Fiber Optical Micro-detectors for Oxygen Sensing in Power Plants

Quarterly Technical Report
October 1, 2005 to December 31, 2005

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Jan. 2006

DOE Award Number: DE-FC26-02NT41582

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ABSTRACT

A reflection mode fiber optic oxygen sensor that can operate at high temperatures for power plant applications is being developed. The sensor is based on the $^3\text{O}_2$ quenching of the red emission from hexanuclear molybdenum chloride clusters. Previously we described a particle-in-binder approach to immobilizing the potassium salt of a molybdenum cluster, $\text{K}_2\text{Mo}_6\text{Cl}_{14}$, at the tips of optical fibers. Compared to previous methods, the particle-in-binder approach affords fibers with greatly improved mechanical properties. We have extensively characterized two fiber sensors at high temperature. We obtain quenching ratios between pure nitrogen and 21% oxygen as high as $3.9\times$ at 70 °C. For the first sensor at 60 °C we obtained a $\pm 1\%$ variation in the quenching ratio over 6 cycles of measurement, and monitored the device performance over 23 days. We were able to operate the second sensor continuously for 14 hours at 70 °C, and the sensor quenching ratio was stable to 5% over that time period. These are promising results for a high temperature fiber optical oxygen sensor based on molybdenum chloride clusters.

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INTRODUCTION

Maximizing the efficiency of the combustion process requires real-time control of the correct fuel/oxygen ratio. This requires the ability to sense oxygen levels over a broad range of concentrations with fast response times. Mussell, Newsham, and Ruud previously reported preliminary studies of the synthesis and optical properties of $\text{Mo}_6\text{Cl}_{12}$ -based clusters relevant to this project ^[1-4]. Mussell described the synthesis of the molybdenum clusters, and Newsham gives a good account of the properties of neutral $\text{Mo}_6\text{Cl}_{12}$ clusters and their salts, in both solution and a sol gel matrix. Newsham's data indicate that the photophysical properties of the clusters are maintained in sol gel matrices. To prepare a fiber optic sensor based on $\text{Mo}_6\text{Cl}_{12}$, Ruud dispersed $\text{Mo}_6\text{Cl}_{12}$ in poly[1-trimethylsilyl-1-propyne] (PTMSP), and used a dipping technique to immobilize the composite at the cleaved end of a silica optical fiber. Ghosh and co-workers ^[5] demonstrated a fast room temperature fiber optic sensor based on oxygen quenching of the luminescence from the PTMSP/ $\text{Mo}_6\text{Cl}_{12}$ composites. While the PTMSP support is adequate for room temperature applications, is unable to withstand the high temperatures associated with combustion in a power plant. To improve the sensor's high temperature performance, we are replacing PTMSP with a thermally stable sol gel matrix that should be able to withstand the higher temperature requirements of the power plant combustion process. The idea of using a sol gel as the support matrix for high temperature oxygen sensor application is not new. Remillard and coworkers have shown that a sol gel supported copper based oxygen sensor can be used in a combustion process ^[6]. With these facts in hand, we anticipate promising results from our design.

EXECUTIVE SUMMARY

A requirement of optical sensors based on luminescence quenching is that the lumophore have a strong luminescence that is efficiently quenched by oxygen, and that oxygen has ready access to the lumophore. For a high temperature sensor, these characteristics must hold over the entire temperature range of interest.

Previously we described a particle-in-binder approach to immobilizing the potassium salt of a molybdenum cluster, $K_2Mo_6Cl_{14}$, at the tips of optical fibers. This new protocol reduced densification and increased the quenching ratios to $\sim 6\times$. Compared to previous methods, the particle-in-binder approach also affords fibers with greatly improved mechanical properties. Having devised a successful protocol for coating the tips of optical fibers via the particle/binder approach, we emphasized in this reporting period the fabrication of fiber sensors to support tests of fiber sensor stability and batch-to-batch variability. We also generated substantial quantities of cluster-containing particles for future sensor fabrication efforts.

We also devised a ballistic pendulum test to characterize the adhesion of the sensing layer at the tip of the fibers and guide our efforts to improve adhesion. Fibers coated using the particle-in-binder approach generally passed the test, indicating the acceptable adhesion. However, fibers tips that were thermally cycled over long periods occasionally delaminated, suggesting the importance of further improvements in adhesion.

In our last quarter we showed measurements of a fiber device with a thermally stable sensor signal which was obtained by manually cycling between nitrogen and oxygen for a little over one hour. In this quarter we have significantly improved the fiber sensor characterization system to allow for quasi real time sensor measurements for an arbitrary time interval, as well as improved the signal to noise ratio of our optical measurements. The major changes to the system we made to the system were as follows:

- (1) implemented an automated gas switching system
- (2) redesigned the gas quartz chamber as a true flow through system with a gas exchange time of ~ 10 s for a gas flow of 200 sccm
- (3) reduced the intensity of “unwanted” light in the emission bandwidth that reaches the detector to a level $1/160$ of the smallest sensor signal in oxygen

During this reporting period we studied in detail the long term performance of two fiber sensors at high temperature, Fiber Sensor 45 at 58 °C and Fiber Sensor 70 at 71.5 °C. Both sensors were fabricated using pre-cured sol-gel particles containing $K_2Mo_6Cl_{14}$ immobilized in an OtMOS/TEOS binder matrix. Our goal was to determine (i) the cycle to cycle stability of the oxygen measurements, (ii) the sensor performance over a period of many hours and (iii) how repeatable is the sensor performance from two independently fabricated sensors using the “same” recipe.

For Fiber sensor 45 we find that at 58 °C during six N_2/O_2 cycles the sensor can clearly resolve the change of 0.5 % absolute oxygen concentration in the 2% - 8.5%, and changes of 1% absolute oxygen concentration in the 8% - 12.5%. From the cycle to cycle variations of the sensor intensity over the 1 hour measurement period we deduce that at 21.1% oxygen there is a ± 1 % variation in the concentration, whereas at 2.1% oxygen

there is a $\pm 15\%$ variation in the concentration. In the 0.1% to 1.0% O₂ range the sensor can clearly resolve the 0.1% changes in *absolute* oxygen concentration at high temperature. These measurements were made in the old measurement setup by manually switching between two gas concentrations.

Sensor measurements at 70 °C for 13.8 hours of cycling between 99.999 % N₂ and 21.1 % O₂ were made in the new optical measurement setup using the automated gas switch in a truly flow through geometry. The data are remarkably stable over time, as the quenching ratio varies from 3.9 to 4.1 over the entire measurement period. One issue that we need to deal with is the continued evolution of the sol-gel matrix during measurements in dry (water free) gas and at high temperature. This leads to a slow background drift in the sensor signal. The performance of Fiber 45 and Fiber 70 are similar. The nitrogen signal intensities are 3 to 4 nW. The pure nitrogen to 21.1 % oxygen quenching ratios are 2.7 at 86 °C and 3.9 at 70 °C. We are encouraged by our ability to be able to independently fabricate two sensors with similar performance.

EXPERIMENTAL

Materials.

All glassware was oven-dried prior to use. Acetonitrile (Spectrum Chemical Company, HPLC grade) was dried over CaH_2 and distilled prior to use. Tetraethyl orthosilicate (TEOS) (Aldrich, 98%), trimethoxy(octyl)silane (OtMOS) (Aldrich, 96%), *n*-trimethoxy(propyl)silane (PtMOS) (Gelest, 98%), triethoxy(octyl)silane (OtEOS) (Aldrich, $\geq 96\%$), (3,3,3-trifluoropropyl) trimethoxysilane (TFP-tMOS) (Gelest), and hydrochloric acid (CCI, electronics grade) were used as received. Fibers were purchased from 3M (FP-1.0-UHT) and Ceramoptec (PUV 1000/1300N), and were handled with gloves in order to minimize surface contamination. Volumes were measured to ± 0.05 .

Cluster-containing Powders for Composites.

mp series, 25-250 μm particles.

Sol-gel solutions containing $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ were aged for 4 – 7 months at room temperature to achieve solid monoliths. The monoliths were then ground using a mortar and pestle and cured at 70°C for 5 days to complete the sol-gel reaction and stabilize the particle against further densification. Three series of cluster containing sol-gel powders were prepared; mp31 with a $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ (cluster source MM5) concentration of 8.6×10^{-3} M, mp29 with a $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ (cluster source FJ17) concentration of 2.1×10^{-3} M, and mp34g-o with a $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ (cluster source FJ17) concentration of 2.3×10^{-3} M.

wlb series, 1–8 μm particles.

To obtain smaller particles than are available from grinding using a mortar and pestle, samples from the mp series were pulverized for 15 minutes using a small stainless steel ball mill (Wig-L-Bug).

Sol-Gel Stock Solutions.

TEOS based binder.

The preparation of a typical TEOS-based sol-gel binder solution is described below. TEOS (100 mL, 0.477 mol) and acetonitrile (70.3 mL) were added to a 500 mL Erlenmeyer flask. With stirring, water (32.3 mL, adjusted to pH=1 with HCl) was added and the solution was stirred for 1 hour at room temperature. The stir bar was removed from the flask and the solution was heated in an oil bath at 70°C for 2.5 hours. The solution was then transferred to a 500 mL glass bottle, capped, and aged at room temperature until use.

Fiber Coating.

Approximately 1 cm of jacket and cladding were mechanically removed to expose the fiber core. The exposed core was wiped with an acetone-soaked Kimwipe to remove residual cladding material and the tip was suspended in stirred acetone for 30 minutes. The fiber was removed, wiped with an acetone-soaked Kimwipe, rinsed with deionized water, and the fiber tip was suspended in a stirred solution of 2M KOH for 60 minutes. The fibers were removed from the KOH solution, rinsed with 5 mL of deionized water, and then the fiber tips were soaked in deionized water for 30 minutes with stirring. The

fibers were removed, rinsed with 5 mL of deionized water, dried using a stream of nitrogen gas, and placed into an oven at 70 °C for at least 30 minutes.

Scotch tape was used to assemble a flat bundle of five fibers with the fiber tips separated by 1 mm. The bundle of five fibers was dipped by hand at a 15° angle (for better coating of tip) into binder/particle mixtures, being careful to maintain the gap between the fiber tips. The fibers were hung vertically (tip-down) and dried under ambient conditions for one hour to promote uniform coating of the fiber tips.

Mechanical testing of composite adhesion.

A qualitative test of adhesion was performed using a stream of nitrogen gas at ~10 psi directed at the coating on the fiber tip and then followed by gently tapping the distal fiber edge on the edge of the laboratory bench top. A ballistic pendulum apparatus (**Figure 8**) was fabricated for more quantitative measurements. Fibers were imaged and weighed before testing, and then tape was used to secure the fiber to a sewing thread. The fiber was attached to the pendulum with the length adjusted so that the metal stop impacted the fiber where the fiber jacket had been removed, ~1 cm above the tip. The distance between the fiber impact point and the upper metal bar was ~22 - 26 cm. The fiber was then set to the desired angle, released, and allowed to impact the metal stop. The fibers were imaged after each test to assess changes in the film morphology. The impact force was calculated by.

$$I = 2m[3gL(1 - \cos(\theta))]^{1/2}$$

where I is the impact force in N·s, m is the mass of the fiber and string in grams, θ is the angle of travel in degrees, g is the acceleration due to gravity (9.8 m/s²), and L is the distance from the pendulum attachment point to the impact point in meters.

Optical microscopy of thin films.

Optical microscopy images were acquired using a Nikon Optiphot2-Pol equipped with a Sony Hyper HAD CCD-IRIS/RGB color video camera (model DXC-151A). The camera was connected to a PC using a Sony camera adapter (model CMA-D2). The images were captured using Hauppauge computer works Win/TV software (version 2.4.17052).

Fiber optic oxygen sensor characterization system

Fiber sensor 45 was characterized for an extended period of time using our “old” unmodified system that is described in detail in the previous report. A brief summary of the system follows. This automated high temperature reflection-mode fiber optic sensor characterization set-up uses a glass “furnace” to heat the tip of the fiber sensor up to ~220 °C and monitor the temperature to better than ± 5 °C using a thermocouple placed 1 – 2 mm. The gas flows are ~100mL/min. However as the residence time of the gas in the glass bulb is uncertain, we are unable to accurately estimate a gas exchange time for the system. We use a Labview program to simultaneously monitor the sensor signal and sensor temperature. The excitation source for the sensor measurements is a 900 μ W, 365 nm UV Nichia LED. Using the dichroic beam splitter and the UV objective lens we are able to couple 300 μ W into the multimode fiber by a UV objective lens. The reflected

phosphorescence (590 – 850 nm) from the tip of the fiber sensor is collected by the photomultiplier tube (PMT). A 45 ° dichroic beam splitter and a 590 nm long wave pass (LWP) filter are used to separate the pump and signal beams. The detection optics/electronics consists of a Hamamatsu R955 and a Stanford SR570 current pre-amplifier. The typical gain of the preamplifier used is 20 $\mu\text{A/V}$. We estimate that a 1 V signal at the voltmeter corresponds to 1 nW of phosphorescence signal from the fiber sensor.

Latest improvements to the optical characterization system

In our previous report we described measurements of a fiber device with a thermally stable sensor signal which were obtained by manually cycling between nitrogen and oxygen over ~ 1 hour. In this quarter we significantly improved the fiber sensor characterization system to allow for quasi real time sensor measurements for an arbitrary time interval, as well as improved the signal to noise ratio of our optical measurements. Fiber sensor 70 was characterized in the new system.

The major changes to the system, which are shown in **Figure 1** were:

- (1) Implementing an automated gas switching system
- (2) Redesigning the quartz chamber as a true flow through system with a gas exchange time of ~ 10 s for a gas flow as low as 200 sccm
- (3) Reducing the intensity of “unwanted” light in the emission bandwidth that reaches the detector to a level 1/160 of the smallest sensor signal in oxygen

The entire optical path from the UV LED to the detector was realigned on a *single* optical bench plate. This has improved our measurements in two ways. First we are now able to make meaningful long term, over several days, sensor measurements because of the improved stability of both the pump power coupled in the fiber sensor as well as the coupling of the output sensor signal to the detector. Secondly, we are able to remove a fiber sensor from the measurement system and reinstall it with a higher degree of reproducibility (repeatability of LED to fiber coupling of better than 1%), which allows for meaningful comparisons between one sensor and another.

Beginning at the UV source, the UV LED, the collimating lens and a UV bandpass filter were placed inside a single stackable lens tubing. This ensures the concentricity of all three components along the optical axis. The output UV beam is now collimated with a 25% variation in the beam size at a distance of 6 cm. The purpose of the UV bandpass filter (Semrock FF01-377/50-25 351/405), which has a 93 % transmission between 351-405nm, is to reduce the unwanted visible light from the UV LED that reaches the detector, see **Figure 2**. Since this visible output from the UV LED in the emission bandwidth of the Mo clusters, 600 – 800 nm, is spectroscopically indistinguishable from the real sensor signal, it sets a bound on the smallest signal we can detect. From the output spectra of the UV diode, we find that the integrated power output of the LED is about 2 μW in wavelength range of 600-800 nm. Without the Semrock visible rejection filter this results in an unwanted signal of about 0.4 nW at the PMT. **Table 1** lists the transmission and reflection parameters for all the relevant optical components. As shown in **Figure 3** the transmission through the Semrock bandpass filter is 93 % in the UV and an average of 5×10^{-5} for 600-700 nm and 3×10^{-3} for 700 -900 nm. We calculate that the unwanted signal from LED should now be only 0.002 nW. The measured

transmission through an optical fiber coated with sol-gel coating without any Mo-cluster, was measured to be about 0.01 nW. This was a PUV fiber with clusterless sol-gel particles in a TEOS/OtMOS sol-gel binder, which mimics a real sensor structure. The measured intensity in emission bandwidth that is 30 times smaller than the intensity in oxygen. A black plastic enclosure now covers the entire optical path and our signal-to-noise ratio is 4 times better than that of old characterization system.

Figure 1: Apparatus for automated high temperature fiber optical oxygen sensor characterization system, for details see text.

Figure 2 LED diode spectrum from Nichia company data sheet. There is 2 μW of unwanted visible signal from the LED itself in the emission bandwidth of the Mo-clusters.

Figure 3 (a) Semrock (FF01-377/50-25) band-pass filter spectrum, with a UV bandwidth 352-403 nm and 93% transmission, (b) enlarged spectrum in the range 500-900 nm, transmission $10^{-6} - 4 \times 10^{-3}$. The filter is used to remove the visible component of the LED output.

	Band-pass filter (700-800) nm	Dichroic Beam-Splitter (~750nm) (Est.)	Lens-fiber coupling (Est.)	Fiber Fresnel reflection (air) (Est.)	Dichroic Beam-Splitter (~750nm)	Fiber-Lens coupling (Est.)	High-pass filter (>590nm)
Transmission	3.4×10^{-3}	--	0.4	--	0.97	0.50	0.92
Reflectance		0.03		0.04			
P = 2 μ W							

Table 1: Reflectance and transmission in visible range for all the optical components used in the system shown in **Figure 1**. For 2 μ W of LED power at 750 nm, the peak luminescence wavelength, we obtain 0.002 nW at the PMT detector.

New gas handling system and sensor chamber

We designed a new gas flow system using a 3–way solenoid valve as an electronic switch (Cole-Parmer Inc. EW-98302-42) to switch between two different gases. The time duration of each gas pulse can be programmed by the switch controller. This system now allows us to perform a long-term gas cycling measurements with flow rate from 100 to 1000 sccm. In addition we now monitor both the input flow into the glass sensor chamber and the output flow from the chamber.

The glass shop fabricated the new quartz sensor chamber, which has a temperature-monitor and a flow-through structure consisting of tube and ball-shape head part, see **Figure 1**. A heating tape was wrapped on the entire cell tube to be able to uniformly heat input gas stream. A sensor tip will be placed on the ball-shape chamber center, which the design does help to achieve uniform gas flow and temperature distribution around the fiber tip. The gas exchange time is around 10 sec and less than 10% flow difference by monitoring input/output flow. The chamber size is $\phi 1.4 \times 6$ cm tubing shape, with one inlet, and a 2.6 cm diameter ball head, with two outlet ports. This quartz material will effectively decrease a potential fluorescence background from the chamber wall. A k-type thermocouple (Omega Inc.) was inserted into one of outlet ports on the ball head close to the fiber tip to monitor flow temperature and was fixed on the port by a shrink tube. 400 °C heating tape was wrapped on the outside of the 19 mL quartz tube. Temperature at 71.5 °C with a ± 1 °C variation was obtained for one day heating.

RESULTS AND DISCUSSION

Composite Approach to Sol-gel Matrices Containing $K_2Mo_6Cl_{14}$ Clusters on Fiber Substrates.

Our emphasis in the past two quarters has been to immobilize molybdenum clusters at the end of high-temperature optical fibers using methods that ensure high luminescence intensity from the clusters and strong quenching of the luminescence in the presence of oxygen. Previously we discovered that despite long aging and drying times, films deposited on substrates continued to evolve when they were tested at high temperatures. In general the quenching ratio decreased, which is consistent with densification of the sol-gel matrix. Our hypothesis is that in these materials, the limiting factor in the quenching process is the diffusion of oxygen to the molybdenum clusters, and that the oxygen diffusivity in the heat-treated sol-gel matrices was low. Both the change in the physical parameters of the sol-gel matrix and the low quenching ratio are problems that must be solved in any practical sensor.

As outlined previously, we developed a composite material approach that involves embedding molybdenum-containing sol-gel particles in a binder that essentially glues the particles to the substrate (**Figure 4**). This approach offers several advantages that will overcome some of the limitations encountered when depositing a homogeneous solution of the cluster in a sol-gel solution. First, by using a preformed and fully equilibrated cluster-containing sol-gel matrix, issues related to the long-term aging of the sol-gel matrix are avoided. Second, the use of small particle sizes should lead to large quenching ratios, since for small particles the diffusivity of oxygen should be dominated by the permeability of the binder. We expected that the binder, a minority component of the matrix, would fill the void space between the small particles and provide good particle-particle adhesion, and that the curing process would lead to little if any net change in the volume of the composite.

Figure 4. Schematic showing the expected morphology resulting from dip or spray coating a slurry of particles in a sol-gel binder solution. The particles correspond to pre-cured sol-gel particles containing $K_2Mo_6Cl_{14}$ clusters.

The materials generated by this approach are promising in that the quenching ratios for some fibers coated with a composite material were $>5\times$. In addition the properties of optical fibers prepared using the particle-in-binder approach are more stable. One problem was not solved by this approach; the adhesion of the composite material to the tip of the fiber was poor, and the fibers that were produced by this method are probably too fragile for most applications. There was a common failure mode for these fibers, after thermal cycling the composite was completely dislodged from the fiber tip. Close analysis of the fibers after failure suggests that in many cases there was a thin sol-gel layer still adhering to the surface. We believe that the failure stems from the shrinkage of the sol-gel binder that leads to a large stress at the interface and eventually catastrophic failure.

The obvious solution to this problem is to remove the source of stress and/or strengthen the mechanical properties of the binder itself. We found that a reliable way to increase the adhesion of the composite to the fiber tip is to use a sol-gel binder that undergoes minimal shrinkage as it cures. Such materials can be prepared by replacing a portion of the TEOS in the sol-gel recipe with alkyltriethoxysilanes such as octyltrimethoxysilane (OtMOS). Reducing the number of functional groups from four to three plus the addition of the alkyl group directly bonded to silicon reduces the cross-link density in the resulting sol-gel matrix and decreases the shrinkage that occurs during curing. Cleaned fibers were coated with a mixture of sol-gel particles and the new binder formulation with ethanol as the co-solvent, cured, and then evaluated by microscopy and by luminescence measurements. As previously shown, these fibers showed improved uniformity, and their adhesion to the tip of the fiber also was improved.

Synthesis of Cluster Incorporated Sol-Gel Powder

Having devised a successful protocol for coating the tips of optical fibers via the particle/binder approach, we emphasized in this reporting period the fabrication of fiber sensors to support tests of fiber sensor stability and batch-to-batch variability. We also generated substantial quantities of cluster-containing particles for future sensor fabrication efforts. Our best quenching and adhesion results were obtained when ball-milled particles (wlb29) were used as the cluster source. Using a monolith with the same room temperature aging time (7 months), cluster source (FJ17), and cluster density (1.3×10^{18} cluster/cm³), we used the ball milling technique to prepare particles of roughly the same size (wlb34g-o, 1 – 8 μm , **Figure 5**).

Figure 5. Dark field optical micrographs of 1 – 8 μm sol-gel particles (cluster source FJ17) prepared by ball milling (a) previously prepared wlb29 (50 $\times$), (b) newly prepared wlb34g-o, (50 $\times$) and (c) wlb34g-o, dark field (100 $\times$).

Multifiber Dip-coating of Fiber Sensors

We moved from single fiber dipping to dip-coating a 5-fiber array to minimize fiber-to-fiber variation (**Figure 6**). In principle, this process can be scaled to allow simultaneous coating of a large number of fibers. Typical results from the simultaneous dipping of five fibers are shown in **Figure 7**. Access to fibers with similar properties enables parallel testing of fibers under a broad range of conditions. Different cluster/sol-gel monoliths were tested to optimize sensor performance and adhesion for each case. The smaller particles obtained using a small ball mill gave better adhesion and sensor performance.

Figure 6. Processing schemes used for coating fiber bundles.

Figure 7. Typical results for simultaneous dip-coating 5 1000 μm diameter fibers with particle / sol-gel binder blends. Image A shows an uncoated fiber for reference. Images B – F are fibers were coated with a mixture of wlb29 powder in an OtMOS/TEOS binder.

Mechanical Testing

Previously we assessed adhesion using crude tests such as lightly tapping fibers on hard surfaces or immersing the fiber tip in a stream of nitrogen gas. These tests were a reasonable indicator of whether the fiber would survive mechanical shocks and the regimen of thermal cycling encountered in measuring sensor performance. We devised a ballistic pendulum test, which allows semi-quantitative adhesion assays for various particle/binder compositions and guides our efforts to improve adhesion. In this test, a pendulum of known mass at rest is allowed to swing through a fixed angle and impact a rigid stop. When the fibers are tested as a function of impact force, the threshold for physical damage to the coated sensor tip provides a measure of adhesive properties. The ballistic pendulum is shown in **Figure 8**.

Figure 8. Design of ballistic pendulum apparatus used to test sol-gel binder/powder coating adhesion to silica optical fiber based sensors.

The fibers were weighed, imaged, and then attached to the pendulum via a piece of sewing thread. Fibers images from representative ballistic pendulum tests are shown in **Figure 9** and details of the experiments and results are shown in **Table 2**. The fibers survive these tests surprisingly well. Films that appear to be cracked prior to testing generally survive, when the angle of travel reached 90°. These flaws may be surface features that do not affect adhesion at the fiber-composite interface.

Figure 9. Images of fibers coated with wlb29 powder in an OtMOS/TEOS binder before and after mechanical testing. A and B are the before and after images of a fiber tested at 30°; C and D are the before and after images from a second fiber tested at 90°. Images E-H are from a single fiber. Image E shows the fiber before testing, and F, G, and H show results after impacting from 30°, 60° and 90°, respectively.

Table 2. Mechanical Testing Results							
Fiber	Binder Used (Aged 5 days)	Powder Used	Cure Parameters (°C, hours)	String, Tape, and Fiber Mass (grams)	Distance to Impact Point (meters)	Angle (degrees)	Impact Force (N-s)
A/B	OtMOS/TEOS (ethanol)	wlb34g-o	70, 16.5	0.2396	0.225	90	0.62
C/D	OtMOS/TEOS (ethanol)	wlb34g-o	70, 16.5	0.2383	0.263	30	0.24
E-H	OtMOS/TEOS (ethanol)	wlb34g-o	70, 16.5	0.2330	0.263	30-90	0.65

Long-term Performance of Fiber Sensors at Elevated Temperature

During this reporting period we studied in detail the long-term performance of two fiber sensors at high temperatures, Sensor I (Fiber 45) at 58 °C and Sensor II (Fiber 70) at 71.5 °C. Our goal was to determine the cycle-to-cycle stability of the oxygen measurements as well as the sensor performance over a period of many hours.

Fiber Sensor 45 at 58 °C

Figure 10: High temperature measurements of Fiber Sensor 45 during six N₂ /O₂ cycles at 58 °C. Blue arrows indicate the introduction of 99.999% nitrogen and red arrows the introduction of 2.1 – 21.1% oxygen. The data demonstrates that the sensor can clearly resolve the change of 0.5 % absolute oxygen concentration in the 2% - 8.5%, and changes of 1% absolute oxygen concentration in the 8% - 12.5% at 58 °C. The luminescent tip contains K₂Mo₆Cl₁₄ sol-gel particles embedded in an OtMOS/TEOS binder matrix, with 1.3 x 10¹⁸ clusters/cm³ (Fiber 45). The coupled pump power is 300 nW at 365 nm and the gas flow rate is 1000 sccm. These measurements were made on the “old” sensor characterization system, with manual gas switching, described in the previous report. Detailed analysis of the measurements from each of the six cycles (labeled 1 – 6 at the bottom of the figure) are shown in the next two figures.

Fiber sensor 45 was selected for repeated N_2/O_2 cycling measurements and to monitor the sensor signal over a period of 24 days. This particular device was chosen due to the high initial sensor signal and the superior morphology and mechanical stability of the Mo-cluster/sol-gel compositing sensing film. The sensor was fabricated using a Ceramoptic UV transparent fiber (PUV-1000/1300 N), which has a 1000 μm silica core. The sensor tip contains $K_2Mo_6Cl_{14}$ sol-gel particles (FJ17 particles 1 – 8 μm in size) embedded in an OtMOS/TEOS binder matrix. The solvent is ethanol and the fiber was hand dipped in the binder/particle solution binder, then cured for 16 hours at 70°C. The tip contains $\sim 1.3 \times 10^{18}$ clusters/cm³. All the sensing measurements on Fiber 45 (**Figures 10, 11, 12, 13, and 14**) were made on the “old” sensor characterization system, with manual gas switching, described in the previous report. A simple gas divider was constructed from a two-way switch and two flow meters, which can read from 100 to 1000 sccm. The total gas flow was kept at a constant 1000 sccm. Pure nitrogen (99.999%) was mixed with either 21.1 % O_2 or 1.0 % O_2 for gas concentrations between 2.1 – 21.1% O_2 or 0.1 – 1.0 % O_2 respectively. Note that the residence time for the gas in the sensing chamber was not well defined in the “old” setup as it was not a true flow-thorough geometry.

Sensing measurements at 58 °C during six N_2/O_2 cycles were made 3 days after sensor fabrication and are shown in **Figure 10**. The data demonstrates that the sensor can clearly resolve the change of 0.5 % absolute oxygen concentration in the 2% - 8.5%, and changes of 1% absolute oxygen concentration in the 8% - 12.5% at 58 °C. Over the 1.05 hour measurement at high temperature the sensor signal was stable, with a 2.1% relative increase in the nitrogen intensity. Note that this change in signal intensity is not due to drift in the coupling of the pump into the sensor or out of the sensor, as the variation in coupled LED pump power has been measured to be less than 1% over 20 hours.

Figure 11: Quenching ratio (intensity in N_2 / intensity in O_2) for 6 N_2/O_2 cycles at 58°C for Fiber Sensor 45. The raw data are from **Figure 10**. The cycle-to-cycle variations correspond to a $\pm 1 - \pm 15$ % uncertainty in oxygen concentration over the entire measurement range from 21.1 - 2.1% oxygen respectively.

In **Figure 11** we have plotted the quenching ratio (signal in nitrogen divided by the signal in oxygen) as a function of oxygen concentration from each of the six cycles of **Figure 10**. The cycle-to-cycle variations over the 1 hour measurement period allow us to gauge the repeatability of measurements. We find that at 21.1% oxygen there is a ± 1 % variation in the concentration, whereas at 2.1% oxygen there is a ± 15 % variation in the concentration based on the intensity change. The larger variation in the measurements at low concentration is due primarily to the accuracy with which we can set the flow meter. We are very encouraged by the repeatability of our results at 58 °C.

We are somewhat puzzled by the slow upwards drift in the nitrogen from the first to the sixth cycle. This is a phenomenon we have observed in a number of sensors during the first few days of measurement. An increase in signal under nitrogen suggests that the heated dry gas flowing over the Mo-cluster/sol-gel composite removes an *in situ* quencher, possibly related to the solvent or byproducts of the sol-gel reaction. One possibility is “drying” or continuing to remove solvent from the sol-gel binder matrix. We are investigating whether curing the sensors in vacuum at 70 °C immediately after coating will improve performance.

The sensitivity of Fiber 45 at low oxygen concentration is shown in **Figure 12**, from 0.1% to 1.0% O₂ in steps of 0.1% at 60 °C. It shows that the sensor can clearly resolve the 0.1% changes in absolute oxygen concentration at high temperature. The quenching ratio at 1% O₂ is about 1.65, consistent with the data in **Figure 11**.

Figure 12: Sensor output signal from Fiber 45 at 60 °C as a function of oxygen concentration: 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, and 1% O₂ (balance is nitrogen). It shows that the sensor can resolve a 0.1% change in absolute oxygen concentration in the 0.1% - 1% range at 60 °C.

Figure 13: Signal from Fiber 45 measured over a period of 23 days, at room temperature (■), 83 °C and 114 °C(■), the lower measurement is 144 °C. The measurement sequence (day 0) began 3 days after the sensor was fabricated. On day 17, the sensor was measured at room temperature, 83 °C and 114 °C, then left at 90 °C for 20.5 hours with the LED blocked. As the sensor signal at room temperature on day 18 is the same as day 17, we conclude that high temperature excursions are not intrinsically harmful to the device. See text for explanation of the drop in signal on day 19. Note that the total UV exposure over the entire 23 days is about 22.5 hours.

Figure 14: Quenching ratio (signal intensity in N_2 divided by 21% O_2) for the measurement sequence described in **Figure 13**. The data demonstrates that after about 17 days and high temperature cycling the sensor response stabilizes.

In order to assess the stability of Fiber sensor 45 over time we tracked its performance over the 23 days period as shown in **Figures 13 and 14**. Day 0 of these two measurement sequences is three days after the sensor fabrication. The sensor signal in nitrogen decreased slowly over the first eight days, while the quenching ratio appears to be leveling off after day 5. No measurements were made from day 10 to day 16, during which time the sensor was stored in laboratory air. On day 17 the sensor was measured at room temperature, 86 °C, then 110 °C, and held at 90 °C for 20.5 hrs without UV exposure in lab air. The purpose of the 90 °C was to determine if high temperature in and of itself is harmful to the sensor. The answer appears to be no. On day 18: the room temperature measurement was repeated, the signal in nitrogen is the same, 4.3 nW, before and after heating while the quenching ratio drops by 10 %. Interestingly the quenching ratio, which is the measurement that will be used for sensing, stabilizes after about 17 days and high temperature cycling.

On day 19 the signal in nitrogen drops to 2.5 nW and does not recover. Sudden loss of signal implies a catastrophic loss of clusters which cannot be easily explained by a chemical process. A mechanical failure such as delamination and loss of the sensing layer at the tip of the fiber is more plausible, but micrographs of the sensor tip taken at day 0 and day 25, see **Figure 15**, show no signs of delamination of the Mo-cluster/sol-gel. We speculate that the composite delaminates from the flat surface at the tip of the fiber, but adhesions of the composite to the lateral surface of the fiber remains intact. This “internal” delamination of the composite likely affects the coupling of UV photons into the composite and the visible signal back to the detector. A better understanding of the drying process as a function of time, temperature and atmospheric pressure may provide insight into delamination, as well as conditions that result in more rapid stabilization of quenching ratios.

Figure 15: The side view of Fiber 45 before (day 0) and after 23 days of room temperature measurements as well heating at high temperature up to 114°C. There are no external signs of delamination and the morphology of the Mo-cluster/sol-gel film does not change.

Fiber Sensor 70 at 71.5 °C

Following our successful high temperature sensor measurements on Fiber 45, we tested the reproducibility of our sensor fabrication technique by fabricating and testing a “clone” of Fiber sensor 45. Fiber sensor 70 was fabricated using a Ceramoptic UV transparent fiber (PUV-1000/1300 N) which has a 1000 μm silica core. The sensor tip contains $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ sol-gel particles (FJ17 particles, 1 – 8 μm in size) embedded in a OtMOS/TEOS binder matrix. The solvent is ethanol and the fiber was hand dipped in the binder / particle solution, then cured for 16.5 hours at 70°C. The tip contains $\sim 1.4 \times 10^{18}$ clusters/ cm^3 . The difference in the fabrication is that this sensor was cured for 0.5 longer than Fiber 45.

Sensor measurements at 70 °C for 13.8 hours of cycling between 99.999 % N_2 and 21.1 % O_2 are given in **Figure 16**. These measurements were made in our new quartz gas cell using the electronic gas switching system and the new optical measurement setup shown in **Figure 1**. The sensor was 19 days old at the start of the measurements. Since we know that the input and output gas flows are the same to better than 5%, we can estimate that the gas exchange time is 10 s for a 200 sccm flow. The temperature stability of the system is 71.5°C $\pm$ 1°C. Note that the 0.4 °C “jitter” in the temperature data is most likely due to digitization errors in the D/A board and could be improved upon by adjusting the voltage input range of the board. Prior to making sensing measurements we determined that the “unwanted” signal from a fiber device without any Mo-clusters, i.e. a fiber with sol-particles in the same binder matrix, was 0.01 nW. This is a factor of 70 larger than our lowest signal in oxygen.

The data in **Figure 16** are remarkably stable over time. The variations sensor signal in nitrogen is synchronous with the temperature fluctuations. On top of this behavior is a slow drift over the 13.8 hours of measurement from 3.1 to 2.9 nW, which is not due to the drift in the optical coupling. We speculate that as in the case of Fiber Sensor 45 it reflects *in situ* curing of the sol-gel binder at high temperature. The oxygen intensity decreases linearly with time from 0.8-0.7 nW and seems to be uncorrelated with the temperature variations. The quenching ratio varies from 3.9 to 4.1 over the measurement period.

The performance of Fiber 45 and Fiber 70 are similar, with nitrogen signal intensities in the 3 to 4 nW range and pure nitrogen to 21.1 % oxygen quenching ratios of 2.7 at 86 °C and 3.9 and 70 °C. Again we believe that the variations between the two sensors are most likely due to evolution of the sol-gel binder with time, gas flow and temperature. These are very exciting results as they demonstrate the feasibility of using Mo-clusters to monitor oxygen at temperature in the 60 – 70 °C range for a period of many hours.

Figure 16: High temperature measurements of Fiber Sensor 70 during 13.8 hours of cycling between 99.999 % N_2 and 21.1 % O_2 at 70 $^{\circ}\text{C}$. These measurements were made in our new quartz gas sensor cell, in which we achieve temperature stability of $\pm 1^{\circ}\text{C}$ for 13.8 hours. In this flow-through cell the gas exchange time is 10 s for a 200 sccm flow. The gas cycling is controlled by a solenoid switch, with 3.6 min in N_2 and 2.3 minutes in O_2 . The variations in the envelope of the sensor signal are synchronous with the temperature fluctuation. The data demonstrates that we can achieve a quenching ratio of 4 ± 0.1 between pure 99.999 % nitrogen and 21 % oxygen over 13.8 hours at $71.5 \pm 1^{\circ}\text{C}$.

CONCLUSIONS

We are encouraged by the measurement results of our two fiber sensors tested at high temperature for extended periods of time. The approach of using $K_2Mo_6Cl_{14}$ immobilized in an OtMOS/TEOS binder matrix appears to give us sensors with reasonably reproducible results for short-term measurements. One issue that we need to deal with is the continued evolution of the sol-gel matrix during exposure to dry (water free) gas as well as high temperature. The time scale for the resultant background drifts on the order of days. We are investigating whether curing the sensors at 70 °C under vacuum will “age” the sensor quickly and results in more stable sensing behavior for long term measurements.

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None.

LIST OF ACRONYMS AND ABBREVIATIONS

HCl – Hydrochloric Acid
MeOH – Methanol; CH_3CN – Acetonitrile
TEOS – Tetraethyl orthosilicate
OtMOS – trimethoxy(octyl)silane
OtEOS – octyltriethoxysilane
TFP-tMOS – trimethoxysilane;
PtMOS – propyltrimethoxysilane

APPENDIX A - ACKNOWLEDGEMENTS

We wish to acknowledge the contribution of Reza Loloee, Michigan State University, towards the gas flow switch box and design of new gas flow through cell and Per Askeland, Michigan State University, regarding discussion on the thermal properties of various sol-gel binders. The Labview program for sensor data acquisition was developed by Mr. Nate Verhanovitz (Troy Research Systems, LLC)