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Spectroscopic detection of Hydrogen peroxide with an optical fiber probe using chemically deposited Prussian blue

Hamed Akbari Khorami [a,b,*], Juan F. Botero-Cadavid [a,b,c], Peter Wild [a,b], Ned Djilali [a,b]

[a] Institute for Integrated Energy Systems (IESVic), University of Victoria, BC,V8 W 3P6, Victoria, Canada
[b] Department of Mechanical Engineering, University of Victoria, BC, V8 W 2Y2, Victoria, Canada
[c] Escuela de Física, Universidad Nacional de Colombia - Sede Medellín, Medellín, Colombia

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ABSTRACT

A novel fiber-optic hydrogen peroxide sensing probe was fabricated using chemically deposited ferric ferrocyanide, often referred to as Prussian blue (PB). The probe features a fast linear response and durability, due to the robustness and purity of the PB film. Potassium ferricyanide was used as a single source precursor in a straightforward chemical deposition of nanostructured PB onto the tip of a multimode optical fiber. Spectroscopic detection of hydrogen peroxide (H_2O_2) was performed based on the reduction of PB to Prussian white (PW) by agents like ascorbic acid, and oxidation of PW to PB by H_2O_2. Measurement of H_2O_2 concentration is based on the changes of the absorption spectrum, under visible light, of PB and PW. The fiber-optic probes exhibit a linear response to concentration on a log-log scale and are found suitable for determining small concentrations of H_2O_2. Multiple tests were performed to investigate the repeatability and durability of a sensor response and though requiring recalibration, the probes were found to remain functional for an extended period of time.

1. Introduction

H_2O_2 is commonly used in many industrial and medical processes such as water treatment plants and disinfection [1,2]. It is also a by-product of oxidative metabolisms [3]. Detection and determination of small concentrations of hydrogen peroxide remains a major challenge in many fields where it plays a main role in a variety of damage mechanisms. For example, H_2O_2 induces cellular damage in human cells [4,5] and its presence can be used to diagnose illnesses such as asthma [6]. It is also believed to be responsible for chemical degradation of polymer membranes in PEM-Fuel cells [7–10]. Conventional techniques to detect H_2O_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 [11]. Electrochemical and spectroscopic techniques on the other hand are able to determine small concentrations of H_2O_2 and have good selectivity [11–16], with spectroscopic techniques being preferred for many biochemical and industrial applications because of their immunity to electromagnetic interference. Spectroscopic detection includes chemiluminescent [17,18], fluorescent [19,20], and absorptive [13,14,21–26] techniques.

The absorptive technique chosen in the present work relies on a detector agent film deposited onto the tip of optical fiber. It affords a small size, flexible fiber-optic sensing probe that is immune to electromagnetic interference. The prepared sensing probe has potential for developing *in-situ* sensors for PEM-Fuel cells, as well as portable biosensors.

PB was chosen as an H_2O_2 indicator for the proposed fiber-optic probe because of its sensitivity and selectivity toward H_2O_2 [13,27]. 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 $Fe_4^{III}[Fe^{II}(CN)_6]_3$ and $KFe^{III}Fe^{II}(CN)_6$ [28,29]. These two chemical forms are commonly known as “insoluble” and “soluble”, respectively [29]. Both insoluble and soluble forms of PB are highly insoluble ($K_{sp} = 10^{-40}$), the difference refers to the simplicity of potassium peptization [30]. Large metal cations and water molecules, as well as other small molecules like H_2O_2, can be accommodated in the open structure of PB [30]. Chemical reduction and oxidation of PB leads to PW (potassium ferrous ferrocyanide) and Berlin green (BG) (ferric ferricyanide), with chemical formula $K_2Fe^{II}Fe^{II}(CN)_6$, and $Fe^{III}Fe^{III}(CN)_6$, respectively [28,30].

The H_2O_2 detection mechanism in the absorptive technique based on PB relies on the redox reactions of PB/PW system, and the evaluation of corresponding changes of the optical properties of the compound. PB will be 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 H_2O_2,

* Corresponding author. Tel.: +1 250 721 6034.
E-mail addresses: hakbarik@uvic.ca (H.A. Khorami), ndjilali@uvic.ca (N. Djilali).

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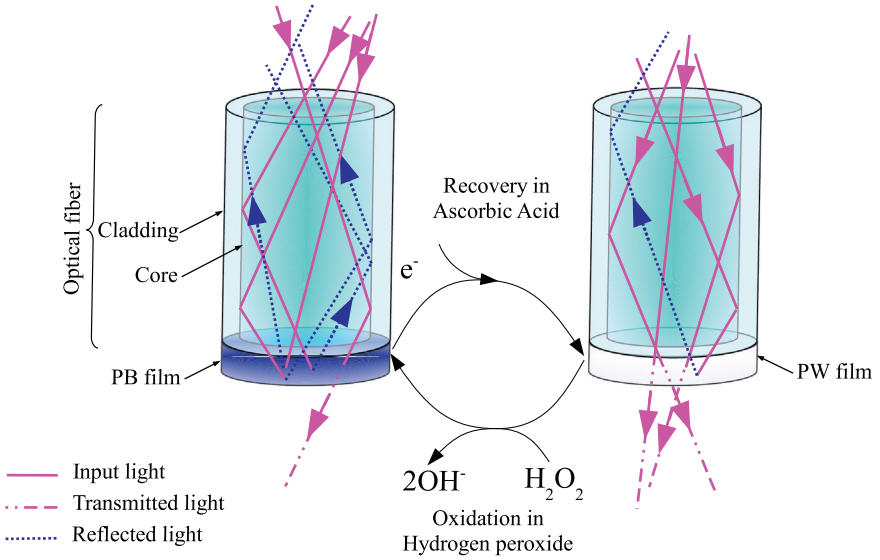

Fig. 1. Detection mechanism of H_2O_2 using a fiber-optic sensing probe based on PB/PW system.

resulting in PB. PB has a strong intervalence charge transfer absorption band near 700 nm because transition from $Fe^{III}Fe^{II}$ to $Fe^{II}Fe^{III}$ states absorbs red photons, and reflects blue light. On the other hand, transparent PW does not have any distinct bands in the visible range of its absorption spectrum [31]. As a result, the increasing absorbance in the visible range while PW is oxidizing to PB by H_2O_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. Fig. 1 illustrates the detection mechanism of H_2O_2 using fiber-optic sensing probe based on chemically deposited PB/PW system onto the tip of an optical fiber.

Generally, PB can be synthesized by electrochemical [28,29,32–34] or chemical [35–40] paths. In the former case, the substrate should be electrically conductive. Considering that optical fibers are made of non-conductive materials, the chemical synthesis of PB would be a more suitable approach. Several chemical methods such as sol-gel [41,42], sonochemichal [37], Photochemical [43], hydrothermal [38], and electrostatic self-assembly [39] have been used to synthesize or immobilize PB nanoparticles and thin films onto non-conductive substrates.

In the present work, a PB thin film was chemically deposited onto the tip of an optical fiber through the single-source precursor approach which, to the best of our knowledge, is the simplest method for synthesizing PB nanoparticles. This method allows the particle size, shape, and porosity to be adjusted by tuning the synthesis parameters such as solution pH, concentration of precursor, temperature and time of synthesis, and reaction environment light [37,43]. After the synthesis of PB, the optical fiber probe was annealed and sensing measurements were performed at room temperature in H_2O_2 buffered solutions with pH 4. Repeatability, durability, and reproducibility of sensor responses were analyzed using multiple sensing probes.

2. Experimental

2.1. Materials

Potassium hexacyanoferrate (III) (product No. 13746-66-2) from Sigma-Aldrich was used as a single-source precursor in an aqueous solution of Hydrochloric acid (HCl) (37%) for synthesizing PB onto the tip of an optical fiber. L-ascorbic acid from Aldrich, (catalog No. 25,556-4), was used as the reducing agent for the PB to PW reaction. Glacial acetic acid, (product No. 00598-468) from Anachemia and Sodium acetate trihydrate, (product No. S-1850) from ACP Chemicals were used to prepare an acetate buffer solution (ABS) at pH 4.0 in which the H_2O_2 solutions and ascorbic acid were prepared. The reducing solution was prepared in ABS with 0.04 mol L^{-1} of L-ascorbic acid. H_2O_2 (30 wt%) from ACP Chemicals was used to prepare the oxidizing solutions at different concentrations in ABS. Sodium hydroxide (NaOH) and Hydrochloric acid (HCl) at concentrations of 0.1 mol L^{-1} were used to adjust the pH of the solutions to the desired values. All chemicals were used as received with no further purification. The water used in the experiments was purified with a four-cartridge purification system (Super- Q Plus, Millipore, Billerica, MA) and had a resistivity of 18.2 MΩ cm. The optical fiber was a multi-mode AFS50/125Y from Thorlabs (Newton, NJ), with core and cladding diameters of 50 μm and 125 μm, respectively.

2.2. Chemical deposition of Prussian blue

The PB film was deposited chemically using the distal end of an optical fiber as a substrate. The optical fiber was cleaved and cleansed with isopropanol. In a synthesis process, 0.25 mmol of $K_3Fe(CN)_6$ were added to 25 mL of an aqueous solution of 0.1 mol L^{-1} hydrochloric acid. 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 done under the fluorescent lamp light exposure. Finally, the optical fiber was left inside the solution to cool to room temperature. The prepared fiber-optic probe was removed from the solution and left at room temperature and relative humidity for one day, and then it was annealed at 100 °C for 15 min.

In the present work, the sensing region with PB was located at the distal end of the optical fiber rather than along the fiber in order to facilitate the eventual integration of the probe into the membrane of a PEMFC. With the distal end PB deposition, the probe operates based on the reflected light from the sensing region and only requires an inlet port into the membrane. In the other case, the operation of the probe would relies on the attenuation of the transmitted light through the optical fiber, similarly to the fiber sensor presented by Hu and Tao [44]; This requires both inlet and outlet ports, which would impose additional design constraints to ensure proper alignment and sealing of the sensing probe within a fuel cell.