A New Quartz Crystal Microbalance Measuring Method with Expansive Frequency Range and Broadband Adaptive Response Capacity

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Abstract: Quartz crystal microbalance (QCM) measuring instruments are suffering from the extremely high requirements for crystal cutting techniques and the incompleteness of measuring parameters. To solve these problems, we proposed a modified measuring method based on quadrature demodulation. This method showed broadband adaptive response, high frequency resolution, and capacity of continuously obtaining both resonance frequencies and dissipation factor (D). The results indicated that at room temperature, the frequency measuring adaptive response was 1–9 MHz while the frequency resolution was < 1 Hz. Moreover, along with the homogenous superimposition of poly acrylic acid (PAA) films at the working electrode, the crystal frequency drifts changed linearly within the measured range. Along with the volatilization of different solvents, the values of measured D were effective and continuous along the time axis. To sum up, this new method is superior over the traditional ones in terms of low material costs and high parameter richness.

Key Words: Quartz crystal microbalance; Broadband adaptive; Quadrature demodulation; Dissipation factor

1 Introduction

Modern analytical chemistry has set increasingly higher requirements for mass measurement precision. Quartz crystal microbalance (QCM) as a new-type resonant mass meter reaches a nanogram-level precision[1] and can be applied in both gas-phase[2] and liquid-phase[3] environments, thus receiving extensive attention from the academic field. To be specific, improved QCM with dissipation monitoring (QCM-D) could perceive the testing sample's conformational change via measuring resonance frequency drift Δf and dissipation factor D. Therefore, it was widely applied in chemistry, biology, medicine, environment, and other fields[4–9].

Despite years of technical development, QCM has not been ideally applied in many regions, especially the cost-sensitive developing countries. The main cause for such low applicability is that most available QCM products necessitate the use of quartz crystals with specific frequency and set high requirements for crystal cutting techniques, and thus raise material cost[10]. Another cause is that the film viscoelasticity in some liquid-phase environments and nonrigid films would largely interfere with the measuring system, so real-time D should be measured to indirectly reflect the viscoelasticity variations and to modify the frequency measurements[11]. However, measurement of D is very complex via traditional methods[8] and is unachievable by most commercial QCM products. Hence, the bottleneck problems in the technical development of QCMs are the effective reduction of material cost and precise measurement of factor D.

In this experiment, based on the quadrature demodulation principle, a measuring approach was designed with broadband adaptive response. This method was realized via both...
simulation and hardware circuit construction. The results show that this method can automatically match the cut-formed quartz crystals within certain frequency range (1–9 MHz) and thus lower the requirements for crystal cutting techniques. Moreover, it can precisely measure the crystal resonance frequencies and obtain the current-state D simultaneously, and thus improve the QCM measurement technique.

2 Measuring principle

2.1 Quartz crystal equivalent circuit model

The theoretical basis for QCM measurement is quartz crystal electrical circuit models, among which the Butterworth-van Dyke (BVD) model is generally applied, as shown in Fig.1a.[9] The followed Fig.1b shows the fitting curve of the equivalent impedance modulus |Z| of an 8 MHz quartz crystal via AT cutting. Theoretically, the variations of the physical properties on crystal surface could induce the drifts of resonance frequency points (series point f_s and parallel point f_p, as shown in Fig.1b)[9], which were generally expressed by the changes of the 4 equivalent parameters in the BVD model. In practice, the general working steps of QCM is as follows. Firstly, it records the frequency point drifts Δf of quartz crystals at both the initial state and the working state (Δf_s or Δf_p, mainly Δf_s); then, equations like Sauerbrey[10] or Kanazawa-Gordon[11] expressions are selected depending on the type of the testing material; finally, the relationships of Δf are quantified with deposit mass Δm or liquid viscosity η to finish the measurement.

2.2 Measuring method

The working principle of the quadrature demodulation is shown in Fig.2. In this way, the quartz crystal is regarded as a two-port network and stimulated by a cosine signal A\text{cos}(\omega t) with vibration amplitude A and angular frequency \omega. Because both the impedance and the phase of the QCM network will directly change with the variation of the excitation frequency \omega, the vibration amplitude and the phase of the followed output signal H(\omega t) will also vary from the excitation signal A\text{cos}(\omega t). To quantify the changes, we use P_s(\omega) to express the vibration amplitude ratio of output and input signals (0< P_s(\omega) < 1) and \phi(\omega) to express the phase shift (–\pi \leq \phi(\omega) \leq \pi), so H(\omega t) can be expressed as follows:

\[ H(\omega t) = P_s(\omega) \times A\text{cos}(\omega t - \phi(\omega)) \]  

Then, H(\omega t) is multiplied by two quadrature excitation signals, A\text{cos}(\omega t) and A\text{sin}(\omega t) respectively, and the product outputs are filtered by corresponding low-pass filters (LPF).

The LPFs can filter out the high-frequency components with angular frequency 2\omega, whose existence can be examined by applying the product-to-sum formula to the products. Therefore, the produced signals I(\omega) and Q(\omega) are validated to be irrelevant to the time variable t, as shown in Eqs. (2) and (3), respectively.

\[ I(\omega) = \text{LPF}[A\text{cos}(\omega t) \times H(\omega t)] = 0.5 \times A^2 P_s(\omega)\cos[\phi(\omega)] \]  
\[ Q(\omega) = \text{LPF}[A\text{sin}(\omega t) \times H(\omega t)] = 0.5 \times A^2 P_s(\omega)\sin[\phi(\omega)] \]  

Subsequently, signals I(\omega) and Q(\omega) are converted to digital signal by analog-to-digital converters (ADC), before processed by a micro-controller unit (MCU) in which the vibration amplitude ratio P_s(\omega) and phase \phi(\omega) at the specific excitation frequency \omega are synthesized as Eqs. (4) and (5).

\[ P_s(\omega) = 2(I(\omega)^2 + Q(\omega)^2)^{1/2}/A^2 \]  
\[ \phi(\omega) = \arctan(Q(\omega)/I(\omega)) \]
Based on the impedance modulus simulation result in Fig. 1, the measurements between vibration amplitude ratios and excitation frequencies in Fig. 3 show that, when the excitation frequency reaches the series resonance frequency $f_s$, the network impedance modulus $|Z|$ is minimized and the amplitude ratios $P_v(\omega)$ of the corresponding response signal is maximized; by contrast, when the excitation frequency reaches the parallel resonance frequency $f_p$, $|Z|$ is maximized and $P_v(\omega)$ of the corresponding response signal is minimized. According to these rules, the $P_v(\omega)$ curve can be determined via adjusting the frequencies of excitation signal and thereby, $f_s$ and $f_p$ can be obtained, then, $D$ can also be deduced if it is needed$^{[11]}$. However, the noise contained in the measured response signals makes precise measurement of the resonance frequency points difficult, so during actual data testing and processing, least squares fitting is used to improve the precision of positioning frequency points, which has made capture precision up to 0.1 Hz.

With the above smooth measurement process, the broadband adaptive response is realized as follows: (1) scan and test in a broad frequency range and preliminarily determine the resonance frequency; (2) shorten the scanning range, reduce the scanning step, and further determine the initial-state fundamental resonance frequency $f_{i0}$ precisely; (3) shorten the scanning range to a smaller range around $f_{i0}$ (usually within $10^4$ Hz), continuously scan frequency to detect the final changes of $f_s$, $f_p$ and $D$. Moreover, during the continuous testing, if the variation of resonance frequencies is out of range, the MCU can dynamically adjust the initial and terminal frequencies by controlling the feedback signal $F$, so the resonance frequency points is always within the scanning range.

3 Experimental

3.1 Instruments and reagents

The hardware connections of the self-made QCM measurement system with broadband adaptive response capacity are shown in Fig. 4, including a frequency generation controller, a frequency scanning signal generation module, a power amplifier module, an impedance matching module, a low-pass filtering and signal conditioning module, an analog-to-digital conversion and data transmission module, and a power management module. Specifically, the frequency generation controller and the data acquisition controller were based on ARM-Cortex M4 kernel embedded processor; the frequency scanning signal generation module was constructed on a direct digital synthesis (DDS, ADI); the frequency scanning range was 0–140 MHz, with the minimum frequency sweep step of 0.001 Hz; the sampling precision of analog-to-digital conversion was 16-bit, with two-channel synchronous sampling; and the final data were uploaded via USB to a personal computer (PC) for processing.

The data processing software in PC was programmed by LABVIEW, with major functions of data acquisition, digital filtering, peak position fitting, graphic display, data storage, and setting experimental parameters (e.g. frequency scanning range, frequency scanning speed, and analog-to-digital conversion parameters).
The quartz crystals (Beijing Chenjing Electronic Co., Ltd., China) adopted 1, 2, 3 and 4 MHz crystals (o.d. 14.00 mm, i.d. 8.30 mm, gold surface), and 5, 6, 7.99, 8, and 9 MHz crystals (o.d. 12.50 mm, i.d. 6.30 mm, gold surface).

The reagents included 0.5% and 0.25% poly acrylic acid (PAA)-ethanol solutions prepared from 25% PAA-ethanol (Sigma-Aldrich Co., Llc.), as well as a 0.25% PAA-ethanol water mixed solution prepared from 1:1 (V/V) ethanol (Sigma-Aldrich Co., Llc.).

3.2 Experimental methods

3.2.1 Crystal fundamental resonance frequency $f_{s0}$ test

A testing crystal was randomly selected and connected to the test system; a wide-range frequency scan was conducted at room temperature to preliminarily determine the resonance frequency; then the frequency scanning range was shortened to improve scanning precision and to determine final $f_{s0}$. Each crystal was initialized only once and all 8 types of crystals were measured in this way.

3.2.2 Crystal resonance frequency $f_s$ continuous test

The frequency was tested per 2 s at room temperature with a sensor of 7.99 MHz fundamental frequency. About 60 s later, 20 µL of 0.25% PAA-ethanol solution was sucked and dripped on surface of crystals, followed by observation of the resonance frequency $f_s$ variations. About 20 min later, once the ethanol was fully volatilized, the test was over and all measured data were processed for plotting.

3.2.3 Multicrystal resonance frequency shifts $\Delta f_s$ test

For a random crystal under test, after initialization of fundamental frequency, 4 µL of 0.5% PAA-ethanol solution was sucked and dripped on the full gold working electrode of this crystal. Then, the crystal should be placed at room temperature without distractions until the surface ethanol was completely volatilized (about 20 min). Next, dripping and measurements were conducted every 20 min and each crystal was tested 10 times before the next one. Finally, after all 8 types of crystals were measured in this way, all measured data were processed for plotting.

3.2.4 Dissipation factor $D$ test

After the adaptive initialization of the 7.99 MHz crystal sensor, 20 µL of 0.25% PAA-ethanol solution was sucked and dripped on the full gold working electrode of the crystal. The measurements were conducted every 1.5 s until 2500 sets of continual data were obtained; after that, the crystal was washed and dried; then 20 µL of 0.25% PAA-ethanol water mixed solution was sucked for repeated tests, and another 2500 sets of continual data were obtained; finally, the data were processed for plotting.

4 Results and discussion

4.1 Single crystal resonance frequency $f_s$

During the process in Section 3.2.2, the changing trend of the quartz crystal series resonance frequency $f_s$ is plotted in Fig.5a. The 30 sets of data measured in the first 60 s before dripping were stable, as $f_s$ fluctuated within (7988562.0 ± 1.0) Hz; upon dripping, $f_s$ drifted largely and declined to 7985768.1 Hz at 101 s, and in the following 10 min, $f_s$ fluctuated slightly but was relatively stable; and then, before ethanol was fully volatilized, $f_s$ largely drifted again and minimized to 7980104.7 Hz at 700 s; in the following 100 s, $f_s$ rebounded to 7983213.8 Hz and gradually increased at average speed of 0.2 Hz s$^{-1}$ until the end of the experiment.

4.2 $f_{s0}$ and correlation between film thickness superimposition and $\Delta f_s$

As shown in Fig.5b, the measurements of $f_{s0}$ of all crystals were consistent with the nominal values, indicating that this
approach was able to adaptively respond to quartz crystals within frequency of 1–9 MHz. Furthermore, along with the increased number of drippings, PAA film was thickening, and the resonance frequency drifts $\Delta f$ of all crystals changed linearly in the range, indicating that the quartz crystals work competently within this range. Therefore, this approach had very low requirements for material consumption and thus was conducive to reduce the material costing.

4.3 Testing results of dissipation factor $D$

As shown in Fig.6, both curves showed that once the reagents were dripped, $D$ increased sharply because of the effects of the liquid viscosity on crystals. Then, during the liquid volatilization, $D$ fluctuated in a certain range but generally decreased, because the effect of liquid viscosity was weakened. After the volatilization, as the effect of PAA thin film deposition on $D$ was slight, $D$ became a little bigger than that at original state and basically stable before the next dripping. Finally, comparing the two curves, the volatilizing speed with ethanol as a solvent was obviously higher than that with ethanol-water (1:1, $V/V$), as the data of Fig.6a were basically stable after 1500 s. Therefore, this phenomenon indicates that this approach can provide both frequency variations and continuous $D$ measurements, and the changing trend of $D$ is consistent with the experimental laws.

5 Conclusions

A new-type quartz crystal microbalance (QCM) testing method is proposed and validated by actual circuits and related experiments. The results show that by this method, the changes of resonance frequency and $D$ factor can be rapidly and continuously obtained, with deviation of frequency measurement smaller than 1 Hz. Moreover, this method can automatically match quartz crystals within frequency of 1–9 MHz, which meets the requirements for low-costing and high-sensitivity QCM analysis appropriately.

References