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An Unexpected Frequency Response of A Piezoelectric Quartz Crystal Sensor to the Density and Viscosity of the Liquid

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Abstract: An unexpected frequency response for a piezoelectric quartz crystal (PQC) sensor to liquid density and viscosity was reported. For a PQC oscillating in a liquid phase, the frequency shifts (Δf) show a wave-shape response to liquid density (ρ) and viscosity (η) in fine structure, if the longitudinal wave effect was not eliminated. This result is different from the well-known linear relationship between of Δf and $(\rho\eta)^{1/2}$. An oscillating frequency-temperature curve of the sensor was observed and explained.

Keywords: Piezoelectric sensor, quartz crystal, liquid property, longitudinal wave.

Studies with the piezoelectric quartz crystal (PQC) sensor became popular after Sauerbrey demonstrated that a quartz crystal could be used as a microbalance[1]. For a PQC sensor operating in liquid phase, its oscillating frequency is also related to the properties of bulk liquid[2,3]. Kanazawa[4] and Bruckenstein[5] showed that the oscillating frequency of a PQC decreases linearly with $(\rho\eta)^{1/2}$, where ρ and η are the density and viscosity of the liquid, respectively. However, oscillating curves in the fine structure of Δf *vs* $(\rho\eta)^{1/2}$ plotting and frequency-temperature curve of the PQC in liquid phase were observed in this work. Understanding the unexpected frequency response to liquid density and viscosity is helpful to improve the frequency stability of the PQC.

Experimental

The PQC detection cells used were illustrated in **Figure 1**. A 5 MHz AT-cut quartz crystal (with disc diameter of 14 mm and gold electrode diameter of 6.5 mm) was used. The quartz crystal disc was fixed to a glass rectangular detection cell (6×6×6 cm) with one side facing the liquid phase. To eliminate the longitudinal wave (LW) effect, a rough glass plane having glass balls with diameter of 2 mm was placed in detection cell (cell B). The PQC was electrically driven to oscillate by a home-made oscillator circuit and its oscillating frequency was recorded by a universal frequency counter.

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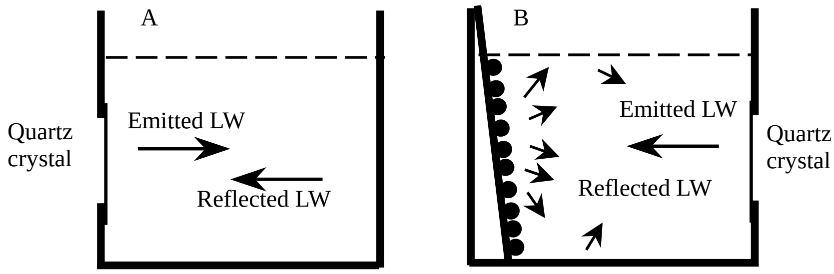
Figure 1 PQC detection cell designs and longitudinal wave effect



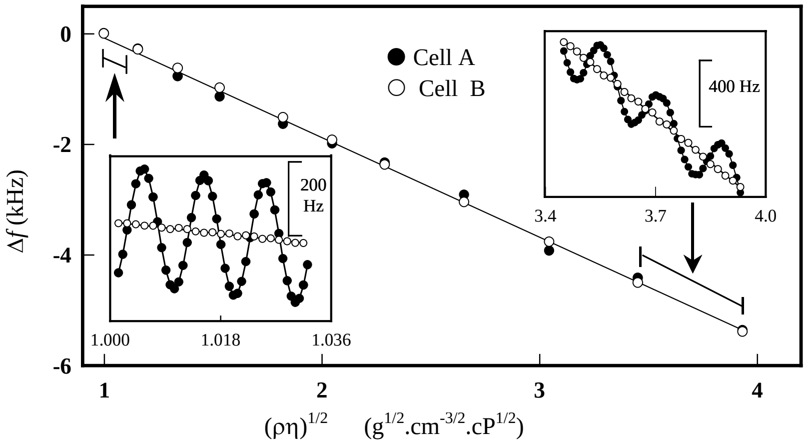
Results and Discussion

In the experiments related to PQC in a liquid phase, the design of detection cell is an important aspect. Bruckenstein[5] suggested a cell design for the PQC in liquid phase, where the quartz crystal disc was horizontally sealed to the bottom of the detection cell, which is widely used in electrochemical quartz crystal microbalance. But oscillating frequency of the PQC in this type cell is sensitive to a slight variation of the liquid height, when evaporation of solvent or addition of solution[6-8]. The reason is that a weak LW is also generated when the AT-cut quartz disc was oscillating in a thickness-shear model (TSM) in liquid phase. The LW can propagate much longer distance (>1 cm) than the TSM wave in the liquid phase and can be reflected by the air/liquid interface. The interference between the emitted and reflected LW on the surface of the quartz disc causes an additional frequency shift, which is a potential error source for PQC frequency measurements.

For the purpose to eliminate the influence of air/liquid interface on the frequency of the PQC, the cell in **Figure 1A** was designed, where the surface of the quartz disc is perpendicular to the air/liquid interface. Indeed, the variation in liquid height above the quartz disc has little influence on the oscillating frequency of the PQC in this cell configuration. However, the PQC in cell A had an unexpected frequency response to liquid density and viscosity. As shown in **Figure 2**, a good linearity was obtained for the plotting of Δf *vs* $(\rho\eta)^{1/2}$ when a large concentration interval was used, which seems to support the well known conclusion that frequency of the PQC decreases linearly with increasing $(\rho\eta)^{1/2}$. Obviously, the fine structure of the plotting Δf *vs* $(\rho\eta)^{1/2}$ is in wave shape (see the small figures), which can not be explained by the theory of Kanazawa[4] and Bruckenstein[5]. It is worthy to note that the fine structure disappeared when a glass plane with glass balls was placed in detection cell (see cell B). This unexpected result is explained below.

For the detection cell in **Figure1A**, the LW emitted from the quartz disc was reflected back quartz disc surface by the cell wall. An interference takes place between the emitted and reflected LW on the surface of the quartz disc. Under the constant liquid conditions, an unaltered interference is expected as the distance between the quartz disc and the wall surface is physically fitted. It is well known that the speed of sound

Figure 2 Frequency shifts of the PQC in cells A (●) and B (○) to density and viscosity of sucrose solutions.

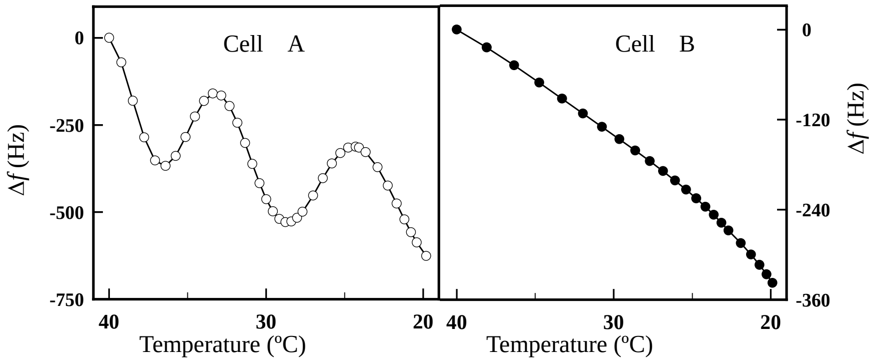


wave in the liquid phase increases with increasing liquid density. Hence, the propagation speed of the LW increases in solution of higher ρ value. As a result, the phase of the reflected LW onto quartz disc varies periodically with increasing liquid density. When the change in $(\rho\eta)^{1/2}$ values is very small, the frequency shifts are mainly due to LW effect and an oscillating curve of *Δf vs* $(\rho\eta)^{1/2}$ was observed. If a large $(\rho\eta)^{1/2}$ step was employed by using a large concentration interval, the frequency variation by the LW is small compared with the large frequency shift rising from the density and viscosity, the plotting of *Δf vs* $(\rho\eta)^{1/2}$ can be treated as a linear correlation.

In the cell design of **Figure 1B**, the LW emitted from the quartz disc was diffused by the small glass balls. The interference between the emitted and reflected LW was significantly weaken due to the differences in phases and directions among the small reflected longitudinal waves. Hence, the LW effect is undetectable in this type cell. The plots of *Δf vs* $(\rho\eta)^{1/2}$ were in good linearity even with small $(\rho\eta)^{1/2}$ interval.

In our opinion, the fine structure of the *Δf vs* $(\rho\eta)^{1/2}$ curve was helpful to understand the long-term stability of the PQC in liquid phase. Usually, temperature fluctuation is the main source for the signal drifts of PQC in a liquid phase. As shown in **Figure 3A,** the frequency temperature curve was in an inclined wave-shape too. The wave-shape frequency temperature curve is also due to LW effect. In the descending temperature process, the density and viscosity of water increase, the distance between the quartz disc and the reflected wall decreases slightly due to the thermal contractility of glass cell body. As a result, the phase of the reflected LW arrived at quartz disc variation periodically with decreasing temperature. Thus, the frequency-temperature curve was in the shape of an inclined wave. Accordingly, the frequency-temperature coefficients were in the range from –100 Hz/°C to 150 Hz/°C. The unexpected large frequency-temperature coefficients were responsible for the baseline draft of the PQC. On the other hand, the positions for near-to-zero temperature coefficient in the peaks and valleys in the frequency temperature curves are variational in each run.

Figure 3 Frequency shifts of PQC cells A (○) and B (●) in water during a temperature descending process



As can be seen in **Figure 3**, frequency of the PQC decreased monotonously in the declining temperature process when cell B was used. The frequency-temperature coefficient of the PQC sensor in water is about 17 Hz/°C in temperature region of 20~40°C, which is much smaller than the maximum in cell A. Hence, the long term stability of the PQC is greatly improved.

The results described above indicated that LW effect is also a potential error source in the perpendicularly placed PQC cell. The fine structure of the plotting of Δf *vs* $(\rho\eta)^{1/2}$ is not in the well-known linear relation if the LW effect occurs. The frequency of the PQC is sensitive to a slight variation in liquid density, such as temperature fluctuation or reagent addition. Hence, elimination LW effect is important in the detection cell design, although such consideration is ignored in most of references. The demonstrations are helpful to design PQC experiments to avoid contributions from the longitudinal wave.

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