

Characterization of a microgravimetric sensor based on pH sensitive hydrogels

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Abstract

The reversible and reproducible phase transition behavior of “stimuli-responsive” or “smart” hydrogels enables their use as materials for chemical and pH sensors in liquids. Using the quartz crystal microbalance (QCM) technique, the principal behavior of hydrogel coated single sensors in dependence of changes in pH is presented. The general sensor properties of polyelectrolytic hydrogels, the detection possibilities and limits, and the response time of such sensors were investigated and discussed.

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1. Introduction

The qualitative and quantitative analysis of multicomponent media present in a lot of industrial processes such as of the chemical, bio technological, pharmaceutical, environmental, and food industry will be most commonly realized with expensive laboratory techniques, for example, chromatography and infrared spectroscopy. These methods are unfavorable because the personnel must be highly qualified and the analyses usually cannot be done in real time. To solve these problems in many special applications, chemical sensors are very attractive. Looking at the current developments in chemical sensors one can distinguish the following three important directions which aim at the improvement of qualitative and quantitative recognition of such sensors. Probably, the trend tried most often are higher-order or higher-number sensors to increase the number of data acquisition channels, and thus the information content [1]. Higher-order are sensors which are disposing about a transduction principle with more than one data acquisition channel or transducer. Higher-number sensors are arrays from a number of single sensors with different sensitivities. The second direction is the improvement of multi-dimensional data processing such as using neural networks for obtain-

ing better qualitative and quantitative results [2]. But the fundamental development in chemical sensors must be the significant extension of the substantial base of sensitive materials. Three relevant kinds of these have been reported in the literature. The first type uses ceramics or glasses such as chalcogenide glasses as sensor materials [3] while in the second kind, common polymers, e.g. poly(vinyl chloride), including plasticizer and different active substances were used [4]. Other less wide-spread polymeric sensor materials are, for example, poly(ethylene glycol)–polystyrene resin bead derivative with various indicator molecules [5] or LiTaO₃ [6]. However, the relatively small substantial base for chemical sensors in liquids restricts the application areas of such devices significantly. Potentially better suitable are smart materials, which show drastic changes in their properties in dependence of special environmental parameters. As the first smart material class, the conductive polymers [7] were introduced. Combinations of these sensor materials in one sensor array are also described [8]. Using these materials in sensor arrays, a lot of beverages such as beers, wines, and milk can be classified, and also several ions can be determined quantitatively [9].

Another class of smart polymers are “stimuli-responsive” or “smart” hydrogels. These materials change their volume, mass and elasticity reversibly in response to a change in the properties of the liquid phase such as temperature [10], pH value [11], solvent composition [12], or salt contents [13]. Specially polymerized hydrogels are sensitive to

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a number of chemical and biochemical species, for example, metal ions [14], surfactants [15,16], urea [17], specific antigens [18], and glucose [19]. Smart hydrogels, utilized as actuator–sensor systems can be used for the automatic regulation of a liquid flow. It could be shown, that the flow rate of a liquid through a hydrogel-based valve depends on the properties of the fluid, like pH, temperature, and concentration of organic compounds in water [20,21]. Automatic microvalves controlled by pH value [22] and electronically controllable microvalves [23] have been presented. However, only in the recent a micro machined pH sensor based on smart hydrogels with a short insight of the sensor behavior has been presented [24].

The aim of this paper is the investigation of the suitability of the microgravimetric transducer principle of quartz crystal microbalance (QCM) for hydrogel-based liquid sensors. The behavior of a polyelectrolytic smart hydrogel in its dependence on changes in pH value, the possibilities and limits of hydrogel coated QCM sensors will be discussed.

2. Experimental

2.1. Materials

As pH sensitive material, a network based on poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA), both from Aldrich, was used. The polymers were dissolved separately in distilled water under stirring at 80 °C (PVA 15 wt.% and PAA 7.5 wt.%). The solutions were then mixed in such a manner that 80 wt.% were PVA and 20 wt.% PAA. The solution was stirred for 1 h at 60 °C and diluted with distilled water to a total amount of solubilized polymer of 5 wt.%. The resulting homogeneous solution was ready for the coating process.

Quartzes (AT, frequency 10.2 MHz, diameter 14 mm) were obtained from Quarz-Technik Müller, Germany. Key-hole patterned gold electrodes (100–200 nm thickness, 5 mm diameter) on a chromium adhesion layer (10 nm thickness) were evaporated using a B30.3-T device from Malz & Schmidt.

2.2. Coating and polymerization procedure

The PVA/PAA solution (5 wt.%) was spin coated onto one side of the resonators (Spincoater Model P6700, Special Coating Systems, Inc.) with 4500 rpm for 60 s. The coating procedure produced a uniform film across the complete resonator surface. Thereafter, the polymer film was dried for 1 h at 45 °C. The cross-linking reaction was thermally induced at 130 °C for 30 min. To remove uncross-linked polymer, an extraction step was performed. However, the adhesion of the cross-linked layer on bare quartz is worse than on gold. This will not influence the performance of the sensor, because due to the energy trapping effect, the oscillation motion is limited to the area covered by the gold electrode.

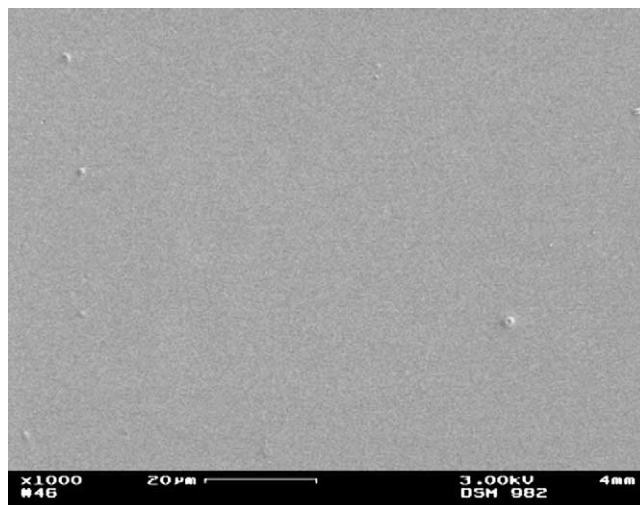


Fig. 1. SEM photograph of a thin hydrogel film coated at an oscillating quartz. The surface is homogeneous. Only a few discontinuities are observable, which are caused by the dust particles.

3. Results and discussion

3.1. Characterization of the polymer films

The surface topography of the polymer films was characterized by scanning electron microscopy (SEM). For cross-linked PVA/PAA the surface is smooth and homogeneous (Fig. 1). The few blisters are caused by dust particles. Quantitative determination of the surface topography of the PVA/PAA films in air was obtained by using atomic force microscopy (AFM) (Fig. 2). Again, it is clearly visible that

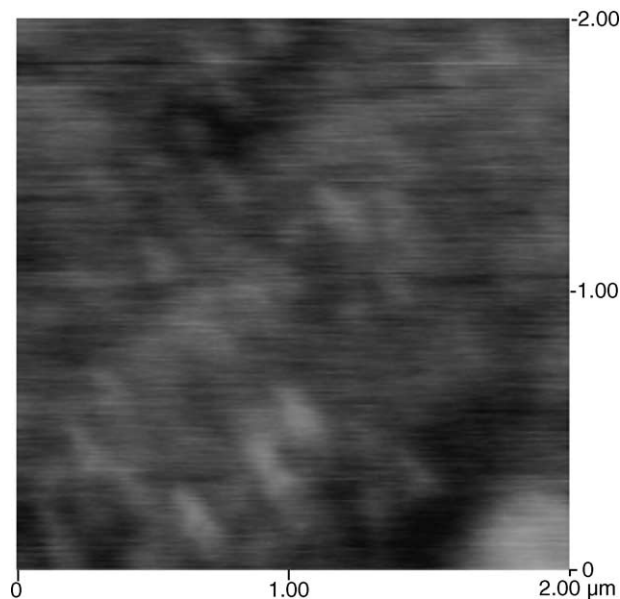


Fig. 2. AFM-photograph of the surface of a thin hydrogel film coated at an oscillating quartz. The PVA/PAA film is very homogeneous. Maximal thickness deviations are 4.7 nm and the roughness R_a is very small with 0.36 nm.

the dry films are very homogeneous. Maximal thickness deviations are 4.7 nm and the mean roughness $R_a = 0.36$ nm is very small. From this finding it can be concluded that the surface roughness of the swollen film will not influence the sensor signal.

The optical thickness of the polymer films was investigated by surface plasmon resonance spectroscopy (SPR). For cross-linked PVA/PAA films the thickness of the dry film is 450 nm. After the extraction step, the dry thickness was reduced by about 15% to 390 nm. The thickness of the polymer film swollen in water (pH 7) was 1.1 μm . This optical thickness gives an idea of the order of magnitude of the film thicknesses.

3.2. Characterization of pH sensitivity of bulky hydrogels

The polyelectrolytic polymer network PVA/PAA is a pH sensitive hydrogel, whose sensitivity is caused by the acidic component poly(acrylic acid). The swelling behavior of the PVA/PAA bulk gel in HCl/NaOH solutions is shown in Fig. 3. When increasing the pH value up to the $\text{p}K_a$ value of acrylic acid (4.7), the hydrogel collapses because the poly-acid groups are in their non-ionic protonated form. Further increase of the pH value causes a swelling of gel since the carboxylic groups are deprotonated. When decreasing the pH from basic to acidic the “deswollen” curve is different from the “swollen” curve. Both characteristics form a hysteresis. Only at pH values above 10 and in the shrunken state up to pH 3 the degree of swelling is independent from the direction of pH change. This swelling behavior is an universal phenomenon in pH-responsive ionized hydrogels. As a reason of this complicated phenomenon, a screening effect has been discussed [25]. By increasing the pH by adding NaOH, the counter ion H^+ in the gel can be replaced by Na^+ ions. At higher pH values, the hydrogel includes excess Na^+ ions, which screen the ionized groups. As a consequence of this screening effect, the distribution of the confirmation of the gel could change to achieve a new swelling equilibrium.

The Young’s modulus, E , of cross-linked bulk PVA/PAA behaves inversely to the swelling degree: E (pH 7) = 1.38,

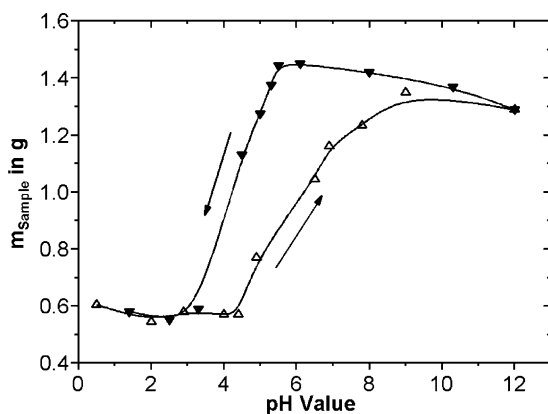


Fig. 3. Swelling behavior of a bulk PVA/PAA network in its dependence on the pH value and on pH gradient.

E (pH 2) = 4.2, and E (pH 11) = 1.24 MPa, respectively. These data show the response of the mechanical properties of the hydrogel towards pH changes. Unfortunately, these values cannot be used in the following discussion, because the relation of the shear modulus of thin layers to Young’s modulus of bulk gels is unknown.

3.3. Characterization of a hydrogel coated quartz in dependence of pH value

3.3.1. Experimental setup

The electrical admittance, Y , of the quartz resonators were measured with a network analyzer (Advantest R3753H or Agilent E5100). When the real part of Y is plotted versus the frequency, one obtains a Lorentzian shaped curve (resonance curve). The maximum of the curve lies at the resonance frequency, f , of the resonator, and the half bandwidth, w is proportional to the damping. In the following, only the changes of f and w accompanying changes of the pH will be discussed. The frequency shift is defined as a complex quantity, $\Delta f^* = \Delta f + i\Delta w/2$ ($i^2 = -1$) because the presence of a layer will in general cause of shift of the center of resonance curve (Δf) and a change of the half bandwidth (damping, Δw). The pH of the solution was measured with a Metrohm 6.0224.100 pH electrode. The temperature was monitored using a temperature sensor type PT 100.

3.3.2. Physical background of QCMB

The QCMB technique is well suited to characterize the properties of thin films, as the complex frequency shift, Δf^* (see above), of the resonator sensitively depends on the surface mechanical impedance. The mechanical impedance, $Z_{M, \text{layer}}^*$, is defined as the ratio of the shear stress to the resulting velocity. For a smooth film of density ρ , thickness d and complex shear modulus G^* undergoing shear deformation at the angular frequency ω . $Z_{M, \text{layer}}^*$ is given by Eq. (1) [26].

$$Z_{M, \text{layer}}^* = i\sqrt{\rho G^*} \tan\left(\sqrt{\frac{\rho}{G^*}} d\omega\right) \quad (1)$$

The presence of a layer with the mechanical impedance $Z_{M, \text{layer}}^*$ will induce a complex frequency shift Δf^* , Eq. (2)

$$\frac{\Delta f^*}{f_0} = i \frac{Z_{M, \text{layer}}^*}{\pi Z_{M, \text{quartz}}} \quad (2)$$

where f_0 is the resonance frequency of the uncoated quartz in air and $Z_{M, \text{quartz}}$ the mechanical impedance of the quartz itself, $Z_{M, \text{quartz}} = 8.849 \times 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$.

At a first glance one could think that the shear modulus of a film could be readily determined by measuring Δf^* and applying Eqs. (1) and (2). However, there are two problems with this approach. First, due to its transcendental form Eq. (1) cannot be solved uniquely for G^* . Second, to yield accurate values for G^* the errors in ρ and d must be very small. Lucklum et al. have discussed this issue in full detail

[27]. Nevertheless, the successful determination of G^* for a variety of systems has been shown [26,28–34].

The complex nature of Δf^* can offer the use of two data acquisition channels:

1. The real part frequency shift, which should be depending at changes of mass and volume of surface load at first approach.
2. The change of the damping (imaginary part of Δf^*), which should be influenced by changes of the shear modulus of the thin hydrogel film.

3.3.3. Behavior of coated hydrogel film

Generally, the hysteresis in the interesting range of volume phase transition at polyelectrolytic hydrogels suggests that these hydrogels are not usable for pH measurements because the degree of swelling depends on the direction of the pH change.

Fig. 4 presents the frequency and damping behavior of the PVA/PAA loaded quartz depending on the pH value. The characteristics of the hydrogel loaded quartz considerably differ from the results at bulk hydrogels. Firstly, the hysteresis behavior of the swelling process is significantly modified. The range of volume phase transition is displaced from about pH 3 to 10 towards pH 1.5 to 3.5. This region does not show any influence of the screening effect. The hysteresis behavior can be only observed at pH values higher than pH 3.5. The shift of phase transition conditions towards the hysteresis free range is essential for the use of PVA/PAA coated quartz crystals as pH sensors because this could offer the possibility to obtain reproducible sensor signals without dependence of the direction of the pH change. An explanation of the displacement of phase transition conditions is very difficult. An influence of the dimension of hydrogel structures at the position of the volume phase transition is known for temperature sensitive hydrogels [35,36]. As a possible reason of this phenomenon a strong dependence of the interaction parameter of polymer network on concentration was discussed. Further investigations in future works will allow a conclusive interpretation of this effect.

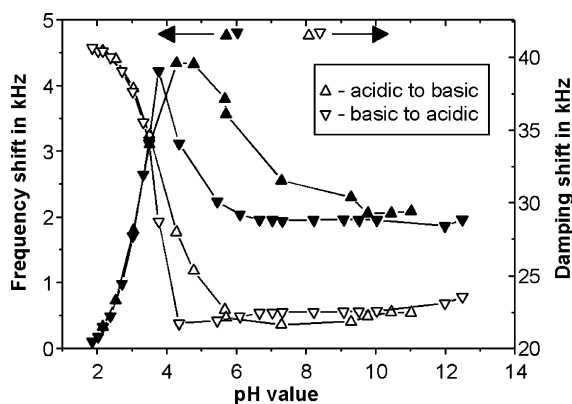


Fig. 4. Behavior of a hydrogel coated oscillating quartz: (\blacktriangle , \blacktriangledown) frequency shift; (\triangle , \triangledown) damping shift.

However, we think it will be confirmed that the dimension of hydrogel structures causes the shift of the phase transition conditions.

The second phenomenon, which is the existence of the hysteresis behavior only above pH 3.5, is according to the described nature of screening effect. In an acidic environment, in which the range of volume phase transition now is placed, an excess of Na^+ ions is not found. Hence, the H^+ counter ions cannot be replaced by the Na^+ ions.

Both sensor signals, the frequency shift and change of damping, show an interesting behavior. Firstly, it can be seen that the damping behavior is opposite to the frequency shift in the region of the volume phase transition. This behavior is in accordance with the prediction of Eq. (1). An increase in the surface load of a quartz crystal should induce a decrease of the resonance frequency. However, the observed frequency shift increases with increasing mass and volume. At a first glance, this behavior apparently contradicts the expected behavior. Essentially, the hydrogel density decreases strongly if it swells and thus increases its volume and mass. As a consequence, the effective surface load decreases during the swelling process.

Furthermore, the behavior of the damping shift is likewise complicated. Obviously the changes of G^* and also ρ induce an overall damping decrease.

The suitability of the PVA/PAA coated quartz as a pH sensor will be destined by their repeatability of the sensor signals. Such behavior is shown in Fig. 5 in the pH range of 2.55–3.45, which possess no hysteresis characteristics. Alterations of pH value result in the highest maximal repeat error, which is for the frequency shift about ± 920 Hz, and for the change of damping ± 1610 Hz. The differences of the absolute values shown in Figs. 4 and 5 can be explained with the different measuring techniques applied: Fig. 4 relates to changes of the real part of the admittance (Y^*) of the quartz crystal, whereas Fig. 5 relates to changes of the modulus of Y^* .

The sensor resolutions of the two measurement values are different because the change of damping is higher than

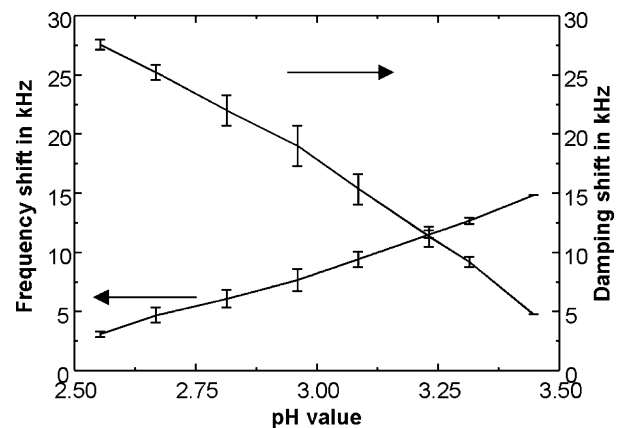


Fig. 5. Sensor characteristics and repeat accuracy of a PVA/PAA coated quartz in the range of pH 2.55–3.45.

the frequency shift. The sensor signal resolution which are obtained amounts for a confidence interval of 95%:

- frequency shift: (13.2 ± 0.62) kHz/pH;
- change of damping: (25.467 ± 1.085) kHz/pH.

In the pH range of 2.55–3.45 these resolutions are equal measurement precisions of about pH 0.002.

As a relevant conclusion, both signals, the frequency and damping shift, can be used as acquisition channels to map the changes of the properties of a hydrogel film coated on a quartz crystal. The sensor characteristics are slightly non-linear, but more point calibrations should be applied for obtaining true measurement results.

The response time of hydrogel-based sensors is governed by the kinetics of the volume change of hydrogels which is based on diffusion phenomena.

To initiate a volume phase transition of hydrogels, two transport mechanisms have to be considered. Firstly, the initiating stimulus such as hydrogen ions must be transported into the polymer network. This modifies the properties of the swelling agent inside the gel. Such penetration happens through a permanent diffusion of solvent into the hydrogel. The typical magnitude of diffusion coefficients D is $\approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [37]. Second, the swelling or deswelling process starts and the diffusion characteristics change towards the so-called cooperative diffusion mechanism. As a result of the additional polymer chain transportation, the cooperative diffusion coefficient D_{Coop} decreases to $\approx 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. However, the swelling process is faster than the deswelling process. This behavior can be attributed to an increase in solvent permeability of gels with swelling. On deswelling the gel the permeability effect is decreased and slows down the shrinking process.

The response time can be observed in Fig. 6, which shows alterations of pH between approximately 3.1 and 1.8. The response time for an increase of pH value, which induces a

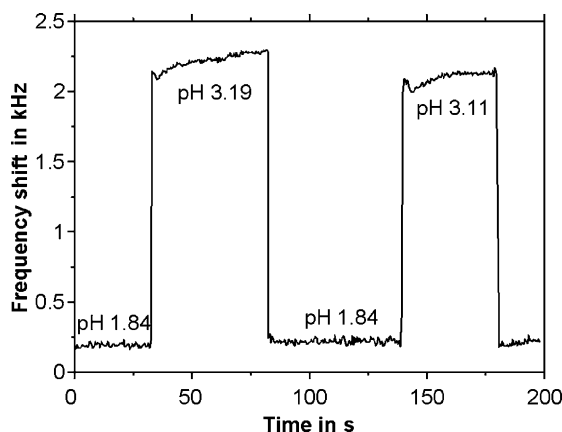


Fig. 6. Response time of a PVA/PAA coated quartz sensor when applying pH steps between 1.84 (0.01 M HCl) and 3.19 (acetate buffer with high ionic strength).

swelling of hydrogel layer, is about 500 ms. Decreasing the pH value, which causes a shrinkage of the PVA/PAA film, results in a response time of about 800 ms. The difference between both cases is small.

Therefore, hydrogel coated quartz crystals are suitable for realization of real-time measurements in liquids.

4. Conclusion

The microgravimetric principle of quartz micro balance is well suited for a precise investigation of the behavior of thin hydrogel films. It is possible to use hydrogel coated quartz crystals as liquid sensors to observe special state values of liquid media in real-time. Two data acquisition channels can be used for the recognition of the sensor behavior. Firstly, the frequency shift is a function of changes in mass and volume of thin hydrogel films. Furthermore, the change of damping depends on the changes in elasticity of hydrogel film.

PVA/PAA coated quartz crystals can be used for pH measurements in the range up to pH 3.5. In this region, measurements with a precision larger than pH 0.005 are realizable. However, it cannot be excluded that ions, particularly cations, will influence the sensor behavior. Such cross-sensitivities must be investigated for the special application case.

The investigations have shown that for polyelectrolyte hydrogels a few of volume phase transition phenomena must be respected. Firstly, the screening effect induces a hysteresis behavior, which limits the range with repeatable characteristic. For PVA/PAA hydrogels the influence of the screening effect is only negligible up to pH 3.5. Secondly, a shift of phase transition condition towards smaller values was observed. The nature of this phenomenon is not yet consistently explicable. If such effects observable for other polymer systems, particularly non-ionic hydrogels, then this effect is a general behavior of thin hydrogel structures.

It might be tempting to extract quantitative information about the shear modulus of the hydrogel layers by combining the SPR and the QCM results. However, as for these systems the relation of optical and acoustical thickness is not fully understood, the discussion will be postponed to a future work.

We believe that the QCM technique is a general suitable transduction principle for the use of hydrogels as sensor materials for the liquid sensors. Furthermore, because smart hydrogels offer a lot of sensitivities across substance and ion concentrations in liquids, they will play an important role in the liquid sensors in nearer future. The volume phase transition behavior of such gels and the fast response times of thin hydrogel structures can allow the development of high sensitive and real-time likely measurement devices. By using an array consisting of different hydrogel-based sensors, multi-compound measuring instruments—so-called electronic tongues—could be realized.

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Biographies

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