UNIVERSITI PUTRA MALAYSIA

RESONANCE FREQUENCY RESPONSE OF QUARTZ CRYSTAL MICROBALANCE WITH DIFFERENT METAL ELECTRODES IN SACCHARIDE SOLUTIONS

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By

SITI SALMIWATI BINTI ABDUL AZIZ

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
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July 2008

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

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July 2008

Chairman : Associate Professor Zainal Abidin Talib, PhD

Faculty : Science

This project investigated the resonance frequency response of Quartz Crystal Microbalance (QCM) with different metal electrodes in different type of liquids. The study investigates the relationship of the density and viscosity of the solutions as a function of the resonance frequency shift (ΔF_w) of the QCMs. The technique used was based on the principle of electromechanical coupling of piezoelectric Quartz Crystal Microbalance.

In this study, QCMs of 10 MHz fundamental frequency with chromium, molybdenum, tungsten and gold electrodes were used to measure their ΔF_w in saccharide solutions. The quartz crystal was clamped between two O-rings in a liquid flow cell. Only one side of the crystal was exposed to the solutions which flow through it propelled by a micro-tube pump. A total of six different saccharide solutions were chosen. The saccharide samples (glucose, fructose, mannose, sucrose, maltose and lactose) were prepared as

solutions with different concentrations. All the measurements were carried out at room temperature, 26.5 ± 0.5 °C.

The research demonstrates that the interaction of the vibrating quartz crystal with the liquid medium is expressed by a decrease in the resonance frequency, which is proportional to the product of the square root of the solution viscosity and density. The increase in the viscosity of the liquid also causes the vibrating mass to increase on the quartz crystal surface, and this make resonance frequency decreases. The aim of the study was to achieve an understanding of the information provided by measuring the shifts in the resonance frequency of the QCM with different metal electrodes (Cr, Mo, W, and Au) in saccharide solutions.

Resonance frequency shift (ΔF_w) of the QCM with gold electrodes was found more responsive compared to chromium, molybdenum and tungsten electrodes in saccharide solutions. The determination of parameter *K*, the coefficient of the equation that governs the relationship between ΔF_w , viscosity and density is one of the major objectives of the project. It was found that value *K* changes with different saccharide solutions in the range of 0.647×10^4-3.234×10^4 $cm^2\ g^{-1}\ s^{-1/2}$.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

RESPON FREKUENSI RESONAN PENIMBANG MIKRO HABLUR KUARTZA DENGAN BERLAINAN ELEKTROD LOGAM DALAM LARUTAN SAKARIDA

Oleh

SITI SALMIWATI BINTI ABDUL AZIZ

Julai 2008

Pengerusi : Profesor Madya Zainal Abidin Talib, PhD

Fakulti : Sains

Projek ini mengkaji respon frekuensi resonan Penimbang Mikro Hablur Kuartza dengan berlainan elektrod logam ke atas pelbagai jenis cecair. Kajian ini mengkaji hubungan antara ketumpatan dan kelikatan suatu larutan cecair sebagai fungsi kepada perubahan frekuensi (ΔF_w) resonan bagi Penimbang Mikro Hablur Kuartza. Teknik yang digunakan berasaskan kepada prinsip hubungan elektromekanik bagi piezoelektrik Penimbang Mikro Hablur Kuartza.

Dalam kajian ini, Penimbang Mikro Hablur Kuartza berfrekuensi asas 10 MHz dengan elektrod logam seperti kromium, molibdenum, tungsten dan emas digunakan untuk mengukur ΔF_w dalam larutan sakarida. Hablur kuartza ini diapitkan dengan dua cecincin dalam tiub sel cecair. Hanya satu permukaan hablur yang dialirkan larutan cecair dipamkan melalui tiub pam mikro. Sejumlah enam larutan sakarida yang berlainan dipilih. Bahan sakarida (glukosa, fruktosa, manosa, sukrosa, maltosa dan laktosa)

disediakan sebagai larutan cecair dengan kepekatan yang berlainan. Semua pengukuran dilakukan pada suhu bilik, 26.5 ± 0.5 °C.

Kajian ini menunjukkan bahawa interaksi getaran hablur kuartza dengan medium kelikatan dapat dinyatakan oleh penurunan frekuensi yang mana adalah berkadar terus dengan punca kuasa dua produk bagi kepekatan dan kelikatan larutan. Peningkatan dalam kelikatan bagi suatu cecair menyebabkan peningkatan getaran jisim ke atas permukaan hablur kuartza dan meningkatkan frekuensi resonan. Kajian ini bertujuan untuk mencapai dan memahami dalam meningkatkan maklumat tentang pengukuran perubahan dalam frekuensi resonan bagi Penimbang Mikro Hablur Kuartza dengan berlainan elektrod logam (kromium, molibdenum, tungsten dan emas) dalam larutan sakarida.

Perubahan frekuensi (ΔF_w) resonan bagi Penimbang Mikro Hablur Kuartza dengan elektrod logam emas menunjukkan respon yang lebih baik berbanding elektrod logam kromium, molibdenum dan tungsten. Penentuan parameter *K* adalah nilai permulaan bagi persamaan yang merangkumi hubungan antara ΔF_w, kelikatan dan ketumpatan adalah objektif utama di dalam projek ini. Kajian menunjukkan bahawa nilai *K* berubah dengan perbezaan larutan sakarida dengan julat antara 0.647×10^4-3.234×10^4 $cm^2\ g^{-1}\ s^{-1/2}$.

DEDICATIONS

For my lovely husband and daughter;
Jumain Bin Arifin
Fatin Najwa Binti Jumain

For my dearest family and siblings;
Abdul Aziz Bin Abdul Razak
Zainun Binti Abdul Hamid

For my supervisor, co-supervisor and friends,

Thank you for their understanding, supporting and encouragement.

-MIE 2008-

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I certify that an Examination Committee met on 4th July 2008 to conduct the final examination of Siti Salmiwati Binti Abdul Aziz on her Master of Science thesis entitle "Resonance Frequency Response of Quartz Crystal Microbalance with Different Metal Electrodes in Saccharide Solutions" in accordance with Universiti Pertanian Malaysia (Hinger Degree) Act 1980 and Universiti Pertanian Malaysia (Hinger Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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Date: 26 August 2008

This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of requirements for the degree of Master of Science. The members of the Supervisory Committee are as follows:

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Date: 11 September 2008

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any degree at UPM or other institutions.

SITI SALMIWATI ABDUL AZIZ

Date: 21 July 2008

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS/NOTATION/GLOSARRY OF TERM

C_f	Sensitivity factor; Hz cm^2 μg^{-1}
D	Dissipation factor
ΔF	Frequency shift; Hz
Δm	The change in mass; g
f_o	Resonance frequency; Hz
F_b	The basic oscillation of quartz; 10 MHz
k_1	Propagation constants, $k = 2\pi/\lambda$; cm^{-1}
L	Thickness of the layer
m	Mass; g
mf	Foreign material mass
mq	Mass of the crystal
n	Number of harmonic (e.g., n = 1 for the fundamental or first harmonic frequency, n = 2 for the second harmonic, and n = 3 for the third harmonic, etc)
R_q	Resistance; Ω
t	Time; s
t_o	Flow time of the solution/solvent; s
v	Volume; cm^{-3}
wt %	Weight percent
z	Function of distance
$\in$	Dielectric constants
κ	Specific conductance

μ_q	Shear modulus of quartz, $\mu_q = 2.947 \times 10^{10}$ N m^{-2}
η	Dynamic viscosity of the Solution; g cm^{-1} s^{-1} or P
η_o	Dynamic viscosity of the Solvent; g cm^{-1} s^{-1} or P
η_w	Dynamic viscosity of the water, $\eta_w = 0.894 \times 10^{-2}$ g cm^{-1} s^{-1} or P
v_o	Velocity of the surface; m s^{-1}
ρ	Density of the solution; g cm^{-3}
ρ_q	Density of quartz, $\rho_q = 2.648$ g cm^{-3}
ρ_w	Density of water, $\rho_w = 0.997$ g cm^{-3}
Au	Gold
Cr	Chromium
Mo	Molybdenum
W	Tungsten
CMC	Critical Micellar Concentration
CTMAB	Centyltrimetylammonium Bromide
ESPS	Electrode-Separated Piezoelectric Sensor
EQCM	Electrochemical Quartz Crystal Microbalance
GPIB	General Purpose Interface Bus
LAL	Limulus Amebocyte Lysate
PQC	Piezoelectric Quartz Crystal
QCM	Quartz Crystal Microbalance
REPS	Ringed-Electrode Piezoelectric Sensor

CHAPTER 1

INTRODUCTION

The development and construction of new chemical sensors, which are specific for particular chemical species, is an active area of research. Many methods have been newly applied to the study of electrochemical interfaces. One of these methods is based on Quartz Crystal Microbalance (QCM) technology. The increased interest in using microbalance has resulted, in part, from the rapid progress in scientific instrumentation. Today, highly sophisticated automatic, microprocessor-controlled devices are available commercially and satisfy most requirements of scientific and technological investigators. Parallel progress in vacuum science and technology has provided a mean of controlling the environment required for many experiments using the QCM (Lu and Czanderna, 1984).

1.1 Quartz Crystal Microbalance (QCM) Characteristics

The QCM earns its name from its ability to measure the mass of thin films that have adhered to its surface. The QCM comprises a thin disk of AT-cut quartz crystal sandwiched between two metal electrodes that established an alternating electric field across the crystal, causing vibration motion of the crystal at its resonance frequency. This resonance frequency is sensitive to mass changes (and other factors) of the crystal and its electrodes (Buttry and Ward, 1992). Quartz is still the most important single crystal serving as transduction element in piezoelectric sensors. Its chemical formula is SiO_2, and it is found in several modifications, constituted of oxygen tetrahedrons with silicon at the center position (Gautschi, 2002).

The schematic of a typical quartz crystal microbalance is shown in Figure 1.1. The metal is deposited on both sides of the quartz plate. The electrical connection is made to the electrode flag by means of a spring clip with attached lead or wire holder. The circular metal electrodes in the crystal center oppose an identical electrode on the other side of the crystal. Electrical connection to the opposing electrode is made to the electrode flag. The crystal and its electrodes are incorporated into a positive-feedback oscillator circuit. The crystal diameter plays an important role in stability. The crystal is generally of 0.538 inches in diameter and electrode diameter is 0.201 inches, although crystals one inch or larger are available. The electrodes finish were polished and not etched. Etched electrode surface can have surface features that are not small as compared with the penetration depth of the acoustic waves in the fluid (O'Sullivan and Guilbuilt, 1999).

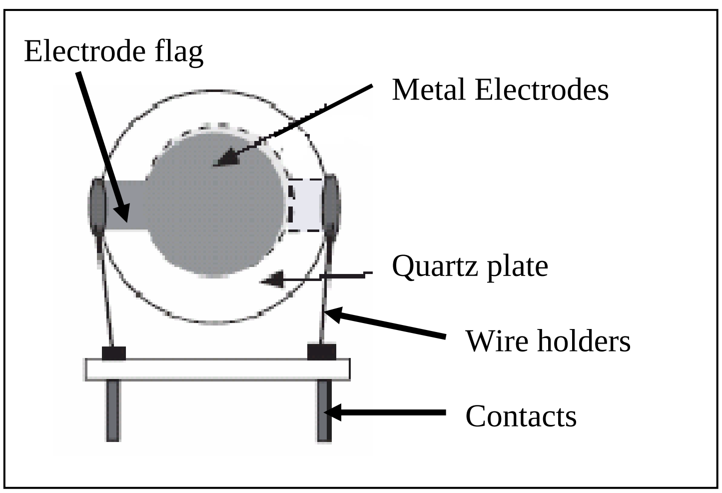

Figure 1.1: Quartz Crystal Microbalance (QCM) (O'Sullivan and Guilbuilt, 1999)

QCM system is typically constructed from piezoelectric materials (quartz in this application) that are incorporated into an oscillation circuit. When a current is applied to the piezoelectric material, the material expands or contracts depending on the magnitude and sign of the electric current. Application of an oscillating current will subsequently result in a mechanical oscillation of the quartz crystal (O’Sullivan and Guilbuilt, 1999).

1.2 Applications of Quartz Crystal Microbalance in Electrochemistry

The QCM is basically a mass sensing device with the ability to measure very small mass changes on a quartz crystal resonator in real-time. The sensitivity of the QCM is approximately 100 times higher than an electronic fine balance with a sensitivity of 0.1 mg. This means that QCM’s are capable of measuring mass changes as small as fraction of a monolayer or single layer atoms. The high sensitivity and real-time monitoring of mass changes on the sensor crystal make QCM a very attractive technique for a large range of applications as a sensor. In research environments, the most common QCM crystal applications include metal deposition monitors, chemical reaction monitors, biomedical sensors, and environmental monitoring applications, etc. Other applications include detection of mass, density, viscosity, adsorption, desorption, and corrosion.

Early applications of quartz crystal microbalance involved the well-documented measurement of metal deposition in high-vacuum metal evaporators, which is still widely practiced. This allow for real-time, rapid measurement of film thicknesses with Angstrom resolution. Recent advances in quartz crystal microbalance methodology in the last decade now allow for dynamic measurements of minute mass changes at surfaces, thin films and electrode interfaces prepared on the quartz crystal, while the surface is immersed in liquid. In fact, operation in liquids is possible, and the response of the QCM is extremely sensitive to mass changes at the solid-solution interfaces. The capability for direct, real-time, highly sensitive mass measurement in liquid phase have led investigators in electrochemistry research to embraced the quartz crystal microbalance as a useful tool, since the crystal metal surface can also serve simultaneously as an electrode.

In most electrochemical experiments, the quartz wafer with its attached electrodes is clamped between two O-rings. Only one side of the wafer and one electrode, which serve both parts of the QCM oscillator circuit and as the working electrode in the electrochemical cell, are in contact with solution. This combine device often is referred to as the electrochemical QCM (EQCM) (Deakin and Buttry, 1989).

The EQCM method can be used to study interfacial processes at the electrode surface which occur to during or after the fundamental electron-transfer events. The low cost and conceptual simplicity of this method signify its development in a diverse variety of commercial and research applications. The piezoelectric property of quartz is utilized to record a frequency change that may be related to a mass change. The method has propagated rapidly, and is now used in many laboratories as a routine tool which is complementary to others normally used by electrochemist. In this respect, the method is reaching maturity fairly rapidly. On the other hand, many of the details of its responses to various situations have yet to be studied carefully. There are such as the influence of