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## Macroporous Smart Hydrogels for Fast-responsive Piezoresistive Chemical Microsensors

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### Abstract

Within this work we present the synthesis and characterization of a pH-sensitive macroporous p(AAm-co-AA) hydrogel with an interconnected channel structure to enhance diffusion of aqueous solutions. The hydrogel is characterized by SEM and mercury porosimetry. Furthermore, the hydrogel is successfully integrated into piezoresistive microsensors measuring the hydrogel swelling due to pH changes. A response time reduction of about 80% compared to sensors with conventional non-porous hydrogels is accomplished.

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*Keywords: microsensor; macroporous hydrogel; chemical sensor; response time*

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### 1. Introduction

The rapidly expanding fields of biomedicine and biotechnology necessitate the development of new smart biocompatible, long-term stable sensor concepts for rapid, cost-effective detection of specific analytes like pH, glucose, proteins and many more [1]. Microdevices with integrated smart hydrogels into a MEMS platform show great potential to meet these requirements. However, hydrogel-based devices which employ hydrogels as chemo-mechanical transducers, and therefore, exploit the volume-phase transition, suffer from long response times due to diffusion-driven processes which primarily determine hydrogel swelling kinetics [2]. This is a serious drawback for the commercialization of hydrogel-based sensors [3]. In this paper we follow a promising route for the reduction of the characteristic response time, i.e. the introduction of an interconnected channel structure into the hydrogel network. Although, chemists

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already proposed this route years ago [4], the utilization in real devices is surprisingly low and not yet reported for MEMS-based chemical microsensors. In this paper we present the synthesis and characterization of a pH-sensitive macroporous poly(acrylamide-co-acrylic acid)-hydrogel (p(AAm-co-AA)) by free-radical copolymerization in the presence of a porogen, the linear polymer Polyethylene glycol (PEG).

## 2. Experimental

### 2.1. Hydrogel synthesis

*Non-porous poly(acrylamide-co-acrylic acid) p(AAm-co-AA):* 1 g Acrylamide (AAm) and 0.3041 g Acrylic acid (AA) were dissolved in 2 g distilled water and mixed with an aqueous solution of 0.0544 g *N, N, N', N'*-Tetramethylethylenediamine (TEMED) and 0.0197 g *N, N'*-Methylenebisacrylamide (BIS) in 1.5 g distilled water. The monomer mixture was filled in an ice-cooled three-necked flask. After stirring for 20 minutes under nitrogen atmosphere, a solution of 0.0865 g Sodium peroxodisulfate in 0.5 g distilled water was added to the monomer solution. The reaction solution was immediately filled in a cooled glass capillary.

*Porous poly(acrylamide-co-acrylic acid) p(AAm-co-AA):* A solution of 1 g AAm, 0.3041 g AA, and 0.4173 g Polyethylene glycol with molecular weight  $M_n = 6000 \text{ gmol}^{-1}$  (PEG 6000) as the porogen, and 2.5 g distilled water was mixed with a solution of 14  $\mu\text{l}$  TEMED, 0.0282 g BIS, and 1 g distilled water. The monomer porogen mixture was filled in an ice-cooled three-necked flask. After stirring for 20 minutes under nitrogen atmosphere, a solution of 0.0216 g Sodium peroxodisulfate in 0.5 g distilled water was added to the monomer porogen solution. The reaction solution was immediately filled in a cooled glass capillary.

After 24 hours all hydrogel samples have been placed in distilled water for 5 days to remove uncrosslinked (sol) fractions and the porogen. The water has been refreshed everyday.

### 2.2. Hydrogel characterization

The synthesized and washed samples of porous and non-porous p(AAm-co-AA) have been freeze-dried (in the water-swollen state), coated with platinum, and investigated with a “Zeiss Neon 40 EsB” Scanning Electron Microscope.

Furthermore, mercury porosimetry was carried out for freeze-dried porous and conventional non-porous hydrogels with a “Porosimeter 2000” (max. pressure 2000 bar) to determine the pore size and pore size distribution. For porosity analysis a contact angle  $\theta = 140^\circ$ , a surface tension  $\chi = 480 \text{ dyn cm}^{-1}$ , and a mercury density  $\rho_{\text{Hg}} = 13.545 \text{ gcm}^{-3}$  (at 20.5 °C) have been considered.

### 2.3. Piezoresistive microsensor

The hydrogel-based piezoresistive microsensor is generally build up on two main components: (i) a piezoresistive pressure transducer ( $5.1 \times 5.1 \text{ mm}^2$ ) measuring the pressure due to hydrogel swelling, and (ii) the pH-sensitive p(AAm-co-AA) hydrogel layer ( $0.9 \times 0.9 \times 0.25 \text{ mm}^3$ ). The hydrogel is confined in the chip cavity (380  $\mu\text{m}$  deep) between a 20  $\mu\text{m}$  thin silicon bending plate and a rigid support mounted on a modified TO8 package as schematically illustrated in Fig. 1. A detailed description of the sensor setup can be found in [4].

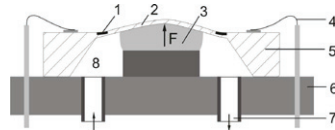


Fig. 1: Schematic cross-sectional view of the piezoresistive chemical microsensor: **1** piezoresistors, **2** 20  $\mu\text{m}$  Si bending plate, **3** p(AAm-co-AA) hydrogel layer, **4** electrical interconnect, **5** Si pressure sensor chip, **6** modified TO8 package, **7** fluidic inlet/outlet, **8** analyte solution.

### 3. Results

#### 3.1. Hydrogel characterization

SEM analysis results clearly reveal that the utilization of PEG 6000 as a porogen leads to an open-porous interconnected network structure (Fig. 2a). The characteristic intrusion curves of the mercury porosimetry (Fig. 2b) show a distinct difference which indicates the different network morphology. From the data of these curves the pore size distribution was calculated (Fig. 2c) using the Washburn equation. The analysis results of non-porous hydrogels show a wide distribution of pore sizes which results from the intrinsic interstices in the gel (nm-range), and pores due to freeze-drying ( $>10\mu\text{m}$ ). In contrast, a narrow pore size distribution with a mean pore diameter of 3.3  $\mu\text{m}$  was found for the porous hydrogel, which is perfectly confirmed by the SEM results.

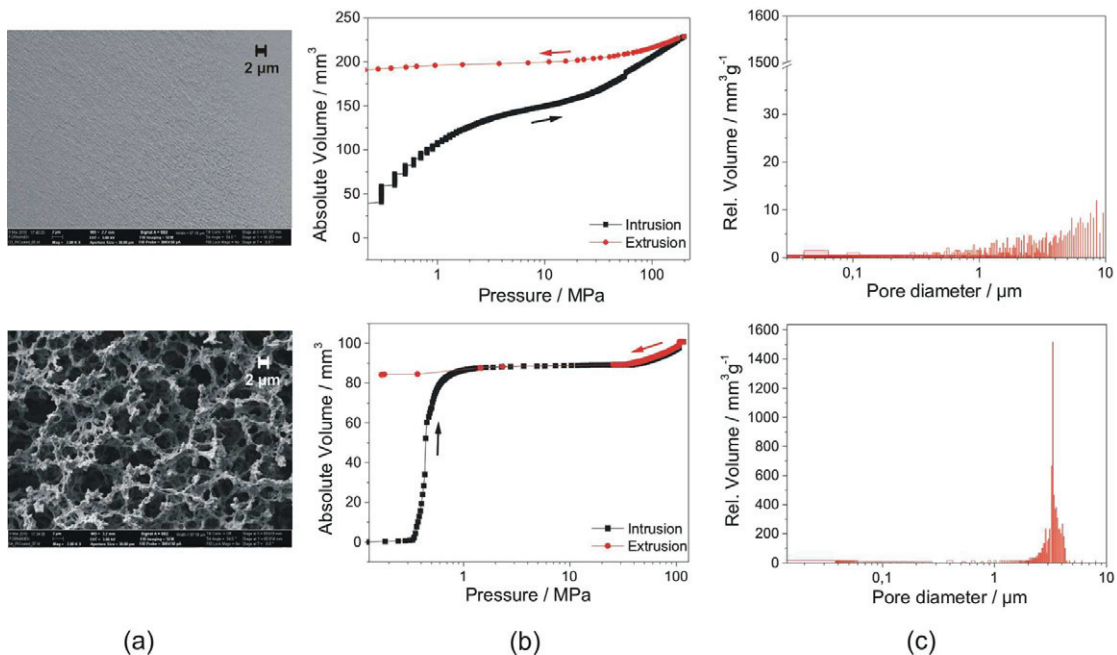


Fig. 2: Results of SEM analysis and mercury porosimetry measurements of non-porous (top) and porous p(AAm-co-AA) hydrogels (bottom); (a) SEM images (Magnification: 2000, scale bar 2 $\mu\text{m}$ ), (b) Intrusion/Extrusion curves, (c) Pore size distribution calculated from the data of (b) by the Washburn equation.

### 3.2. Sensor performance

Fig. 3a shows the normalized time-dependent sensor output signal for a pH transition between pH 7 and pH 5 for the conventional non-porous and the macroporous hydrogel. For the sensor using the macroporous hydrogel the equilibrium of the sensor signal is reached about 5 times faster compared to a sensor with non-porous hydrogel. The water loss during the shrinking process is also more pronounced for the macroporous hydrogel due to the higher water content at equilibrium because of the porous network structure (higher sensitivity). The sensor output signal for cyclic pH changes between pH 5 and pH 7 for the macroporous hydrogel (Fig. 3b) reveals a stable and reproducible sensor performance.

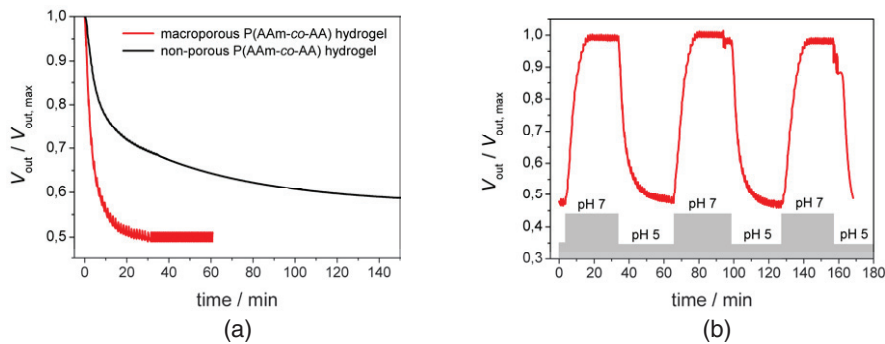


Fig. 3: Time-dependent normalized sensor output signal; (a) output signal of macroporous and non-porous p(AAm-co-AA) hydrogels for a pH change between pH 7 and pH 5, (b) normalized sensor output signal for cyclic pH changes between pH 5 and pH 7 for the macroporous hydrogel.

### 4. Conclusions

Macroporous p(AAm-co-AA) hydrogels were synthesized by use of PEG 6000 as a porogen. A mean pore diameter of 3.3  $\mu\text{m}$  was determined by mercury porosimetry and approved by SEM analysis. The macroporous hydrogel was integrated into a piezoresistive microsensor. A response time reduction of about 80% was observed compared to sensors with non-porous hydrogels.

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