

Optical dissolved oxygen sensor utilizing molybdenum chloride cluster phosphorescence

Ruby N. Ghosh,^{1,a)} Per A. Askeland,² Sage Kramer,³ and Reza Loloee¹

¹Department of Physics, Michigan State University, East Lansing, Michigan, 48824, USA

²Composite Materials Center, Michigan State University, East Lansing, Michigan, 48824, USA

³Department of Physiology, Michigan State University, East Lansing, Michigan 48824, USA

(Received 1 April 2011; accepted 29 April 2011; published online 1 June 2011)

We report on an optical oxygen sensor for aqueous media. The phosphorescent signal from the indicator, $\text{K}_2\text{Mo}_6\text{Cl}_{14}$, immobilized in a polymer matrix, is quenched by ground state $^3\text{O}_2$. Continuous measurements ($\Delta t=10$ s) over 36 h in oxygen atmospheres (0%–21%) were obtained with a signal to noise ratio better than 150. Photobleaching was not observed over $\sim 13\,000$ measurements. The sensor response at 10, 22, and 37 °C water is governed by bimolecular collisional quenching, as evidenced by a linear fit to the Stern–Volmer equation for dissolved oxygen in the range $0 < [\text{O}_2] < 3 \times 10^{-4}$. © 2011 American Institute of Physics.

[doi:10.1063/1.3595483]

Quantitative monitoring of dissolved oxygen (DO) in aqueous media is necessary for a wide range of chemical and biological processes. These applications require sensitive, precise, continuous monitoring, without restrictions on the frequency of measurement or total number of data points. The measurement process should have no cross sensitivity to other chemical species in the liquid, be operable in either flowing or stationary media, and be minimally affected by changes in environment. Present techniques for direct measurement of DO utilize one of two physical principles, electrochemistry or luminescence. Electrochemical devices result in analyte consumption, require a flowing stream and are intrinsically coupled to the properties of the media such as ionic species concentration. Common optical indicators are the Ru (II) complexes^{1,2} and Pt or Pd porphyrins.^{1,3–5} Although Ru (II) complexes are widely employed; they have a strong temperature dependence and suffer from photobleaching.¹ The Pt and Pd porphyrins are significantly more robust; they require complex synthetic processes to shield the optical indicator from deleterious interactions with other constituents in the media.⁵

The optical and physical properties of molybdenum chloride clusters are eminently suited for optical detection of molecular oxygen.⁶ In solution the clusters exist in the form $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4\text{L}_2$, where L is either a ligand or solvent molecule. The challenge arises in how to preserve the photophysical properties of singly solvated monomers in solution^{7,8} during the synthesis of a solid state sensing film where the clusters are dispersed and immobilized in an optically transparent and oxygen permeable matrix. Absorption of a UV photon via the broad absorption band (300–400 nm) promotes the cluster to an excited electronic state with spin triplet symmetry. Spontaneous emission to the singlet ground state is spin forbidden, resulting in phosphorescent emission with a long half-life, ~ 180 μs .^{7,8} Alternatively the phosphorescence can be quenched by a molecule with spin triplet symmetry, i.e., $^3\text{O}_2$. Detection of molecular oxygen involves monitoring either the emission intensity or lifetime (τ) of the excited state. The specificity of the molybdenum chloride

clusters to molecular oxygen is determined by quantum mechanics, a unique property not shared by the organometallic Ru (II) complexes. The emission band extends from 600 to 900 nm. The phosphorescence lifetime or intensity increases with decreasing oxygen concentration due to bimolecular collisional quenching.

From a device perspective the broad absorption and emission bands, large Stokes shift (~ 300 nm) and long excited state lifetime of the molybdenum chloride clusters provide unique engineering advantages. First, an inexpensive UV light emitting diode (LED) with a color glass filter is used as the pump beam, without need for a monochromatic excitation source. Second, a fast, cost effective Si avalanche diode with a 600 nm long wavelength filter is used for detection. Third, the phosphorescence or emission lifetime is readily monitored using phase sensitive techniques, which can be implemented using a simple phase locked loop configuration,⁹ thereby eliminating the need for a bulky optical fluorometer.

We have previously reported on a reflection mode fiber optic oxygen gas sensor, using molybdenum chloride indicators, for measurements in the 0%–21% range.⁶ For aqueous applications we have developed a unique sensing film composed of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ clusters caged in a hydrophobic, oxygen permeable polymer matrix.^{10,11} The salts of the molybdenum chloride cluster, synthesized at 350 °C,¹² are the lumiphore of choice due to their optical and thermal stability. Acetonitrile solutions of $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ mixed with a photocurable silicone polymer [(acryloxypropyl)-methylsiloxane-dimethylsiloxane copolymer] are applied on a UV transparent quartz substrate. UV photo initiation, catalyzed by benzoin ethyl ether, immobilizes the solvated optical clusters in the silicone resin, followed by a vacuum bake to evaporate residual solvents. Optical isolation from ambient light is provided by a final opaque coating, (vulcanized silicone with carbon black). The hydrophobic nature of both the top coating and the support matrix of the sensing film acts to deter biofouling. The sensing substrate is mounted in a watertight sensor head, with the front face in contact with the aqueous media. A UV transparent polymer fiber bundle is butt

^{a)}Electronic mail: ghosh@pa.msu.edu.

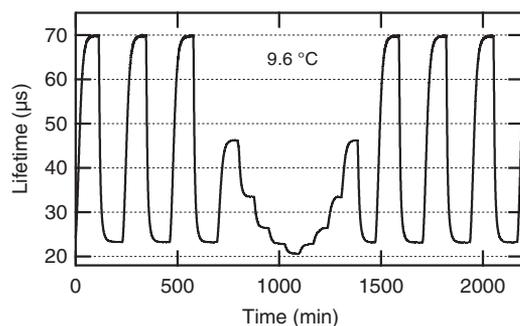


FIG. 1. Optical DO sensor signal (lifetime) over 36 h ($\delta t=10$ s) in 10 °C water. The sensor was cycled between N_2 , ($O_2 < 0.001$), $\tau=70 \mu s$, and laboratory air (20.9% O_2), $\tau=23 \mu s$, for three complete cycles at the beginning and end of the measurement period. From 700 to 1400 min oxygen gas, 4.4%, 10%, 16%, 21%, 26%, 21%, 16%, 10%, and 4.4%, was bubbled into the water. For the 36 h period the sensor signal is repeatable, does not show signs of hysteresis and there is no evidence of photobleaching for >13 000 measurements.

coupled to the back of the quartz substrate for reflection mode optical measurements.

The DO concentration is determined by monitoring the lifetime of the phosphorescent emission from the $K_2Mo_6Cl_{14}$ indicator. For field applications, lifetime monitoring was chosen in favor of intensity measurements as it is largely unaffected by stray light which can vary with time, especially outdoors. A compact phase fluorometer, TauTheta Model MFPPF-100, supplies the excitation source (365 nm LED with a 10 nm bandpass filter) and detector (Si APD with a 600 nm long wave pass filter) while a 1 mm diameter bifurcated fiber bundle couples light into and out of the sensor head. The emission lifetime was monitored at 5 KHz with a 0.5 s integration time. Certified O_2 mixtures, balance N_2 , were bubbled into the vessel at 0.2–0.5 l/min using an aeration stone to ensure rapid dissolution of O_2 in the water.

Continuous sensor measurements over a 36.5 h period ($\Delta t=10$ s) are shown in Fig. 1. The water temperature was maintained at 9.6 °C. In order to ascertain the device stability the sensor response at the two extremes of oxygen concentration, the absence of oxygen (99.999% N_2) and laboratory air (20.9% O_2), were measured. We obtain lifetimes of $(69.74 \pm 0.10) \mu s$ and $(23.21 \pm 0.08) \mu s$ in 0 and 21% O_2 , respectively, from three complete cycles over ~ 700 min at both the beginning and end of the 36 h experiment. A quantitative measure of the sensor performance is provided in Table I; the device signal to noise ratio (S/N) ≥ 150 for either low or high oxygen concentrations.

A complete calibration curve was obtained, between 700 and 1400 min (see Fig. 1), by sequentially bubbling oxygen mixtures of 4.441%, 10.00%, 16.15%, 21.5%, 26.06%, 21.5%, 16.15%, 10.00%, and 4.441%. The DO concentration in the water bath was calculated using the Henry's Law coefficients.¹³ The raw lifetime data of Fig. 1 converted to

TABLE I. Statistics on the DO sensor performance at the extremes of oxygen concentration over 36 h at 10 °C (see Fig. 1).

	No. of cycles	Lifetime (μs)	Signal/noise
N_2 ($<0.001\%$ O_2)	6	69.74 ± 0.10	175
Laboratory air (20.9% O_2)	6	23.21 ± 0.08	150

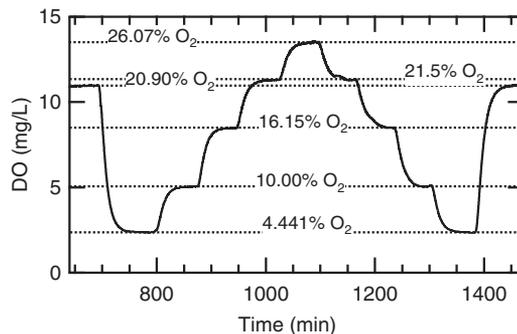


FIG. 2. DO concentration at 10 °C from the data in Fig. 1. As a guide to the eye lines are drawn at 26, 21.5, 20.9, 16, 10, and 4.4% O_2 . Minimal hysteresis is observed between data points taken for increasing vs decreasing oxygen concentrations.

DO in units of mg/L is given in Fig. 2. As a guide to the eye the signal levels at 4.4%, 10%, 16%, and 21% are indicated. Flat, reproducible steps are observed at each oxygen level with minimal hysteresis while increasing and decreasing the oxygen concentration. The sensor can resolve absolute changes in DO of 0.02 mg/L in the 0–2 mg/L range, of 0.03 mg/L in the 2–5 mg/L range, and of 0.05 in the 5–13 mg/L range. Note that the overall stability of our device is given in Table I where we compare the sensor lifetime at the beginning and end of the measurement sequence.

Photobleaching of the indicator is a problem frequently encountered with optically based chemical sensors. It has been reported for the Pt and Pd porphyrines^{3,4} and the Ru (II) organometallic oxygen indicators.² Photobleaching limits the total number of measurements possible with a single sensor film forcing the choice between frequent measurements over a short period or a sparse data set during a long experiment. The >13 000 data points obtained from the $K_2Mo_6Cl_{14}$ sensing film given in Fig. 1, show no evidence of photobleaching. Note that the optical transitions of the cluster arise from states localized in the $[Mo_6Cl_8]$ core, which has little ligand character;⁷ thereby minimizing interactions between the indicator and its environment.

DO monitoring occurs over a range of temperatures, shown in Fig. 3 is the response of a *single* sensor film in 9.65, 21.6, and 37.1 °C water. The measured lifetime is plotted as a function of molar oxygen concentration, $[O_2]$, to show the linearity of the response at all three temperatures. The quenching of a luminophore by a simple bimolecular

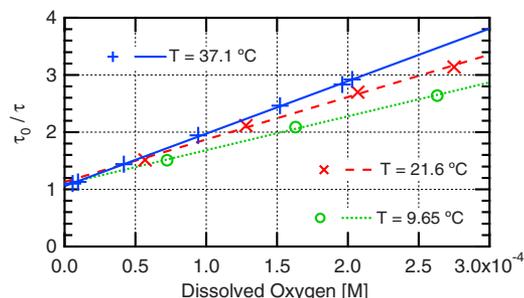


FIG. 3. (Color online) DO sensor performance at 9.6, 22, and 37 °C as a function of molar oxygen concentration. The data were fit to the Stern-Volmer equation, without including the point at $[O_2]=0$. The suitability of the sensing material for DO monitoring at industrial and biologically relevant temperatures are demonstrated by the linearity of the fit.

TABLE II. Photophysical parameters and fit to the Stern–Volmer equation from Fig. 3. τ_0 is independently measured. The intercept of 1 and linearity of the fit shows that bimolecular collisions dominate the oxygen quenching process with minimum indicator/matrix interactions.

Temperature (°C)	Intercept	K_{SV} (M^{-1})	τ_0 (μs)
9.65	1.09 ± 0.05	5900 ± 250	69.7
21.6	1.13 ± 0.06	7400 ± 300	65.4
37.1	1.05 ± 0.01	9195 ± 85	46.0

collisional process can be modeled with the linear Stern–Volmer equation¹⁴

$$\tau_0/\tau = 1 + K_{SV}[O_2], \quad (1)$$

where τ_0 and τ are the emission lifetimes in the absence and presence of the quencher respectively, K_{SV} is the overall dynamic quenching constant and $[O_2]$ was determined from thermodynamics as previously described. At each temperature τ_0 was determined experimentally using 99.999% N_2 . The least-squares fit to the data at 10, 22, and 37 °C is given by the dotted, dashed and solid lines in Fig. 3 where the measurement at $[O_2]=0$, or τ_0 is not included in the fit to avoid double counting. The fitting parameters and measured τ_0 are tabulated in Table II.

At all three temperatures we obtain a good fit to the linear Stern–Volmer equation with an intercept of one. The statistics of the intercept and slope (K_{SV}) given in Table II, demonstrate that the optical properties of the $K_2Mo_6Cl_{14}$ cluster trapped in its support matrix are not adversely affected by the external environment. The room temperature oxygen quenching rate constant for solvated $[Mo_6Cl_8]Cl_6^{2-}$ ions in acetone^{7,8} is $6300 M^{-1}$, which compares well with the value of K_{SV} for our solid state sensing film in water. The natural or unquenched lifetime of metal-halide clusters has a negative temperature coefficient,¹⁵ consistent with our data. Caging the $K_2Mo_6Cl_{14}$ cluster in a photocured silicone polymer preserves the essential photophysics of the singly solvated monomer.

We have developed an optical technique based on the phosphorescence quenching of molybdenum chloride clusters by 3O_2 , to monitor DO in aqueous media. Continuous real-time data is possible with our reflection mode fiber optic sensor as photobleaching was not observed for >13 000 measurements. In accordance with theory the device response is linear over the 10–37 °C temperature range. Our cost effective DO sensor is well suited for continuous environmental water monitoring, fermentation process control, aquaculture and biomedical applications.

We thank C. Weeks for technical contributions. This research was supported in part by State of Michigan under Grant No. 06-1-P1-0452.

- ¹S. M. Borisov and O. S. Wolfbeis, *Chem. Rev.* **108**, 423 (2008).
- ²B. D. MacCraith and C. McDonagh, *J. Fluoresc.* **12**, 333 (2002).
- ³S. M. Borisov, G. Nuss, and I. Klimant, *Anal. Chem.* **80**, 9435 (2008).
- ⁴S. Scheicher, B. Kainz, S. Kostler, M. Suppan, A. Bizzarri, D. Pum, U. Sleytr, and V. Ribitsch, *Biosens. Bioelectron.* **25**, 797 (2009).
- ⁵A. Y. Lebedev, A. V. Cheprakov, S. Sakadzic, D. Boas, D. F. Wilson, and S. A. Vinogradov, *ACS Appl. Mater. Interfaces* **1**, 1292 (2009).
- ⁶R. N. Ghosh, G. L. Baker, C. Ruud, and D. G. Nocera, *Appl. Phys. Lett.* **75**, 2885 (1999).
- ⁷J. A. Jackson, C. Turro, M. D. Newsham, and D. G. Nocera, *J. Phys. Chem.* **94**, 4500 (1990).
- ⁸M. D. Newsham, Ph.D. thesis, Michigan State University, 1988.
- ⁹V. Vadde and V. Srinivas, *Rev. Sci. Instrum.* **66**, 3750 (1995).
- ¹⁰R. N. Ghosh, R. Loloee, P. A. Askeland, C. T. Weeks, S. P. Kramer and C. Kramer, US Provisional Patent No 61/410,254 (November 4, 2010).
- ¹¹R. N. Ghosh, S. P. Kramer, P. A. Askeland, and R. Loloee, *Adv. Mater.*, “Dissolved oxygen sensing films based on molybdenum chloride phosphorescence in a silicone polymer” (unpublished).
- ¹²C. T. Yang, D. N. Hay, L. Messerle, and D. J. Osborn, “Bis(Hydroxonium) Tetradechlorohexamolybdate Hexahydrate (Chloromolybdic acid), $(H_3O)_2[Mo_6(\mu_3-Cl)_8Cl_6] \cdot 6H_2O$, and Hexamolybdenum Dodecachloride, Mo_6Cl_{12} ,” *Inorg. Synth.* (in press).
- ¹³M. L. Hitchman, *Measurement of Dissolved Oxygen* (Wiley, New York, 1978).
- ¹⁴*Fiber Optic Chemical Sensors and Biosensors*, edited by O. S. Wolfbeis (CRC, Boca Raton, 1991), Vol. II, Chap. 10.
- ¹⁵Y. Saito H. K. Tanaka, Y. Sasaki, and T. Azumi, *J. Phys. Chem.* **89**, 4413 (1985).