

Multi-sensor system based on phase detection, an LED array, and luminophore-doped xerogels

V.P. Chodavarapu, R.M. Bukowski, S.J. Kim, A.H. Titus, A.N. Cartwright and F.V. Bright

An optical multi-sensor system based on the excited-state lifetime of luminophore doped xerogels is described. The system is based on the novel concept of combining addressable surface-mount light-emitting diode (SM-LED) arrays with doped xerogel thin films; each SM-LED in the array is coated with a different xerogel-based sensor element. Each sensor element exhibits a unique response profile to the target analyte. A prototype system with a 2×2 LED array is presented, with three of the LEDs coated with xerogel-based sensing layers, each layer having a different sensitivity and response profile to oxygen (O_2).

Introduction: Frequency-domain (phase angle) measurements provide an attractive and practical approach for developing chemical sensors for many environmental, medical and industrial applications [1, 2]. This detection modality yields sensors that are insensitive to various operating parameters including luminophore photobleaching or wash-out, variation in the excitation intensity, or light scattering [2]. In this Letter, we demonstrate the use of an addressable LED array for an O_2 sensitive multi-sensor system. This system provides three unique response profiles for the same target analyte (i.e. diversified response). The operating principle behind the O_2 sensors is the quenching of a luminescent molecule (tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II), $([Ru(dpp)_3]^{2+})$) sequestered within a nanoporous xerogel [3].

In the case where the luminescent molecules emit with a single excited state lifetime (τ_0) in the absence of a quencher from within the xerogel and all luminescing luminophores are equally accessible to the quencher molecules, one can write [2]:

$$\tau_0/\tau = 1 + \tau_0 k_q Q \quad (1)$$

which relates the excited state luminophore lifetime at any quencher concentration (τ) and τ_0 to the luminophore-quencher bimolecular quenching constant (k_q) and the quencher concentration (Q). When luminophores are excited by sinusoidally modulated light the excited state lifetime (τ) is given by:

$$\tau = (1/2\pi f) \tan \theta \quad (2)$$

In this expression, f represents the linear modulation frequency (in Hz) and θ is the phase angle (in degrees) associated with the emission. Thus, measurement of θ provides a way to determine the quencher concentration in a sample.

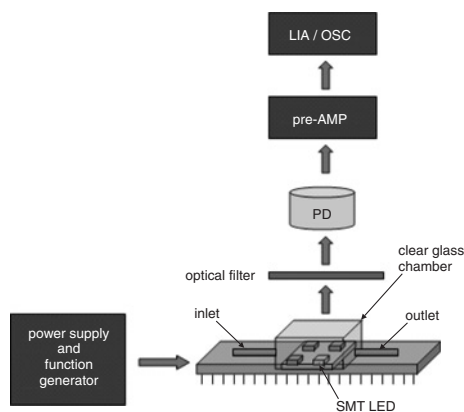


Fig. 1 Block diagram of multi-sensor system

PD: photodetector; pre-AMP: preamplifier; LIA/OSC: lock-in-amplifier or oscilloscope

Fig. 1 presents a simplified block diagram of the sensor system. The individual LEDs (length = 1.6 mm, width = 800 μ m) are arranged in a 2×2 array in a DIP package each of which can be accessed using an external switch. Crosstalk is reduced by using epoxy between the LEDs. The array consists of three blue LEDs (λ_{peak} : 468 nm, Stanley

Electric Co., Inc.) and one amber LED (λ_{peak} : 595 nm, Matsuhita Electronics, Ltd.). The system also uses a silicon photodiode (Thorlabs, Inc.) as the detector followed by a preamplifier. The output is recorded by using a lock-in-amplifier, an oscilloscope or an appropriate phase detection device. In the current embodiment the frequency range of the system is 1–100 kHz.

Sensor materials and fabrication: Three sol–gel derived, xerogel-based sensor elements were used in this work. Sol 1 was created by mixing 1.026 ml of *n*-octyltriethoxysilane (C8-TriEOS), 0.724 ml of triethoxysilane (TEOS), 1.35 ml of ethanol and 0.40 ml of 0.1 M HCl. Sol 2 was created by mixing 0.598 ml of *n*-propyltrimethoxysilane (C3-TriMOS), 0.500 ml of trimethoxysilane (TMOS), 1.35 ml of ethanol and 0.40 ml of 0.1 M HCl. Sol 3 was created by mixing 0.684 ml of methyltrimethoxysilane (C1-TriMOS), 0.500 ml of TMOS, 1.35 ml of ethanol and 0.40 ml of 0.1 M HCl. Each sol solution was sonicated for 1 h.

Sensor elements are formed by mixing 80 μ l of each sol solution with 20 μ l of 0.4 mM $[Ru(dpp)_3]^{2+}$ dissolved in ethanol. Approximately 20 μ l of the luminophore-doped sol solutions is deposited onto the face of LEDs 1, 2 and 3, respectively. The xerogels were allowed to form and age for two weeks under ambient conditions. Fig. 2 is a photograph, taken through the optical filter (Newport: FSQ-OG550), of the sensor array when LED 1 is powered with 3 V and 6 mA. Each of the sensors will operate satisfactorily over the entire range of O_2 concentrations, but each sensor element exhibits a different sensitivity to O_2 . This difference in sensitivity is due to differences in k_q within each xerogel [4, 5].

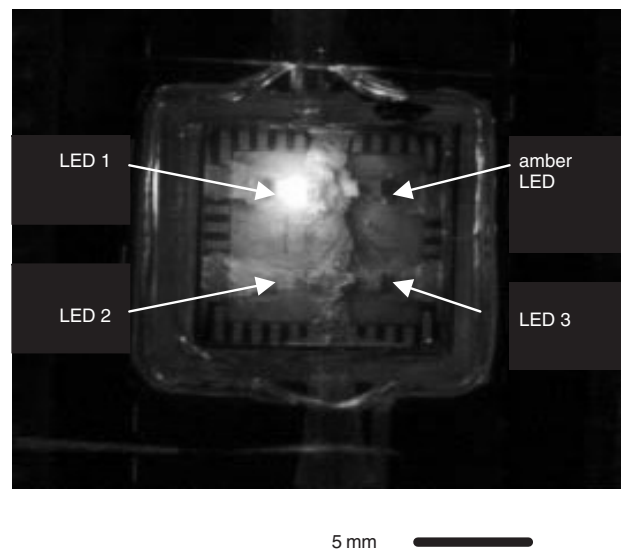


Fig. 2 Photograph of emission from single xerogel-based sensor element

Experimental results and discussion: The sensor response was measured against gaseous O_2 concentration at room temperature. The LED modulation frequency was 20 kHz. During the initial experiments, only one LED was powered at a time. The amber LED is used to generate the phase signal reference; eliminating the need for two optical filters, which would be needed if just the blue LED were used for the excitation and reference [1]. Each measurement cycle consists of two phase measurements (a) blue LED turned on (θ_{total}) and (b) amber LED turned on ($\theta_{instrument}$). The phase angle associated with the luminescence from the xerogel sensor elements is $\theta_{total} - \theta_{instrument}$.

Fig. 3 shows the effects of O_2 concentration on the phase angle from the three sensors. As expected the phase angle decreases ($[Ru(dpp)_3]^{2+}$ lifetime decreases) as the O_2 concentration increases ((1) and (2)). These data represent five separate sets of measurements that were recorded over a one month period of time, indicating very good stability and reproducibility. Fig. 4 presents the Stern-Volmer plots (i.e. τ_0/τ against O_2 concentration) for the three sensors. The solid lines passing through the points are the best fits to the Stern-Volmer model (1) or Lehrer [6] models (sensors 2 and 3). The error bars are a reflection of the imprecision in multiple measurements over the course of a month. Again, the different sensitivities (slopes) arise from differences in k_q , the transport properties of O_2 within the xerogels [4, 5].

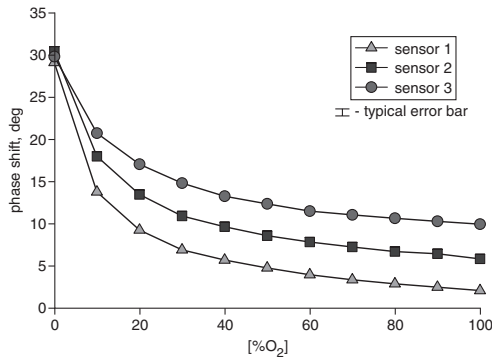


Fig. 3 Phase response of individual O_2 responsive sensor elements (typical error bar shown)

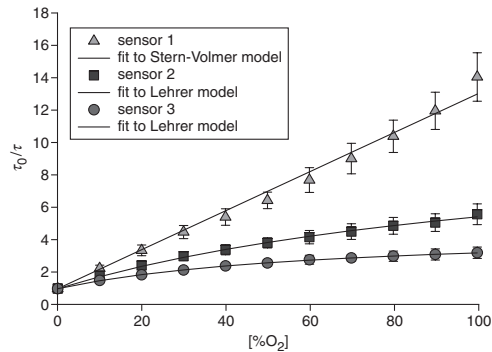


Fig. 4 Stern-Volmer plots for individual O_2 responsive sensor elements

Conclusion: An optical multi-sensor system based on phase detection is reported. The system has an LED array, a single photodetector, a phase measurement device, and three O_2 responsive sensors with different response profiles. Multiple sensitivities combined with phase

detection enables the development of a powerful sensing system that improves accuracy and reduces uncertainty.

Acknowledgments: This work was generously supported by the Johnson & Johnson Focused Giving Program and National Science Foundation (BES-0330240 to A.H. Titus and CHE-0315129 to F.V. Bright).

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13 June 2005

Electronics Letters online no: 20052142

doi: 10.1049/el:20052142

V.P. Chodavarapu, S.J. Kim, A.H. Titus and A.N. Cartwright (Department of Electrical Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA)

E-mail: ahtitus@eng.buffalo.edu

R.M. Bukowski and F.V. Bright (Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA)

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