

Fiber Optical Micro-detectors for Oxygen Sensing in Power Plants

Quarterly Technical Report
July 1, 2005 to September 30, 2005

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October 2005

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 immobilized the potassium salt of a molybdenum cluster, $\text{K}_2\text{Mo}_6\text{Cl}_{14}$, in a sol-gel matrix and showed that the luminescence is stable after 54 hours at 200 °C, but the quenching ratios were low and the films delaminated after thermal cycling due to densification of the matrix. Three new approaches to solve decreased quenching over time and delamination of films off fiber tips were investigated. In the first approach $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ embedded in cured sol-gel particles were incorporated into a TEOS based sol-gel. These gave enhanced quenching (6×), but delaminated. Our second approach was to use a commercial cyanoacrylate glue to immobilize the particles onto the tip of an optical fiber. This gave better adhesion and good quenching initially, but eventually the glue degraded upon heating. Our third approach was to use a 55% OtMOS/ TEOS sol-gel binder. Films based on this new sol-gel binder show high quenching (~6×) and superior mechanical stability even after thermal cycling. Sensor measurements on an optical fiber containing $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ embedded in cured sol-gel particles were obtained from 100 to 25 °C. The signal intensity in nitrogen was stable at 2.8 ± 0.2 nW, and the quenching ratio (ratio of signal in N_2 vs. 21 % O_2) varied from 4.4 to 6.9X. 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 immobilized the potassium salt of a molybdenum cluster, $K_2Mo_6Cl_{14}$, in a sol-gel matrix and showed that the cluster luminescence is stable after 54 hours at 200 °C. However, the quenching ratio for these materials decreased from 4 to 1.5 due to densification of the sol-gel matrix, and the films often delaminated from substrates after thermal cycling. To address the decrease in quenching we prepared a slurry of pre-cured sol-gel particles containing $K_2Mo_6Cl_{14}$ dispersed in a sol-gel solution and deposited the slurry on planar substrates and optical fibers. This new approach reduced densification and increased the quenching ratios to $\sim 6\times$. To address delamination we tested the use of a commercial cyanoacrylate glue. While the initial results were promising, cyanoacrylates degraded during thermal treatment and proved to be incompatible with $K_2Mo_6Cl_{14}$. More successful was a modification of the sol-gel binder to reduce its shrinkage while curing and reduce stress at the substrate/sol-gel interface. Using this strategy, we obtained luminescent films that do not delaminate with thermal treatment to 58 °C, have high quenching ratios even at 58 °C ($\sim 6.5\times$), and are stable over time. The lower crosslink density also allows oxygen to more easily diffuse to and quench the cluster by opening up the sol-gel pore structure.

The automated reflection-mode high temperature (up to 220 °C) fiber sensor test set-up was brought on line during this period. Extensive sensor measurements on an optical fiber containing $K_2Mo_6Cl_{14}$ dispersed in a TEOS based sol-gel binder were made between room temperature and 100 °C. In pure nitrogen the signal is 2.8 ± 2 nW and the quenching ratio (signal in N_2 vs 21% O_2) varied from 4.4 to 6.2 X over the temperature range. We obtained a ~ 3 nW output signal for ~ 300 μ W of incident pump power; 10^{-5} is a very reasonable power conversion efficiency for a fiber sensor. In addition the signal level in synthetic lab air was a factor of 40 larger than the autofluorescence, which sets a lower bound on the smallest detectable signal from the sensor. The absolute magnitude of the sensor signal, the degree of quenching and the signal to noise ratio of this sensor are very encouraging in terms of practical implementations of our device.

However the long term mechanical stability of this first sensor we have tested at high temperature was poor. Following an extended series of high temperature measurements the device failed due to delamination of the cluster containing composite from the fiber tip. Subsequently, a series of fibers using mixtures of OtMOS and TEOS binders were prepared. We are in the process of characterizing these sensor, the initial results are promising. At 60 °C the cluster/sol-gel composite continues to adhere to the end of the silica fiber and the signal level in pure nitrogen is 4 nW, slightly higher than that for the previous fiber sensor.

Dr. Po Zhang, the postdoctoral associate developing the fiber sensors will be presenting a talk entitled, "High Temperature Oxygen Sensing Using $K_2Mo_6Cl_{14}$ Luminescence " at the International IEEE Sensors Meeting (<http://ewh.ieee.org/tc/sensors/sensors2005/>), in

Irvine, CA Oct. 31 – Nov. 3, 2005. His talk will be in the “Optical Sensors for High Temperature & Environmental Applications” session.

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%), 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.

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. These monoliths were then ground using a mortar and pestle and cured at 70 °C for 5 days to complete the sol-gel reaction and minimize further densification of the sol-gel matrix. Two series of cluster containing sol-gel powders were prepared; mp31 with a $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ (MM5) concentration of 8.6×10^{-3} M and mp29, with a $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ concentration (FJ17) of 2.1×10^{-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) ball pestle.

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.

55% OtMOS/TEOS based binder.

The preparation of a typical 55% OtMOS / TEOS sol-gel binder solution is described below. TEOS (5.84 mL, 26.0 mmol), OtMOS (8.16 mL, 31.6 mmol), and the co-solvent (see below) were added to a 20 mL scintillation vial and stirred. Water (3.2 mL, adjusted to pH=1 with HCl) was added and the solution was stirred at room temperature until clear (~15 minutes). The bottle was then sealed using a Teflon lined cap. The solution was diluted 1:1 v/v with an additional portion of the co-solvent to decrease the viscosity of the solution. The solution was then aged at room temperature until used. For binder solutions with acetonitrile as the co-solvent, deionized water (864 mL, 0.480 mol) and dry acetonitrile (18.4 mL, 0.352 mol) were pre-mixed in a brown glass bottle. For binder solutions using ethanol as the co-solvent, deionized water (864 mL, 0.480 mol) and ethanol (20.0 mL, 0.352 mol) were pre-mixed in a brown glass bottle while stirring.

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 Kim Wipe to remove residual cladding material and the tip was suspended in stirred acetone and for 30 minutes. The fiber was removed, wiped with an acetone-soaked Kim Wipe, 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.

Fibers were dipped by hand at a 15° angle (for better coating of tip) into composites and allowed to dry under ambient conditions for one hour while hanging vertically to maximize coating uniformity on the tip.

Preparation of fiber M (TEOS binder and mp31).

A paste containing 60 w/w% was prepared by adding a known mass of TEOS-based sol-gel solution aged at room temperature for 70 days to a predetermined mass of mp31 powder to obtain a light yellow paste. The paste was then mixed with gentle grinding in a small vial to increase homogeneity. A clean dry fiber was then dipped at an angle of 15° and hung vertically for 1 hour to achieve a uniform coating and pre-dry the film. The pre-dried film was cured at 70 °C for 12 hours.

Preparation of fiber 10 (cyanoacrylate glue and mp31).

A clean dry fiber was dipped into a small bead of super glue placed on a quartz slide leaving a relatively large bead of glue on the tip of the fiber. The coated tip was then gently touched to the quartz slide to remove much of the glue leaving a thin coat (~5 µm) on the tip. The pre-coated tip was then dipped into a small amount of powder, removed, allowed to dry for 5 – 10 seconds and then dipped again into the powder. After the second dipping the coated fiber was hung vertically and allowed to dry for 15 minutes under ambient conditions. The pre-dried fiber was then placed into an oven at 70 °C for 30 minutes to completely cure the film.

Preparation of fibers 26, 27, 32, 33, 45, and 46 (55% OtMOS / TEOS and wlb29).

A paste containing 60 w/w% was prepared by adding a known mass of room temperature aged 55% OtMOS / TEOS based sol-gel solution to a predetermined mass of wlb29 powder to obtain an off-white paste. The paste was then mixed with gentle grinding in a small vial to increase homogeneity. A clean dry fiber was then dipped at an angle of 15° and hung vertically for 1 hour to achieve a uniform coating and pre-dry the film. The pre-dried film was cured at 70 °C for 12 hours. Fibers 26, 32, and 45 used the sol-gel binder containing ethanol as the co-solvent and fibers 27, 33, and 46 used the sol-gel binder with acetonitrile as the co-solvent. Fibers 26, 27, 45, and 46 used 5 – 6 day old sol-gel binder and fibers 32 and 33 used sol-gel binder aged at room temperature for 12 days.

Mechanical testing of composite adhesion

All fibers were tested for mechanical stability before measurements in nitrogen or oxygen by first gently tapping on the edge of the bench top followed by a gentle stream of nitrogen gas. All fibers used in this report withstood mechanical testing with little or no loss of coating.

Optical microscopy of thin films.

Polarized 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 viewed using a Sony Trinitron color video monitor. Images were taken using Hauppauge computer works Win/TV software (version 2.4.17052).

Absorption spectroscopy.

Samples were prepared by weighing 2 - 3 mg of $\text{Mo}_6\text{Cl}_{12}$ in a small sample vial. The compound was then dissolved in a small amount of dry acetonitrile and transferred to a 10 mL volumetric flask. The volumetric flask was filled to the mark, stoppered, and shaken to insure a homogenous solution. Typical concentrations were 1.7×10^{-4} M. Absorption spectra were measured using a Perkin-Elmer Lambda 40 series double beam UV/vis spectrometer. Data analysis was performed using the UV Win lab (version 2.80.03) software package supplied with the instrument and plotted using Microsoft Excel. Solutions were placed into a 1 cm pathlength quartz cuvette with a separate cell containing only solvent as a reference.

Fluorescence measurements

The fluorescence measurements were performed using a Fluorolog-3 instrument from Instruments S.A., Inc. The system includes a single Czerny-Turner excitation spectrometer with a 1200g/mm ruled grating blazed at 330nm and a single Czerny-Turner emission spectrometer with a 1200g/mm holographic grating blazed at 630 nm. The excitation optics consists of a 450W ozone free Xe lamp, followed by a 270-380 nm bandpass filter (Oriel 1124). A Si photodiode is used to continuously monitor the lamp signal. The detection optics consists of 603.2 nm long wave pass filter (CVI) followed by a multi-alkali photo multiplier tube (Hamamatsu R928) with photon counting electronics. Data processing was performed using the Datamax (version 2.2) software package supplied with the instrument. Spectra were obtained by exciting at 313 nm and scanning the emission monochromator from 550 to 850 nm.

Measurements of cluster fluorescence in solution were performed by placing the solution in a quartz cuvette sealed with an airtight septum. Spectra were measured in laboratory air and high purity nitrogen (AGA, Inc, 99.999%). Prior to obtaining spectra, all gases were bubbled through the solution for 10 to 15 minutes at a rate of ~ 10 mL / min. via a glass pipette inserted through the septum. For the measurements of the potassium salts in HCl a glass pipette was used to bubble oxygen into the solution.

The measurements of the $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ emission from Mo-cluster / sol-gel composite films were made in the quartz cuvette sealed with an airtight septum. Nitrogen gas with purity 99.999% was used to obtain the luminescence spectra in a non-oxygen environment. The oxygen measurements (21% oxygen in nitrogen) were performed using 99.999% purity

gas. The nitrogen and oxygen were injected bias a needle passing through the septum and allowing the gas in the cuvette to equilibrate for 10 min. An external gas flow switch was designed and built to conveniently change the gas environment without needing to touch the spectrometer compartment. This switch allows us to be completely certain that the sample does not move during repeated gas exchange.

The *in-situ* measurements of the $K_2Mo_6Cl_{14}$ emission from Mo-cluster / sol-gel composite films, as a function of temperature were made in the same quartz cuvette described above. A platinum microheater (part 32 208 172 from Heraeus Sensor Technology) was attached with a thermally conducting epoxy resin (Ther-O-Bond/1500 hardener) to the backside of the quartz slide. The epoxy is allowed to cure for at least four hours in air at room temperature. Electrical connection to the Pt heater was made by microwelding 5 mill thick Cu wire to the 5 mill thick legs of the Pt microheater. The electrical leads were then threaded through the septum. The microheater was powered with a regulated voltage supply. We determined the heater temperature by monitoring the heater resistance, and using the resistance versus temperature curves for a standard 100 ohm Pt thermometer. The thermal impedance of the quartz slide was independently determined by gluing a Pt thermometer to the front of a quartz slide, and monitoring the temperature of the front side of the slide in the quartz cuvette under the same gas flow conditions used during spectroscopy. Thus, by monitoring the backside heater resistance we know the temperature of the front side of the slide to ± 5 °C.

Fiber optic oxygen sensor characterization system

The automated high temperature reflection-mode fiber optic sensor characterization set-up shown in Figure 1 was brought on-line during this period. The ceramic “furnace” allows us to heat the tip of the fiber sensor up to ~ 220 °C and using a thermocouple placed 1 – 2 mm from the fiber tip we are able to monitor the temperature to better than ± 5 °C. Using typical laboratory gas flows, ~ 100 ml/min, the estimated gas exchange time in the ceramic “furnace” of < 10 s, which will allow us to determine the time response of the sensor. 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 is 20 μ A/V. We estimate that a 1 V signal at the voltmeter corresponds to 1 nW of phosphorescence signal from the fiber sensor.

Our long term goal is to develop an inexpensive, portable sensor characterization system. Note that because the clusters have a very wide absorption band (300 – 400 nm) we are able to use an inexpensive (\$6) UV LED as the excitation source. Back in 1999, our only choice was to use a \$30,000 HeCd laser for excitation. Using the LED we are able to achieve a comparable excitation intensity in the high temperature fiber as what we used

for the room temperature sensor [5]. We are currently using a photo multiplier tube as the detector to allow us to do spectroscopy. In the future we will take advantage of the broad emission band of the clusters (590 – 900 nm) to replace the PMT with an inexpensive Si photodiode.

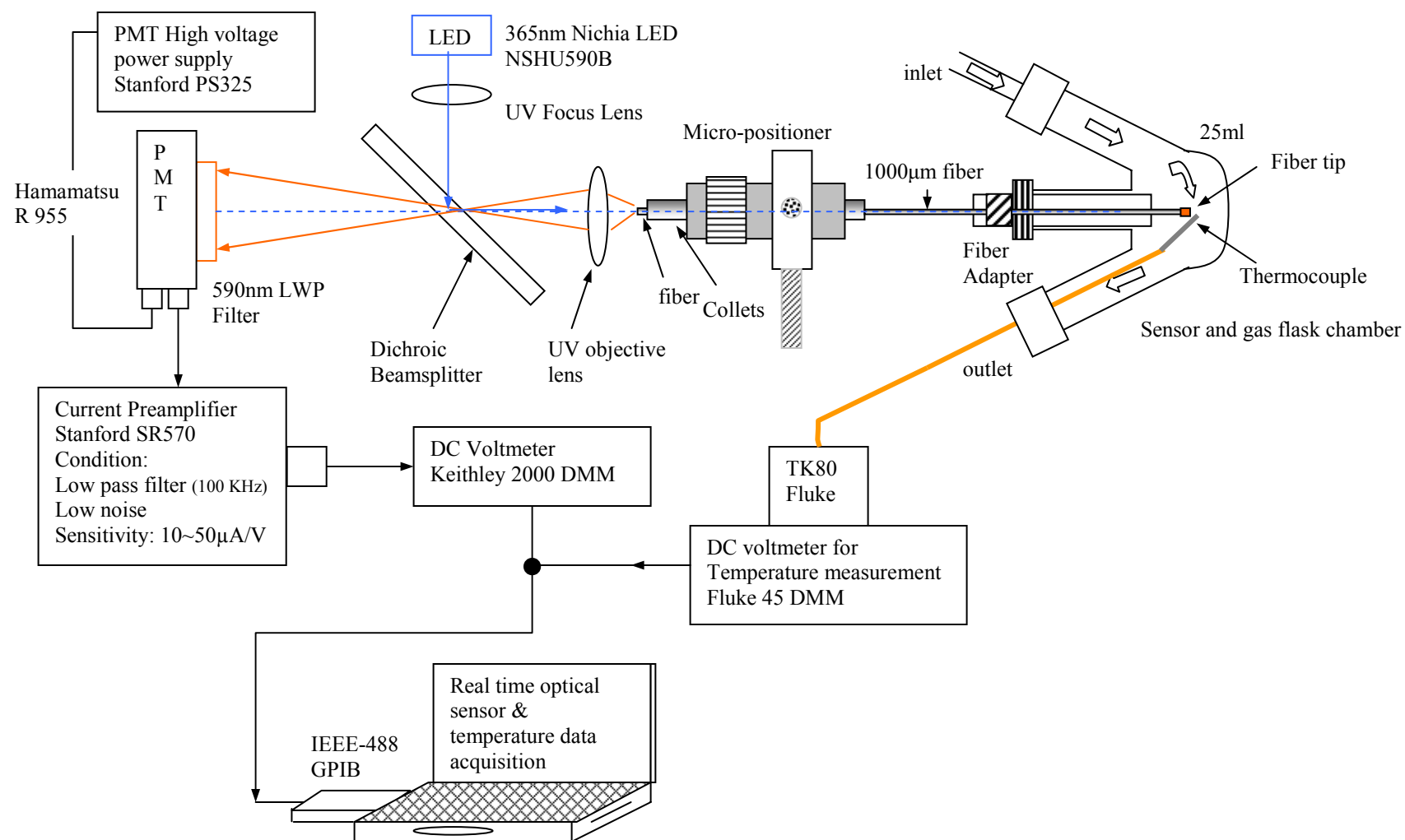


Figure 1. High temperature fiber sensor characterization system.

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 in our last report, 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 2**). 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.

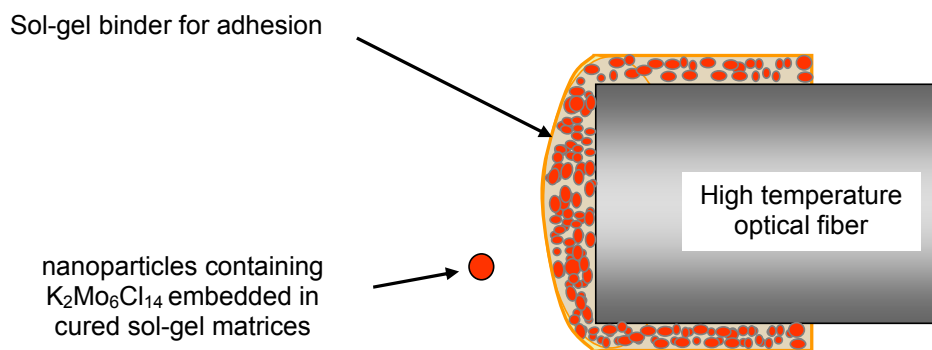


Figure 2. Schematic showing the expected morphology resulting from dip or spray coating a slurry of particles in a sol-gel binder solution. The particles correspond to pre-cured sol-gel particles containing $K_2Mo_6Cl_{14}$ clusters.

The materials we 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 optical fibers have more stable properties using the particle in binder approach. 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 investigated two approaches. In the first we altered the chemistry used in the sol-gel binder to reduce binder shrinkage during curing. Minimizing shrinkage should improve adhesion by reducing the stress at the interface between the composite and the fiber. In the second, we took a somewhat unusual approach and briefly investigated the possibility of using commercial adhesives to glue the sol-gel particles to the fiber surface. If successful, this would simplify sensor fabrication since most glues cure rapidly.

We elected to use a commercial cyanoacrylate adhesive (super glue) to test the notion that the sol-gel particles could be glued directly to the end of the fiber. This process simply requires coating the tip of the optical fiber with glue and then depositing the sol-gel particles containing the molybdenum complex onto the surface of the fiber. Curing is completed in minutes. The resulting fibers are quite interesting and not surprisingly, there is excellent adhesion of the glue and particles to the surface of the fiber. As shown in the second panel of **Figure 3**, the particles appear to cover the surface although the uniformity of the coating is poor, partly due to the use of large particles. The uniformity of the coating seems inferior to the control sample shown in the top panel. The luminescence intensities from these fibers in nitrogen and oxygen yield high quenching ratios that approach those of solutions. However, there are two significant problems with this approach. The first is that the fiber-particle interface is a thin layer of glue, and particle-particle adhesion is poor. Not surprisingly, the composite material at the tip of the fiber was easily abraded from the surface. Using more glue (Fiber 10) resulted in a high luminescence intensity and quenching ratio, but the luminescence from the composite degraded over time, suggesting a deleterious chemical interaction between the glue and the clusters. The latter result prompted us to reconsider sol-gel solutions as binders.

A more 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

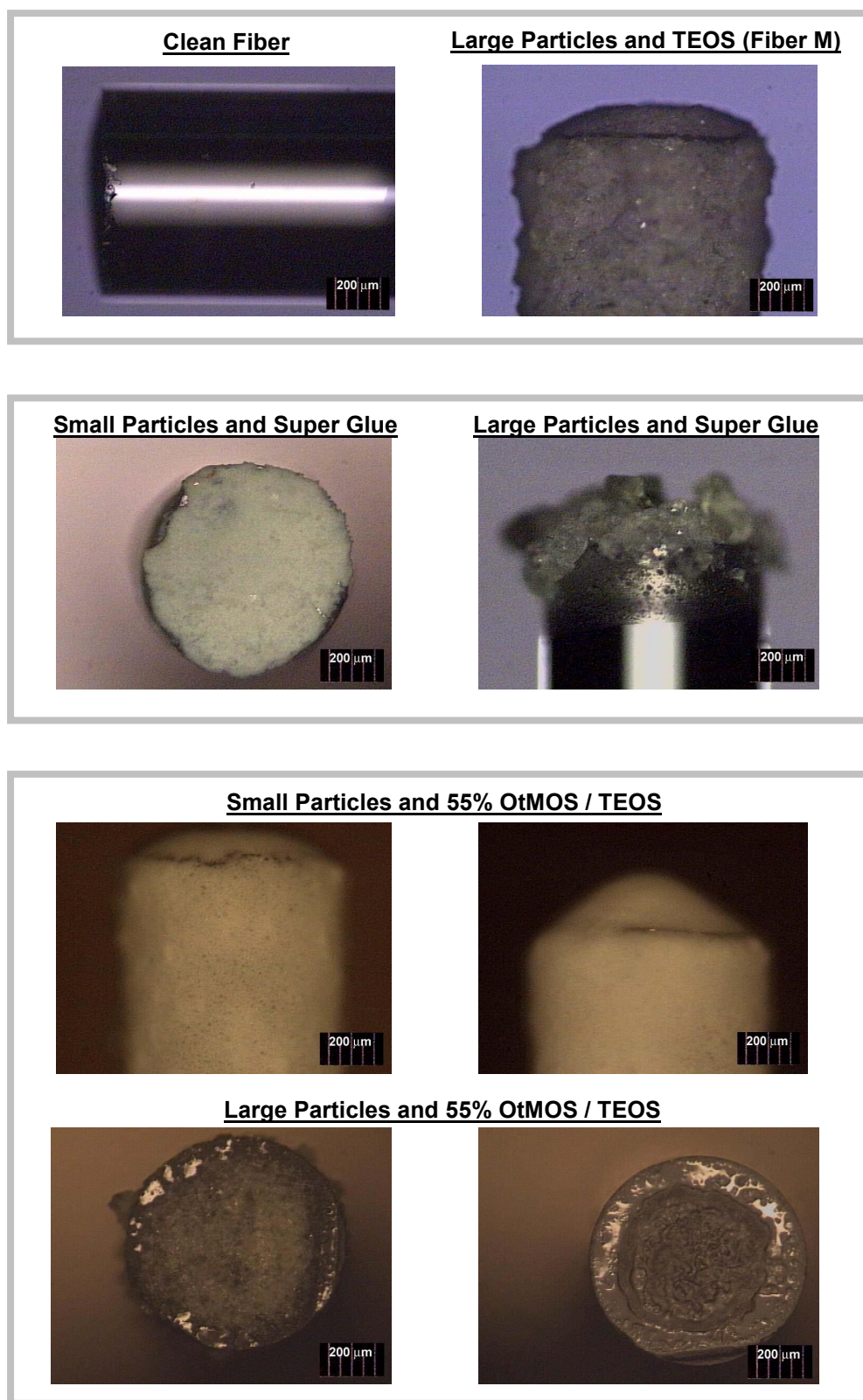
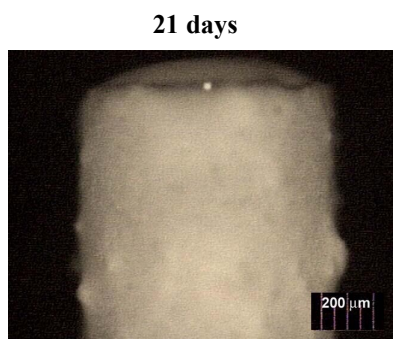
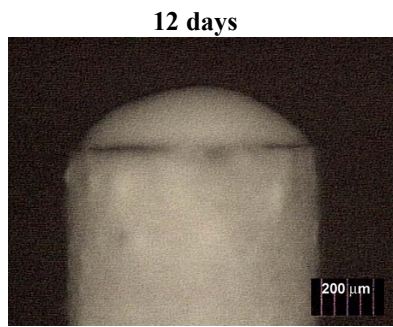
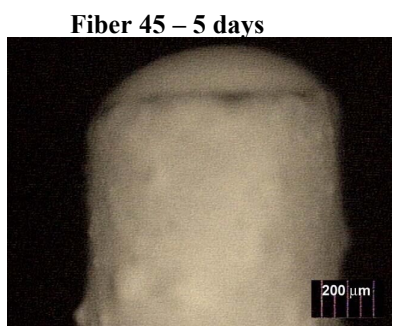
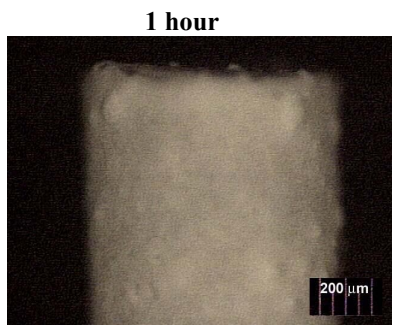


Figure 3. Images showing the range of results obtained from coating with different binders and particle sizes. Large particles are 25-250 μm and small particles are 1-8 μm . Note that high temperature sensor data for Fiber M are described in the next section.

Ethanol
55% OtMOS / TEOS and wlb29



Acetonitrile
55% OtMOS / TEOS and wlb29

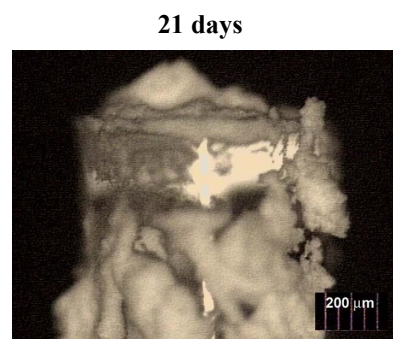
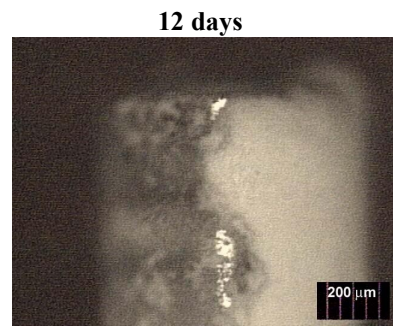
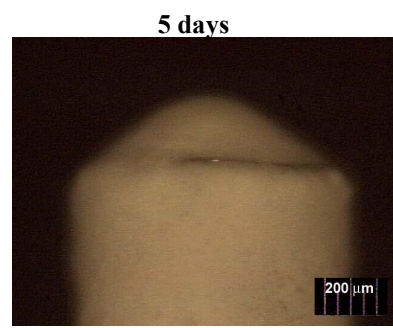
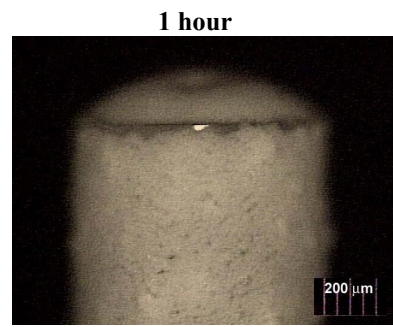


Figure 4. Images showing the range of film properties and adhesion obtained by varying the sol-gel aging time and co-solvent. The binder composition is 55% OtMOS / TEOS and the diameter of the particles are 1-8 μm for all samples shown.

particles and the new binder formulation, cured, and then evaluated by microscopy and by luminescence measurements. As shown in the bottom four photos in **Figure 3**, these show improved uniformity, and their adhesion to the tip of the fiber also was improved. **Figure 4** shows further examples of this modified approach, contrasting the use of acetonitrile and ethanol as co-solvents. All of the samples used finely powdered sol-gel particles and all show excellent coating and adhesion to the fiber surface.

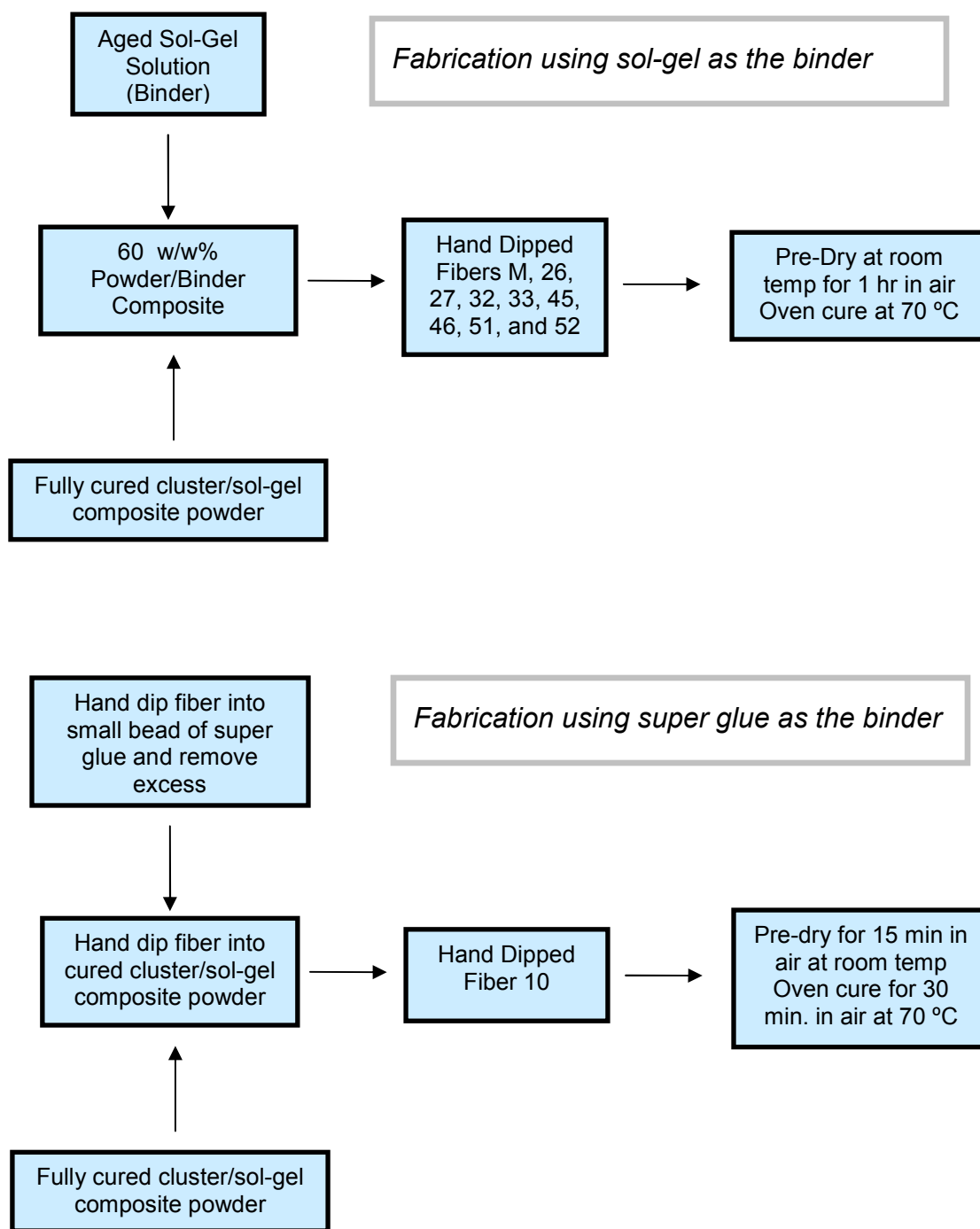


Figure 5. Processing schemes used for fibers. Different cluster/sol-gel monoliths were tested to optimize sensor performance and adhesion for each case. Larger particles sizes gave better adhesion and sensor performance for fiber M and 10. The smaller particles obtained using a small ball mill gave better adhesion and sensor performance.

High temperature fiber sensor measurements.

The oxygen sensing characteristics of one of our first successful fiber sensors prepared using a sol-gel binder to immobilize sol-gel particles embedded with $\text{K}_2\text{Mo}_6\text{Cl}_{14}$ are shown in **Figures 6 – 11**. The data are from Fiber M (see **Figure 3**), a fiber sensor with large particles using a TEOS binder, and span the temperature range of 100 °C to room temperature. There are 4×10^{18} clusters/ cm^3 in the composite, which formed a $\sim 100 \mu\text{m}$ thick hemispherical cap on the end of the fiber. The sensor was characterized in the measurement setup shown in **Figure 1** under the following conditions. First using a 900 μW , 365 nm LED as the pump source, we were able to obtain a net coupling efficiency of 33% by coupling 295 μW of UV power into the optical fiber. Secondly, the gas flow rate was maintained at ~ 1000 sccm. Thirdly, the temperature of the fiber sensor was monitored continuously with a thermocouple to ± 1 °C. During the course of each measurement, the maximum temperature drift was ~ 3 °C over 30 minutes.

Our first goal was to determine if elevated temperatures adversely affect the sensitivity of sensor by examining the sensor output in pure nitrogen and synthetic air (21% oxygen, balance nitrogen) which are the end points of our concentration range. Figures 6 – 10 show the sensor response to alternating pulses of 99.999% N_2 and 21.1% O_2 at 100, 81, 60, 41 and 23 °C respectively. The signal intensity in nitrogen is stable over the entire temperature range, 2.8 ± 0.2 nW or a variation of $\pm 7\%$. **Figure 11** shows that the sensor signal is relatively unaffected by a ramp up, followed by a ramp down in temperature.

The quenching ratio, or the signal in pure nitrogen divided by that in 21% oxygen, is a measure of the sensitivity of our sensor. We find that the quenching ratio increases from 4.4 to 6.9X from room temperature to 72 °C, and then decreases slightly to 6.2X at 100 °C (see **Figure 12**). The temperature dependence of the quenching ratio is due primarily to the temperature sensitivity of the sensor signal in oxygen. We have previously shown that the quenching ratio of the potassium salt in solution, following 4 hours of heating at 200 °C was 13.2X and are quite satisfied to be able to reach half that value for the clusters immobilized in the matrix. We are currently investigating whether the temperature dependence of the sensor a reversible process due to a temperature dependent permeability of oxygen in the sol-gel matrix or that the physical structure of the sol-gel binder matrix is continuing to evolve with heat cycling.

The absolute magnitude of our sensor signal is very encouraging in terms of practical implementations of our device. We obtain a ~ 3 nW output signal for $\sim 300 \mu\text{W}$ of incident pump power; 10^{-5} is a very reasonable power conversion efficiency for a fiber sensor. Autofluorescence or the magnitude of the signal in our measurement bandwidth due to fluorescence from a length of fiber without any cluster on the tip sets a lower bound on the smallest signal we can detect from our sensor. For our current 15 cm long fiber sensor, we have 0.011 nW of autofluorescence, which is a factor of 40 smaller than the ~ 0.4 nW signal in oxygen.

Fiber M was thermally cycled above room temperature for a cumulative 7 hours in either nitrogen or oxygen. In addition the cluster containing sol-gel composite at the end of the fiber tip was exposed to a total of at least 15 days of 365 nm UV radiation in laboratory air. Following the series of experiments shown in **Figures 6 -12**, we found that the bulk of the cluster containing sol-gel composite had delaminated from the fiber tip; however a

thin sol-gel film still remained on the tip. As discussed in the previous section this is due to the shrinkage of the sol-gel binder during curing, so we have chosen to replace a portion of the TEOS binder with OtMOS. Initial optical and mechanical characterization of the fibers prepared with this technique (see **Figure 4**) are quite promising. At 60 °C the cluster/sol-gel composite continues to adhere to the end of the silica fiber and the signal level in pure nitrogen is 4 nW, slightly higher than that for Fiber M.

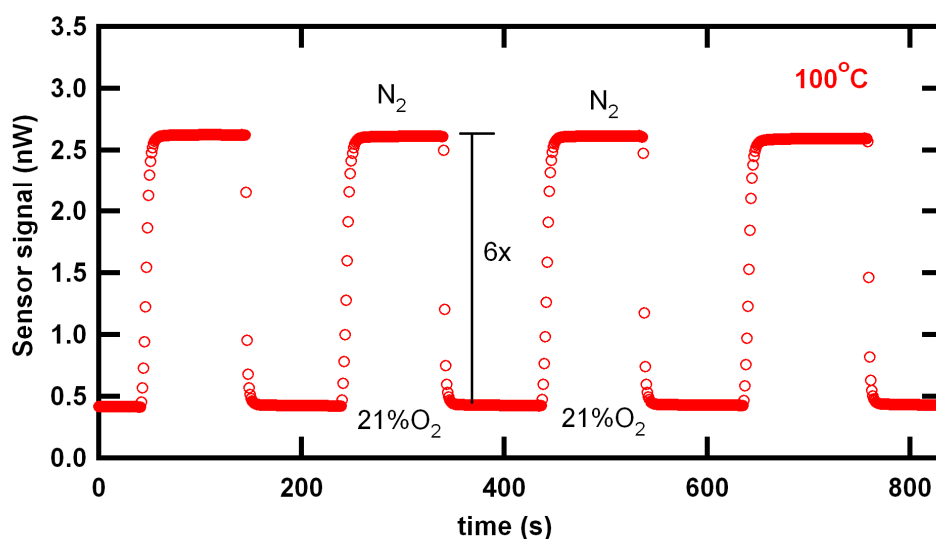


Figure 6. Fiber sensor measurements at 100 °C demonstrating quenching of 6.1X between pure nitrogen and 21% oxygen (balance nitrogen). The sensor signal is large, in the nanowatt regime with the signal magnitude in oxygen ~40 greater than the measured autofluorescence. The luminescent tip contains $K_2Mo_6Cl_{14}$ sol-gel particles embedded in a sol-gel binder matrix, with 4×10^{18} clusters/cm³ (Fiber M). The coupled pump power is 295 W at 365 nm and the gas flow rate is 1000 sccm.

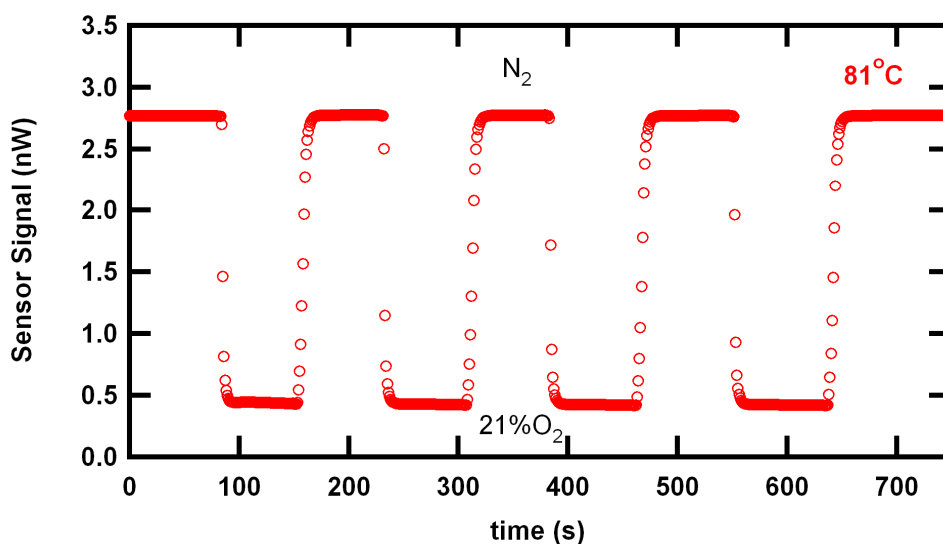


Figure 7. Fiber sensor measurements at 80 °C demonstrating quenching of 6.4X between pure nitrogen and 21% oxygen (balance nitrogen) for Fiber M. The measurement conditions are the same as Figure 6.

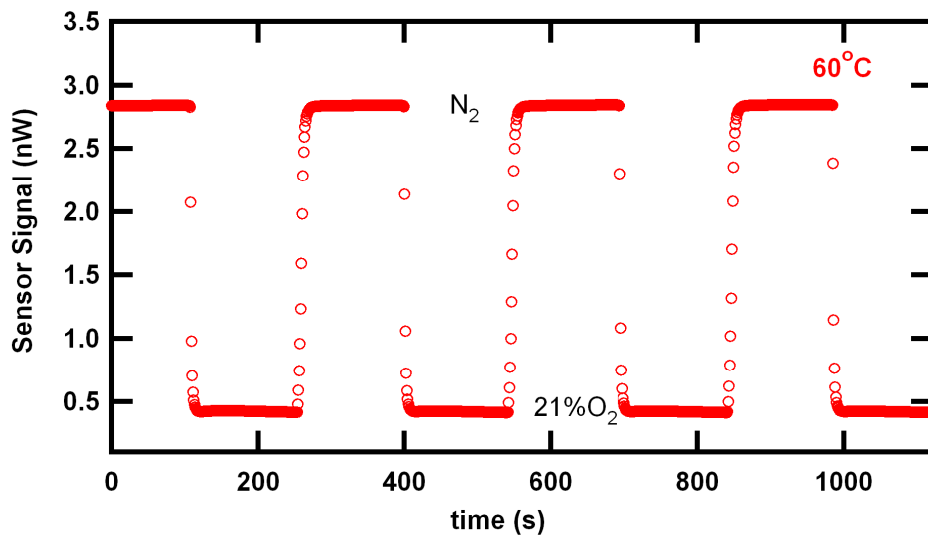


Figure 8. Fiber sensor measurements at 60 °C demonstrating quenching of 6.8X between pure nitrogen and 21% oxygen (balance nitrogen) for Fiber M. The measurement conditions are the same as Figure 6.

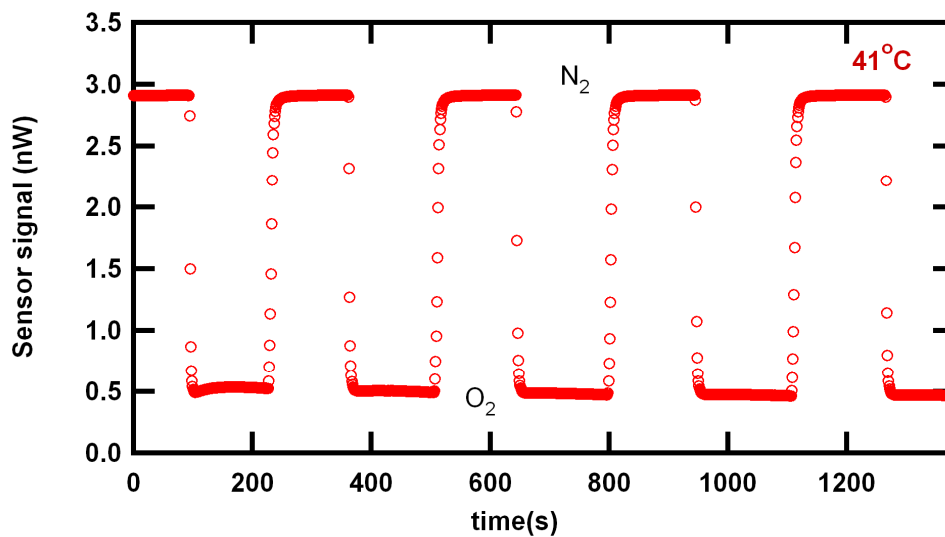


Figure 9: Fiber sensor measurements at 41 °C demonstrating quenching of 5.9X between pure nitrogen and 21% oxygen (balance nitrogen) for Fiber M. The measurement conditions are the same as Figure 6.

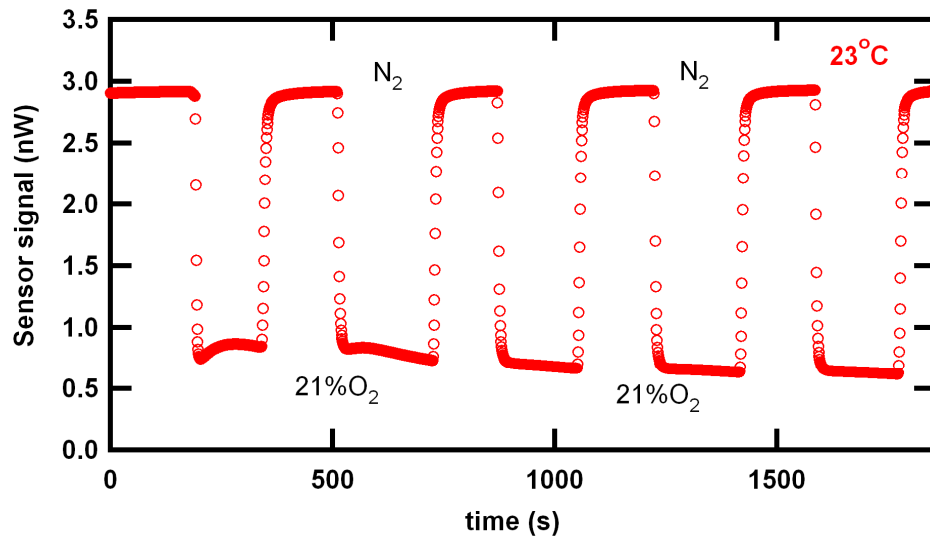


Figure 10. Fiber sensor measurements at room demonstrating quenching of 4.4X between pure nitrogen and 21% oxygen (balance nitrogen) for Fiber M. The measurement conditions are the same as Figure 6.

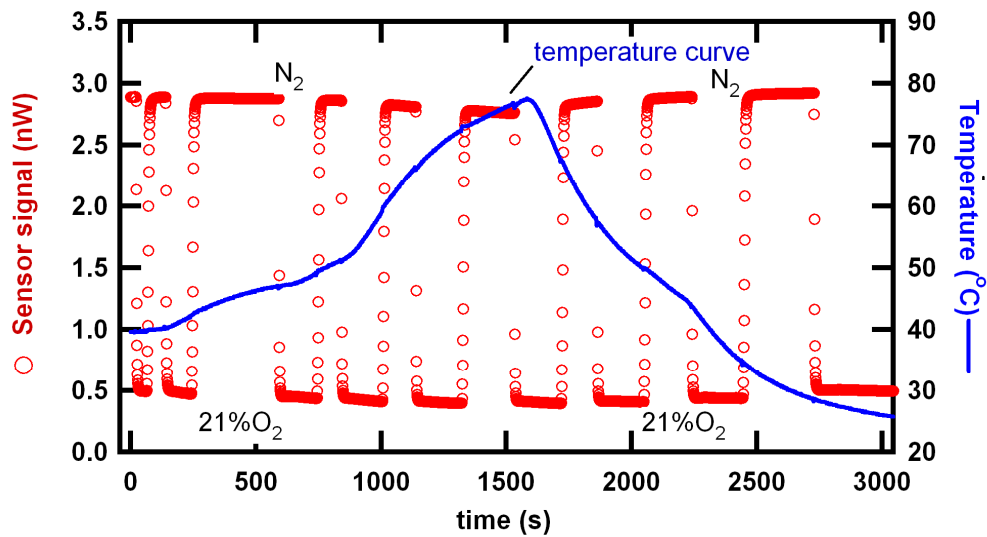


Figure 11. Fiber sensor measurements while scanning the temperature from 23 °C to 76 °C and then back down to 23 °C for fiber M. The data demonstrate that the sensor signal is relatively unaffected by the temperature ramp; the signal magnitude in N₂ decreases by 5% from 23 °C to 76 °C, whereas the quenching ratio varies by 25 %. The measurement conditions are the same as in Figure 6.

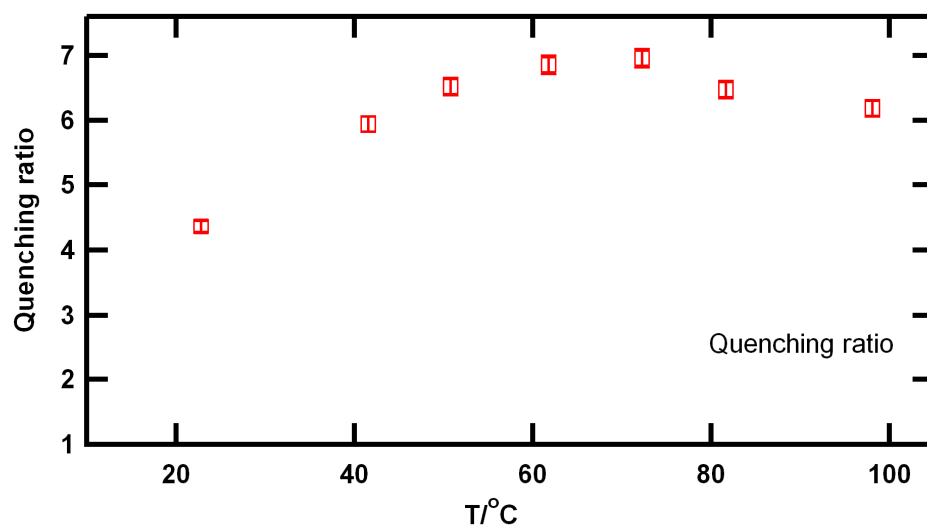


Figure 12. Quenching ratio (signal intensity in N₂ vs 21% O₂) as a function of temperature for Fiber M, from the data in Figs. 6 – 10. These measurements show that in the temperature range of 50 to 100 °C the quenching ratio is relatively independent of temperature, varying by $\pm 6\%$.

CONCLUSIONS

Three new approaches to solve decreased quenching over time and delamination of films off fiber tips were investigated. In the first approach the particles were incorporated into an aged TEOS based sol-gel. The measurements from our first fiber sensor to be tested up to 100 °C are very encouraging in terms of the absolute magnitude of the sensor signal, the degree of quenching and the signal to noise ratio. However after extensive thermal cycling the film delaminated. Our second approach was used a commercial cyanoacrylate glue to immobilize the particles however the glue degraded upon heating. Our third approach was to use a 55% OtMOS/ TEOS sol-gel binder. These films show excellent quenching (~6×) and superior mechanical stability after thermal cycling to 58 °C. We are in the process of fully characterizing the optical and mechanical properties of these new fiber sensors.

REFERENCES

- [1] R. D. Mussell, Ph. D. thesis, Michigan State University (East Lansing), **1988**.
- [2] M. D. Newsham, Michigan State University (East Lansing), **1988**.
- [3] M. D. Newsham, M. K. Cerreta, K. A. Berglund, D. G. Nocera, *Mater. Res. Soc. Symp. Proc.* **1988**, 121, 627.
- [4] C. J. Ruud, Ph. D. thesis, Michigan State University (East Lansing), **1999**.
- [5] R. N. Ghosh, G. L. Baker, C. Ruud, D. G. Nocera, *Appl. Phys. Lett.* **1999**, 75, 2885.
- [6] J. T. Remillard, J. R. Jones, B. D. Poindexter, C. K. Narula, W. H. Weber, *Appl. Opt.* **1999**, 38, 5306.
- [7] J. C. Sheldon, *J. Chem. Soc.* **1960**, 1007.
- [8] L. M. Robinson, H. Lu, J. T. Hupp, D. F. Shriver, *Chemistry of Materials* **1995**, 7, 43.
- [9] A. W. Maverick, J. S. Najdzonek, D. MacKenzie, D. G. Nocera and H. B. Gray, *J. Am. Chem. Soc.*, **1983**, 105, 1878.
- [10] T. Azumi and Y Saito, *J. Phys. Chem.*, **1988**, 92, 1715.

BIBLIOGRAPHY

None.

LIST OF ACRONYMS AND ABBREVIATIONS

HCl – Hydrochloric Acid

MeOH – Methanol

CH₃CN – Acetonitrile

TEOS – Tetraethyl orthosilicate

APPENDIX A - ACKNOWLEDGEMENTS

We wish to acknowledge the contribution of Reza Loloee, Michigan State University, towards the gas flow switch box and calculation of high temperature gas flow rate 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)