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Chang-Soo Kim

Missouri University of Science and Technology, [ckim@mst.edu](mailto:ckim@mst.edu)

Dae-Hyuk Kwon

Byung-Ki Sohn

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## A NEW PH-ISFET BASED DISSOLVED OXYGEN SENSOR

Chang-Soo Kim\*, Dae-Hyuk Kwon\*\* and Byung-Ki Sohn\*

\* Sensor Technology Research Center, Kyungpook National University, Taegu 702-701, KOREA

\*\* Dept. of Electronic Engineering, Kyungpook Sanup University, Kyungsan-gun 713-900, KOREA

### SUMMARY

A new dissolved oxygen sensor based on pH-ISFET has been discussed. A platinum working electrode surrounding a pH-sensing gate of the pH-ISFET electrolyzes dissolved oxygen, resulting in a corresponding pH change. The pH-ISFET can determine dissolved oxygen concentration through detecting this pH change.

### INTRODUCTION

There have been increasing interests in miniaturizing dissolved oxygen sensors for rapid response and on-line measurements. Lots of efforts have been made by using integration technology and micro machining technology. Miniaturization of the Clark type oxygen sensor[1-3], however, is difficult because the precise control of thickness and permeability of hydrophobic polymer gas membrane through which gas molecule can permeate is a critical problem, and composition of the internal filling solution in a small reservoir changes with use. Moreover, the decrease of sensor dimension inevitably results in a low signal-to-noise ratio[4] because the amount of signal current is directly proportional to the working electrode area.

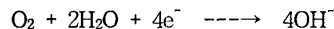
A feasibility study on a simple alternative approach by incorporating a pH-ISFET without gas permeable membrane has been described in this paper.

### OPERATIONAL PRINCIPLES

The combination of a potentiometric sensor principle with that of an amperometric sensor leads to the sensing principle of a new dissolved oxygen sensor based on a pH-ISFET.

A conventional amperometric Clark type sensor reduces an oxygen molecule by the following reaction at working electrode(cathode) surface when the working electrode is held at reduction potential

of oxygen versus the reference electrode(anode).



An electrochemical current flows between the two electrodes, giving current output related to the dissolved oxygen concentration. A pH change by the generation of hydroxyl ions(OH<sup>-</sup>) as well as a current flow between the two electrodes occurs simultaneously. The conventional Clark type oxygen sensor determines dissolved oxygen concentration by measuring this electrochemical current, while a pH change is of importance in the proposed sensor.

When the working electrode surrounds a pH-sensing gate of a pH-ISFET as shown in Figure 1, a pH variation due to oxygen reduction will occur at a small local area in close proximity to the pH-sensing gate. The pH-ISFET, a well-known pH sensor, then detects this pH

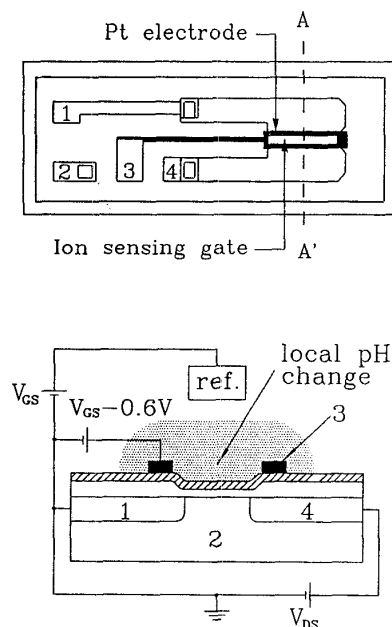


Figure 1. Cross-section and layout of a sensor chip.(1.source 2.substrate 3.Pt working electrode 4.drain, not to real scale)

variation that is logarithmically proportional to the oxygen content. This method is very attractive because the sensor can be used as either a pH sensor or a dissolved oxygen sensor whether the working electrode that surrounds the pH-sensing gate is used or not.

### EXPERIMENTAL & RESULTS

Figure 2 is a voltammogram of the two electrode system which is composed of a platinum working electrode and a Ag/AgCl reference electrode. The Ag/AgCl reference electrode used was not an integrated one but a sleeve type single junction electrode. In the curve of air-saturated solution, a plateau around  $-0.6V$  means that the reduction of oxygen occurs ideally.

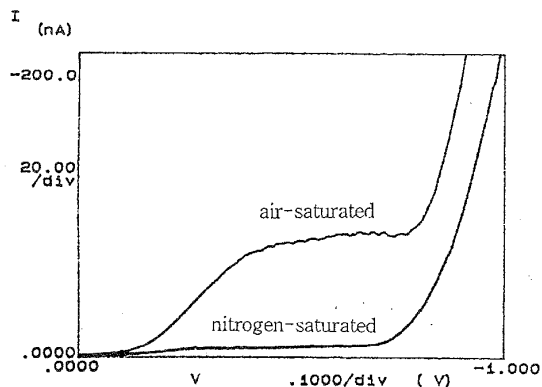


Figure 2. Voltammograms measured in nitrogen-saturated and air-saturated solution.

The sensor was immersed in a sample solution and operated in constant drain current ( $I_{ds}=150\mu A$ ) and constant drain voltage ( $V_{ds}=3V$ ) mode with only a Ag/AgCl reference electrode at first. An output voltage shift of the sensor began when a  $-0.6V$  voltage pulse, reduction potential of oxygen, was applied to the working electrode. This voltage shift occurred even in a nitrogen-saturated solution which contained no dissolved oxygen to be electrolyzed. This is considered to be a change of electric field which is caused by the two gate electrodes (reference and working electrode) having different potentials, thereby changing the bias condition of the FET device. This can be seen in Figure 3. In Figure 3, a solid line and a dashed

line correspond to the  $I_{ds}$ - $V_{ds}$  characteristics of the FET operating with reference electrode only and reference and working electrode together, respectively.

The voltage shift increased as the dissolved oxygen content in solution increased, when the pulse was applied. This voltage increment corresponds to the pH variation near pH-sensing gate according to the oxygen reduction. The output reaches a steady-state within about one minute and then returns to the initial position as the pulse is removed.

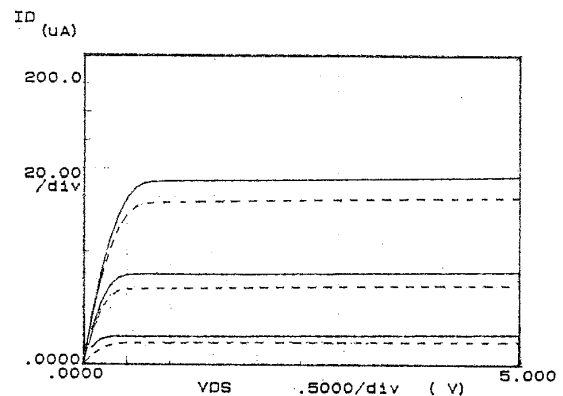


Figure 3.  $I_{ds}$ - $V_{ds}$  characteristics of the sensor operating with reference electrode only (—) and reference and working electrode together (---)

Figure 4 is an calibration curve measured in phosphate buffer solution (pH7.4, 0.01M). All measurements in this study were made in a static solution to exclude any affects of flow or agitation of the solution. It is suggested that the increase of working electrode area leads to a higher sensitivity[5] as the more hydroxyl ions can be generated.

### DISCUSSION

Table 1 summarizes a general description of a conventional Clark type sensor and the proposed sensor. It is not easy to declare that one has much better characteristics than the other one because both types have their own advantages and disadvantages over the other one.

The Clark type sensor is quite advantageous considering that it is not sensitive to the buffering

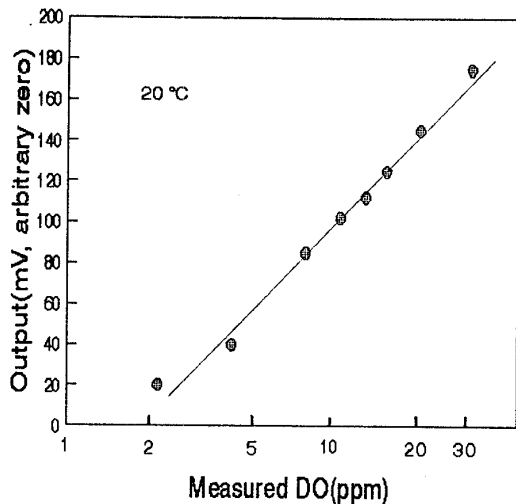


Figure 4. A calibration curve measured in phosphate buffer solution (pH 7.4, 0.01M)

capacity of the sample solution and the electrode surface will not be contaminated by other chemical species during measurements since the gas permeable membrane covers the whole sensor surface.

In a view of miniaturization and smart sensor compatibility, it is considered that the proposed sensor is a better configuration. The decrease of a sensor dimension inevitably results in a low signal-to-noise ratio as well as a small current output of the amperometric sensor and requires a very accurate integrated current-voltage converter,

while a potentiometric sensor has less dependence of such problems on sensor size. It was found that both sensors had a considerable flow dependence. The Clark type sensor had a so-called diffusion errors when there was no sample solution convection, thereby displaying a lower concentration than the real oxygen concentration in the sample. While the proposed sensor showed some decreased output with fluctuations when the sample solution was stirred.

It is expected that the flow sensitivity and electrode surface contamination can be reduced by

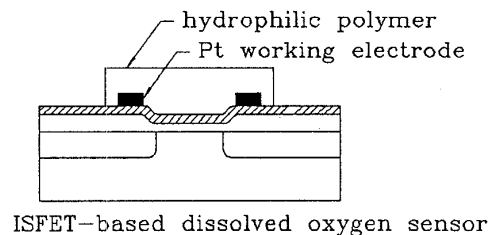
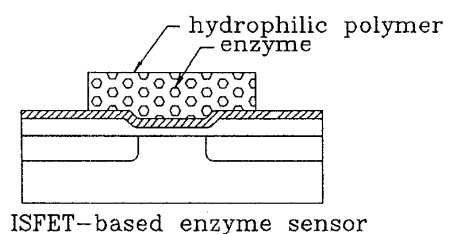


Figure 5. Structural similarity between an ISFET-based dissolved oxygen sensor and an enzyme sensor.

	Clark type sensor	Proposed sensor
Principle	Electrolysis current	Nernstian voltage
Precision	Linear response	Logarithmic response
Buffer capacity dependence	Independent	Dependent
Flow dependence	Dependent	Dependent
Sensitivity (in size respect)	Decrease (as size decrease)	Constant
Signal-to-noise ratio (in size respect)	Decrease (as size decrease)	Constant
Miniaturization & smart sensor compatibility	Relatively bad	Relatively good

Table 1. A General description of the Clark type sensor and the proposed sensor.

incorporating a hydrophilic polymer layer as shown in Figure 5. This configuration is quite similar with an ISFET-based enzyme sensor, in both cases a pH variation occurs in a local region near the gate of the pH-ISFET. The difference is that the pH variation is generated by the enzyme molecules uniformly trapped in a hydrophilic membrane in case of the ISFET-based enzyme sensor and by the platinum working electrode which electrolyzes oxygen in case of the dissolved oxygen sensor.

#### CONCLUSION

The preliminary results suggested that the proposed sensor, based on a combinational principle of an amperometric sensor (Clark type oxygen sensor) and a potentiometric sensor (pH-ISFET),

could determine the dissolved oxygen content.

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