Fiber Optic Oxygen Sensor for Power Plant Applications

Ruby N. Ghosh[a1], D. J. Osborn[b] and Gregory L. Baker[b]
[a]Center for Sensor Materials, Michigan State University, East Lansing, MI 48864, USA
[1]ghosh@pa.msu.edu
[b]Dept. of Chemistry, Michigan State University, East Lansing, MI 48864, USA

Summary

We report on the development of a fiber based oxygen sensor for power plant applications. The sensor utilizes quenching of the bright red fluorescence from inorganic molybdenum chloride (Mo_6Cl_{12}) clusters by ground state $^3O_2$, as shown in Fig. 1. We are developing a reflection mode fiber sensor by immobilizing the Mo_6Cl_{12} clusters in an oxygen permeable sol-gel matrix at the far end of a Au clad high temperature silica fiber (continuous operation to 700 °C), as shown in Fig. 2. In contrast to organic indicators these metal halide compounds are well-suited for oxygen sensing schemes in harsh environments. In this paper we report on the high temperature photophysical parameters of the Mo_6Cl_{12} clusters obtained via absorption and emission spectroscopy in a controlled gas environment.

Motivation

Combustion processes in power plants require the correct mix of fuel and oxygen to maximize the heat extracted from the fuel and to minimize the emission of pollutants. Real time monitoring of oxygen is an efficient way to control boiler operation and reduce emissions. Time resolved measurements of oxygen in energy plants is difficult because of the high temperature (> 300 °C) and chemically reactive environments. Silica fiber based oxygen sensing strategies that utilize the oxygen quenching of metal halide compounds provide a potential solution. The advantages of the Mo_6Cl_{12} cluster are: (a) insensitivity of the cluster luminescence to changes in the external environment due to the confinement of the radiative transitions to the octahedral Mo core, (b) robustness of the cluster to temperatures in excess of 650 °C as well as repeated cycling, (c) rapid (< 1 s) response to changes in oxygen concentration and (d) insensitivity to other gaseous species present in the exhaust stream due to the triplet nature of the quenching process.

Results

The structure of the Mo_6Cl_{12} cluster is shown in Fig. 1. Absorption of UV photons through out the broad 300-400 nm absorption band results in bright red luminescence (600-900 nm) from the cluster excited state. We measured the absorption and emission spectra of thin films of the cluster as a function of oxygen concentration and observed efficient quenching of the luminescence signal by a factor of 5.5 upon introduction of 20% oxygen into an inert (<0.005% O_2) environment (see Fig. 3). In addition the emission lineshape is independent of oxygen concentration, allowing us to use the integrated (600-900 nm) emission intensity as the sensor signal. To immobilize the molybdenum clusters on silica surfaces we prepared the corresponding acetonitrile complex and deposited the resulting oil on lightly etched (HF) silica. On drying, the clusters strongly adhere to the surface. Sol-gel deposition of the clusters allows for control over the cluster to cluster separation, which is important for oxygen permeability at high temperatures.

The quartz cell shown in Fig. 4, which has an upper temperature of 600 °C, was used to obtain high temperature spectroscopic data of Mo_6Cl_{12} thin films from the UV to the near IR, in a controlled gas environment. Measurements of the cluster photophysical parameters, such as quenching time constant and luminescence life time, as a function of temperature and oxygen concentration allow us to optimize the design of the high temperature fiber oxygen sensor.

Figures

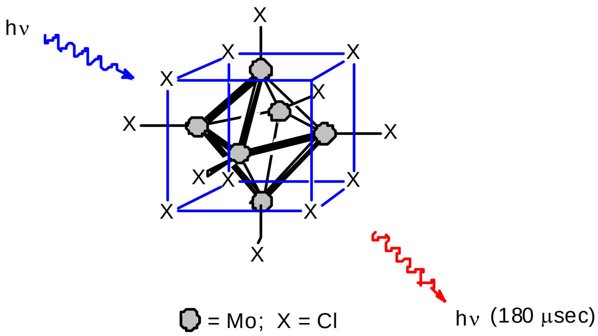


Fig. 1 Schematic of the Mo_6Cl_{12} cluster. UV (300-400 nm) irradiation promotes the cluster to an excited state, resulting in a red luminescence that is efficiently quenched by $^3O_2$. The photophysics of interest is confined to the octahedral Mo core, unaffected by the external environment.

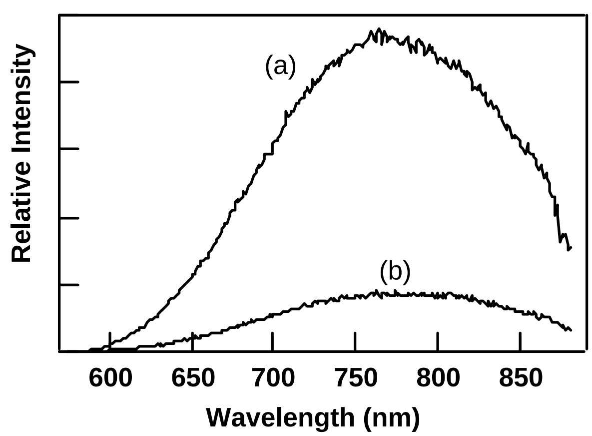
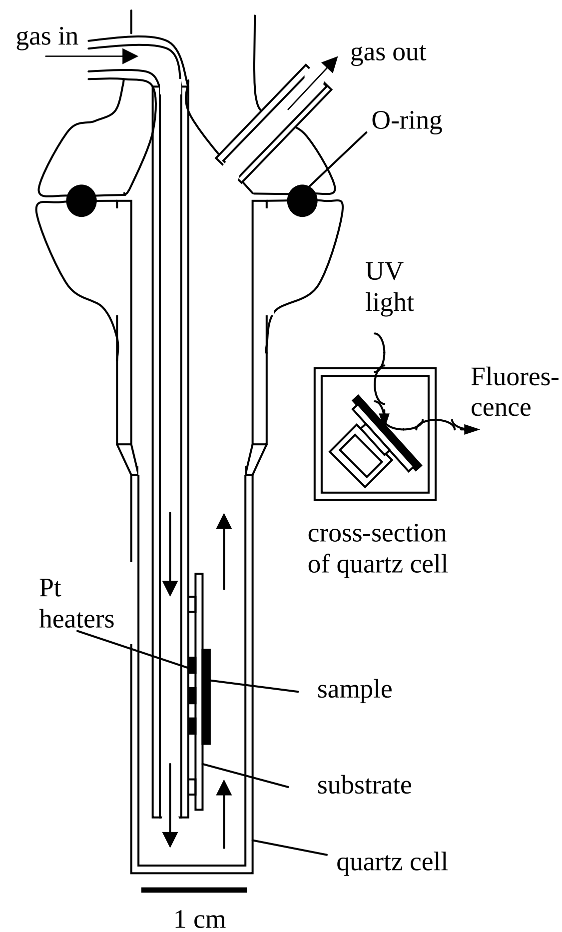


Fig. 3. Emission spectra of the Mo_6Cl_{12} cluster demonstrating quenching by oxygen, (a) inert (<0.005% oxygen) environment and (b) 20% oxygen environment. Pump wavelength is 313 nm.

Fig. 4 Quartz sample cell for high temperature (up to 600 °C) emission and absorption spectroscopy in a controlled gas environment. A thin film of the cluster is deposited on an oxidized Si substrate. The sample temperature is controlled by three Pt heaters and a thermocouple mounted on the back of the substrate.



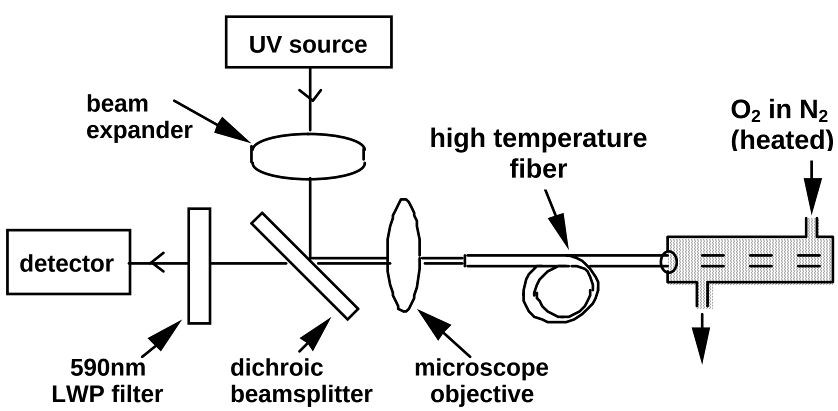


Fig. 2. Measurement setup for testing the reflection mode fiber optic sensor.