Fiber-optic oxygen sensor using molybdenum chloride cluster luminescence

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We report on a reflection-mode fiber-optic oxygen sensor based on the $^3O_2$ quenching of the red emission from hexanuclear molybdenum chloride clusters. Measurements of the probe operating in a 0%–21% gaseous oxygen environment have been obtained, a range suitable for biological and automotive applications. The luminescence signal increases with decreasing oxygen concentration in accordance with theory. We observe clearly resolvable steps in the sensor response for changes of 0.1% absolute oxygen concentration in the 0%–1.0% range. The response time of the fiber probe is theoretically predicted to be 1 s. © *1999 American Institute of Physics.* [S0003-6951(99)01445-X]

The quantitative detection of oxygen is important for industrial, automotive, and medical applications. In these environments the advantages of fiber-optic chemical sensors are that they: can probe remote locations, are immune to electrical interference, and may be miniaturized into small, flexible probes. Oxygen quenching of the fluorescence from organic and organometallic compounds has been used to develop a number of fiber sensors.[1–5] However, a drawback of these indicators is that the chromophores often degrade and have a limited operational temperature range. A copper containing zeolite probe for oxygen detection at 500 °C is described in Ref. 6. We report here on a fiber-optic oxygen sensor that utilizes the fluorescence from hexanuclear molybdenum chloride clusters.

The photophysics and physical properties of Mo_6Cl_{12} and related metal halide compounds[7] are well suited for oxygen sensing schemes. The extended cluster array has a quasiperovskite structure, composed of an octahedral core of molybdenum atoms with eight face bridging chlorides and four axial chlorides, which are shared among neighboring cluster subunits.[8] When dissolved in solution the clusters exist in the form $[Mo_6Cl_8]Cl_4L_2$ where L is either a solvent molecule or another ligand. Absorption of UV photons through the broad 300–400 nm absorption band raises the cluster to an excited electronic state.[9] Emission of red luminescence from the excited state is efficiently quenched by ground state $^3O_2$,[9] as shown in Fig. 1. Due to the long cluster lifetime (>100 μs) and large Stokes shift (> 300 nm), the luminescence is easily detectable by integrating over the broad emission band. In addition, simple filtering techniques are used to separate pump and signal beams. The clusters can withstand repeated cycling and show no signs of decomposition to temperatures in excess of 600 °C. In solution, the emission intensity of the clusters has been shown[9] to increase with decreasing oxygen concentrations ranging from 10^{-5} to

10^{-2} M. Thus, the clusters are ideal luminescent probes for detection of gaseous oxygen concentrations ranging from 0.09% to 90% at 1 atm, an important compositional range for medical and industrial processes.

We have developed a molybdenum chloride based fiber sensor by immobilizing the clusters at the end of a silica optical fiber. Polymer and silica-bound hexanuclear Mo halide clusters have been reported as sensitizers for $^1O_2$ generation and oxygen detection in liquids,[10,11] however for gas sensing applications, the polymer matrix needs to have a high permeability to ensure fast response times. Poly [1-trimethylsilyl-1-propyne] (PTMSP) has the highest gas permeability coefficient of any known polymer.[12] For a 100 μm film the measured permeability implies an oxygen diffusion constant of 10^{-4} cm^2/s or a diffusion time of 1 s. PTMSP's mechanical properties, environmental stability, and thermal stability make it an ideal matrix for oxygen sensing schemes. The molybdenum chloride clusters were dispersed in a PTMSP matrix to obtain: Mo-cluster/PTMSP composites. We report here on a reflection mode fiber-optic sensor based on Mo-cluster/PTMSP composites for real time (time constant $t \leqslant 30$ s) monitoring of oxygen in a 0%–21% gaseous environment.

The luminescence properties of the Mo-cluster/PTMSP composite (1.0×10^{20} clusters/cm^3 composite) were initially characterized by spin coating films onto a quartz slide. Fig-
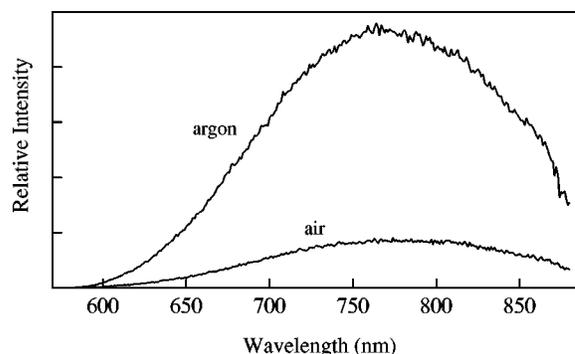
FIG. 1. Luminescence spectra from Mo-cluster/PTMSP composite film demonstrating quenching by oxygen: (a) argon environment and (b) laboratory air (~20% oxygen).

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ure 1 shows the luminescence spectra of the slide in (a) a sealed cuvette flushed with argon and (b) laboratory air (~20% oxygen). The emission spectra of the composite film has the same line shape as that obtained from Mo_6Cl_{12} in methanol.[13] As previously observed,[10] immobilization of the cluster in a polymer matrix does not add nonradiative pathways to the lumophore, since the photophysics of interest is due to electronic transitions confined to the $[Mo_6Cl_8]^{4+}$ cluster core. The luminescence signal in an argon atmosphere is 5.5 times greater than that in air, demonstrating oxygen quenching of the emission from the Mo-cluster/PTMSP composite film.

The sensor was fabricated from a commercially available multimode fiber, FT-1.5-UMT from 3M Specialty Optical Fibers, which is designed for UV to visible transmission. The large core diameter (1500 μm) and high numerical aperture (0.39) of the fiber allows for efficient excitation and collection of the luminescence from the clusters immobilized at the back face of the fiber. The cleaved surface of the fiber was cleaned in a UV–ozone photoreactor for 30 min, and then immediately transferred into a He-atmosphere drybox.

PTMSP adheres poorly to the silica fiber. To improve adhesion we devised a two-layer scheme for depositing the Mo-cluster/PTMSP composite onto the optical fiber by first using a thin ''primer'' layer of poly[(1-trimethylsilyl-1-propyne)-*co*-(1-(4-azidobutyldimethylsilyl)-1-propyne)] (PTMSP–N_3, azide content 2%).[14] After dip coating the fiber tip with a 1 wt % solution of PTMSP–N_3 in toluene, the primer layer was dried and cross linked at 250 °C for 8 hs. A transparent bead (~100 μm) of the Mo-cluster/PTMSP composite was then applied by dipping the primed fiber tip into a 2 wt % coating solution. The coating solution was prepared by dissolving Mo_6Cl_{12} in acetonitrile and removing the solvent to give a yellow oil, presumably $[Mo_6Cl_8]Cl_4(CH_3CN)_2$.[15] Known amounts of the oil were added to tetrahydrofuran solutions of PTMSP to obtain the desired concentrations for dip coating. The composite bead was first allowed to dry overnight, and was then further dried under vacuum at ambient temperature for 1 h. Composites prepared by this protocol were mechanically stable and adhered well to the fiber end.

The fiber sensor was pumped by a 325 nm HeCd gas laser. The reflected luminescence was collected at the front end of the fiber with a Hamamatsu R955 photomultiplier tube (PMT). Separation of the signal and pump beams was accomplished using a 45° long wave pass (LWP) dichroic beamsplitter and a 590 nm LWP filter. The PMT therefore integrates all the luminescent photons in a 590–880 nm bandwidth. The output power from the sensor was determined by multiplying the luminescence line shape (Fig. 1) with the spectral responsivity of the PMT. The sensor was exposed to controlled environments with varying oxygen concentrations by enclosing the last 5 cm of the fiber in a flow through cell.

Data from two different 1.5 m long fiber sensors Fiber Probe 1 and Fiber Probe 2, 2.95×10^{19} and 1.31×10^{19} clusters/cm^3 composite respectively, are shown in Figs. 2 and 3. The input pump power for all the measurements is 0.5 mW, which corresponds to a power density of 9 mW/cm^2 in the fiber. The response of Fiber Probe 1 to 0%–21% oxygen
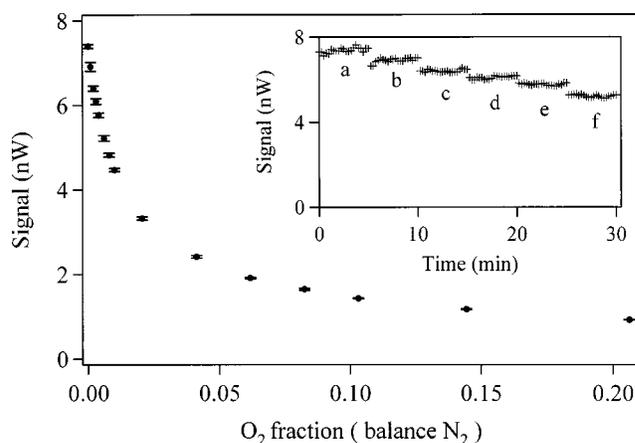

FIG. 2. Output signal from Fiber Probe 1. (Inset) Signal as a function of time for (a) 0%, (b) 0.10%, (c) 0.20%, (d) 0.30%, (e) 0.40%, and (f) 0.61% O_2; the balance gas is N_2.

environments is shown in Fig. 2. A commercial ten step gas divider was used to blend 99.999% purity nitrogen gas with O_2/N_2 mixtures containing 20.63% or 1.01% oxygen. Note that within the 6 Hz measurement bandwidth the standard deviation is less than 2% of the signal. In the inset to Fig. 2 the sensor is shown cleanly switching between well defined plateaus corresponding to 0%, 0.10%, 0.20%, 0.30%, 0.40%, and 0.61% O_2, the balance gas is N_2. The data demonstrate that the sensor can clearly resolve changes of 0.1% absolute oxygen concentration in the 0%–1% range, changes of 0.5% absolute oxygen concentration in the 1%–4% range, and changes of 1% absolute oxygen concentration in the 4%–10% range. Autofluorescence, which is less than 4% of the integrated signal from 590 to 880 nm, has been subtracted from all the data. This low autofluorescence level from such a long fiber length suggests that the sensor could be used in probing remote locations. From the inset to Fig. 2, we find that an upper bound to the sensor switching time is 30 s. This is not the intrinsic response time of the sensor but an upper limit set by the response time of the gas mixing system. We estimate a lower bound to the sensor response time to be 1 s from the oxygen permeability of PTMSP and a film thickness of 100 μm.

In liquid environments the quenching of the cluster luminescence by oxygen has been shown[9] to obey the Stern–Volmer equation in the range $10^{-5} < [O_2] < 10^{-2}$ M
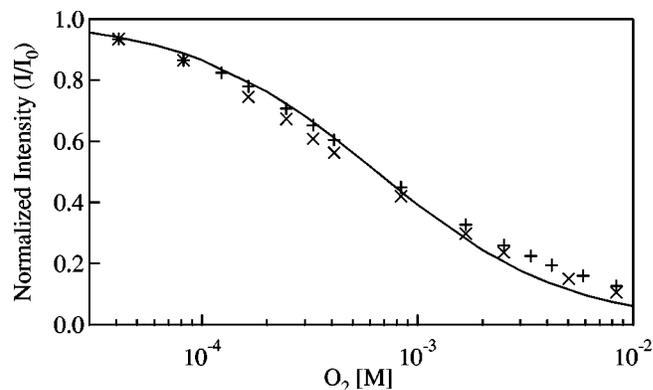

FIG. 3. Normalized output signal from Fiber Probe 1 (+) and Fiber Probe 2 (×). Solid line is a least squares fit to Eq. (1) with $k_q\tau_0 = 1550$.

$$I/I_0 = (1 + k_q \tau_0 [O_2])^{-1}, \tag{1}$$

where I and I_0 are the luminescence intensity in the presence and absence of oxygen of concentration $[O_2]$, k_q is the quenching rate constant, and τ_0 is the luminescence lifetime in the absence of oxygen. In Fig. 3 we demonstrate that the Stern–Volmer relationship is also valid for clusters in a solid state PTMSP polymer matrix. The normalized luminescence intensity I/I_0 is shown for the two fiber sensors, where ideal gas behavior at room temperature has been assumed to obtain the molar oxygen concentration. In the absence of oxygen, or a pure N_2 environment, the sensor signal is 7.40 and 5.10 nW for Fiber Probes 1 and 2, respectively. Note that the error bars, which are smaller than the symbols, have been omitted for clarity. From our lifetime measurements of solid state composite films and previous measurements of the clusters in solution[9,13] we estimate that for our fiber sensors $50\,\mu\text{s} < \tau_0 < 180\,\mu\text{s}$ and $2 \times 10^6\,\text{M}^{-1}\,\text{s}^{-1} < k_q < 3 \times 10^7\,\text{M}^{-1}\,\text{s}^{-1}$. A least squares fit of the data in Fig. 3 yields $k_q \tau_0 = 1550$, consistent with our estimates. In addition, although the two fiber sensors differ in cluster concentration by a factor of 2, they have essentially the same normalized response characteristic. The data in Fig. 3 demonstrate that for concentration below 3×10^{19} clusters/cm^3 composite the photophysics of the clusters is not adversely effected by immobilization in the PTMSP matrix and self quenching is not an issue.

The stability of the fiber sensor was investigated by cycling between pure nitrogen and 21% oxygen environments. The response in a 21% oxygen environment is repeatable with time, while in a nitrogen environment we observe a slow decay of the signal for time periods greater than 40 min. We attribute this behavior to the UV photoxidation processes in the Mo-cluster/PTMSP composite, which can be limited by lowering the concentration of residual peroxides in PTMSP.[14]

In conclusion, we have demonstrated a reflection-mode fiber-optic oxygen sensor based on the quenching of the red luminescence from hexanuclear molybdenum chloride clusters, that can detect 0.1% changes in absolute oxygen concentration with a response time of $1\,\text{s} < t < 30\,\text{s}$. The low autofluorescence from the sensor allows for the use of long fiber lengths to probe remote locations. We envision that the following changes in sensor design will improve its performance. First, we have demonstrated that the 0.5 mW pump power for the fiber probe can be provided a UV lamp, thereby enabling development of a completely portable benchtop fiber optic oxygen sensor. Second, the cluster luminescence can withstand repeated cycling and is largely impervious to varying environmental conditions. The present probe is thermally stable to 200 °C, limited by the polymer matrix. Since Mo_6Cl_{12} is synthesized[8] at 1000 °C, immobilization of the clusters in a porous sol–gel matrix will enable oxygen sensing in gaseous environments at elevated temperatures as well as liquid environments with varying salinity and pH.

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