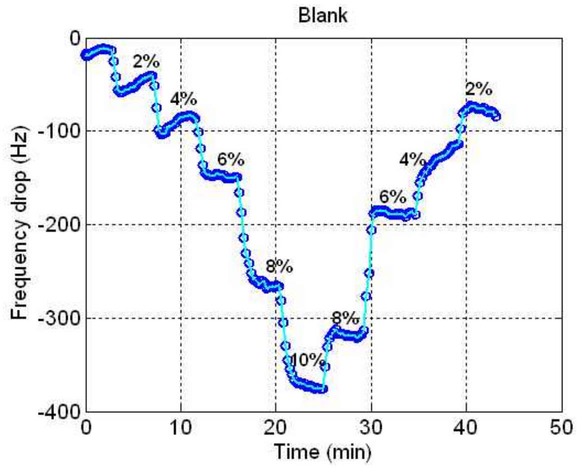

Figure 3. Frequency variation of blank QCR at different water contents.

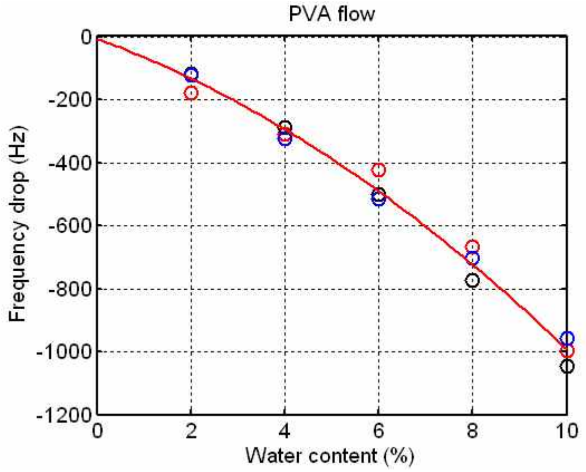

Figure 4. Frequency shifts of PVA coated QCR at different water contents.