

# Fiber Optic Sensors for Hydrogen Peroxide Vapor Measurement

H. Akbari Khorami, P. Wild, N. Djilali

**Abstract**—This paper reports on the response of a fiber-optic sensing probe to small concentrations of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) vapor at room temperature.

$\text{H}_2\text{O}_2$  has extensive applications in industrial and medical environments. Conversely,  $\text{H}_2\text{O}_2$  can be a health hazard by itself. For example,  $\text{H}_2\text{O}_2$  induces cellular damage in human cells and its presence can be used to diagnose illnesses such as asthma and human breast cancer. Hence, development of reliable  $\text{H}_2\text{O}_2$  sensor is of vital importance to detect and measure this species.

Ferric ferrocyanide, referred to as Prussian Blue (PB), was deposited on the tip of a multimode optical fiber through the single source precursor technique and served as an indicator of  $\text{H}_2\text{O}_2$  in a spectroscopic manner. Sensing tests were performed in  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$  vapor mixtures with different concentrations of  $\text{H}_2\text{O}_2$ .

The results of sensing tests show the sensor is able to detect  $\text{H}_2\text{O}_2$  concentrations in the range of 50.6 ppm to 229.5 ppm. Furthermore, the sensor response to  $\text{H}_2\text{O}_2$  concentrations is linear in a log-log scale with the adjacent R-square of 0.93. This sensing behavior allows us to detect and quantify the concentration of  $\text{H}_2\text{O}_2$  in the vapor phase.

**Keywords**—Chemical deposition, fiber-optic sensors, hydrogen peroxide vapor, prussian blue.

## I. INTRODUCTION

**H**YDROGEN peroxide ( $\text{H}_2\text{O}_2$ ) is used in a broad range of applications such as aseptic processing of food and pharmaceuticals, water treatment plants, and industrial effluents for decontamination and disinfection [1], [2]. On the other hand, excessive  $\text{H}_2\text{O}_2$  is also a health hazard because it plays a leading role in a variety of damage mechanisms [3]. Therefore, detection and measurement of  $\text{H}_2\text{O}_2$  concentrations both in liquid and vapor phases is crucial.

Conventional techniques to detect  $\text{H}_2\text{O}_2$  comprise titrimetric, colorimetric, and gasometric methods which, in general, require complex equipment and time consuming sample preparation, or have poor selectivity and limits of detection. Electrochemical and spectroscopic techniques on the other hand are able to determine small concentrations of  $\text{H}_2\text{O}_2$  and have good selectivity [4]–[8], with spectroscopic techniques being preferred for many biochemical and industrial applications because of their immunity to

electromagnetic interference. Spectroscopic detection includes chemiluminescent [9], [10], fluorescent [11], [12], and absorptive [6], [13] techniques.

Recently, fiber-optic sensing probes based on Prussian blue (PB) have shown reliable response to  $\text{H}_2\text{O}_2$  concentrations in a liquid phase [14], [15]. A PB-based fiber-optic sensing probe fabricated through the layer-by-layer electrostatic self-assembly (ESA) of PB has been used successfully to detect  $\text{H}_2\text{O}_2$  in a vapor phase [16]. However, this device was not able to determine concentrations of  $\text{H}_2\text{O}_2$  in the vapor phase. In this paper, detection and determination of  $\text{H}_2\text{O}_2$  concentrations in a vapor phase using a fiber-optic sensing probe based on chemically deposited PB is demonstrated.

PB was chosen as an  $\text{H}_2\text{O}_2$  indicator for the proposed fiber optic probe because of its sensitivity and selectivity toward  $\text{H}_2\text{O}_2$  [6], [17]. PB is a ferric ferrocyanide with the basic face-centered cubic crystalline structure consisting of iron ions linked by the cyanide groups with two chemical forms  $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$  and  $\text{KFe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$  [18], [19]. These two chemical forms are commonly known as “insoluble” and “soluble”, respectively [19]. Both insoluble and soluble forms of PB are highly insoluble ( $K_{\text{sp}} = 10^{-40}$ ), the difference refers to the simplicity of potassium peptization [20]. Large metal cations and water molecules, as well as other small molecules like  $\text{H}_2\text{O}_2$ , can be accommodated in the open structure of PB [20]. Chemical reduction and oxidation of PB leads to Prussian white (PW) (potassium ferrous ferrocyanide) and Berlin green (BG) (ferric ferricyanide), with chemical formula  $\text{K}_2\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CN})_6$ , and  $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$ , respectively [18], [20].

The  $\text{H}_2\text{O}_2$  detection mechanism in PB-based fiber-optic sensing probes relies on the redox reactions of PB and its reduced state, PW, and the measurement of corresponding changes of the optical properties of the compound. PB is reduced to PW in the presence of a strong reducing agent, such as ascorbic acid. The reverse reaction happens when PW is exposed to a strong oxidizing agent, such as  $\text{H}_2\text{O}_2$  resulting in PB. PB has a strong intervalence charge transfer absorption band near 700 nm because transition from  $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}$  to  $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$  states. On the other hand, transparent PW has no distinct bands in the visible range of its absorption spectrum [21]. As a result, the increasing absorbance in the visible range while PW is oxidizing to PB by  $\text{H}_2\text{O}_2$  can be used to detect the presence of this oxidant. Moreover, the initial PW state can be recovered by exposing PB to ascorbic acid.

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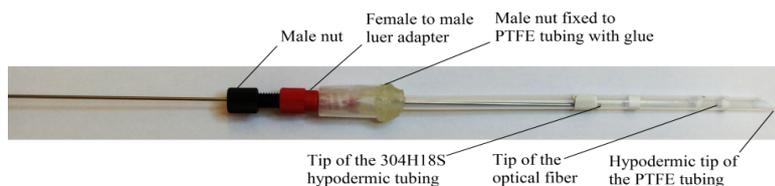


Fig. 1 PB-based fiber-optic sensing probe

## II. EXPERIMENTAL PROCEDURE

### A. Materials

Potassium hexacyanoferrate (III) (or potassium ferricyanide) was used in an aqueous solution of 0.1 M hydrochloric acid (HCl) for synthesizing PB through a chemical process. L-ascorbic acid was used as the reducing agent for the PB to PW reaction. Sodium phosphate dibasic and potassium dihydrogen phosphate were used to prepare phosphate buffer solution (PBS) at pH 2 in which ascorbic acid solutions were prepared.  $\text{H}_2\text{O}_2$  (30 wt%) and distilled water (18.2 M $\Omega$  cm) were used to prepare solutions for generating  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$  vapor phase. All chemicals were used as received. The sources of the chemicals are documented in Table I.

TABLE I  
SOURCE OF CHEMICALS

Chemicals	Product No.	Source
Potassium ferricyanide	13746-66-2	Sigma-Aldrich
L-ascorbic acid	25,556-4	Aldrich
Sodium phosphate dibasic	7558-79-4	EM science
Potassium dihydrogen phosphate	7778-77-9	Caledon
Hydrogen peroxide	4060-1-05	Caledon

### B. Sensor Fabrication

The PB-based fiber-optic sensor was prepared using chemical deposition of a PB film onto the tip of a multimode optical fiber. As reported in our previous work [14], 10 mM of potassium ferricyanide, as a single source precursor, was added to 25 mL of an aqueous solution of 0.1 M HCl. The optical fiber was immersed in this prepared mix, and was kept at 40°C under continuous stirring at 300 rpm for 10 hours. The synthesis process was performed with exposure to fluorescent lamp light. Finally, the optical fiber was left in the solution to cool to room temperature. The prepared fiber-optic sensor was then removed from the solution and left at room temperature for one day. The sensor was then annealed at 100 °C for 15 min.

The PB-based fiber-optic sensor was integrated into a sensing probe for testing in  $\text{H}_2\text{O}_2$  vapor. A short length of PTFE tubing was cut diagonally to form a hypodermic needle, and the other side of the PTFE tubing was positioned and fixed into a male nut using glue. The PB-based sensor was passed through the 304H18S hypodermic tubing such that the tip of the fiber was positioned beyond the distal tip of the hypodermic tubing. The 304H18S hypodermic tubing with the optical fiber was passed through a male nut, flangeless ferrule,

and female to male Luer adapter to seal the sensing probe. Then, the sensing probe was assembled by connecting the 304H18S hypodermic tubing and PTFE tubing using the adapter and fixed nut, as shown in Fig. 1.

Using this sensing probe, it is possible to withdraw the fiber-optic sensor into the PTFE tubing to protect the tip of the fiber from damage when the fiber is passing through a parafilm membrane into the flask containing the  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$  vapor. The sensor position can be adjusted to extend beyond the PTFE tubing when the fiber is immersed in ascorbic acid solution. The sensing probe is sealed before every sensing measurement by tightening the male nut.

### C. Sensing Test and Instrumentation

Sensing tests were performed by alternately exposing the sensing probe to an ascorbic acid solution and  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$  vapor, for recovery and oxidation steps of the PB/PW system. Fig. 2 illustrates the experimental setup. During the sensing test the light is generated by a white light source (Dunedin, FL LS-1, OceanOptics), is carried through the arm 1 (i.e. the common arm) and arm 1 to the tip of the fiber-optic sensor. Part of the scattered light from the PB/PW film on the tip of the fiber is collected by the optical fiber and guided back through the common arm and arm 2 into an optical fiber spectrometer (USB2000, OceanOptics), which measures the intensity of the light in a wavelength range of 370 to 1048 nm. The reflected spectrum was sampled at a frequency rate of 1 Hz using the software Spectra- Suite (OceanOptics, Dunedin, FL). The integrated values of intensity over the full range of the spectrometer (i.e. 370 to 1048 nm) were evaluated to study the response of the PB/PW system during both the oxidizing and the reducing steps.

$\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  were mixed in the Erlenmeyer flask with different weight ratios to generate different concentrations of  $\text{H}_2\text{O}_2$  in the vapor phase. The mouth of Erlenmeyer flask was sealed with 2 sheets of parafilm. The tested concentrations of  $\text{H}_2\text{O}_2$  in liquid and vapor phases are given in Table II [16].

TABLE II  
 $\text{H}_2\text{O}_2$  CONCENTRATIONS IN LIQUID AND GAS PHASES [16]

Concentration in liquid phase ( $\text{H}_2\text{O}_2$ wt%)	Concentration in vapor phase ( $\text{H}_2\text{O}_2$ ppm)
20	229.5
15	164.6
10	105.2
5	50.6

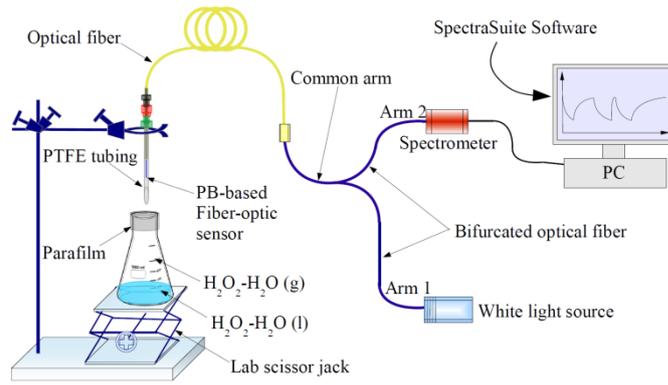
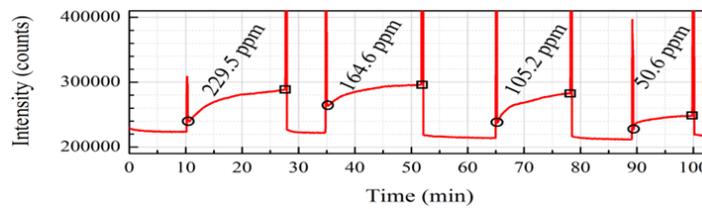


Fig. 2 Experimental setup

Fig. 3 Intensity response of the sensing probe to  $\text{H}_2\text{O}_2\text{-H}_2\text{O}$  vapor with different concentrations of  $\text{H}_2\text{O}_2$ 

### III. CALCULATION OF $\text{H}_2\text{O}_2$ VAPOR CONCENTRATION

To calculate the concentration of  $\text{H}_2\text{O}_2$  in a  $\text{H}_2\text{O}_2\text{-H}_2\text{O}$  vapor mixture in equilibrium with  $\text{H}_2\text{O}_2\text{-H}_2\text{O}$  liquid mixture, the partial vapor pressure of  $\text{H}_2\text{O}_2$  needs first to be determined. The partial vapor pressure of each component of an ideal mixture of liquids may be calculated using Raoult's law (1).

$$P_i = P_i^* X_i \quad (1)$$

where:  $P_i$  is the partial vapor pressure of component  $i$  in the liquid mixture,  $P_i^*$  is the vapor pressure of the pure component  $i$ , and  $X_i$  is the mole fraction of component  $i$  in the liquid mixture. However, the  $\text{H}_2\text{O}_2\text{-H}_2\text{O}$  system does not obey Raoult's law because the hydrogen bonding and interaction of the molecules with each other cause a system far from the ideal mixture. In this case, the activity coefficient of the component,  $\gamma_i$ , has to be inserted into Raoult's law (2):

$$P_i = P_i^* \gamma_i X_i \quad (2)$$

Partial vapor pressure of pure  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  can be calculated from (3) and (4), respectively [22].

$$\begin{aligned} \log_{10} P_{\text{H}_2\text{O}_2}^* &= 24.8436 - 3511.54/T - 4.61453 \log_{10} T \\ &- 3.60245 \times 10^{-3} T - 7.73423 \times 10^{-6} T^2 + 1.78355 \times 10^{-8} T^3 \\ &- 2.27008 \times 10^{-13} T^4 \end{aligned} \quad (3)$$

$$\begin{aligned} \log_{10} P_{\text{H}_2\text{O}}^* &= 19.389127 - 2861.9133/T - 3.2418662 \log_{10} T \\ &- 1.0799994 \times 10^{-4} T - 7.9189289 \times 10^{-6} T^2 + 1.5411774 \times 10^{-8} T^3 \\ &- 8.1926991 \times 10^{-12} T^4 \end{aligned} \quad (4)$$

Also, the activity coefficient of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  can be calculated from (5) and (6), respectively [23].

$$\ln(\gamma_{\text{H}_2\text{O}_2}) = \frac{x_{\text{H}_2\text{O}}^2}{RT} \left( \frac{B_0 + B_1(3 - 4X_{\text{H}_2\text{O}}) + B_2(1 - 2X_{\text{H}_2\text{O}})(5 - 6X_{\text{H}_2\text{O}})}{+ B_3(1 - 2X_{\text{H}_2\text{O}})^2(7 - 8X_{\text{H}_2\text{O}})} \right) \quad (5)$$

$$\ln(\gamma_{\text{H}_2\text{O}}) = \frac{(1 - x_{\text{H}_2\text{O}})^2}{RT} \left( \frac{B_0 + B_1(1 - 4X_{\text{H}_2\text{O}}) + B_2(1 - 2X_{\text{H}_2\text{O}})(1 - 6X_{\text{H}_2\text{O}})}{+ B_3(1 - 2X_{\text{H}_2\text{O}})^2(1 - 8X_{\text{H}_2\text{O}})} \right) \quad (6)$$

where:  $B_0, B_1, B_2, B_3$  are functions of temperature [16], [23],  $R$  is the universal gas constant, and  $T$  is the absolute temperature.

Assuming the  $\text{H}_2\text{O}_2\text{-H}_2\text{O}$  vapor mixture is an ideal gas, the concentration of  $\text{H}_2\text{O}_2$  in the vapor mixture may then be calculated using Dalton's law (7) and the Ideal gas law (8).

$$P_i = y_i P_t \quad (7)$$

$$P_t = \frac{n_t RT}{V_t} \quad (8)$$

where:  $P_i$  can be calculated by combining (2), (3), and (5),  $y_i$  is the mole fraction of the component  $i$  in the vapor mixture,  $n_t$  is the total amount of the vapor in mole, and  $V_t$  is the total volume of the vapor mixture.

By inserting (8) into the (7) and replacing  $y_i$  by its equivalent term,  $(n_i/n_t)$ , the  $\text{H}_2\text{O}_2$  concentration can be obtained as (9), in which  $MW_{\text{H}_2\text{O}_2}$  is the molecular weight of  $\text{H}_2\text{O}_2$ .

$$C_{\text{H}_2\text{O}_2} = \frac{P_{\text{H}_2\text{O}_2} \text{MW}_{\text{H}_2\text{O}_2}}{RT} \quad (9)$$

#### IV. RESULTS AND DISCUSSION

The intensity of the reflected light from the distal end of the sensing probe during its exposure to  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$  vapor at different concentrations of  $\text{H}_2\text{O}_2$  is shown in Fig. 3. The circles and squares indicate the instant at which the sensing probe was exposed to  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$  vapor and ascorbic acid, respectively. The intensity of the reflected light starts rising after the exposure of the sensing probe to  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$  vapor due to oxidation of PW to PB. Following the immersion of the sensing probe in ascorbic acid, the intensity decreases as the ascorbic acid reduces the PB to PW.

The intensity response of each individual test was brought to the origin of the time axis at the moment of exposure to  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{O}$  vapor, and an inverse exponential curve fitted to the data, as shown in Fig. 4. For each concentration, the characteristic response time ( $\tau$ ) (i.e. the time elapsed for the signal to reach 63% of the intensity of the plateau state) was extracted from the inverse exponential curve and plotted in Fig. 5. This plot shows that the probe exhibits a linear response to  $\text{H}_2\text{O}_2$  concentration on a log-log scale. This linear behavior suggests that this sensing probe can be used not only to detect the presence of  $\text{H}_2\text{O}_2$  vapor but also to quantify the concentration of  $\text{H}_2\text{O}_2$  in the vapor phase.

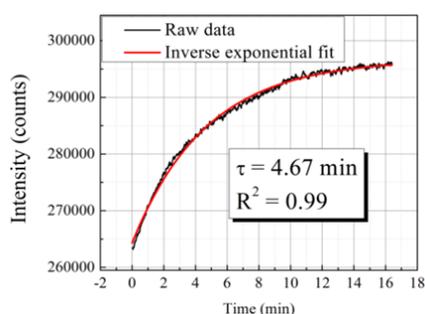


Fig. 4 Intensity response to 164.6 ppm  $\text{H}_2\text{O}_2$

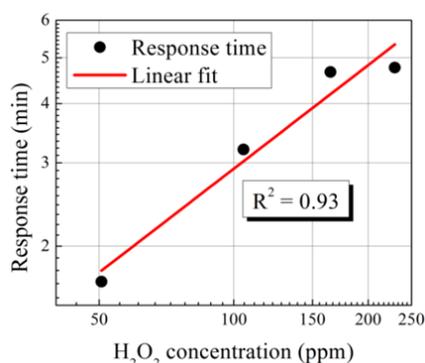


Fig. 5 Time response versus  $\text{H}_2\text{O}_2$  concentration

#### V. CONCLUSION

Detection and measurement of small concentrations of  $\text{H}_2\text{O}_2$  in the vapor phase has been demonstrated. The sensor shows a linear response to the  $\text{H}_2\text{O}_2$  concentration on a log-log scale with the adjacent R-square of 0.93. The sensor features fast and reliable responses and is suitable to be used in industrial applications.

#### ACKNOWLEDGMENT

The authors gratefully acknowledge funding provided by the Natural Sciences and Engineering Research Council of Canada (NSERC).

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