# High Temperature Oxygen Sensing using $K_2Mo_6Cl_{14}$ Luminescence

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***Abstract*– A reflection mode optical sensing system for monitoring oxygen in high temperature gas flows, 25-220°C and 500 sccm, is presented. The sensor is based on $^3O_2$ quenching of the red emission from $K_2Mo_6Cl_{14}$, one member of a family of hexanuclear molybdenum chloride clusters. One advantage of using inorganic Mo-clusters as the lumophore is the lack of sensitivity to gases typically present in a coal-fired boiler due to the triplet nature of the transition from the excited to ground state. The sensor is prepared by dip-coating fiber tip in a sol-gel solution containing $K_2Mo_6Cl_{14}$ particle clusters. Drying and aging yields a composite film with $K_2Mo_6Cl_{14}$ immobilized in a porous silica matrix. The composite film deposited on a planar substrate was characterized via in-situ spectroscopic measurement up to 200°C. The emission intensity is constant following 56 cumulative hours of heating at 200°C, demonstrating long-term stability at high temperature.**

## I. INTRODUCTION

Real time and *in-situ* monitoring of oxygen gas concentration at high temperature in aerospace engine testing and during combustion processes is of significant importance. Optical fiber sensors based on fluorescence detection are a powerful technique to realize these objectives. The development of fiber optic oxygen chemical sensor has been continuing for more than a decade. Its merits over conventional electrochemical devices are small size, rapid response, the potential for multiplexing several sensors and the capability to probe remote harsh environment. However, current sensors based on organic and organometallic lumophores are limited to low temperatures and typically have a poor time responses.[1,2] A copper containing zeolite optical probe for indirect detection of oxygen at high temperature is described in Ref. 3. We have previously reported on a room temperature metal-halide cluster based fiber oxygen sensor[4], and more recently the immobilization of these clusters in a sol-gel matrix[5]. Here we describe the oxygen sensing capabilities of a high temperature $K_2Mo_6Cl_{14}$/sol-gel composite, as well as the measurement set-up for characterizing fiber optic sensors at elevated temperatures.

The sensor is based on $^3O_2$ quenching of the red emission from $K_2Mo_6Cl_{14}$, one member of a family of hexanuclear molybdenum chloride clusters. UV irradiation (300 – 400 nm) promotes the cluster to an excited electronic state. The red (600 – 900 nm) phosphorescence of the excited state is efficiently quenched by ground state triplet oxygen, where the degree of quenching decreases with increasing oxygen concentration.[4] The sensor signal is obtained by simply integrating up all the photons in the emission band.

In order to develop a fiber based oxygen sensor for high temperature applications, we have immobilized the potassium salt $K_2Mo_6Cl_{14}$ form of the cluster in an oxygen permeable sol-gel matrix. The details of the sol-gel processing are described in Ref. 5. We present here *in-situ* measurements of the emission intensity of the cluster/sol-gel composite at temperatures up to 210 °C, as well as the long term stability of the films following thermal cycling.

## II. EXPERIMENTAL

The absorption measurements were made using a Perkin-Elmer Lambda 40 series double beam UV/vis spectrometer. The emission spectra were obtained with a Fluorolog-3 instrument from Instruments S.A., Inc. The excitation beam was centered at 313 nm (with a 5 nm bandpass) and the emission monochrometer was scanned from 550 to 850 nm in 2 nm steps. The emission spectra have been corrected for both the spectral response of the emission grating and the photomultiplier tube.

The cluster/sol-gel films were deposited on quartz slides as described in Ref. 5, to evaluate the optical properties of the resultant films as a function of oxygen concentration and temperature. The emission spectra in different gas environments were taken in a specially fabricated quartz cuvette, with a gas inlet and outlet port to allow for measurements in a "flow through" configuration. A Pt microheater attached to the backside of the quartz slide was used to vary the film temperature from 25 to 210 °C. The temperatures we report here are that of the sensing film itself after accounting for the thermal conductivity of the quartz slide. Our experimental set-up allows us to obtain *in-situ* emission spectra while varying gas composition and the temperature of the sensing film.

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## III. RESULTS

Three different heat cycling experiments were performed on several $K_2Mo_6Cl_{14}$/sol-gel films on flat substrates to investigate the thermal stability of the films. The cluster concentration of all the films is $3 \times 10^{18}$ clusters/cm$^3$. Shown in Fig. 1 is the room temperature emission spectrum for film A after a total of 36 hours at 200 °C. The line shape of the film is essentially unchanged after heating compared to that of the unheated clusters in solution.

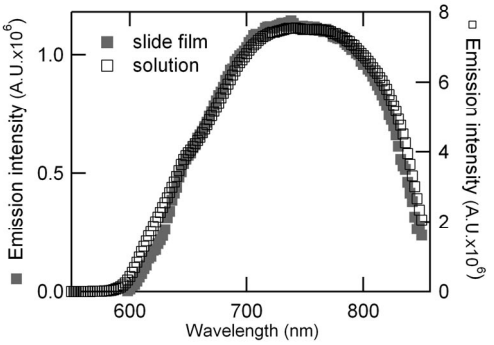


**Fig. 1**: Room temperature emission spectra of $K_2Mo_6Cl_{14}$ in $CH_3CN$ (□) and $K_2Mo_6Cl_{14}$ (■) in a sol-gel matrix (film A) following 36 hours at 200°C. Thermal cycling & sol-gel immobilization does not adversely affect the optical properties of the lumophores.

Fig. 2 shows the integrated emission intensity of the same film prior to heating and after 12, 17, 22, 34, 44, 56 hours of heating at 200 °C. The integrated emission intensity or sensor signal is obtained by integrating the emission spectra from 550 to 850 nm. The emission signal remains relatively constant after each cycle, demonstrating long-term thermal stability. In addition the data in Figures 1 and 2 show that neither thermal cycling nor sol-gel immobilization, alter the photophysics of the luminescent clusters.

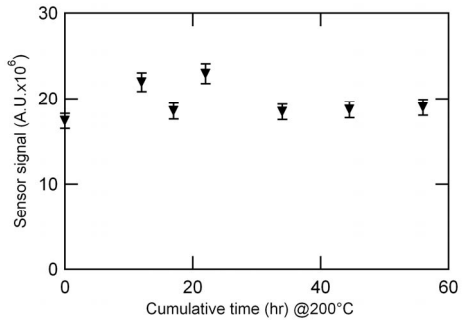


**Fig. 2**: Integrated emission intensity (550~850nm) from the $K_2Mo_6Cl_{14}$ sol-gel film of Fig. 1 after a total cumulative heating at 200°C of 56 hours. All measurements were taken at room temperature, after heating at 200°C for the indicated time. The data demonstrates the long-term survivability of the sensing film following repeated cycling to 200°C.

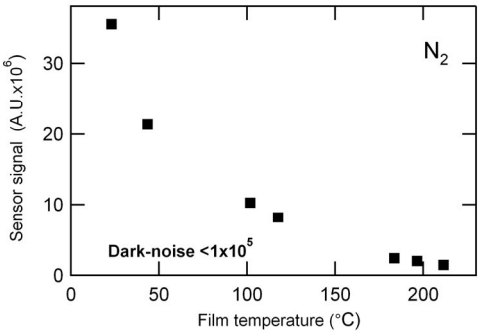


**Fig. 3**: *In-situ* measurements of the integrated signal intensity from a $K_2Mo_6Cl_{14}$ sol-gel film (film B) as a function of temperature. The dark noise is <10% of the signal at 210°C, demonstrating that there is sufficient signal/noise ratio for the high temperature sensor operation.

The sensor signal in nitrogen from a second film at 23, 43, 102, 118, 183, 196 and 211 °C are shown in Fig. 3. This data was obtained from *in-situ* measurements of the emission spectra at the indicated temperature. Although the signal decreases with temperature, at 200 °C the noise level is less than 10% of the signal.

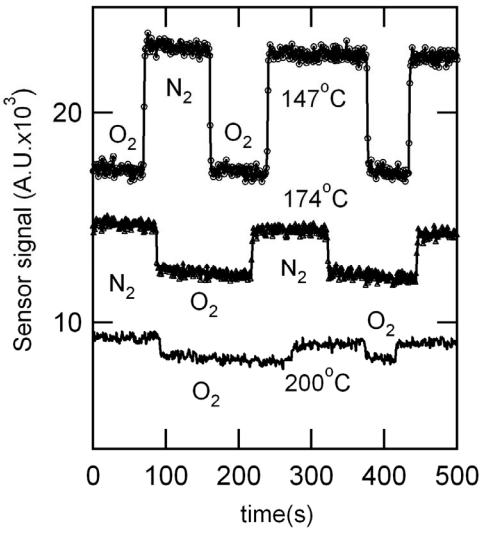


**Fig. 4** Oxygen quenching measurements from a $K_2Mo_6Cl_{14}$/sol-gel film (film C) at 147°C, 174°C and 200 °C. The emission intensity at 674 nm was monitored in real time while alternating between a pure $N_2$ and 20.7% $O_2$ gas environment. The response time of the film is fast, ~ 1 second, at high temperature.

Oxygen quenching measurements from a third film at 147, 174 and 200 °C are shown in Fig. 4. The sensing film was pumped at 313 nm with a 5 nm bandwidth. The emission intensity was monitored at 674 nm (within a 5 nm bandwidth) while alternating the gas in the measurement chamber between pure nitrogen (99.999 %) and 20.7 %

oxygen (balance gas is nitrogen). The quenching ratio (signal in $N_2$ vs 21 % $O_2$) remains at 1.4 X, even though the magnitude of the emission intensity decreases between 147 and 200 °C. As the time interval between data points is 0.5 s, the response time of the sensing film is fast at high temperature, on the order of 1 s.

We have successfully coated the end of a silica based optical fiber with the cluster/sol-gel composite film, see inset to Fig. 5. The optical fiber is designed to operate at temperatures of up to 150 °C in the UV to visible wavelength range. For a 1 µm thick cluster/sol-gel film on this 200 µm diameter fiber we estimate that there are ~$10^{11}$ clusters on the end face of the fiber. Based on the data in Figs 3 and 4 and our previous fiber sensor results[4], there are enough photons within our signal/noise ratio for oxygen sensing at 200 °C.

Fig. 5 shows the measurement set up we have developed to characterize the reflection – mode fiber sensors in a heated gas stream from 25 to 220 °C. A 365 nm UV Nichia LED with an output power of 900 µW, is coupled into the multimode fiber by a UV objective lens. The measured coupling efficiency is ~ 33 %. The reflected phosphorescence (590 – 850 nm) from the tip of the fiber sensor is collected by the photomultiplier tube. A 45 ° dichroic beam splitter and a 590 nm long wave pass (LWP) filter are used to separate the pump and signal beams. Note that because the clusters have a very wide absorption band (300 – 400 nm) we are able to use an inexpensive UV LED as the excitation source.

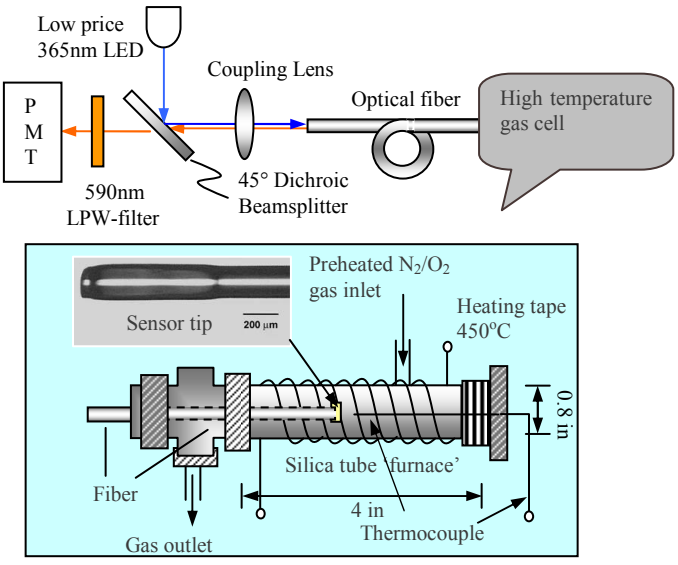


**Fig 5:** Schematic of the reflection mode fiber optic oxygen sensor measurement system. The working end of the fiber sensor is placed in a flow through gas cell that can be heated up to 220 °C. The gas exchange time is < 10 s. **inset**: optical micrograph of a fiber sensor tip.

The sensor probe is mounted inside a temperature-controlled flow through gas chamber using a fiber adapter. The heated gas stream, 25 to 220 °C (at atmospheric pressure) impinges upon the sensor tip at a flow rate of ~ 500 sccm. The gas exchange time in the gas cell is <10 s. A thermocouple was installed within 1 mm of the fiber sensor tip to monitor the gas temperature.

## IV. CONCLUSIONS

We are developing an intensity based reflection – mode fiber optical sensor for oxygen detection at elevated temperatures. The sensor is based on the oxygen quenching of the phosphorescence from $K_2Mo_6Cl_{14}$ clusters immobilized in a porous sol-gel matrix. The emission intensity from the cluster/sol-gel composite is relatively constant after 56 cumulative hours of heating at 200 °C. The photophysics of the clusters was shown to not be effected by thermal cycling or sol-gel immobilization. The clusters were successfully deposited on the tip of a high temperature fiber, and a flow through system for heated fiber sensor measurements was developed. *In-situ* spectroscopy of cluster/sol-gel composite films up to 210 °C show that there are sufficient photons within our signal/noise ratio for real time fiber optic based sensing at elevated temperatures.

## ACKNOWLEDGMENTS

The authors acknowledge the contribution of Reza Loloee, Michigan State University, towards development of the heated fiber test cell. This article was prepared with the support of the National Energy Technology Lab - U. S. Dept. of Energy, under Awarded No. DE-FC26-02NT41582. However, any opinions, findings, conclusions, or recommendation expressed herein are those of the authors and do not necessarily reflect the view of the DOE.

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