Application of Sensitive Hydrogels in Chemical and pH Sensors

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Summary: In the present work, pH-sensitive poly(vinyl alcohol)/poly(acrylic acid) (PVA/PAA) blends as well as hydrogels based on poly(N-isopropylacrylamide) (PNIPAAm), which are sensitive to organic solvent concentration in aqueous solutions, were used in silicon micromachined sensors. A sensitivity of approximately 15 mV/pH was obtained for a pH sensor with a 50 μm thick PVA/PAA hydrogel layer in a pH range above the acid exponent of acrylic acid (pK_a=4.7). The output voltage versus pH-value characteristics and the long-term signal stability of hydrogel-based sensors were investigated and the measurement conditions necessary for high signal reproducibility were determined. The influence of the preparation conditions of the hydrogel films on the sensitivity and response time of the chemical and pH sensors is discussed.

Keywords: hydrogels; pH-sensitive; sensors; solvent composition; swelling;

Introduction

Hydrogels are used for a variety of applications where environmental sensitivity is needed. Hydrogels consist of a crosslinked polymer network that can contain large amounts of a solvent. By controlling the functional groups along hydrogel's backbone chains, the amount of solvent uptake, and thus the dimensions of the gel, can be affected by environmental stimuli, such as solvent composition, pH value, temperature, ionic strength, and electric field.

The swelling ability of pH-sensitive hydrogels depends on the functional acidic or basic groups on the polymer backbone. Due to the dissociation of these groups and the influx of counterions, the concentration of ions in the hydrogel is higher than in the surrounding solution. This causes a difference in osmotic pressure and results in a solution flux into the hydrogel and, consequently, a swelling. The interaction and repulsion of charges along the polymer chain also lead to an

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increase in swelling. Hydrogels with acidic groups will be ionised at higher pH, thus an increase in pH leads to an increase in swelling. When basic groups are used, the hydrogel will swell by lowering the pH. The degree of swelling depends on the amount of groups, crosslinking density, and the hydrophilicity of the monomers.[1-4] Hydrogels are capable to reversibly convert chemical into mechanical energy and are used as active sensing components in micro-electro-mechanical systems (MEMS).[5-7]

In the present work we propose an approach for pH and chemical sensors based on such swellable hydrogels, using a mechano-electrical transducer with piezo-resistive elements. The characteristics and the long-term signal stability of such sensors are investigated.

Experimental

The following hydrogel systems were used in this work:

1. *Poly(vinyl alcohol)/poly(acrylic acid) (PVA/PAA) blends*: The swelling degree of these hydrogels changes steeply with the change of the pH value of the measuring species: it is at minimum in acids and takes its maximum in bases.[1, 2] PVA and PAA polymers obtained from Aldrich Chemical Co. were dissolved separately in distilled water under stirring at 80°C (PVA 15 wt% and PAA 7.5 wt%). For hydrogel formation, the solutions are then mixed in such a manner that 80 wt% were PVA and 20 wt% PAA. This mixture is stirred for 1 h at 60°C to manufacture a homogeneous solution. Thin films of PVA/PAA blends were deposited by spin-coating onto the silicon wafers covered with a 550 nm thick PECVD silicon oxide film which served as convenient substrates. Finally, the dried hydrogel films were isothermally annealed in an oven at 130°C for 20 min.
2. *Hydrogels on basis of the N-Isopropylacrylamides (NIPAAm)*: Hydrogels on PolyNIPAAm (PNIPAAm) basis react sensitively on changes of the concentration of organic components in aqueous solutions. [3] The crosslinked PNIPAAm-hydrogels were prepared by free radical polymerization of NIPAAm in water with *N,N'*-methylene-bisacrylamide (BIS; BIS content: 4 mol%) as the crosslinking agent. A solution of NIPAAm, BIS (overall monomer concentration: 0.53 mol/l) and potassium peroxodisulfate as the initiator ($3x10^{-3}$ mol/mol monomer) were cooled to 0°C and purged with nitrogen for 15 min. The *N,N,N',N'*-tetramethylethylenediamine as the accelerator

($3x10^{-3}$ mol/mol monomer) was added and the solution was immediately transferred into a Petri dish to get hydrogel foils. After 17 h reaction time at 20°C, the gels were separated and washed with water for one week.

For the design of chemical and pH sensors a sensor chip with a distortable thin silicon membrane is used (Fig. 1). The chip surface contains the electronic components: piezoresistors metallization and bonding islands. The hydrogel itself is brought into a cavity at the backside of the silicon chip and closed with a cover. This cavity on the backside of the chip is wet etched, a silicon nitride mask was used as an etch resist. Therefore, only the backside of the chip comes in contact with the measuring species, whereas the frontside with the electronic components is protected from it. In this case, the long-term stability of the sensor is solely determined by the stability of the hydrogel characteristics.

Figure 1 illustrates the operational principle of hydrogel-based sensors. The swelling or shrinking processes of the hydrogel are monitored by a corresponding change in piezoresistance of an integrated Wheatstone bridge inside a rectangular silicon membrane. The membrane deflection causes a stress state change inside the membrane and therefore a change of the resistivity of the resistors. This changes proportionally the sensor's output voltage.[8]

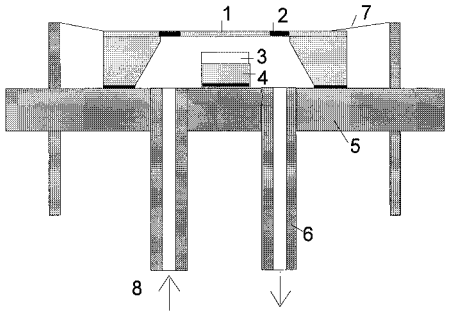

Figure 1. Operational principle of hydrogel-based sensors
1 bending plate; 2 mechano-electrical transducer (piezoresistive bridge);
3 swellable hydrogel layer; 4 Si platform;
5 socket ; 6 tube ; 7 interconnect; 8 solution.

The sensor chip is bonded to a socket with inlet and outlet flow channels. The aqueous solution to be measured is pumped through the inlet tubes into the silicon chip cavity. In order to obtain a sufficient measuring signal, the 50 µm thick PVA/PAA-hydrogel layer is located on a silicon platform to achieve a small enough gap between dry (absolutely unswollen) hydrogel and the silicon membrane. The hydrogel layers were spin coated on the Si wafer, dried and then crosslinked. For PNIPAAm chemical sensors, 250 µm thick hydrogel foil pieces were used. The

dried PNIPAAm-foils were prepared by evaporation of water at room temperature and then cut into pieces of 1 mm x 1 mm.

Results and discussion

The sensor's output voltage was measured during the swelling of the PVA/PAA hydrogel layer under influence of solutions with different pH values, as shown in Fig. 2. A hysteresis was obtained for cycling from acidic to basic conditions and vice versa. The hysteresis loop widened with increasing number of measuring cycles. During the first pH increase the hydrogel layer abruptly swelled at pH values above the acid exponent of acrylic acid (pK_a=4.7). Then the threshold value pH_1 shifted to higher pH values with increasing number of measuring cycles. The downward threshold pH_2 for pH value decrease processes shifted to lower values. The hysteresis and the widening the hysteresis loop with increasing number of cycles could be caused by a screening effect.[9] With increasing the pH values by adding base, the counterions H^+ in the gel can be replaced by cations. At higher pH values, the hydrogel includes excess cations, which screen the ionized groups. This effect is disappearing only at low pH values.

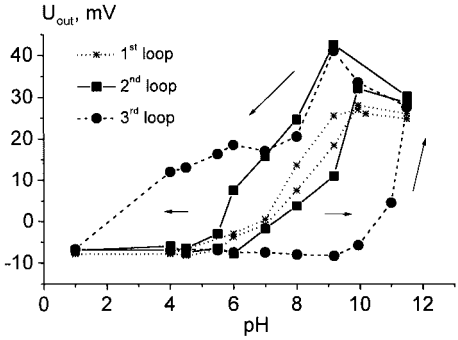

Figure 2. Sensor output voltage as a function of pH value.

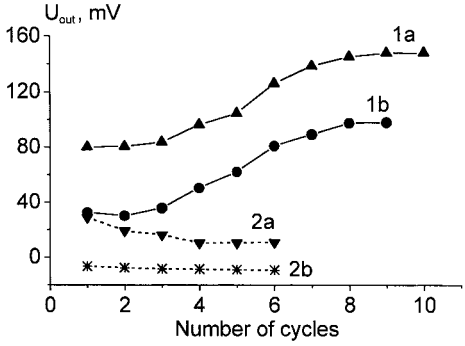

Figure 3. Sensor output voltage:
1 - at pH=11 (a) and at pH=7 (b) for alternate pH 11...7; 2 - at pH=11 (a) and at pH=1 (b) for alternate pH 11...1.

In order to investigate the reproducibility of the sensor response, pH1 and pH11 or pH7 and pH11 solutions were pumped alternatively. The resulting sensor response is shown in Fig. 3. On

the one hand, the amplitude of the signal at pH11 (curve 2a) became smaller after the first cycles in acid solution until it became almost constant. On the other hand, the signal amplitude at both pH11 and pH7 (curves 1a und 1b) increased steadily from cycle to cycle at cycles between values pH=7 and pH=11. After several cycles of alternating immersions in the pH7 and pH11 solutions, the signal at pH11 reached its saturation. This behaviour shows clearly that hydrogel based sensors can favorably be used only in certain limited pH value region besides the region of the hysteresis loop. Preferably, sensors for low and for high pH values are useful. As expected by this behaviour, the sensor response is reversible at low pH values after initial conditioning in deionized water (Fig. 4). For a high signal reproducibility, the dry hydrogel layer should be placed in deionized water for more than 1 day. Before starting the measurements, the water uptake of hydrogel must reach its full saturation.

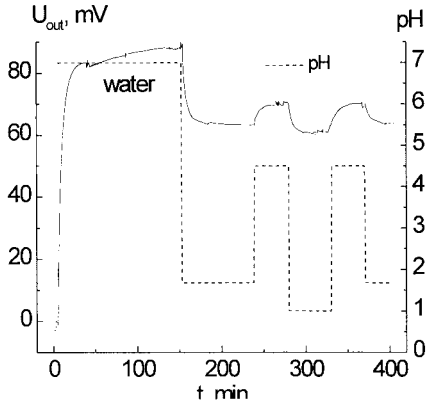

Figure 4. Sensor output voltage at alternating pH changes.

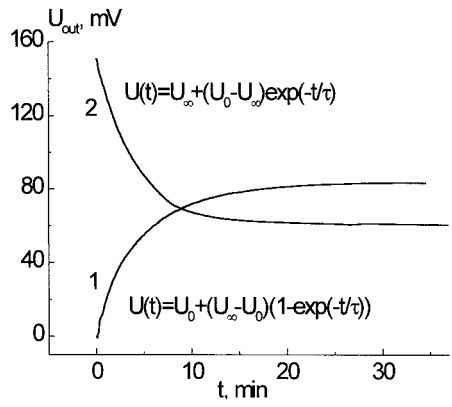

Figure 5. Sensor output voltage during: 1) swelling process of a dry hydrogel in deionized water, 2) deswelling process (from pH11.5 to pH1).

Beside the sensitivity and signal reproducibility, the response time is one of the most crucial aspects for sensor implementation. The sensor response time is determined by the polymer layer thickness as well as by the hydrogel swelling kinetics. The latter depends on the rates of diffusion of three species in the gel structure. First, solutes which are not excluded from the gel will diffuse into the gel. Second, base or acid must diffuse into the gel to spark its swelling or

collapse. Third, water must enter or leave the gel. The kinetics is complicated because three these different mass transfer processes occur, often simultaneously. The mechanisms for swelling and shrinkage are different, since shrinkage occurs more quickly than swelling.[1, 10, 11] It was found that the time dependence of the deswelling process is identical with that one of the swelling process of a dry gel in deionized water.[1] Figure 5 shows the sensor's output voltage during the rapid swelling of dry hydrogel layer in deionized water (curve 1). The behaviour can be described by means of an exponential increase, which gives a time constant τ_1=5 min. The time dependence of the rapid deswelling process from pH11.5 to pH1 yields also τ_1=5 min (Fig. 5, curve 2), indicating that both processes are determined by the diffusion of water into the gel and out of the gel, respectively. It can be shown, that hydrochloric acid diffuses into the gel much faster than the rate at which the gel shrinks, indicating that the diffusion of water out of the gel, rather than ion exchange, limits the shrinkage.[10]

In contrast, during the slow swelling of the dry hydrogel layer in solution with pH=11.5, water and sodium hydroxide uptake occur at the same rate suggesting that ion exchange is the rate limiting step during swelling. In this case the swelling behaviour is described by a time constant of τ_2=80 min. Time constants in the same order of magnitude $\tau \geq 80$ min were found also for slow swelling processes both from pH1 to pH11.5 and from pH7 to pH11.5 as well as for slow deswelling process from pH11.5 to pH7. The latter is determined by the decay of the electrostatic repulsion between the polycarboxylate groups within the network. The sensor response time can be shortened by using a thinner hydrogel layer which needs also thinner silicon membrane of the chip for a sufficient sensor output signal.

The same sensor concept was also applied to chemical sensors for the measurement of solvent concentrations in aqueous solutions. For this purpose, the pH sensitive PVA/PAA was replaced by PNIPAAm. Fig. 6 shows the

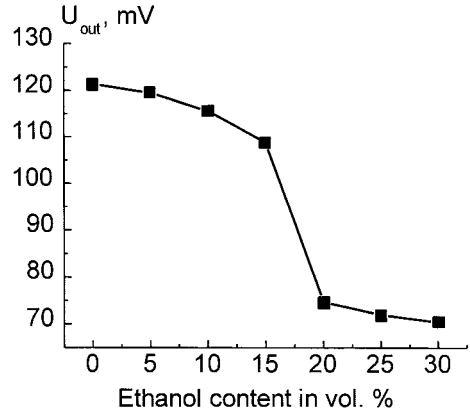

Figure 6. Output voltage of PNIPAAm based sensor in aqueous mixtures of ethanol.

characteristic of such a organic solvent concentration sensor. The sensor's output voltage was measured during the swelling of the hydrogel under influence of water solutions with different ethanol contents. The volume phase transition occurs at about 20 vol% of ethanol. This value corresponds to that one of PNIPAAm which was found for the swelling degree defined as the ratio between the masses of swollen and dry hydrogel.[3] For this sensor, the time constant describing swelling behaviour was determined to be $\tau \geq 60$ min.

Conclusions

We have demonstrated the operational principle of hydrogel-based chemical and pH sensors. To realize pH sensors, PVA/PAA blends which show a pH value dependant swelling behaviour were used as chemo-mechanical transducers. The hydrogel swelling leads to a bending of a thin silicon membrane and, by this, to an electrical output voltage of the sensor chip. For a pH sensor with a 50 µm thick PVA/PAA hydrogel layer, a sensitivity of approximately 15 mV/pH was obtained in a pH range above the acid exponent of acrylic acid (pK_a=4.7). Sufficient signal reproducibility was found both in the low and the high pH value regions besides the hysteresis loop. A similar sensor design was also used for chemical sensors on PNIPAAm basis for measuring the content of organic solvents in aqueous solutions. It was found that an initial conditioning in deionized water is necessary for high signal reproducibility. In order to shorten the sensor response time, the hydrogel film preparation and the film thickness have to be optimized.

Acknowledgments

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