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# Electrochemical and Hydrodynamic Interferences on the Performance of an Oxygen Microsensor with Built-in Electrochemical Microactuator

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## Abstract

*An in situ self-diagnostic technique for a dissolved oxygen microsensor is proposed in an effort to devise an intelligent microsensor system with an integrated electrochemical actuation electrode. With a built-in platinum microelectrode that surrounds the microsensor, two kinds of microenvironments (oxygen-saturated or oxygen-depleted phases) can be created by water electrolysis depending on the polarity. The functionality of the microsensor can be checked during these microenvironment phases. The polarographic oxygen microsensor is fabricated on a flexible polyimide substrate (Kapton®) and the influences of electrochemical and hydrodynamic conditions on the sensor responses have been investigated.*

## Keywords

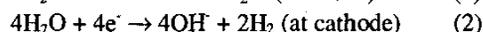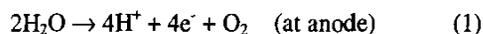Electrolysis, self-diagnosis, polyimide.

## INTRODUCTION

An ideal biosensor for long-term continuous monitoring should meet the following requirements: simple structure, immunity to motion artifacts, sufficient sensitivity for reliable measurements, robustness and stability over long periods of time, biocompatibility, and dependable diagnosis and/or calibration methods to check its functionality and accuracy. Apart from long-term stability or biocompatibility, it should be emphasized that development of a novel *in situ* diagnosis technique without any externally coupled apparatus is one obstacle to the realization of an unattended intelligent microsensor system. Consequently, we present a novel self-diagnosis concept for a dissolved oxygen microsensor by using an integrated electrochemical microactuator toward built-in intelligence of the microsensor system.

## ESTABLISHMENT OF ELECTROCHEMICAL MICROENVIRONMENT

The principle of the novel diagnosis method proposed herein is based on water electrolysis at noble metal electrodes as shown in Figure 1 [1]. Oxygen or hydrogen can be generated by the electrolysis of water in a controlled manner by applying voltage or current through a generating electrode (GE) and counter-generating electrode (GE').

Reactions occurring at the anode and cathode are as follows:

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2 \quad \text{(at anode)} \qquad (1)$$

$$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2 \text{ (at cathode)} \qquad (2)$$

Accumulation of these dissolved gas molecules at the generating electrode, in turn, rapidly establishes a microenvironment of oxygen saturation or hydrogen saturation. The accumulation and saturation of hydrogen molecules takes place after the depletion of oxygen. An oxygen microsensor in close proximity to the surrounded generating electrode can be confined in a controlled microenvironment. A two-point self-diagnostic procedure for the oxygen sensor can then be performed, with the high point diagnosis being established in an oxygen-saturated phase, and the low point diagnosis in an oxygen-depleted phase, respectively. These transient perturbations of the microenvironment are expected to equilibrate rapidly with the surrounding solution medium.
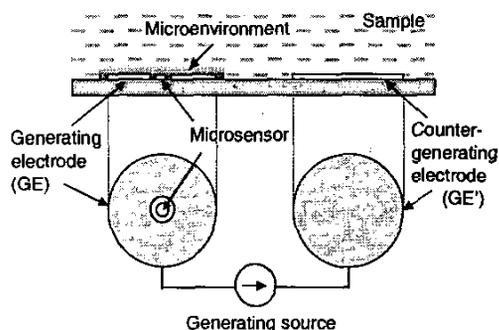


**Figure 1. Concept for a novel oxygen sensor with *in situ* self-diagnosis capability. The microenvironment is generated by a generating electrode (GE) which surrounds the microsensor. Oxygen-saturated or oxygen-depleted phases can be established by water electrolysis depending on the polarity.**

## EXPERIMENTS

We designed and fabricated polarographic micro-oxygen sensors on flexible polyimide substrates (Kapton®). The basic electrochemical three electrode cell configuration was adopted to avoid the ohmic voltage drop through the electrolyte between the anode and cathode. All elec-

trodes were designed to be geometrically symmetric to assure diffusional mass transport of electrochemical species in all radial directions. The conventional Clark oxygen sensor contains a reference electrode (RE) and a working electrode (WE) located in the same compartment filled with an internal electrolyte gel which is encapsulated by a hydrophobic, electrically non-conducting membrane. To circumvent the technical difficulties of photolithographic formation of the reliable double-layered membrane (electrolyte gel / hydrophobic membrane), we did not use any membrane in this study.

Figure 2 shows the layout and cross section of the concentric type electrode configuration. The middle electrode serves as the working electrode at which dissolved oxygen molecules are cathodically reduced. The generating electrode is wrapped around the working electrode; this configuration will establish oxygen-saturated or oxygen-depleted microenvironments during self-diagnosis phases. Proceeding from inside to outside, the next concentric circle can be used as the reference electrode. The outermost electrode in Figure 2 is the counter electrode (CE) of this three-electrode cell. It is placed at a distance from the working electrode to minimize electrochemical interference of byproducts generated at the counter electrode. The counter-generating electrode, not shown, is located even more remotely from the working electrode for this same reason.
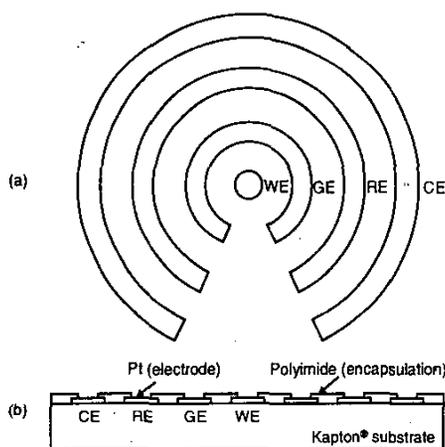


**Figure 2. Concentric 3-electrode oxygen sensor with total diameter of 200 micron meter, (a) Layout of exposed electrodes (not to scale), (b) cross-sectional view after fabrication on a flexible Kapton® substrate.**

The sensor was placed in a measuring vessel and the solution was saturated with different oxygen/nitrogen gas ratios at room temperature. Oxygen tension in the bulk solution was monitored with a commercial oxygen meter (Instech, SYS203). All measurements were done in a sta-

tionary solution to prevent any solution convectional effects.

A custom set of electrochemical instrumentation has been employed. A potentiostat (Gamry Instruments, FAS1) and a galvanostat (Gamry Instruments, 750) were used to bias the 3-electrode oxygen microsensor and to operate the generating electrodes, respectively. These two modules were plugged into one control PC and operated in a floating-ground mode to prevent electrical interference between the two modules. The cathodic potential for oxygen reduction (-0.7 V vs. Ag/AgCl) was chosen from the plateau region in a traditional voltammogram. To control the microenvironment near the working electrode of the oxygen microsensor, constant currents were forced between the pair of generating and counter-generating electrodes.

A script was written to perform a procedure for the establishment of microenvironments. The diagnosis procedure involved a simultaneous gas-generating phase during sensor operation. By this procedure, monitoring of any changes in the microenvironment during the preceding generating phase is possible by comparing real-time measurements with the sensor's baseline response, which reflects the background oxygen content. After each measurement, the solution was equilibrated to a defined baseline value by bubbling with a fixed ratio of oxygen and nitrogen gases and magnetically stirring.

### RESULTS AND DISCUSSION

The generating phase was performed during the normal operation of the sensor. Once the limiting current condition at a given bulk oxygen content had been achieved after application of the oxygen reduction potential to the sensor, the generating current were applied to the generating electrode for 90 seconds. The limiting current level (the baseline during the response) reflects the bulk oxygen content around the sensor. Various time responses during the generating phase are shown in Figure 3. Simultaneous operation of the potentiostatic instrument (for biasing the oxygen microsensor) and the galvanostatic instrument (for driving the generating current) produced a quasi steady-state response during the generating phase. It can be seen that the responses during each generating phase approaches the limiting current levels of the oxygen-saturated solution and then gradually returns to the original level of bulk oxygen content. As the generating current density increases the corresponding response increases. With the current density higher than 16 $mA/cm^2$, tarnish on the generating electrode surface and damage to the polyimide encapsulation were observed occasionally in some of the devices. For comparison the response to oxygen-saturation was recorded shortly after the completion of these measurements in the air-saturated case in the same solution.
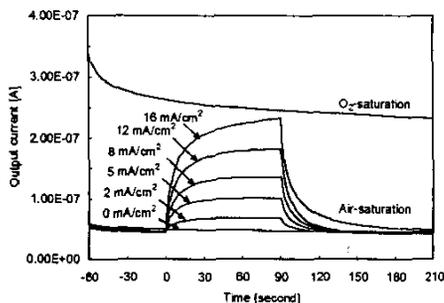
**Figure 3.** Typical quasi steady-state responses during the simultaneous oxygen-generating phase; effect of the oxygen-generating phase with various current densities in air-saturated phosphate buffer solution (pH 7.4, 10 mM), with a sensor response to oxygen-saturated solution for comparison.

At a given temperature, the limiting current magnitude in the oxygen-saturated solution (100% oxygen-saturation) is limited to 4.76 times of that in the air-saturated solution (21% oxygen-saturation) at 1 atm. During the generating phase with higher generating current densities, however, responses exceeding this limit were observed. The most plausible explanation for this is the supersaturation of the electrochemically generated oxygen in the microenvironment covering the working electrode [2]. The concentration of the electrochemically generated oxygen near the oxygen-evolving anode surface can exceed the standard oxygen solubility in water at 1 atm without the formation of gas bubbles. The pH changes in the microenvironments according to equations (1) and (2) are also expected to have contributed to this exaggerated response, since the oxygen catalytic activity of the platinum working electrode is influenced by pH [3]. Subsequently, the oxygen catalytic activity of the platinum working electrode should be enhanced by the lower pH induced in the microenvironment during this phase.

To observe the overall influence of.pH and supersaturation, the generating phase was performed in an oxygen-saturated solution. The lower curve in Figure 4 is a plot of the percent changes of response during the oxygen- generating phase with respect to the baseline at the oxygen-saturated solution. At the highest current density the response was almost doubled from the baseline (response to the oxygen-saturated solution), suggesting that either the stoichiometric coefficient was increased or supersaturation was established, or both. To further investigate the influence of the pH changes during the oxygen-generating phase, measurements were performed in solutions with different pH buffering capacities. The response magnitudes in a 1 mM buffer solution were most pronounced, which implies that in stronger buffer solutions the pH changes

were suppressed to minimize the perturbation of the stoichiometric coefficient of oxygen reduction. At the highest current density, the responses during the generating phase were similar with the oxygen-saturation value (theoretically 476%) in 10 mM and 100 mM buffer solution.
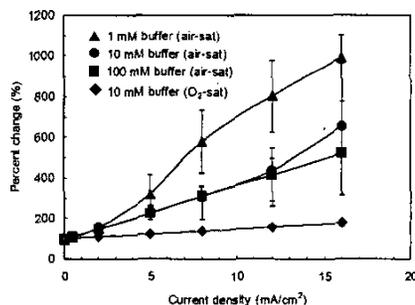


**Figure 4.** Percent changes in the sensor responses (ratio of the steady-state value at t=90 with respect to the base line at t=0) according to the oxygen-generating current density in various pH buffering capacities, with those in an oxygen-saturated solution for comparison.

Other factors may have contributed to the exaggerated responses; first, a considerable concentration-driven convection by the oxygen molecules diffusing from the generating electrode could enhance the mass transport of oxygen in the stagnant solution, thereby increasing the limiting current value of the oxygen-saturated solution. A second factor may be "feedback" of electrochemically generated oxygen generated from hydrogen peroxide [4], a byproduct of oxygen reduction at the working electrode. Hydrogen peroxide is being oxidized to oxygen at the anodic generating electrode and contributes to the oxygen-rich microenvironment.

$$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^- \qquad (5)$$
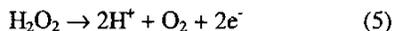
Thirdly, the possibility of temperature elevation around the microsensor due to high current densities. The generation of gas bubble has not been monitored during this study. Further analysis of these factors is necessary to adapt the proposed system for practical applications.

The effect of stirring on the microenvironment was also investigated. As expected, the magnitude of response diminished with energetic stirring of the solution as in Figure 5. The response of the same sensor without solution stirring is given for comparison. Note the increased baseline produced by stirring. This result allows us to ascertain that the contribution of electrical interference to the response by the potentiostat operating the oxygen microsensor and the galvanostat operating the generating electrode pair is negligible.
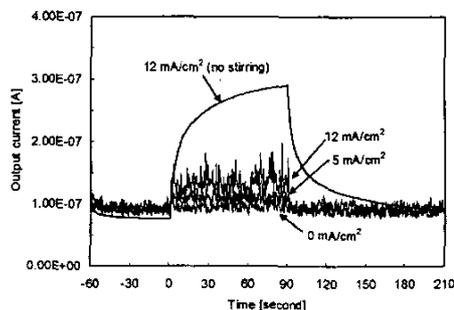
**Figure 5. Effect of vigorous solution stirring in air-saturated phosphate buffer solution (pH 7.4, 10 mM), with a sensor response to a stationary solution for comparison.**

Figure 6 shows the quasi-steady state responses during the oxygen-depleting phase. Analogous to the generating phase, the sensor responses during depleting phases approach the limiting current levels at nitrogen-saturation, followed by a return to the original level of bulk oxygen content. As the current density increases the corresponding response decreases. It should be noted that the responses with the current density higher than 5 mA/cm² remains without significant decrease beyond this level. This implies that the oxygen depletion has not been completely accomplished with the given electrode geometry over the entire current density range. The higher pH in the microenvironment during the depleting phase is assumed to further decrease the sensor response due to the reduction of catalytic activity of the working electrode to reduce oxygen.

## CONCLUSION

The concept of an *in situ* self-diagnosis for a dissolved oxygen microsensor is proposed in an effort to devise an intelligent microsensor system with an integrated electrochemical actuation electrode. The sensor responds properly during both the oxygen-generating and oxygen-depleting phases. Incorporation of a Clark type microsensor structure should minimize the effects of pH and hydrodynamic perturbation during this procedure. The integrated electrochemical actuator is a useful tool for achieving built-in intelligence of the dissolved oxygen microsensor.
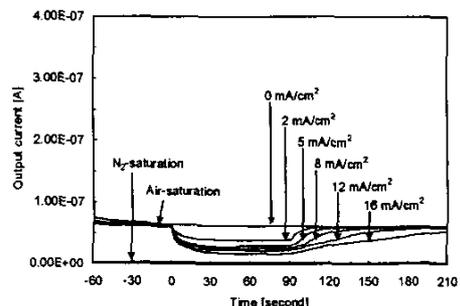


**Figure 6. Typical quasi steady-state responses during the simultaneous oxygen-depleting phase in air-saturated phosphate buffer solution (pH 7.4, 10 mM); effect of the oxygen-depleting phase with various current densities, with a sensor response to nitrogen-saturated solution for comparison.**

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