

A Mass/Heat Flow Sensor Combining Shear Mode Resonators with Thermoelectrics: Principles and Applications.

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Abstract -We describe a new way to monitor chemical and biological processes occurring in thin films interacting with gases and liquids, using a mass/heat flow sensor. The thin films may be metals, polymers, paints or coatings, chemical samples, proteins, catalysts, or monolayers. Changes in mass and in coating stiffness as well as heat generated by chemical or biological process *on or in* the film are measured with high sensitivity. We call the technique “Quartz/Crystal Microbalance/ Heat Conduction Calorimetry” (QCM/HCC).

INTRODUCTION

Many chemical processes occur in a thin solid film exposed to a fluid (gas or liquid) when components of the fluid either adsorb or react on the surface or dissolve in the film. In this paper we present the principles and a few applications of quartz crystal microbalance/heat conduction calorimetry (QCM/HCC), a new technique that measures mass changes, heat flows, and viscoelastic damping in the thin film [1, 2]. The mass measurement sensor is a 5 MHz transverse shear mode resonator, or quartz crystal microbalance (QCM). The QCM is thermally coupled to a heat sink through a Peltier thermopile used as a heat flow sensor. The combined sensor is placed in an adiabatic thermal environment for stability.

In the first generation of quartz crystal microbalance/heat conduction calorimetry (QCM/HCC) developed at Drexel University[3], a QCM is coated with a thin (0.1-10 μm) sample and exposed to a slow flow of (probe gas)/N₂ mixture at ambient pressure. Three quantities are measured simultaneously: (a) the mass change $m(t)$ (to $\pm 2 \text{ ng/cm}^2$), (b) the thermal power $P(t)$ (to $\pm 50 \text{ nW}$), and (c) the change in motional resistance $R(t)$ when the sample film takes up, releases, or reacts with the probe gas. Data reduction yields the sorption enthalpy, the sorption isotherm, and changes in loss compliance for the fluid/film combination, as well as rates of sorption or reaction. Sensitivities are suitable for detection of single layers of molecules.

EXPERIMENTAL

The mass/heat flow sensor and its associated sample chamber for the Drexel QCM/HCC are shown in Fig. 1. A photograph

of the new mass/heat flow sensor for the Masscal¹ apparatus is shown in Fig. 2. The sample film is applied to the top of the QCM. When the probe gas is absorbed in the film, the mass increase is monitored with the QCM. The corresponding heat of absorption flows from the film through the QCM to the thermopile, where it is detected as a DV voltage (*vide infra*).

For the mass and loss compliance measurements, a 2.54 cm diameter 5 MHz QCM from Maxtek (Santa Fe Springs, CA) is driven with a Maxtek PLO-10 phase locked oscillator [4]. Films less than 10 μm thick are prepared by spin-coating, spray-coating, or electrochemical deposition. The thin-film limit of transverse shear mode oscillators is assumed, and checked with measurements at various film thicknesses. In this limit, the Sauerbrey equation [5] is used to calculate mass change per unit surface area $\Delta m/A$ from the frequency shift Δf :

$$\Delta f = -\{2f_0^2 / (\mu_q \rho_q)^{1/2}\} \Delta m/A \quad (1)$$

where μ_q and ρ_q are the shear modulus and density of quartz and f_0 is the resonance frequency of the bare resonator. In the thin film limit it can also be shown that measuring the motional resistance of the bare resonator, R_{mQ} , and of the film-coated resonator, R_{mQf} can yield the film's loss compliance J'' through the relationship

$$R_{mQf} - R_{mQ} \propto h_f^3 \rho_f^2 J'', \quad (2)$$

where h_f = film thickness and ρ_f = film density. Here $J'' = G'' / (G'^2 + G''^2)$, where G' and G'' are the shear storage modulus and shear loss modulus, measured at f_0 .

For the heat flow measurements, commercial thermoelectric cooling plates based on the Peltier effect are used as heat flow detectors. The TCP's in the Drexel apparatus are from Melcor (Trenton, NJ). In heat conduction calorimetry [6, 7], the relationship between thermal power or heat flow, dQ/dt , and TCP output voltage U is given by the Tian equation,

¹ Masscal Corporation, Chatham, MA 02669. Masscal was formed to commercialize the QCM/HCC. See www.masscal.com

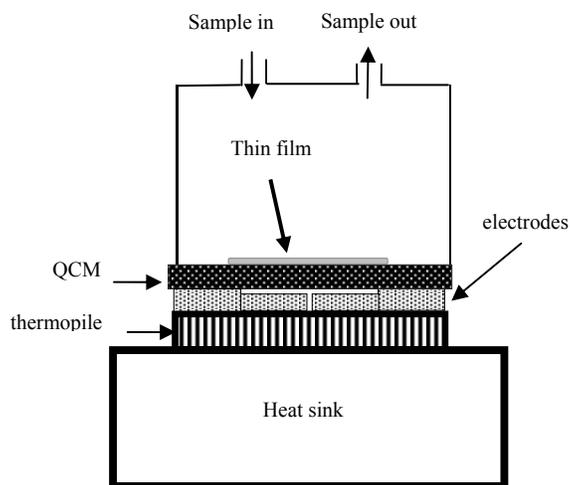


Fig. 1. The mass/heat flow sensor and its accompanying sample chamber.



Fig. 2. A photo of the mass/heat flow sensor assembly in the Masscal QCM/HCC

$$dQ/dt = \epsilon[U + \tau dU/dt] \quad (3)$$

where U is the thermopile voltage, τ is the calorimeter time constant (~ 50 s in the Drexel apparatus), and ϵ is an experimentally determined calibration constant.

A two-component gas flow comprising mass flow controllers produces the input gas stream [3]. The carrier gas is N_2 , and for water or organic solvents a second N_2 stream is passed through a bubbler to produce saturated vapor. The two streams are combined in different amounts to enable variable partial pressures of the volatile component to be introduced to the sample chamber under computer control. In a typical experiment, a period of constant vapor activity is followed by a step to a new vapor activity. Equilibration times of 100–3000 s are common.

One polymer extensively studied in our laboratory is a cyclic aliphatic polyetherurethane with the trade name Tecoflex [8]. This polymer was shown to have attractive gas sorption characteristics in QCM sensor studies[9]. Fig. 3 shows the mass uptake in a $8.5 \mu\text{m}$ film of Tecoflex exposed to water vapor at 25.00°C in five steps of relative humidity from 0 to 80%. Each step lasted 150 s, so a complete cycle lasted 1500 s. Fig. 4 shows four complete cycles of the corresponding thermal power signals for the same experiment. Note that each step in increasing relative humidity give a mass increase in the film and a corresponding exothermic thermal power pulse, whereas on a decrease in humidity the thermal power pulse is endothermic. Time integration of the thermal power trace give the heat changes ΔQ for each step change in water vapor activity, and the corresponding changes in film mass give the change Δn in the number of moles of water absorbed or released; their ratio is the molar enthalpy of sorption $\Delta_{\text{sorption}}H$ of water vapor in the polymer film. An extensive set of measurements of this quantity gives values for $\Delta_{\text{sorption}}H$ for water in Tecoflex of -44 ± 5 kJ/mol, comparable to the heat released when one mole of water vapor condenses to the liquid state.

To test the sensitivity of the QCM/HCC, we measured the energetics of formation of a single self-assembled monolayer of butanethiol on a gold surface [3, 10]. The experimental strategy was to expose a clean gold surface (the top electrode of the QCM) to butanethiol, injected into the sample chamber using a gas syringe pump. The mass change (Fig. 5), thermal power (Fig. 6), and motional resistance signal (Fig. 7) were monitored as the thiol group bound to the gold surface to form a self-assembled monolayer. The butanethiol was introduced at ~ 6300 s, and all three signal channels show significant responses well above the noise level. The change in mass from Fig. 5 is $0.084 \mu\text{g}$, within 15% of that calculated for the formation of a single self-assembled layer of butanethiol on gold. The measured enthalpy of formation of the self-assembled monolayer is -180 ± 40 kJ/mol. The motional resistance increase due to the formation of the monolayer is $1.0 \pm 0.2 \Omega$.

The sorption of water by pharmaceutical film coating materials has also been studied[11]. The purpose of this study was to quantify water sorption by thin films used as tablet coating materials, in order better to predict the shelf life and durability of film coats. The coatings on pharmaceutical tablets must dissolve in water in order to release the drug, but they must also resist high humidity at elevated temperatures in order to retain mechanical integrity during their shelf life. Generic film coat materials such as cellulose acetate butyrate and ethyl cellulose with varying amounts of triethyl citrate plasticizer were coated on a QCM and subjected to varying relative humidities both at 25°C and 40°C , and mass change, heat absorption, and motional resistance changes were

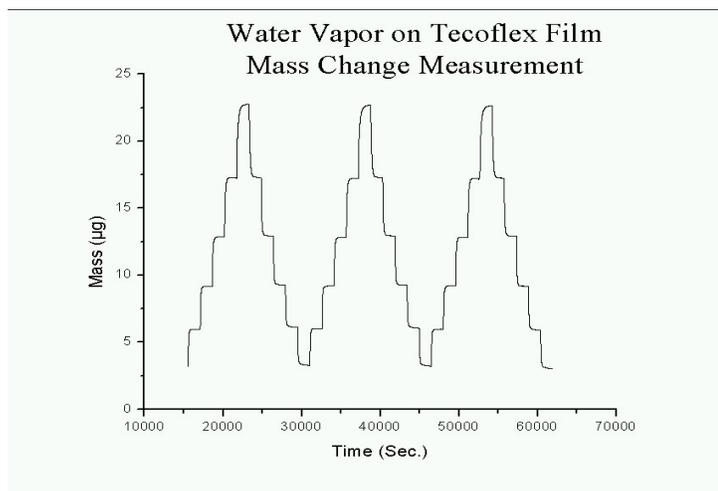


Fig. 3. Water vapor uptake in 8.5 μm film of Tecoflex. Water vapor activity is varied in 5 steps between 0.0 and 0.80.

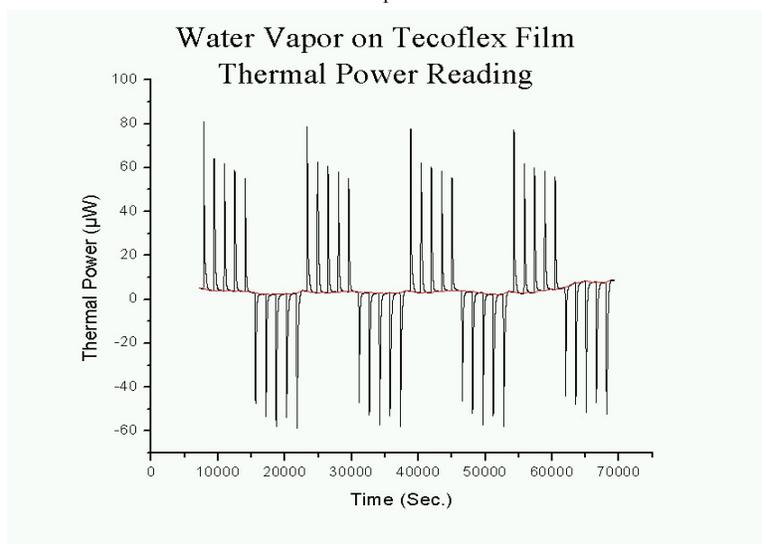


Fig. 4. Thermal power signal corresponding to the mass signal in Fig. 3

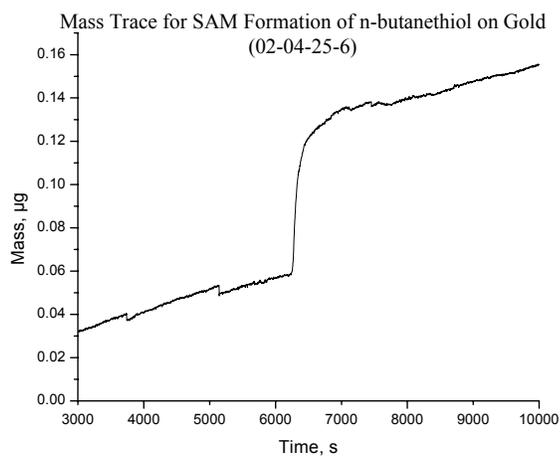


Fig. 5. Butanethiol vapor introduced to a bare gold surface on the QCM at 6300 s: mass signal.

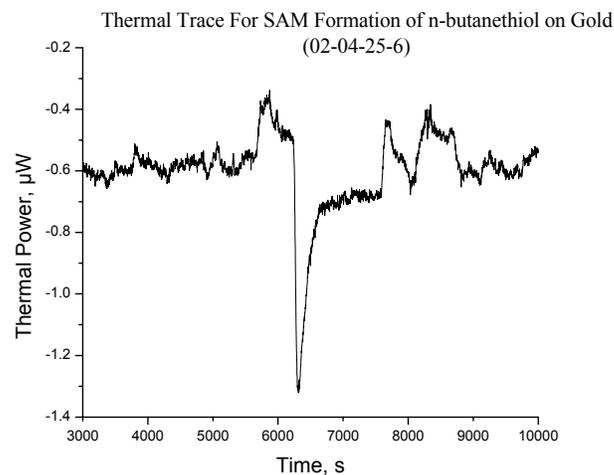


Fig. 6. Thermal power trace in butanethiol experiment of Fig. 5. Note the exothermic signal at 6300 s corresponding to the bonding of the thiol to the gold surface.

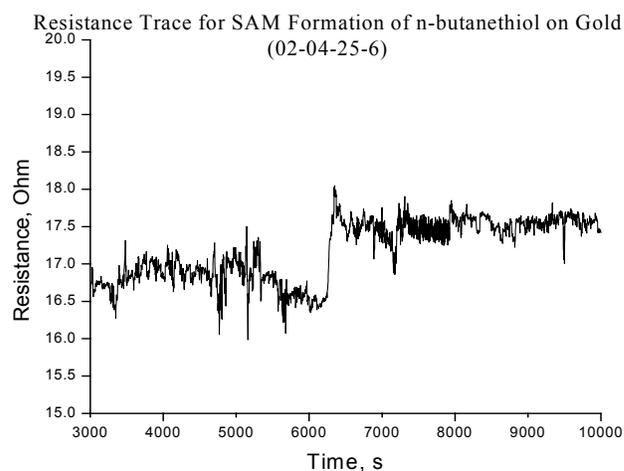


Fig. 7. Motional resistance signal for the experiment shown in Figs 5 and 6.

measured. It has been possible to determine water sorption isotherms and sorption enthalpies in films as thin as 3 μm by this technique. The absorption of water vapor significantly softens the film coat (i.e., increases its compliance).

In the past few years other applications of the QCM/HCC in our laboratory have included:

- thermodynamics and dynamics of hydrogen storage in thin palladium films[3];
- rates and energetics of surface-catalyzed reactions (hydrogenation of ethylene on palladium)[3];
- thermodynamics and dynamics of the interaction of water with thin protein films – useful in understanding protein folding and stability of pharmaceutical protein formulations[12, 13].

Potential chemical applications include

- a sensor for monitoring the drying and curing of paints, coatings, and finishes;
- characterizing the thermodynamic stability of nanoscale structures important in nanotechnology;
- evaluating the sorption properties of highly porous materials;
- monitoring heterogeneous reaction rates and surface poisoning of heterogeneous catalysts.

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