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Chang-Soo Kim

Missouri University of Science and Technology, ckim@mst.edu

Jongwon Park

Xinbo He

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An Intelligent Dissolved Oxygen Microsensor System with Electrochemically Actuated Fluidics

Jongwon Park, Xinbo He, Chang-Soo Kim

Dept. of Electrical & Computer Engineering, University of Missouri-Rolla, USA, jp7r9@umr.edu

Dept. of Electrical & Computer Engineering, University of Missouri-Rolla, USA, xhfxd@umr.edu

Depts. of Electrical & Computer Engineering and Biological Sciences, University of Missouri-Rolla, USA, ckim@umr.edu

Abstract

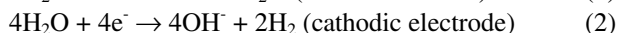
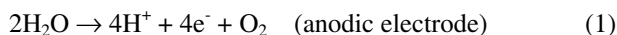
A new dissolved oxygen monitoring microsystem is proposed to achieve *in situ* intelligence of the self-calibration by using an electrochemically actuated fluidic system. The electrochemical actuation based on water electrolysis plays two critical roles in the proposed microsystem. First, the electrochemically generated gases serve as the calibrants for *in situ* 2-point calibration/diagnosis procedure of the microsensor in a chip. Secondly, the electrochemical generation and collapse of gas bubbles provide a driving force of the bidirectional fluidic manipulation for sampling and dispensing of sample solution. A microsystem including a dissolved oxygen micromicroprobe, electrochemical actuators, and a fluidic structure are prepared by microfabrication technology and its performances are characterized.

Keywords

oxygen, hydrogen, water vapor, electrolysis, bubble.

INTRODUCTION

A proper *in situ* diagnosis and/or calibration technology should be developed to overcome the instabilities of biochemical sensors such as baseline drift and sensitivity degradation. An “electrochemical actuation” based on water electrolysis can provide novel functionalities to several types of biochemical microsensors. The electrolysis reactions occurring at the anodic and cathodic calibration electrodes are as follows:



Recently an approach to manipulate the oxygen microenvironment for *in situ* self-diagnosis of dissolved oxygen microsensor was reported [1]. A calibration electrode was integrated in proximity of the amperometric dissolved oxygen sensor with no oxygen permeable membrane. This initial design, however, suffered from the pH artifact, as in the reactions (1) and (2), and the supersaturation of electrochemically generated dissolved oxygen at the microenvironment during the electrolysis. Although the pH artifacts can be circumvented by employing an oxygen permeable membrane to the oxygen

sensor (i.e. being a Clark type sensor) or using other types of sensors immune to pH, still the influence of supersaturation needs to be solved.

Another application of the electrochemical gas generation is to provide mechanical forces for microsystems. Several electrochemical microactuators have been reported for several exemplary fluidic devices. Gas pressure was electrochemically generated to change the deflection of micromechanical diaphragms [2, 3, 4] or to operate valve structures [5, 6, 7]. A micromachined electrochemically driven syringe, capable of bidirectional fluidic motions, was introduced as well [8, 9].

We adopted the gas bubble generation technique to achieve the *in situ* sensor calibration and the bidirectional fluidic sampling and dispensing simultaneously. A fluidics chip composed of an elastic cover layer, an electrode substrate, and a commercial fiber optic oxygen microprobe, was fabricated and characterized.

EXPERIMENTS

Figure 1 shows simplified microsystem operation. A pair of calibration electrodes generates oxygen and hydrogen bubbles galvanostatically within a fluidic channel to allow the 2-point *in situ* diagnosis/calibration procedure. The sensor tip was sequentially provided a high-point diagnosis/calibration environment being established within an oxygen bubble (100% oxygen) and a low-point environment within a hydrogen bubble (0% oxygen). These bubbles also serve as indicators of the flow driven by the bubble volume expansion generated within the actuation chamber.

The electrochemically actuated syringe is based on the fluidic displacement during the gas bubble generation according to the reactions (1) and (2). The syringe (water electrolysis cell) consists of a pair of an actuation chamber (oxygen bubble chamber) and its counter-chamber, and a pair of calibration electrodes. The volume of bubbles can be controlled galvanostatically for reproducible fluidic manipulations with appropriate actuation currents (magnitude and/or duration). The area of the counter electrode was about five times larger than that of the actuation electrode to reduce the current density, thereby

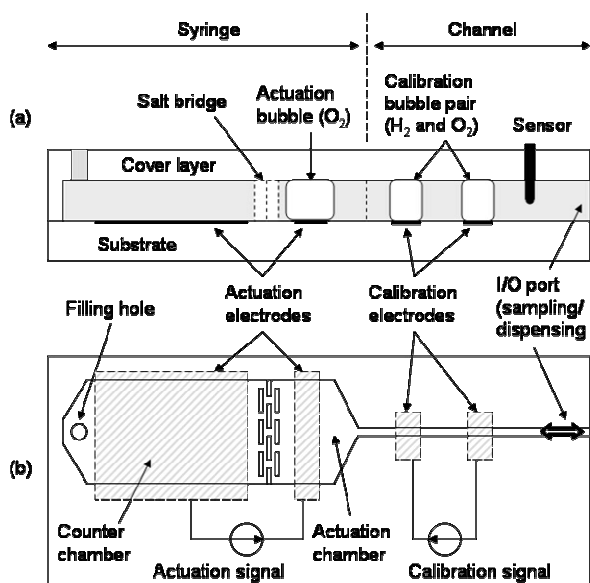


Figure 1. (a) A simplified cross-section and (b) a layout of the fluidics chip composed of an on-chip syringe (sampling and dispensing of sample solution) and an on-chip calibrator (2-point *in situ* self-diagnosis/self-calibration of oxygen microsensor). Both the syringe and the calibrator is based on an electrochemical actuation (water electrolysis). A commercial fiber optic microprobe was used.

minimizing undesirable volume expansion due to the hydrogen bubble generation in the counter chamber. With proper actuation current with reverse polarity, the oxygen bubble can be collapsed to react back to water. The resulting reverse flow drives the sample solution to flow into the microsystem through the I/O port. The overall size of the fluidics chip was relatively large to initially test out the proposed concept. The volume of the actuation chamber was about 50 μl . The width and length of the channel were 1.5 mm and 15.0 mm, respectively. The height of the syringe and channel cavities was about 200 μm .

The filling hole was used to initially fill the syringe cavity and the channel with sample solution and was sealed off. The I/O port is for the sampling/dispensing of sample solution. A salt bridge structure was designed between the chambers to effectively separate the gases by providing a diffusion barrier, while maintaining an electrical contact.

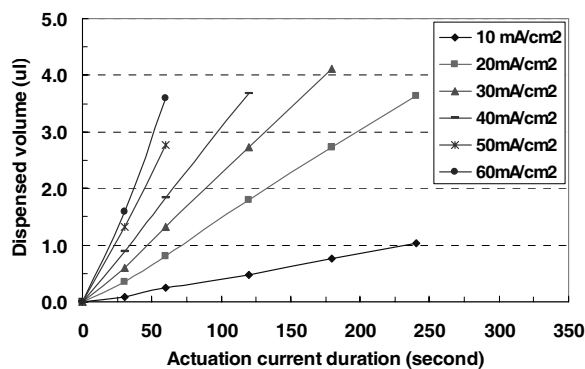
The chip consists of a cover layer, a substrate, and a sensor microprobe. A thick photoresist (MicroChem, SU-8) was used to prepare a template for the molding process of a polydimethylsiloxane (PDMS) cover layer (Corning, Sylgard 184) to define the fluidics structure. The thick photoresist was patterned on a borosilicate glass substrate to have a thickness of about 200 μm . The PDMS was cast onto the glass substrate and cured for 24 hours at room temperature in a vacuum desiccator. The thickness of the PDMS cover layer was about 75 μm . The substrate was a

silicon wafer with a silicon nitride layer coating. A platinum/titanium thin film (150 nm/25 nm) was deposited by e-beam evaporation and patterned by lift-off technique to define the electrode. The PDMS cover layer was attached to the substrate by simply pressing on the substrate to seal the interface between the PDMS and the silicon nitride layer. The relatively large fluidics patterns on the cover layer allowed a manual alignment with the electrode substrate.

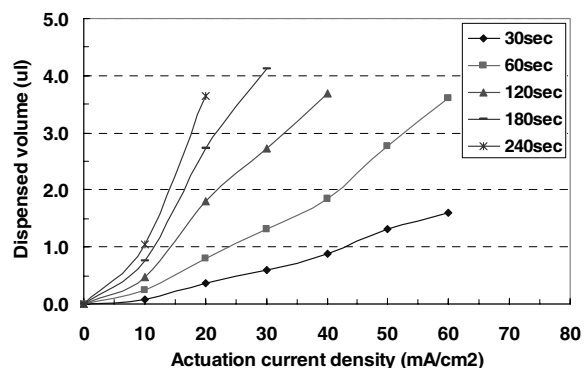
A commercial fiber optic oxygen microprobe (WPI MicroTip) was located in the channel. The microprobe was positioned with a micromanipulator to be perpendicular to the channel to access to the sample solution. The sensor measures the luminescence lifetime of immobilized luminophore as the oxygen dependent parameter to avoid problems that are inherent with intensity-based measurements [10]. This sensor was chosen due to its small microprobe size and immunity to pH. Before the fluidics measurement, a standard sensor calibration procedure was performed with nitrogen-saturated and air-saturated solutions according to the manual [10]. Shortly after this procedure, the microprobe was inserted to the fluidics channel. A pair of calibration bubbles (oxygen and hydrogen) was formed at the anodic and cathodic calibration electrodes by a galvanostatic operation. The calibration current was turned off after the generation of the calibration bubbles. Time responses of the sensor were obtained as the calibration bubbles move along the channel during the volume expansion of the actuation bubble (oxygen). The high-point calibration was made with the distal tip of the microprobe being enclosed in the oxygen bubble and the low-point calibration in the hydrogen bubble. The sample solution used was 0.1 M K_2SO_4 throughout all experiments.

RESULTS AND DISCUSSION

By gently pressing the PDMS cover layer onto the substrate, the elastic and “sticky” cover layer made a satisfactory sealing with the substrate surface without causing a leakage problem. The presence of the microprobe tip within the channel hardly interrupted the movement of bubbles and solution since the diameter of the distal tip was only about 50 μm . Two important parameters in the microfluidic actuation will be the duration and magnitude of the actuation current. Figure 2 (a) and (b) show the dispensed volumes with respect to the actuation current. The volume expansion of oxygen actuation bubble (hence the dispensed solution volume) had a reasonably good linear relationship with respect to the duration and density of the actuation current. Compared to the dispensing rate, the rate of solution withdrawal was much smaller. The most likely explanation for this fact is the difficulty in effective contact of the electrode with the solution to let the oxygen to react back to water [9]. In actual applications, the frequency of this combined procedure of actuation and



(a)



(b)

Figure 2. Dependence of the dispensed solution volume on (a) the actuation current density and (b) the actuation current density. An oxygen bubble was generated in the actuation chamber of the syringe to provide a driving force of the displacement of solution through the channel.

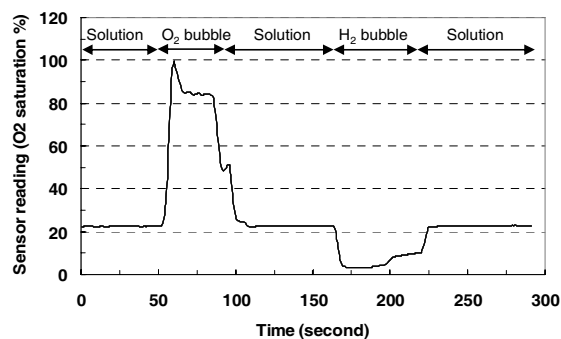
calibration can be determined depending on the stability of sensor during operation.

Figure 3 shows a typical time response of the sensor. The sensor readings showed a rapid increase just after the contact of the microprobe tip with the oxygen bubble, while it showed a decrease in the hydrogen bubble. The flat responses, before and after the calibration bubble phases, represent the oxygen partial pressure of air-saturated sample solution (21% oxygen). A steep decrease of the oxygen bubble response was observed during the oxygen bubble phase. These facts suggest a possible inter-diffusion of the oxygen (from the bubble to the solution) and water vapor (from the solution into the bubble). The oxygen partial pressure (pO_2) at a given temperature can be described as follows;

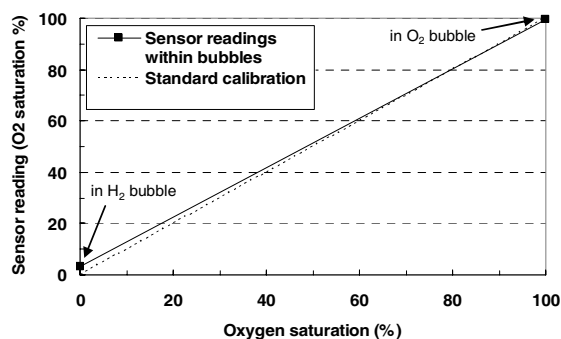
$$pO_2 = O_2 \text{ fraction} \times (\text{Barometric pressure} - p_{H_2O}) \quad (3)$$

in which the O_2 fraction and the p_{H_2O} mean the volume ratio of oxygen in the sample media (e.g. 0.21 in the air)

and the partial pressure of water vapor, respectively. Without further calibration current (i.e. no more oxygen supply), a decrease in O_2 fraction and an increase in p_{H_2O} within the oxygen bubble can cause a decrease in pO_2 . A gradual increase of the response during the hydrogen bubble phase (i.e. recovery to the air-saturation level) suggests the oxygen diffusion from the solution into the hydrogen bubble. These facts should be taken into account for the precise calibration procedure for either gaseous or dissolved oxygen. To achieve the novel *in situ* self-calibration/self-diagnosis functionality, a more thorough investigation will be required to find the optimum calibration current (density and duration) based on understanding of the diffusion behaviors of the related species (oxygen, hydrogen, and water) and the dynamic internal pressure of electrochemically generated bubbles at a given channel geometry.



(a)



(b)

Figure 3. (a) A typical time response of the microsensors obtained in the fluidics chip and (b) a comparison of calibration results obtained with the standard procedure (---) and with the fluidics chip (—). The sensor properly responds to the oxygen microenvironments with respect to the location of the gas bubbles (and the air-saturated sample solution (0.1 M K_2SO_4). The initial values from the time responses (i.e. the highest value during the oxygen bubble phase and the lowest value during the hydrogen bubble phase) were plotted in the fluidics chip curve.

CONCLUSION

A simple fluidic structure with actuation electrodes has been adopted in this study to test the feasibility of using the controlled oxygen microenvironment within the channel for a novel functionality. The system demonstrated sensor readings comparable to those obtained by the standard calibration procedure. The use of a simple fluidic structure combined with the water electrolysis was able to circumvent the influence of supersaturation as in the previous study [1]. Further studies are needed on the influence of water vapor and the internal pressure of bubbles. The method is regarded to be potentially applicable to oxygen and hydrogen gas sensors for both gaseous and dissolved phases.

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