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Oscillating Frequency Response of a Langasite Crystal Microbalance in Liquid Phase

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Abstract: The frequency responses of a langasite crystal microbalance (LCM) in liquid phase were investigated. It was shown that the LCM possessed much stronger oscillating ability in liquid phase than that of the commonly used quartz crystal microbalance (QCM). The frequency shifts of the LCM to the changes in mass loading, as well as viscosity and density of the liquid were measured. The LCM was applied to monitor the adsorption process of an ionic liquid film to ethanol vapor.

Keywords: Piezoelectric sensor, langasite crystal, frequency response, ionic liquid.

Studies with the microbalance sensor became popular after the original works of Sauerbrey in 1959[1]. Near half a century was passed, piezoelectric quartz crystal is the absolutely predominating piezoelectric material in microbalance due to its excellent physical and chemical properties. Hence, a quartz crystal microbalance (QCM) is in fact the standard term for microbalance mass sensor. The QCM is well known for its high sensitivity to mass change on its surface. The QCM is a useful tool for solution chemistry and bioanalysis[2-6]. But the application of the QCM in a liquid phase is limited to low viscosity solution because it ceases oscillation in liquid of high viscosity.

Langasite ($La_3Ga_5SiO_{14}$) crystal is an excellent material for laser devices. It is also one of the perspective crystalline materials for various applications in acousto-electron and piezoelectric devices[7]. As a piezoelectric material, langasite has a higher electromechanical coupling coefficient and lower acoustic losses than those of quartz. Langasite does not undergo phase transformation up to the melting temperature of 1470 °C. Langasite resonator can be operated up to high temperature of 900 °C[8].

In this work, the oscillation characteristics of langasite resonator in liquid phases was investigated. The oscillating frequency responses of the langasite crystal microbalance (LCM) to the changes in surface mass, density and viscosity of liquid phase were reported. The LCM possesses a much better oscillating ability than QCM. The application of the LCM in heavy viscous loading of an ionic liquid film was demonstrated.

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Experimental

Langasite single crystals were grown up by using the Czochralski system in the State Key Laboratory of Crystal Materials in Shandong University. The resonator devices were prepared from polished langasite plates cut from a langasite crystal. The diameter of the Y-cut resonators was 18 mm. The thickness of the plates was 213 and 152 μm for the resonators with fundamental frequency of 6.3 and 8.8 MHz, respectively. Two "key-hole" shaped gold electrodes with a diameter of 8 mm were evaporated in center of the Y-cut langasite plates. The langasite crystal disc was fixed to a slant of a glass trapezoid detection cell with one side facing the liquid phase. The resonator was electrically driven to oscillate by a home-made oscillator circuit and its oscillating frequency was recorded by a universal frequency counter. Ionic liquid of 1-butyl-3-methylimidazolium chloride ($[BuMIm]^+[Cl]^-$) was synthesized in our lab.

Results and Discussion

In the measurements of frequency-mass coefficients of the LCM in liquid phases, the electrochemical deposition process of Ag from 10^{-3} mol.L^{-1} Ag^+ ammonia solution was monitored. The depositing mass was also determined from the electricity amount during the electrolysis by a coulometer. As can be seen in **Figure 1**, the frequency shifts (Δf) are in good linearity with the mass change ($\Delta m/A$), where A is the area of the electrode on the LCM. The frequency-mass coefficients are –57.9 and –112.6 Hz.μg.cm^{-2} for the LCM with fundamental frequency of 6.3 and 8.8 MHz, respectively. As a control, the frequency-mass coefficient of an AT-cut 9 MHz quartz crystal was measured in the same experimental conditions. According to the Sauerbrey equation, the mass sensitivity of LCM is about 2/3 of that of the QCM of the same fundamental frequency. The slightly lower sensitivity is due to the fact the density of langasite is 5.84 g.cm^{-3}, which is greater than the density of quartz of 2.63 g.cm^{-3}.

Figure 1 Dependence of frequency shifts of LCM on surface mass loading in electrochemical depositing Ag from 10^{-3} mol.L^{-1} Ag^+ ammonia solution.

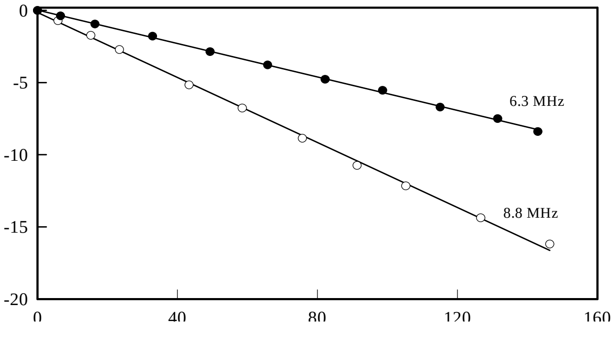
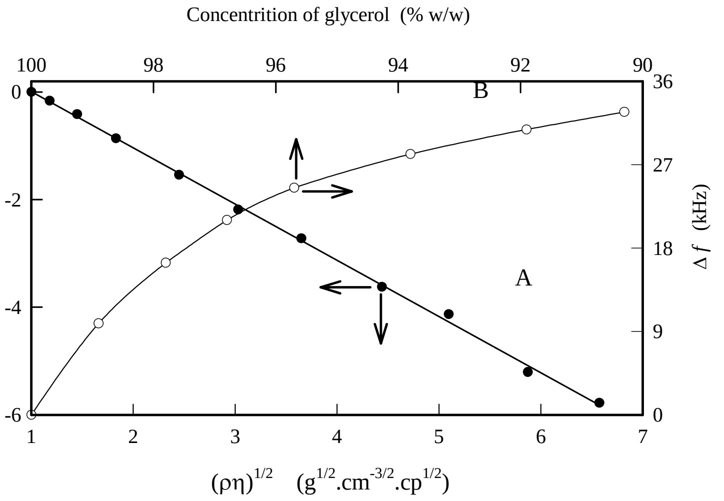


Figure 2 Dependence of frequency shift of LCM with fundamental frequency of 6.3 MHz on the viscosity and density of glycerol aqueous solutions.



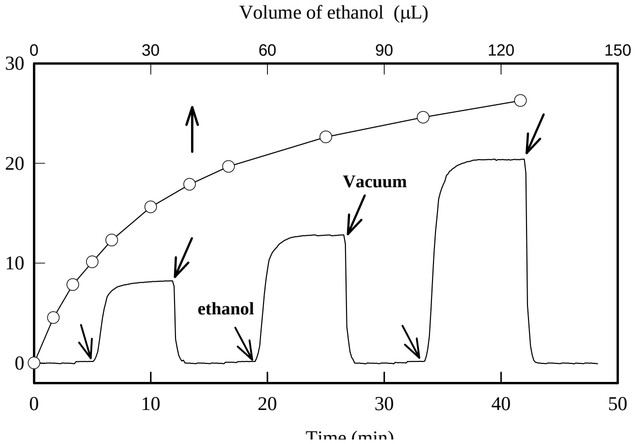
(A) with one face contact liquid, (B) two faces immersing in liquid.

Similar to QCM, the frequency of the LCM is also related to the density (ρ) and viscosity (η) of the liquid phase. As shown in **Figure 2**, the frequency shifts of LCM are in proportional to $(\rho\eta)^{1/2}$. As the fundamental frequency of the LCM increases, the influence of viscosity and density of the liquid increases.

It should be noted that the LCM exhibits an excellent oscillating ability in high viscosity liquid. For example, a QCM of 9 MHz ceases oscillation in contact with 70% glycerol solution. As shown in **Figure 2**, the LCM can oscillate stably even immersion in 100% glycerol with two faces contact with the liquid phase. Hence, the LCM possesses a much better oscillating ability than that of the QCM, especially in heavy viscosity liquids. This characteristic is helpful to apply the microbalance sensor in high viscous system.

As an example, an ionic liquid film of ($[BuMIm]^+[Cl]^-$) was prepared on the surface of LCM by spreading 1 μL 50% ethanol solution. The LCM was put into a closed glass box of volume of 2 L. The box was vacuum dried until a stable baseline was obtained. A certain amount of ethanol was brought into the box by dry nitrogen. As illustrated in **Figure 3**, the frequency of the LCM with ionic liquid modified increases when it was exposed to ethanol vapor. The frequency increases can be mainly ascribed to the lower of the viscosity of the ionic liquid during the adsorption process. The adsorption isotherm is in the Langmuir shape. When the box was vacuum dried again, the frequency of the LCM drops as the viscosity of the ionic liquid film increases.

Figure 3 Frequency responses of the 6.3 MHz LCM with ionic liquid modified film to ethanol vapor and the adsorption isotherms.



The results described above indicated that LCM is a promising piezoelectric sensor. Despite a slightly lower mass sensitivity to surface mass change than the QCM, the oscillation ability and frequency stability of the LCM are much better than that of the QCM, especially in heavy viscous liquids. The applications of the LCM depend greatly on the commercialization of langasite resonators and the development to the related theoretical and experimental methods.

Acknowledgments

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