Chapter 13
Optical Sensing of Dissolved Oxygen

Masoud Ghandehari, Gamal Khalil, Filip Mlekicki, Alex Sidelev and Mohsen Hossein

Abstract We present the application of Platinum Porphyrin for in situ measurements of dissolved oxygen using optical fibers. The method employs a sensor compound composed of Porphyrin luminescent indicator in a gas permeable substrate. The compound is used along with optical fibers for both illumination and detection of fluorescence lifetime which is calibrated to changes in ambient oxygen concentration.

13.1 Introduction

It is projected that by 2030 $35 billion will be spent on cleaning up 5000 contaminated sites (EPA 2006). Among the dozens of remediation techniques that exist for treating these site conditions, monitored natural attenuation (MNA) is often the preferred method of cleanup. The natural attenuation capacity of a soil and groundwater environment is monitored, tested, and enhanced in order to degrade the entrapped contaminants by natural (physical, chemical, and biological) processes. The success of this technique is based on three basic activities: site

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M. Ghandehari (✉)
New York University, Six Metrotech Center, Brooklyn, NY 11201, USA
e-mail: masoud@nyu.edu

M. Hossein
e-mail: mhossein@nyu.edu

G. Khalil
Department of Aeronautics & Astronautics, University of Washington,
Box 352250, Seattle, WA 98195, USA
e-mail: gekhalil@gmail.com

F. Mlekicki
Chromosense LLC, One Metrotech Center, Brooklyn, NY 11201, USA
e-mail: filipmlekicki@gmail.com

A. Sidelev
Parsons, 100 Broadway, New York, NY 10005, USA
e-mail: a.sidelev@gmail.com

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characterization, treatment or enhancement, and the capacity to monitor the parameters of interest in order to determine the overall success of the remediation (Bergman 1968; Baleizão et al. 2008; Eich et al. 2010).

The potential for monitoring innovations in this area comes from the fact that most samples are currently taken through a rather lengthy manual process which uses several pieces of mechanical equipment and observation wells. These analyses are time-consuming and therefore costly, and error-prone due to the physical extraction of samples for analysis. Certain monitoring pain points can be addressed with the development of robust in situ monitoring tools that track parameters common to most MNA projects. These geochemical parameters include pH, oxidation-reduction potential and contaminant concentrations. In the applications involving aerobic bioremediation O_2 is a critical geochemical parameter.

In this chapter we show how coupling the photo-physical properties of Platinum Porphyrin (Eich et al. 2010; Khalil 2004) along with the utility of optical fiber technology can be used to the quantitative assessment of subsurface oxygen in situ. The chemical stability of Porphyrin is an attractive feature of the fluorinated porphyrin compounds for the intended long term applications.

13.2 Sensor Molecules for Sensing Dissolved Oxygen

The luminescence of conjugated organic and metallo-organic molecules is quenched by oxygen (McDonagh et al. 1998), an effect that can be used to monitor oxygen concentration by monitoring either the luminescence intensity or the intensity decay rate. Several molecules are known to be sensitive to oxygen concentration. These sensor molecules are commonly embedded in a hydrophobic polymeric or solgel matrix permeable to oxygen diffusion. Most commercial oxygen sensor molecules in this category are based on luminescence quenching of ruthenium complexes (Wang and Wolfbeis 2016). The most recent commercial development for measurement of dissolved oxygen is based on our porphyrin research (Sweet et al. 2002; Khalil et al. 2005).

13.2.1 Detection Method: Intensities and Lifetimes

The concept of using luminescence changes to monitor oxygen concentration was originally developed with the goal of monitoring the oxygen concentration in blood and other fluids. It was conceived as a tiny volume of oxygen-permeable polymer with a luminescent indicator at the tip of an optical fiber (Klukowska 2004). The lifetime (duration) of emission of the luminescent indicator and the diffusion rate of oxygen in the host (which can be a polymer including solgel) are designed so there is a measurable change in the luminescence level, such that the anticipated oxygen pressure range can be accurately measured. The host matrix functions as a carrier for the

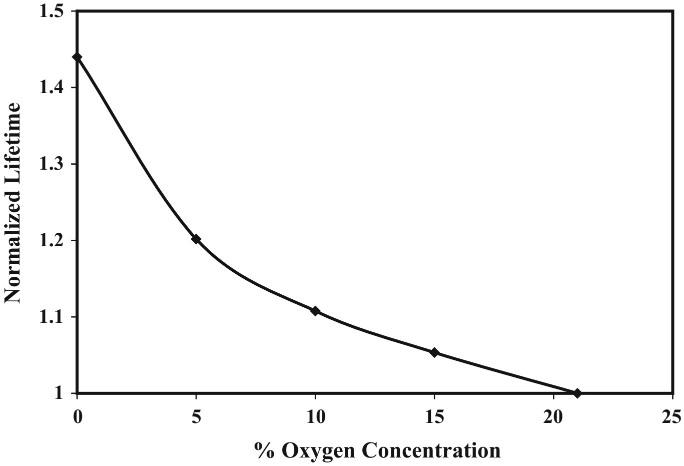

Fig. 13.1 Fluorescence lifetime (normalized versus value at 22% O_2) versus Oxygen concentration

indicator and provides interaction sites for the oxygen sensing. The preferred method for measuring oxygen is based on measuring the fluorescence intensity versus time as it decays. The phosphorescent intensity upon removal of the excitation light source is

$$I(t) = I_0 e - t/\tau \tag{13.1}$$

τ is the phosphorescent lifetime and is the inverse of the overall phosphorescence rate of decay. A calibration curve is generated by plotting the observed τ at known oxygen concentrations. Measured τ values will be used to determine oxygen level (Sweet et al. 2002).

Determinations of quenching based on luminescence rate of decay avoid several problems that arise when determinations are based on intensity measurements, including light source intensity fluctuations, index of refraction shifts, optical geometry variations, variations in film thickness, and sensor molecule concentration due to aging. Lifetime measurement of porphyrins (Fig. 13.1) can be easily accomplished using instruments made with reliable and inexpensive solid-state components. Integration of luminescence energy at three different points along the decay time provides a reliable measurement of luminescence lifetime.

13.2.2 Simultaneous Sensing of Temperature

An independent temperature sensitive sensor molecule will be needed since the luminescence is also function of temperature (Acquaye 2006; Barbarulo et al. 2005; Baleizão et al. 2008; Norris et al. 2008; Venturini et al. 2015; Wang and Wolfbeis 2014, 2016). This is the important for long-term applications where the temperature will vary. Photo-physical properties of luminescent organic and metallo-organic compounds provide lifetime based systems where an oxygen sensitive and a temperature sensitive sensor molecule may be embedded in the same matrix.

The temperature sensor is a tris(β-diketonate) phenanthroline europium complex, with absorption peaked at 370 nm and sharp emission peak at 615 nm. Lifetime of this compound varies between 350 and 50 μs over the temperature range 5–45 °C, for a derivative of −5.3 μs/°C. The oxygen and the temperature sensors have maximum absorption in the range 370–400 nm (Fig. 13.2) but emission spectra, which do not overlap (Fig. 13.3).

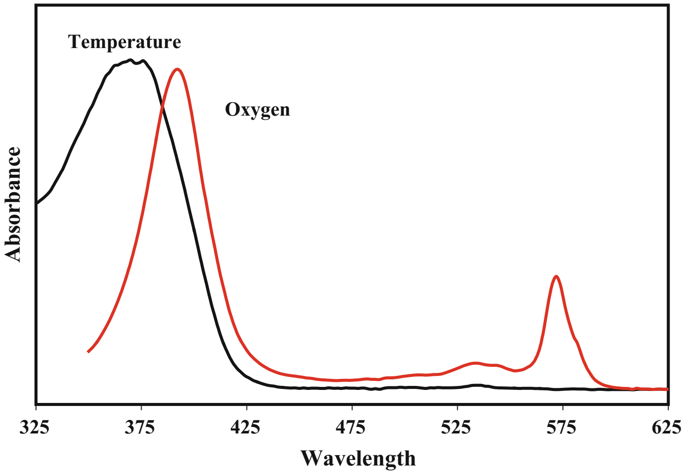

Fig. 13.2 Absorption peaks of the oxygen and temperature sensor molecules

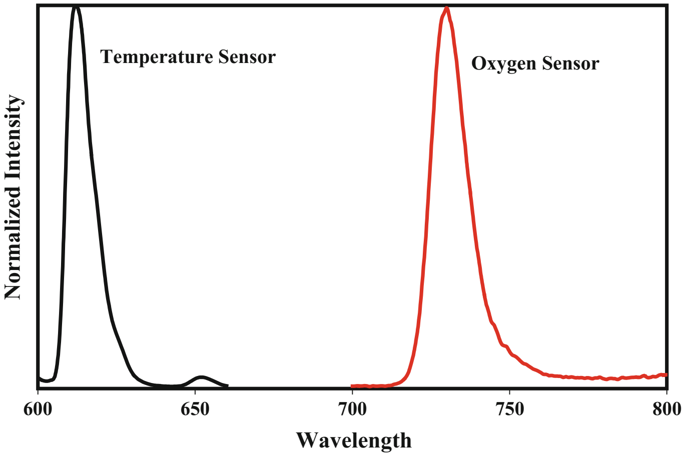

Fig. 13.3 Emissions peaks corresponding to the absorption peaks shown in Fig. 13.2

The example shown here is platinum-tetra (pentafluorophenyl)porpholactone [PtTFPL], recently developed in our labs. This compound has a principal absorption band at 390 nm and a red-shifted phosphorescence at 740 μm. In the flouro-isopropyl-butyl (FIB) polymer PtTFPL has a lifetime flourescence range of 42.7–6.6 μs in going from 0 to 21% oxygen.

13.3 Experimental Results in Dry and Saturated Soil

Experiments were conducted in a chamber (Fig. 13.4) filled with sand which was tested dry and at various level of saturation while the Oxygen concentration was varied. This was achieved by releasing methane from a valve (Fig. 13.4) embedded in the soil. Results of these experiments for the case of wet sand are shown in Fig. 13.5; note the slower rebound to the natural condition is observed. The x-axis

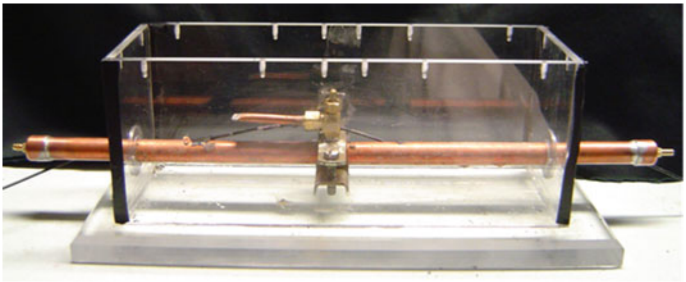

Fig. 13.4 Test chamber showing copper pipe with holes and valve

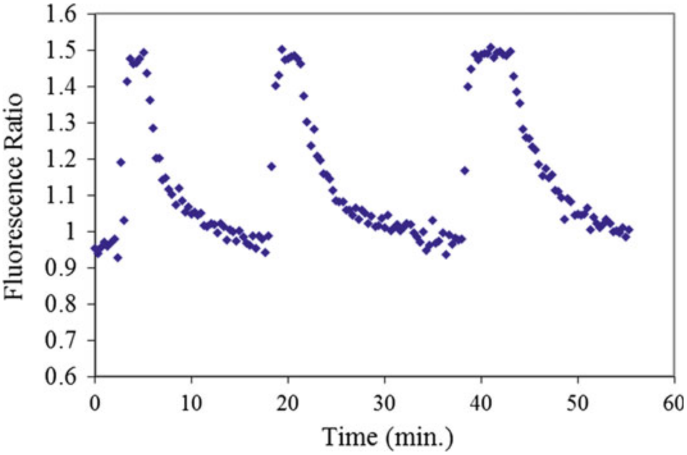

Fig. 13.5 Response to variation of oxygen concentration in wet sand. Vertical axis is the ratio of fluorescence lifetime versus the lifetime before gas was released

is time, and the y-axis is the normalized response of the sensor. The longer relaxation time of the sensor response in wet sand is expected since the moisture in the sand tends to trap gases, making the diffusion rate of gases through liquids much slower than through air.

13.3.1 Choice of Sensor Molecule

The proper choice of the sensing compound, allows one to tune for a desired detection range of dissolved oxygen concentration. Good dynamic range can be achieved by employing sensor molecules with different triplet state lifetimes. For example, a luminescent dye with a long excited state lifetime is suitable for application with high O_2 concentration, as would be the case in sandy soil, while a short-lived luminescent dye is better for lower O_2 concentration, as may be the case in clay. The relationship between sensitivity and the sensor molecule excited state lifetime is shown in Table 13.1.

The luminescence efficiency of porphyrin compounds is typically between 20 and 30%. Variations of the above compounds have demonstrated stability, and are commercially available from several suppliers, including Frontier Scientific (Ogden, UT), Aldrich (Milwaukee, WI) and Molecular Probes (Eugene, OR).

13.3.2 Choice of Host Matrix

In the case of polymeric hosts, the Porphyrin sensor compounds can be immobilized in polymer matrices that form the fiber tip or the cladding for the optical fiber along the length. The host polymer has two functions: (1) to hold the porphyrin indicator close to the optical fiber in order to be excited by the incident energy, either at the tip or by evanescent field energy, and (2) to provide interaction sites for the oxygen. In general, oxygen sensitivity is polymer-dependent; different polymers elicit different response characteristics. Figure 13.6 shows results of a study on the oxygen sensitivity of various host polymers. It is possible to "tune" the sensitivity

Table 13.1 Optical properties of the sensor molecules

Luminescent dye	Lifetime (μs)	Sensitivity	Application
PtTPP	0.124	45	λ_{ex} 510 nm–λ_{em} 650 nm
PdTPP	1.4	20	λ_{ex} 554 nm–λ_{em} 680 nm
PdTFPP	1.8	20	λ_{ex} 540 nm–λ_{em} 650 nm
TaTPP	2.5	45	λ_{ex} 565 nm–λ_{em} 710 nm
HfTPP	10.8	NA	λ_{ex} 540 nm–λ_{em} 650 nm

λ_{ex} Excitation λ_{em} Emission

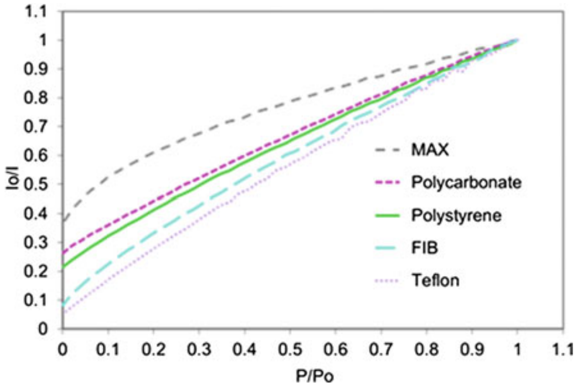

Fig. 13.6 Stern-Volmer oxygen sensitivity in various polymers

for detecting a certain oxygen level by and response time by selecting the appropriate polymer. The sensing compound can therefore be matched with a particular sensor molecule that has an optically emissive triplet state lifetime appropriate to the application.

13.4 Conclusion

This chapter demonstrated the utility of a porphyrin sensor molecule for sensing dissolved oxygen, and a europium complex for temperature sensing and calibration. Both are embedded in the same polymer which is applied to an optical fiber for remote in situ monitoring of subsurface oxygen. The proposed approach has two main desirable features: inherently robust composition of the sensor molecules, and the internal calibration strategy made possible through fluorescence lifetime measurements. Response of the fiber optic oxygen sensor was tested in a chamber filled with sand, testing the sensor response in dry and saturated condition.

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