



# Increasing QCM sensitivity based on high molecular weight porous polymer films



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## ABSTRACT

High molecular weight porous poly(methyl methacrylate) (PMMA) films sensitive to water vapor were produced on a QCM crystal by first dip coating the quartz crystal into polymer solutions containing both PMMA and poly(ethylene oxide) (PEO). After drying, these films were leached with water to remove the PEO which created porous PMMA films. The most sensitive film to water vapor contained both high molecular weight PMMA and PEO as film components. Porous PMMA films made from high molecular weights of both components comprising PMMA/PEO blended polymers had higher water vapor sensitivities. The molecular weight of the PMMA in a nonporous film only had a small effect on its water vapor sensitivity. The approach used in this research is a general and can be used to increase the sensitivity of gas sensors in which the polymer that is leached by water (or other solvent) contains a functional group sensitive to a targeted volatile species.

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## 1. Introduction

In general, the analytical sensitivity of a QCM technique depends upon two factors – the resonant frequency of the AT-cut crystal that is responding to the analyte and the effective surface area on the crystal that is available for a sensing the analyte [1,2]. One way to increase the analytical sensitivity of a QCM based technique is to use a QCM crystal that has a high resonant frequency [3]. A second approach is illustrated by using aluminium metal whose surface responds to water vapor. In this example aluminium was deposited on the AT-cut quartz crystal and the aluminium film was “electro-drilled” to form a large number of empty shafts whose internal surface area detected water vapor [4]. Here we describe an extension of this concept that uses an aqueous chemical approach to form porous structures that are attached to the surface of the QCM crystal and whose pores sense the target analyte. It is based on a conventional AT-cut quartz crystal quartz crystal upon which we form a porous film that provides both a large internal and external pores that sense the target analyte. In such porous films, both the analytically sensitive surface and interior regions contribute to the frequency change.

Here, we describe a method that is a variation of one we used earlier that was based on a non-aqueous approach [5]. We showed

that water vapor sensitive porous PMMA polymer films could be created by removing one of the components in a blended polymer film consisting of PMMA [6] and poly(D, L-lactide) (PDLL). Then the PDLL was removed from the blended polymer by hydrolysis using aqueous nitric acid. This approach produced porous PMMA films that gave a sensitive, novel way to determine water vapor in a gas phase.

Here we use aqueous chemistry to create water vapor sensitive PMMA porous structures. These are created by removing PEO from a film that initially contained a blended polymer of PMMA and PEO [7]. The PEO was removed by leaching the blended polymer film with water, leaving behind the porous PMMA structures that were sensitive to water vapor.

We note that the magnitude of the steady state frequency response of films with porous interior and exterior structures are independent of the film's geometry. Below we report the analytical water vapor responses of porous PMMA films produced by varying the molecular weights of both PMMA and PEO films.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Chemicals and solutions

All chemicals were obtained from the Aldrich Chemical Co. Inc., and were used as received. PMMA with molecular weights of ~120,000 and ~996,000 and PEO with molecular weights of ~35,000, ~400,000 and ~2,000,000 were used. PEO polymer solu-

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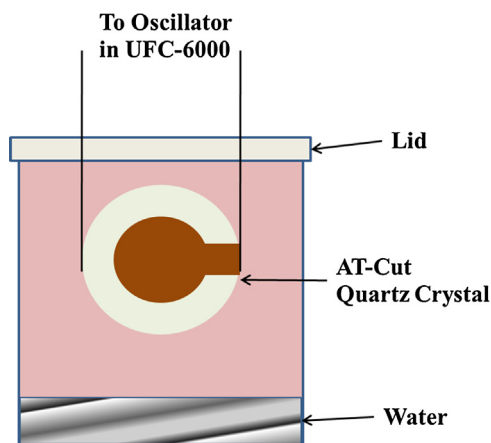


Fig. 1. QCM Cell Used for Water Vapor Experiments.

tions were made by dissolving PEO in methylene chloride and acetone (1:1 volume ratio) mixture. PMMA solutions were made by dissolving PMMA in acetone. PMMA:PEO solutions contained 1:1 mixture of 0.04 g of polymers per 2 ml of solvent. This solution was then diluted as needed with acetone to produce final solutions in which the QCM crystal was dipped. Films of varying thickness were prepared by diluting initial dipping solutions that had the desired film thickness. An ultrasonic bath (Fisher scientific CPN-952-518) was used to dissolve the polymers overnight.

## 2.2. Apparatus

10 MHz AT-cut quartz crystals were purchased from Jameco Electronics (part number 14381). The crystals were mounted on a 49/U base inside a sealed electrostatic shield. This shield was cut from the base, the crystals were washed twice with acetone, and then allowed to dry in air until their resonant frequency was constant ( $\pm 1$  Hz) before use.

Experiments involving liquids (3 ml) were carried out using a (11 cm<sup>3</sup>) plastic jar (Loew Cornell #1021078) (See Fig. 1). Film coated QCM crystals were suspended in the space above the aqueous solution in the jar. For the drying process, silica gel was used in the same size plastic jar. Contact wires on the crystal were used to position the crystal.

QCM resonant frequency measurements were made using the Model# UFC-6000 EQCM/QCM apparatus from Stanley Bruckenstein Chemical Consulting and Services, LLC. It uses an AT-cut resonant frequency oscillator that is controlled by a 10 MHz AT-cut quartz crystal. The latter crystal is the one used in QCM experiments. The device uses a digital countdown circuitry based upon a 20 MHz crystal oscillator that provides the necessary information for data sampling. The QCM data were recorded at one second intervals using software provided with the Model# UFC-6000. Experiments were carried out at ambient temperature.

## 2.3. Procedure

### 2.3.1. Dip coating films on QCM crystals

QCM crystals were dip coated in solutions containing the desired constituents in the film. The dip coating process consisted of dipping the QCM crystal vertically into the solution, leaving it there for three seconds, then removing it vertically into air and finally drying the film in a desiccator with silica gel to form the Blended Polymer Film (BPF). Its mass was determined from the resonant frequency of the dried film that was coated on the QCM crystal using the Sauerbrey equation which relates quartz crystal resonant frequency to the masses attach to the surface of the crystal (Sauerbrey, [1]).

### 2.3.2. Removing PEO from PMMA/PEO blended polymer films to produce porous PMMA films

PEO was removed (leached) from PMMA/PEO films coated on the QCM crystal by dipping the crystals into water for 1 h. The film coated QCM crystals were then dried in a desiccator containing silica-gel. The crystal's resonant frequency was then measured. This procedure was repeated until the crystal's resonant frequency became constant to within a few Hz, which signalled the total removal of PEO from the film and thus leaving behind a porous PMMA film.

## 2.4. Measurement of water vapor sensitivity

We define the QCM's water vapor sensitivity as the slope of a plot of the water vapor resonant frequency of the QCM crystal in the gas phase vs. the resonant frequency of the leached polymer film that detects the water vapor. Difference frequencies were calculated from difference of individual resonant frequencies. The slope is dimensionless.

Pure PMMA, pure PEO and porous PMMA films were studied. Film-coated QCM crystal measurements of water sensitivity were made using the arrangement of the coated QCM crystal in the jar containing water shown in Fig. 1. Water vapor equilibrium between the film and gas phase were assumed when the QCM crystal resonant frequency became constant to within  $\pm 15$  Hz. All experimental data were fitted as straight lines whose least square's parameters are shown in all figures.

## 3. Results and discussion

### 3.1. Effect of PEO molecular weight of on the water vapor sensitivity of nonporous PEO films

Fig. 2 plots the water vapor response of three pure (nonporous) PEO films having different molecular weights of 35,000, 400,000 and 2,000,000. The two films formed from the two lower molecular weights of PEO had identical water vapor sensitivities. However, the film formed from the PEO film whose PEO molecular weight was 2,000,000 had a dramatically higher water vapor sensitivity, 3.4 times larger than the other films.

If we assume the packing in all porous films is the same (determined by the PMMA) structure, the difference in water sensitivity (the molecular weight effect) depends on the geometry of PEO molecules. i.e., low molecular weight PEO films are more compact than high molecular weight polymer films. Thus high molecular weight PEO films have more vacancy volume than low molecular weight PEO films.

### 3.2. Effect of molecular weight in a leached PMMA/PEO blended polymer on its water vapor sensitivity

Fig. 3 shows the water vapor sensitivities of three porous PMMA films made from PMMA/PEO blended polymers all having a PMMA molecular weight of 996,000 but having PEO molecular weights of 35,000, 400,000, and 2,000,000. The ratio of water vapor sensitivities for films made with a PEO molecular weight of 2,000,000 compared to one made with PEO of 35,000 is 2.5 and 1.7 for PEO 400,000.

We believe the water vapor sensitivity is directly related to the number and size of vacancies in a leached blended polymer. Thus, PEO is leached while PMMA is not. Only the molecular weight (size) of PEO can have significant effects on the film's water vapor sensitivity.

We recognize that a pure PEO could form a film with a higher water vapor sensitivity than porous PMMA films. However a pure

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