

50. Internationales Wissenschaftliches Kolloquium

September, 19-23, 2005

**Maschinenbau
von Makro bis Nano /
Mechanical Engineering
from Macro to Nano**

Proceedings

Fakultät für Maschinenbau /
Faculty of Mechanical Engineering

Startseite / Index:

<http://www.db-thueringen.de/servlets/DocumentServlet?id=15745>

Impressum

- Herausgeber: Der Rektor der Technischen Universität Ilmenau
Univ.-Prof. Dr. rer. nat. habil. Peter Scharff
- Redaktion: Referat Marketing und Studentische Angelegenheiten
Andrea Schneider
- Fakultät für Maschinenbau
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- Redaktionsschluss: 31. August 2005
(CD-Rom-Ausgabe)
- Technische Realisierung: Institut für Medientechnik an der TU Ilmenau
(CD-Rom-Ausgabe) Dipl.-Ing. Christian Weigel
Dipl.-Ing. Helge Drumm
Dipl.-Ing. Marco Albrecht
- Technische Realisierung: Universitätsbibliothek Ilmenau
(Online-Ausgabe) [ilmedia](#)
Postfach 10 05 65
98684 Ilmenau
- Verlag:  Verlag ISLE, Betriebsstätte des ISLE e.V.
Werner-von-Siemens-Str. 16
98693 Ilmenau

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ISBN (Druckausgabe): 3-932633-98-9 (978-3-932633-98-0)
ISBN (CD-Rom-Ausgabe): 3-932633-99-7 (978-3-932633-99-7)

Startseite / Index:

<http://www.db-thueringen.de/servlets/DocumentServlet?id=15745>

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Output Characteristics of Silicon Piezoresistive pH Sensors based on Polymer Hydrogel: Simulations and Experiments

ABSTRACT

THIS PAPER PRESENTS THE STUDY OF A SILICON PIEZORESISTIVE pH SENSOR, which operation relies on the pH sensitive swelling of a polymer hydrogel. The pH-sensitive poly(vinyl alcohol)-poly(acrylic acid) (PVA-PAA) hydrogel was used for this aim. The pH sensor behaviour under swelling of polymer hydrogel had been simulated using finite element method (ANSYS). Free swelling experiments and mechanical tests of PVA-PAA hydrogel have been performed in order to prove the simulation results. Based on the simulation analysis, pH sensors have been realised using a rigid mesh fabricated by micromachining technology. The sensor characteristics, such as the silicon membrane deflection and output voltage, have been measured. There was a good relative agreement between static simulations and experimental results. However, the sensor time response is four times longer than predicted by simulation.

1. INTRODUCTION

A POLYMER GEL CONSISTS OF AN ELASTIC CROSS-LINKED POLYMER WITH A fluid filling the interstitial space of the network. Polymer gels can easily be deformed by external physical and chemical stimuli and can generate a force or execute work to the exterior. If such responses can be translated from the microscopic level into a macroscopic scale, a conversion of chemical free energy into mechanical work should be realized. These energy-conversion systems belong to so-called smart materials and have great potential that might be applied to actuators [1], sensors [3-6], chemical valves [2], and delivery controllers. That is why there has been an ever-increasing interest in this type of materials during recent years. Among them, pH sensitive hydrogels are chemomechanical systems that change in response to change in pH. Many attempts were made to combine this type of gel with microstructures having mechanical sensitive elements. Several studies on this aim have been carried out. R. Bashir et al. designed and fabricated a pH microsensor using hydrogel and

silicon cantilever [3]. I. S. Han et al. reported about a miniature biosensor for glucose concentration measurement in blood using the combination of a pressure transducer and a pH glucose gel [4]. Recently, S. Herber also developed a hydrogel biosensor for monitoring carbon dioxide pressure in stomach of human body connecting it to a silicon piezoresistive pressure transducer [5-6]. However, these studies have just focused on the use of pH sensitive gels for concrete applications but not delved into the aspects of material modelling techniques required for the design and optimization of devices. For this reason, a detail investigation of the polymer gel behaviour is crucial to establish reliable models for predicting the device characterizations.

In this paper, a hyperelastic material model for polymer hydrogels is applied to simulate the hydrogel based pH sensor behaviour by finite element method using ANSYS. In order to support the simulation, free swelling experiments and mechanical tests of PVA-PAA hydrogel have been performed. A FE model was developed and calculated for the sensor design. As a result, the pH sensors were realized by exploitation of the commercial piezoresistive pressure transducers. The sensor output characterization such as sensor membrane deflections, output voltage and sensor response time were measured and compared to the simulation results.

2. MATERIAL BEHAVIOUR OF HYDROGELS

2.1. Material characterization

As mentioned above, polymer gels include a polymer network and interstitial solutions. The network of polymer molecules holds the liquid in place and so gives the gel its rigidity. Gels are wet and soft and look like a solid material, but are capable of undergoing large deformations. This is in contrast with most industrial materials, such as metals, ceramics, and plastics, which are dry and hard.

Therefore, the material properties were determined experimentally.

First, free swelling experiments were performed. The measured hydrogel strain is a function of pH value and is varying from some percentages at low pH levels to 34% at pH11 [7]. The

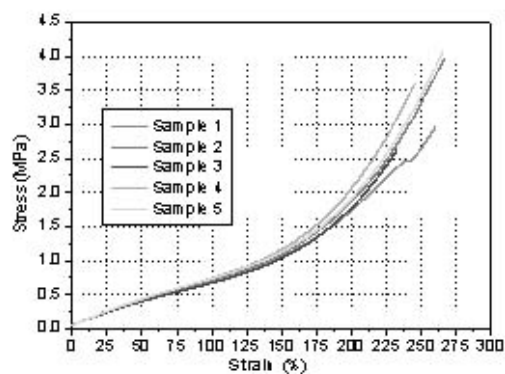


Fig.1. Stress– strain characteristic of PVA-PAA hydrogel preserved in pH1

results of this investigation showed that hydrogel strains are large and recoverable. The hydrogel strain vs. pH value relation is used for sensor simulation.

Furthermore, the stress–strain characteristic of gels preserved at pH1 solution resulting from a test of uniaxial extension was determined by applying increasing forces and by detecting the related strains, up to a strain of 250%. The relationship between stresses (force per unit unstrained cross-section) versus strains (percentage variation of the sample length) is shown in Fig. 1. It presents the typical non-linear behaviour of rubber-like materials [8]. On the basis of this probing the real insight of material nature of polymer hydrogel was gained supposed as reason to establish its appropriate material model.

2.2. Material model of polymer hydrogel

The development of the material model of polymer hydrogel materials has been an active research area for many years. Very recently, a number of constitutive models have been developed addressing different experimental observations. As shown above, one can be defined that polymer hydrogels are belonging to rubber-like materials. Under such circumstances, hyperelastic models are often adequate for predicting its mechanical response. For hyperelasticity, mechanical properties are characterized by a strain energy function, which is a scalar function of either a strain or a deformation tensor [9]. The strain energy describes the work stored in the body is expressed as:

$$W = W(\lambda_1, \lambda_2, \lambda_3) \quad (1)$$

where $\lambda_1, \lambda_2, \lambda_3$ are principal stretch ratios of actual and initial lengths.

The energy function is determined by the thermodynamics theory as follows [8]:

$$W = \frac{1}{2} NkT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad (2)$$

where N is number of chains per unit volume in the network, k is Boltzmann constant and T is absolute temperature. The quantity NkT is equivalent to the shear modulus of material.

One of these models is the finite-elastic constitutive model for active polymer gels of Marra et al [9]. This model has been shown to couple the large deformation mechanical behaviour with the volume change/actuation behaviour based on Mooney-Rivlin equation.

Using the theory of continuum mechanics, the strain energy function for an isotropic material is in the following form [10]:

$$W = C_1(I_1 - 3) + C_2(I_2 - 3) = C_1(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + C_2(\lambda_1^2\lambda_2^2 + \lambda_1^2\lambda_3^2 + \lambda_2^2\lambda_3^2 - 3) \quad (3)$$

where I_1 and I_2 are the first and second strain invariants, C_1 and C_2 are material constants having dimension of MPa.

If incompressible material is assumed, I_2 can be rewritten as:

$$I_2 = \lambda_1^2 \lambda_2^2 + \lambda_1^2 \lambda_3^2 + \lambda_2^2 \lambda_3^2 = \lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2}$$

In case of uniaxial deformation the stretch ratios can be expressed as:

$$\lambda_1 = \lambda \text{ and } \lambda_2 = \lambda_3 = \lambda^{-1/2}$$

Then, the derivative of strain energy function with respect to a strain component determines Cauchy stress (force per unit unstrained area):

$$T_1 = 2 \left(\lambda - \frac{1}{\lambda^2} \right) \left(C_1 + C_2 \frac{1}{\lambda} \right) \quad (4)$$

For polymer hydrogels, when combining the uniaxial mechanical extension with volume change due to actuation by chemical stimuli, the Cauchy stress can be expressed as [9]:

$$T_1 = 2 \left(\lambda - \frac{1}{\lambda^2} \right) \left(\Lambda^{-1} C_1 + \Lambda C_2 \frac{1}{\lambda} \right) \quad (5)$$

where Λ is the swelling ratio of polymer hydrogel, i.e., the size ratio between swollen and fully contracted states. Eq (5) is called the modified Mooney - Rivlin equation

For an acidic gel like poly(vinyl alcohol)-poly(acrylic acid) (PVA-PAA), it will fully contract in acidic solutions, i.e., at low pH values like pH1 and fully expanded in base solutions i.e. at high pH values. In this work, the starting state of polymer gels used for pH sensors is in the fully contracted state since gel is preserved in pH1 solution. Therefore $\Lambda = 1$, and eq. (5) again becomes eq. (4).

The physical values of the constants C_1 and C_2 are determined mathematically using results of uniaxial extension test in section 2.1 based on the Mooney-Rivlin plot [8].

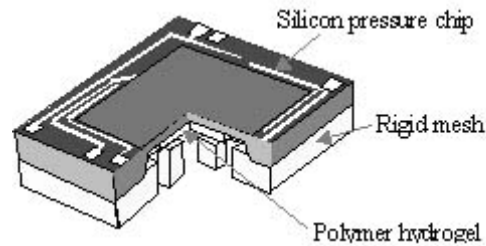


Fig.2. Hydrogel pH sensor viewed from the top

3. SENSOR MODEL AND FINITE ELEMENT SIMULATION

3.1. pH sensor design

A thin layer of PVA-PAA hydrogel is placed in the cavity of a piezoresistive pressure transducer between the upper silicon diaphragm and a lower silicon rigid mesh. It is known

that swelling of polymer hydrogel in polyelectrolyte solutions mostly depends on diffusion of hydrogen ions. Hence, the gel response is relatively slow. Kinetics of gel swelling is a function of both gel dimension and diffusion coefficient, hence, the response time is proportional to square of its dimension [11]. Therefore, in order to decrease the reaction time constant the gel dimension was chosen to be smaller than silicon diaphragm one. Because of the gel is fixed in the hard square frame, the force exerted by gel swelling acts only on the silicon diaphragm. This makes the gel deformations similar to the uniaxial extension test. Due to gel swelling, the diaphragm will be bent causing the stresses in it. The output voltage can be determined as [12]:

$$U_{out} = -\frac{U_{cc}}{2} \pi_{44} (\sigma_l - \sigma_t) \quad (6)$$

where U_{cc} is the applied voltage, π_{44} is the piezoresistive coefficient (for (100) silicon $\pi_{44} = 138.1 \times 10^{-11} \text{Pa}^{-1}$), σ_l and σ_t are the longitudinal and transverse stress, respectively.

3.2. Finite element simulation

The finite element model is built by using the commercial package software ANSYS, which offers a built-in hyperelastic material and geometric modeling capability [10]. Only a quarter of the model is considered due to sensor symmetry. The solid45 element is used to model the silicon chip and the silicon rigid mesh, the hyper58 one is used for the hydrogel piece. The contact49 element is applied to maintain the model continuity and present the force caused by hydrogel swelling to the silicon diaphragm. In order to model the chemically caused hydrogel swelling, we have used its equivalence to the thermal extension. Equivalent strain due to swelling is determined by free swelling experiment [7]. According to this assumption, we easily use the thermal

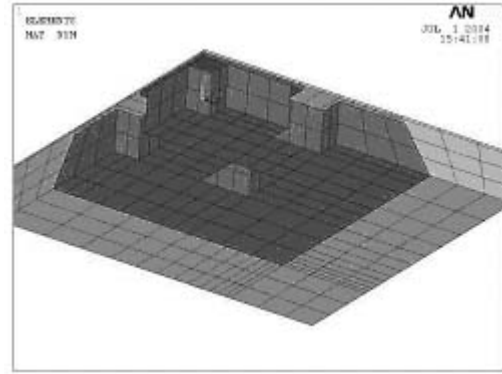


Fig.3. FE model of hydrogel pH sensors (viewed from the bottom)

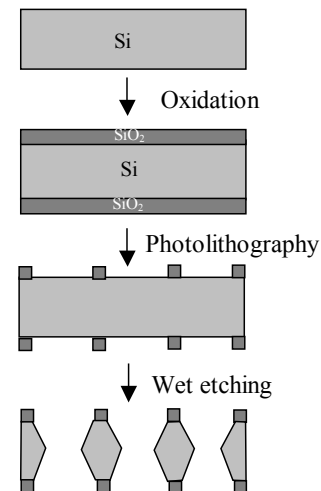


Fig. 4: Technological flow for fabricating silicon rigid mesh

expansion term offered by ANSYS to simulate the swelling phenomenon. The viscous behaviour of polymer gel was neglected in this study since the focus was brought to the static behaviour. The FE model of sensor is shown in figure 3.

4. SENSOR REALISATIONS

4.1. Gel preparation

Gel has been produced by deposition of PVA/PAA polymer solution then, dry polymer film was peel-off cut into the small square slabs before being baked in the oven at 130 °C for 20 minutes. The baked PVA/PAA slabs were soaked in deionized water to get equilibrium swelling and subsequently in buffer pH1 solution to be in the least swollen state.

4.2. Rigid mesh fabrication

In this work, the rigid meshes have been made by micromachining technique. They were fabricated using a 3 inches n-type <100> 320 μm thick single polished silicon wafer. First, the wafer was wet oxidized for 8 hours to grow a 1.5μm thick SiO₂ layer. The oxide was patterned on both sides of the wafer by photolithography to create etch-masks for holes. Subsequently, the wafer is immersed in KOH 30% solution for etching holes from both sides. The last step was dicing of the wafer resulting in the rigid meshes with outer dimensions corresponding to those of the silicon chip cavity. The technological fabrication sequence of silicon meshes is shown in figure 4 and a photograph of the manufactured meshes is shown in figure 5.

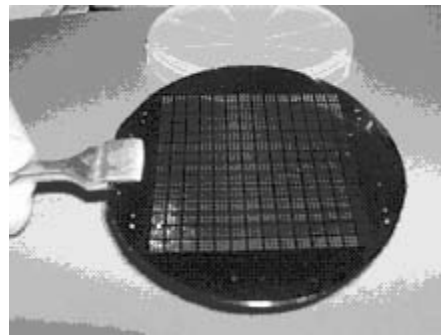


Fig.5. Mass produced silicon meshes

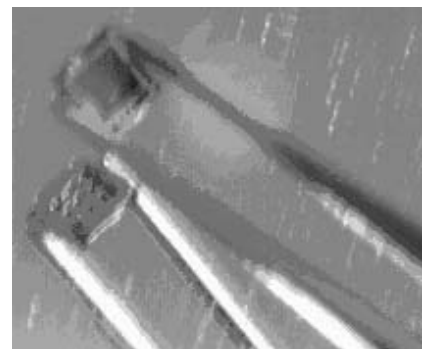


Fig.6. Built-up piezoresistive pH sensor

4.3. Sensor assembly

In this process, the 40μm thick gel was placed inside the cavity of a commercial pressure chip (AE series, Aktivsensor, Stahnsdorf, Germany). Membrane dimensions are 3x3mm² with a

thickness of 20 μm . In order to complete the sensor, the rigid mesh made by silicon micromachining technique was bonded to the chip using two-component epoxy. A photo of a built-up sensor is shown in figure 6.

4.4. Experimental validations of the model

First, the sensor diaphragm deflection was measured using Nano Microscan method (NMS). In this measurement, pH solutions were poured into and drawn out of the sensor successively. For the measurement of the sensor output voltage, which is a main characterization of piezoresistive pH sensor, a voltage of 5V is applied to sensor. Output voltage is displayed on a multimeter and the measurement data is acquired by computer. These measurements have been described in details in [12].

5. RESULTS AND DISCUSSIONS

5.1. Membrane deflection

Firstly, we look at the sensor membrane deflection, which is a direct result of hydrogel swelling. Figure 7 shows the membrane deformation obtained by both FEM (ANSYS) and NMS. The illustrated pictures are according to strain case of 34%, which is the maximum strain of hydrogel in this work and equivalent to pH11. Both images are correlative with each other and revealed that the sensor, namely the silicon membrane, exhibited good response under swelling of PVA/PAA gel. The maximal membrane deflection was calculated as 15.1 μm while the measured value was about 14.3 μm for this case.

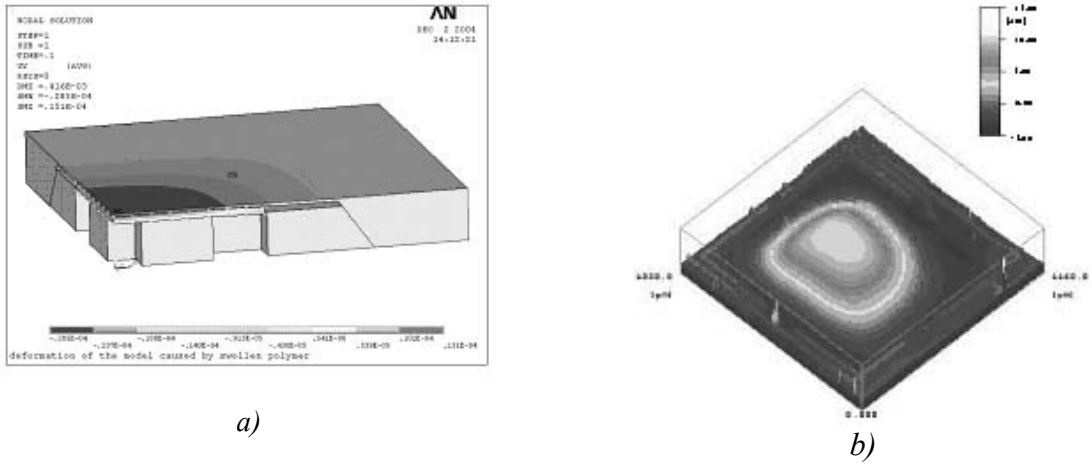


Fig. 7. Sensor membrane deflection: a) FE simulation, b) measurement

Figure 8 shows the comparison between the calculated and measured deflection corresponding to hydrogel strain and pH value in the range of 4 to 11. There is a leap between pH4 and pH5 in this graph because transition occurs here when pH value rises above the dissociation constant of PAA ($pK_a = 4.7$). It means that the ionization process of polycarboxylic groups within the polymer network happened and created the electrostatic repulsion leading to a significant increase of swelling. In our case, the polycarboxylic groups were fully ionized at pH 11. That means that the gel gets the maximum expansion here. As can be seen from figure 8, the measured membrane deflection appeared to be well-suited for the calculations.

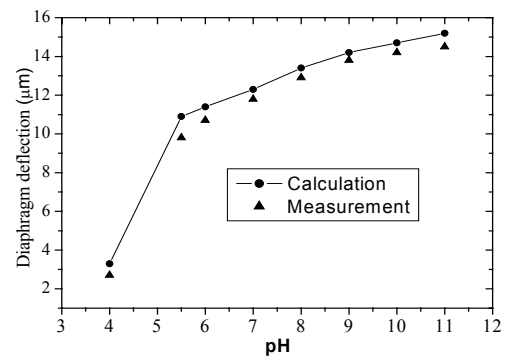
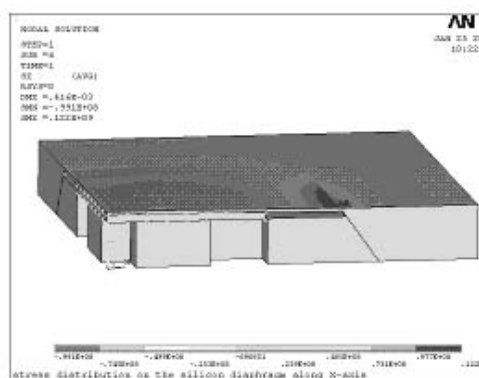


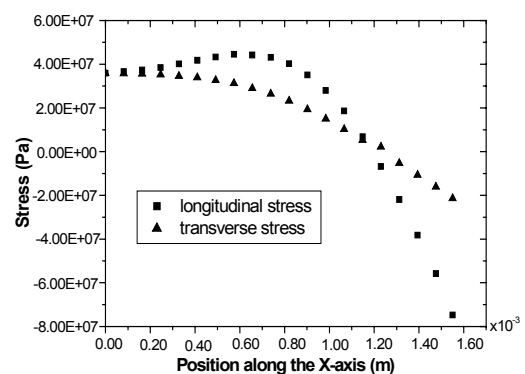
Fig.8. Comparison of calculated and measured of silicon membrane deflections

5.2. Membrane stresses and output voltage

Here, the silicon membrane stress obtained by ANSYS, shows a plot of the stress contours of silicon membrane for the case of the highest hydrogel strain value of 34% is shown in figure 9a. Due to the symmetry involved in the problem, the in-plane stress along the Z-direction and X-direction of silicon membrane were found to be exactly equal to each other. The plot of longitudinal and transverse stresses along one direction for this case is also presented in figure 9b.



a)



b)

Fig. 9. Stress distribution in sensor membrane:
a) contour plot, b) longitudinal and transverse stress

It is seen from this plot that the longitudinal stress gradient is higher than the transverse one. The maximum stresses, corresponding to the hydrogel’s maximum strain, are two orders of magnitude less than the maximum tensile strength of silicon ($\sigma_{\text{yield}} = 7 \text{ GPa}$). Thus, the pH sensor can operate safely in the pH range 1...11. Based on these results, the sensor output voltage can be predicted using eq. (6).

A measurement result of long term sensor output voltages using changes in pH values from 1 to 12 and vice versa is shown in figure 10.

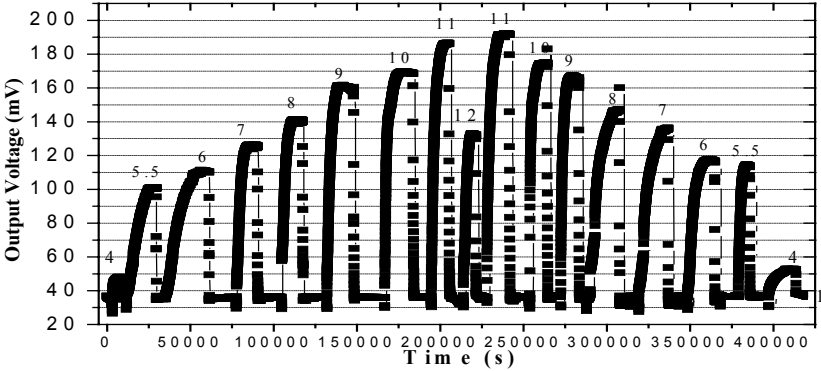


Fig. 10. Long-term sensor output voltage

In this measurement pH1 solution was used as reference. The sensor output voltage show a reproducible response to pH value changes.

Increase and following decrease of pH causes a slight hysteresis. Similar to deflection graph, there is a large difference of the output voltage near pH4. With increasing pH, the ionization degree is going up and hence the output voltage increases. However, as the pH further increases, the gel swelling tends to decrease due to the osmotic pressure difference of free ions inside and outside decreases. As a result, when the pH value exceeds 11, the effect of ionic strength surpassed the effect of the electrostatic repulsion between the polycarboxylate groups making the gel deswelling and consequently leading to the lower output voltage at pH 12.

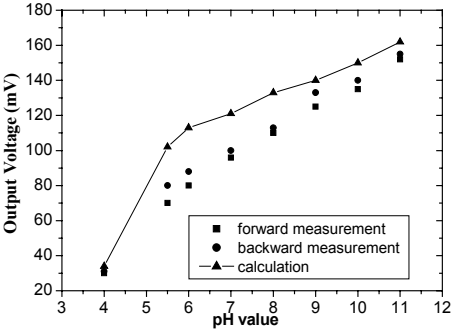


Fig.11. Comparison of calculated and measured sensor output voltages versus pH

Measured and calculated output voltages show good agreement between simulation and experiment results of this output characterization (fig.11).

5.3. Sensitivity and response time

Sensitivity and response time are main criteria of a sensor. As can be seen from the long term output voltage the sensor sensitivity was about $30\mu\text{V}/\text{pH}$ in the pH range above the dissociation constant of PAA.

The sensor response time is illustrated in figure 12a for pH5.5 and pH11 solutions (measurements started at pH1). Because of the rate-limiting of diffusion processes, the mechanical readjustments of gel depend on the pH range. As a result, the response time at pH5.5 is longer than at pH11. It is probable that the much more amount of hydroxyl groups in high pH solutions leads to the stronger and faster ionization process and results in the faster response time at pH11. The calculated results of this characterization are shown in figure 12b for comparison. It can be seen that the measured response time is evaluated about four times longer than the calculated one for both cases. Possibly, this difference is caused by using free-swelling experiments for the simulation problem. It should be reminded that gel was immersed alone into the solution in this experiment, the diffusion process and hence the response took place more quickly. However, when placed in silicon chip, the gel was clamped in a very small volume of sensor cavity leading to the difficult penetration of solution ions into polymer network, therefore resulting in the longer response time. In addition, the gel extension was assumed happening immediately. Due to the reasons mentioned in section 3.1 the sensor response time can be improved by using the thinner hydrogel layer. However, it must be correlative with the silicon membrane thickness for sufficiently good agreement.

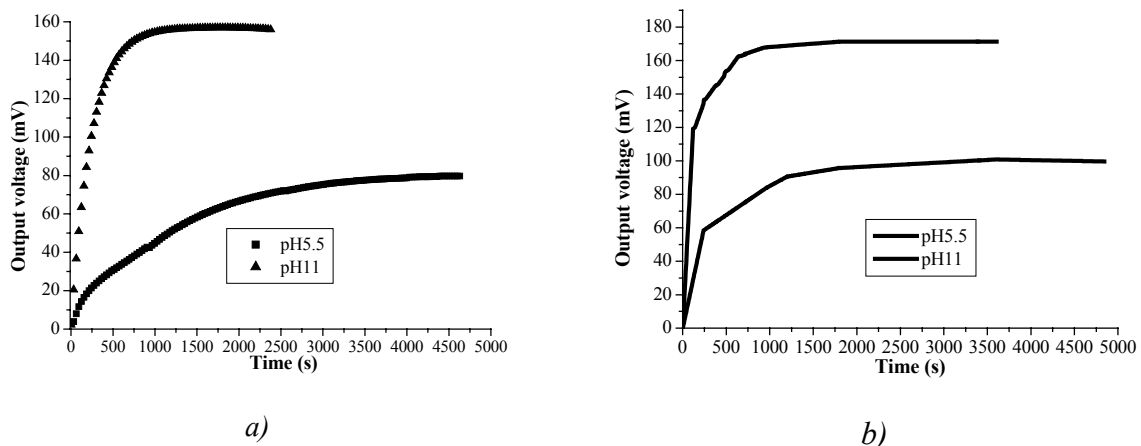


Fig.12. Time dependent sensor output voltage: a) measurement, b) FE calculations

6. CONCLUSIONS

Evaluations of the output characterisations of the silicon piezoresistive pH sensor have been performed. The sensor operational principle relies on the pH sensitive swelling of poly(vinyl alcohol)-poly(acrylic acid) (PVA-PAA) hydrogel. The hyperelastic model applied for polymer hydrogel was used to simulate the sensor behaviour by finite element method (ANSYS). Free swelling experiments and mechanical tests of PVA-PAA hydrogel have been carried out in order to prove the simulation results. The pH sensors have been realised using a rigid mesh fabricated by micromachining technology. The main sensor characteristics, such as silicon membrane deflection, output voltage and response time have been computed and measured. A relatively good agreement was found in comparing static simulations and experimental results.

ACKNOWLEDGEMENTS

This work was supported by German Research Council (DFG) as project C11 of SFB 287. The authors also would like to thank Dipl.-Ing. Marco Luniak of the Electronics Packaging Laboratory (IAVT) for performing the nanofocus microscan measurements.

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