Dissolved Oxygen Sensing in a Flow Stream using Molybdenum Chloride Optical Indicators

Reza Loloee[1], Per A. Askeland[2] and Ruby N. Ghosh[1]
[1]Department of Physics and Astronomy
[2]Composite Materials and Structures Center
Michigan State University
East Lansing, USA
loloee@msu.edu, paskeland@msu.edu, ghosh@msu.edu

Abstract—**Dissolved oxygen concentration is considered the most important water quality variable in fish culture. Reliable and continuous (24/7) oxygen monitoring of dissolved oxygen (DO) in the 1 – 11 mg/L range would be of great benefit to the aquaculture industry. We briefly review selected DO sensors from both the Clark and optical sensor categories as well a comparing their differences, both advantages and disadvantages. We introduce our fiber optic technique for continuous monitoring of DO levels in a flowing aqueous stream. An inorganic molybdenum chloride compound was used as the optical indicator in the oxygen sensitive material. The reflection mode fiber sensor is based on the ability of oxygen to quench the red luminescence of the molybdenum chloride indicator. The advantage of our broad-band, optical dissolved oxygen sensor is shown and discussed.**

I. INTRODICTION

There exists a need for spatially and temporarily resolved measurements of oxygen concentration in a wide variety of biological applications ranging from measuring oxygen levels in a bioreactor during cell growth, determining the distribution of microbes in soil samples based on oxygen consumption as a function of the distance from the air/soil interface, and round the clock monitoring of dissolved oxygen concentration for successful fish cultures. During cell growth in a fermentor a commercial amperometric or Clark type sensor is used to monitor oxygen. These probes have a diameter ranging from 12 to 25 mm and a time response of ~90s. This time response is inadequate to monitor some of fermentation processes, where a response time below 1s would be preferred. In the area of microbial ecology and bioremediation, there is a need for spatial resolution at the tens of microns scale to monitor the migration of cells in the direction of a chemical gradient (chemotaxis). Miniaturized amperometric microelectrodes have been used in studying chemotaxis [1] by repeated insertion of the microsensor tip into the semi-solid gel. These sensors, based on pulled glass pipettes, are extremely fragile. A preferred method would be to insert an array of robust sensors into the gel to obtain a time resolved map of oxygen concentration.

Aquaculture is an important source of economic livelihood in several parts of the United States. A recent report from the Southern Regional Aquaculture Center, states "dissolved oxygen concentration is considered the most important water quality variable in fish culture" [2]. The concentration of dissolved oxygen in a fish pond or tank is a function of fish activity (i.e. feeding), water depth, and environmental conditions. It also can change very rapidly over the course of a day. If left unchecked DO concentrations in intensive fish production facilities can easily fall below critical levels resulting in high fish mortality rates. An array of sensors located in fish rearing units operating continuously would greatly improve production capabilities and reduce risk of catastrophic failure.

In this report, we provide a brief review of different types of DO sensors presently available and current research activity occurring in this field. We then describe our newly developed optical DO sensor, along with our experimental procedure, results and discussion of our study.

II. TYPES OF DO SENSORS

Dissolved oxygen sensors are classified in three categories; i) Polarographic or Clark DO sensors which measure DO directly through an electrochmical reaction. The Clark sensors which have been used for decades, use gold or platinum as the cathode and silver as the anode. ii) Galvanic DO sensors which are basically a Clark sensor with exception of using Silver or platinum as the cathode and lead, iron or zinc as the anode. Galvanic DO sensors provide a faster response time compared to the first group. iii) Optical DO sensors, which are relatively new with respect to the Clark sensor and typically consist of an optical fiber with a sensor tip that is a thin film of oxygen-sensitive–fluorescent materials.

Table 1

Company/ product	Sensing Materials i) Indicator ii) Matrix	Range	Response time Second
In-Situ / RDO [5]	i) Platinum Porphyrin Lumiphore ii) Polyester	0-20 mg/l	12
Global water / D-Opto [6]	i) Ruthenium compounds ii) Not Avialable (NA)	0-25 mg/l	<60
YSI Hydrodata Ltd / YSIROX [7]	NA	0-25 mg/l	NA
HACH / LDO [8]	i) Platinum based Luminophore ii) polystyrene coat	0-20 mg/l	NA
Ocean Optics / FOXY [9]	i) Ruthenium compounds ii) sol-gel matrix	0-40.7 ppm	35-45
Research Group			
Z.Y. Tao et al. [10]	i) tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) ii) tetramethoxysilane or tetraethoxysilane and monoalkylsiloxanes	NA	NA
C. McDonagh et al. [11]	i) Ruthenium complex ii) porous hydrophobic sol–gel matrix	6 ppb-100%	~a few min
H. S. Voraberger et al. [12]	i) Ruthenium(II)-tris(4,7-diphenyl-1,10-phenantroline) perchlorate ii) polysulfone (PSU) and polyetherimide (PEI)	0-100%	59-107
H. L. Pang et al. [13]	i) tris(4,7-diphenyl-1,10-phenanthroline)ruthenium (II) ii) tetramethyl orthosilicate and dimethoxy dimethylsilane	0.05-40 mg/l	1.1-2.1 min
F. G. Gao et al. [14]	i) Tris(4,7diphenyl-1,10-phenanthroline)ruthenium(II) chloride ii) Silicon matrix	NA	NA

In the fiber-optic DO sensor, a light-emitting diode (LED) is used to provide the incident excitation energy, typically between 300-500 nm, to illuminate the oxygen-sensing material. The excited optical indicator will fluoresce by emitting photons at higher wavelenght (emission intensity). As oxygen molecules arrive, the energy of the excited state will be transferred to the O_2 molecules and the fluorescence signal will decrease or completely vanish depending on the relative oxygen concentration. This process is referred to as fluorescence quenching. In most DO sensors, an optical fiber is used to transmit collect the excitation and emission signals between the O_2 sensing materials, LED, and the photo-detector used to collect the emitted photons.

Oxygen quenching of the fluorescence from organic and organometallic compounds has been used to develop a number of dissolved oxygen fiber sensors, which are reviewed in ref. 3 and 4. The most commonly used lumophore has been $Ru(dpp)3^{2+}$. However, two of the drawbacks of this indicator is its small Stokes shift (20 nm difference between the excitation and emitted light) [11] and potential chromophore degradation with time.

Each category of DO sensor described thus far has various advantages and disadvantages. The Clark DO sensors are cheaper; however they require frequent calibration, frequent replacement of membrane and electrolyte, flowing water, and can exhibit substantial drift in natural systems due to biofilm buildup across the membrane. Fiber optic oxygen sensors on other hand, offer a number of advantages over the commonly employed Clark type sensors and galvanic oxygen sensors. The fiber optic devices can be very long to probe remote locations, are immune to electrical interference, less prone to fouling and calibration drift and may be miniaturized into small flexible probes. Single sensors can be placed in an array to provide spatially localized information whose content is determined by the size of each individual sensor and the density of devices in the array. While more than 90 industries manufacture DO sensors less than 10% of them produce optical DO sensors. Examples of companies manufacturing optical DO sensors are provided in Table 1 along with some of the current research being conducted in this field [5-14].

The details of the sensing materials used by industry is given in literature. One of the major problems with organic based sensing materials such as the Ru compounds, is photo-bleaching. We define photo-bleaching as the loss of fluorescence due to repeated exposure to UV light over long period of time, thereby decreasing the sensitivity of the sensing material to dissolved oxygen.

We have developed and implemented a portable, inexpensive fiber-optic oxygen sensor based on the $^3O_2$ quenching of the red emission from hexanuclear molybdenum chloride indicators [15, 16]. Our sensor shows exceptional promise for long term continuous use without susceptibility to photobleaching.

III. Experimental Procedure

The sensing film consists of $K_2Mo_6Cl_{14}$ indicators embedded in an oxygen permeable sol-gel matrix. The sensor (shown in Fig. 1) was fabricated by dipping the cleaved fiber end into a 2.2 μM indicator containing n-octyltrimethoxysilane / tetraethyleorthosilane sol-gel solution followed by curing at 70 °C under vacuum for 24 hours. The fiber sensor is operated in reflection mode, pumped by a 365 nm UV light emitting diode and using a photo-detector to collect the reflected luminescence. Fig. 2 shows the experimental setup used to generate a flowing water stream,

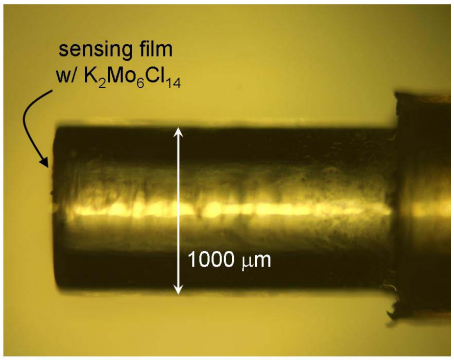

Figure 1 Photograph of the fiber sensor tip, with a sensing film (1 – 5μm) composed of $K_2Mo_6Cl_{14}$ in a OTMOS/TEOS sol-gel matrix

with a well controlled and adjustable DO level, to characterize our dissolved oxygen sensor performance.

In this experiment, oxygen was introduced into the stream by bubbling 21% O_2 (balance N_2) gas through a diffuser. Pure N_2 gas is used to remove oxygen from the stream. The water temperature and flow rate were controlled.

IV. Results and Discussion

The photophysics of the molybdenum chloride indicator is well suited for optically based oxygen sensing. As shown in Fig. 3, the $K_2Mo_6Cl_{12}$ indicator (dissolved in acetonitrile) is excited (pumped) by UV photons ($\lambda_{Excitaion}$ = 365 nm) to its excited triplet state. The excited state then decays to the ground state by emission (fluorescence) of a red luminescence peaked around $\lambda_{Emission}$ = 700 nm, which is efficiently quenched by ground state $^3O_2$. The emission spectra was obtained by pumping at 365 nm and collecting the spectra from 500-850 nm. The large Stokes shift ($\Delta\lambda = \lambda_{Emission} - \lambda_{Excitation}$) of > 300 nm of our indicator is a great advantage as it simplifies the design of the reflection mode fiber sensor; a simple band pass filter can be used to easily separate the excitation and emission signals.

These inorganic indicators show no signs of photobleaching, and once immobilized in a sol-gel binder are not susceptible to leaching into the analyte of interest, thereby making them ideal candidates for long-term monitoring of dissolved oxygen (DO).

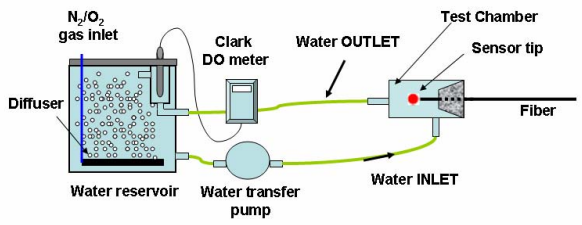

Figure 2. Schematic of the experimental system. The fiber sensor monitors the dissolved oxygen level of flowing water (~600 ml/min) inside a quartz chamber. The downstream DO concentration is measured with a commercial Clark meter.

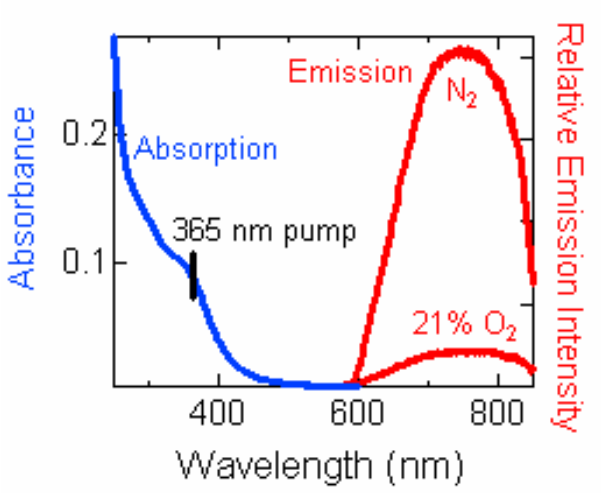

Figure 3. Absorbance and emission spectra of the $K_2Mo_6Cl_{14}$ optical indicator, showing quenching of the emission intensity by 9X between 0.000 (pure N_2) and 21.0 % oxygen.

We expect the oxygen concentration inside the thin (1 – 5 μm) sensing film shown in Fig. 1, to quickly equilibrate with the surrounding water, leading to a fast sensor response. The fiber sensor output was validated using a commercial Clark electrode DO meter [17] located downstream from the optrode. The device response while cycling the DO concentration between 0 and 7.3 mg/l for several hours is very good and stable. Under atmospheric conditions in an open body of water the rate at which oxygen dissolves in water is a slow process. In our experimental setup, this rate is determined by the inlet gas flow, the size of the bubbles produced by the diffuser and the water flow rate.

As the intrinsic response time of the optical sensor is expected to be ≤ 60s based on previous experiments [15], we believe our measurements are currently limited by the dissolving rate of oxygen in the experimental setup.

V. Conlusion

Oxygen quenching of the fluorescence from organic and organometallic compounds has been used to develop a number of fiber sensors. We reviewed several product and related research project which are summarized in table 1. The most commonly used lumophore has been $Ru(dpp)3^{2+}$. However, this indicator has a small Stokes shift (20 nm) and is susceptible to photo-bleaching. We have developed a new dissolved oxygen sensor using reflection-mode fiber-optic oxygen sensor based on the molecular oxygen ($^3O_2$) quenching of the red luminescence from the $K_2Mo_6Cl_{12}$ indicator. This oxygen sensing material enables us to work with a large Stokes shift parameter (> 300 nm) and the luminescence is detectable by integrating over a broad emission band. In addition the lack of degradation and long tem stability of the indicator suggests that our sensor technology is well suited for long term continuous operation.

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