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Detection of hydrogen peroxide using an optical fiber-based sensing probe

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ABSTRACT

A sensing probe for hydrogen peroxide (H_2O_2) in solution at low concentrations has been developed by deposition of Prussian blue dye in a multi-layer structure of polyelectrolytes onto the tip of a multi-mode optical fiber. The sensing mechanism of this optrode (optical electrode) relies on the oxidation of Prussian white (reduced form of Prussian blue) in the presence of hydrogen peroxide. The sensing capabilities of the probe can be recovered by *ex situ* reduction of Prussian blue to Prussian white using ascorbic acid. A first set of experiments yielded a linear-log relationship between the peak intensity of the reflected light and the concentration of hydrogen peroxide. The intensity of the light, relative to the intensity at immersion, showed an inverse exponential dependency on the time required to reach the saturation for each H_2O_2 solution tested. Subsequent experiments in which the sensing probe was exposed to H_2O_2 solutions with different concentrations, showed that only the time-dependent behavior of the intensity of the light remained. Furthermore, the response time for the intensity to reach 63% of its peak value was found to be linearly dependent on the concentration of the H_2O_2 in a log–log scale. Reproducible results were for H_2O_2 concentrations ranging from 10 μmol L^{-1} up to the maximum concentration tested of 1 mmol L^{-1}. This range of concentrations makes this sensing probe suitable for the remote detection of H_2O_2 as a by-product of biological reactions and electrochemical reactions in polymer electrolyte membrane fuel cells.

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1. Introduction

Hydrogen peroxide (H_2O_2) is a highly reactive oxidant that plays an essential role in many chemical, industrial, medical, environmental, and biological processes. It is used as a disinfectant due to its antimicrobial properties, and in bleaching of textiles, paper pulp, hair, and teeth [1,2].

H_2O_2 also plays an important role in biological and environmental processes. In biological processes, H_2O_2 is often the intermediate product of enzymatic reactions and its monitoring allows the control of bioreactions [2–4]. H_2O_2 is also one of the by-products of cellular processes such as phagocytosis [5], which are used in medical diagnosis of pulmonary illnesses including asthma [6]. Finally, H_2O_2 is also found in rain water [7], causing acidity, which can alter the equilibrium of an ecosystem [8].

H_2O_2 can be produced as part of the electrochemical reactions in a polymer electrolyte membrane fuel cell (PEMFC) [9]. Localized measurements of H_2O_2 concentrations in PEMFCs have not been possible to date, but it has been detected in the exhaust gases [10], in the drain water from the cathode [11], and by *in situ* electrochemical techniques in the ionomeric membrane [12]. The role played by H_2O_2 in PEMFCs has been extensively investigated since it is believed to be a precursor of hydroxyl ($HO^{\bullet}$) and hydroperoxyl ($HOO^{\bullet}$) radicals, which have been linked to the accelerated chemical degradation of Nafion® – the proton conductive membrane used in many PEMFCs [13–22].

Conventional techniques for detection of H_2O_2 include titration, colorimetry, and gasometry [2,23,24]. Although these methods are used in many applications, they are not well suited to the detection of small concentrations of H_2O_2 such as those occurring in a PEMFC. The rate of production of H_2O_2 in a PEMFC has been estimated to reach values of up to 0.7×10^{-6} mol cm^{-2} s^{-1} on the cathode side. This rate of production is highly dependent on operating conditions such as relative humidity and temperature [25].

Electrochemical techniques are well suited determining small concentrations of H_2O_2 [26], but can suffer interference from other reactive oxygen species [27,28]. Furthermore, these techniques are susceptible to electromagnetic interference (EMI) in environments such as a PEMFC.

Spectroscopic techniques including chemiluminescence [29–31], fluorescence [5,32–35], and absorptive techniques [7,26,36–42] can also be used for detection of H_2O_2 at low

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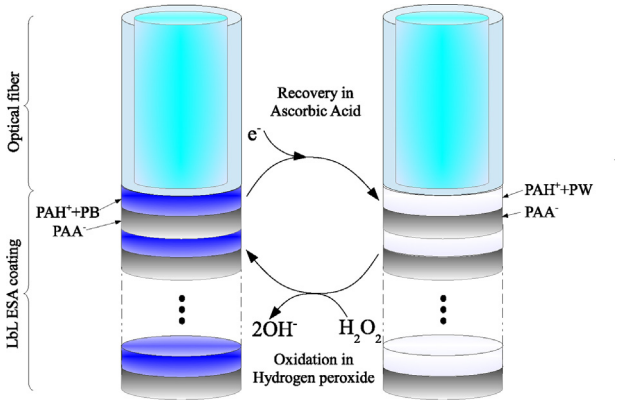

Fig. 1. Scheme of hydrogen peroxide sensing using the Prussian blue/Prussian white system in a layer-by-layer electrostatic self-assembled structure coating the tip of the optical fiber probe.

concentrations. These techniques have been integrated with optical fibers, making possible the development of sensors with high sensitivity and many of the advantages of optical fibers, such as small size, high selectivity, and immunity to EMI [26,29,40–46]. In addition, some absorptive-based approaches involve the use of low-cost reagents, which because of their absorbance in the visible and near infrared region of the light spectrum allows the use of readily available light sources and detectors [41,42].

The use of optical fiber sensors has been successfully demonstrated for the measurement of temperature and relative humidity in PEMFCs using fluorescent and phosphorescent methods [47,48], and fiber Bragg gratings [49]. In the present work, an optical fiber sensing probe for H_2O_2 was developed. The reagents employed in this absorptive-based technique, as well as the proposed technique of immobilization are compatible for use in PEMFCs.

1.1. Sensing mechanism

The mechanism of detection of H_2O_2 relies on the metallic hexacyanoferrate compound Prussian blue (PB). PB ($Fe_4(Fe(CN)_6)_3$) has a cubic crystalline structure in which C atoms of cyanide ions surround Fe(II) ions while the N atoms surround Fe(III) ions [50]. PB can be reduced electrically or chemically to Prussian white (PW), by applying a voltage of 0.2 V vs. SCE [51] or in the presence of strong reducing agents such as ascorbic acid [52]. In a similar way, the chemical oxidation of PW can be achieved by exposing it to H_2O_2 which makes it revert back to the PB form.

The spectrum of absorption of PB spans part of the visible and near infrared and has its maximum at 720 nm. Conversely, the absorbance of PW is almost negligible and appears transparent to the visible light [50,53,54]. Thus, the oxidation of PW to PB increases absorbance the 400–900 nm range. Moreover, the intensity of the absorbance reaches a maximum at low pH and decreases with increasing pH [55].

The absorbance properties of the PB/PW system have been used in optical biosensors [53–55]. In this work the scheme of detection of H_2O_2 follows the one illustrated in Fig. 1.

1.2. Polyelectrolyte multi-layered films

Nano-sized multi-layer films fabricated by the electrostatic self-assembly (ESA) of polyelectrolytes, in a layer-by-layer (LbL) deposition technique, have been the subject of a number of studies because of their simplicity, low-cost, and flexibility in applying multiple substrates regardless of the material and geometry [56–59]. LbL ESA deposition is based on the immersion of a substrate whose surface is electrostatically charged into a solution of a polyelectrolyte with the opposite electric charge. Due to the effect of electrostatic forces, the polyelectrolyte is adsorbed onto the surface until the charge is neutralized, creating a layer where the outermost surface has the opposite charge. The excess non-adsorbed material is rinsed away using a proper solvent, which is followed by the immersion into a solution with a counter polyelectrolyte. This procedure is repeated to fabricate a multi-layered structure.

LbL ESA deposition allows a variety of materials to be immobilized within the multi-layered structure. By immobilizing gold colloids, dyes and enzymes, and fluorophores, the LbL ESA deposition of polyelectrolytes has allowed the fabrication of biosensors and filters among others devices [26,60–62]. By modifying the template of deposition it is also possible to fabricate microcapsules that allow drugs to be released in a controlled manner [63]. It is also possible to tailor the permeability properties of the multi-layers. This is achievable by modifying parameters during the deposition of the layers such as concentration, pH and ionic strength of the precursor solutions, and also by applying thermal treatments and capping layers at different pH to the multi-layer structure [63]. In this manner it is possible to alter features such as the thickness of each layer (ranging in values from 5 to 80 Å), the smoothness and porosity of the surface, and the interaction between opposite charges creating a looser structure [41,58,64]. An approach to H_2O_2 detection using an optical fiber probe, whose distal end was coated with an LbL ESA structure of polyelectrolytes immobilizing PB, has been previously presented by Del Villar et al. [41,42] and served as a starting point for the developments presented here. Del Villar et al. reported a time-dependent relationship between the concentration of H_2O_2 solutions and the change in intensity of the reflected light due to the oxidation of PW. The ratio between the difference of two intensities, 10% and 90% of the maximum value, and the elapsed time within these intensities was found to increase with H_2O_2 concentration. While this linearization of the response fits the experimental data and allows the concentration to be quantified, it does not correlate with the phenomenology of the change in absorbance. To build on this initial proof of concept, measurement and response as function of concentration need to be established, and the impact and possible dependence on the intensity of the light source investigated.

The current work presents an optical fiber based sensing probe for H_2O_2 immobilizing PB in a multi-layered structure of polyeelectrolytes by LbL ESA deposition. Multiple experiments were performed to determine the response of the probe as a function of intensity of the reflected light and H_2O_2 concentration, as well as to establish a better phenomenological understanding of its operation. The role of the ESA multi-layer structure immobilizing the PB/PW reagent in limiting the underlying transport processes is also clarified.

2. Materials and methods

2.1. Materials

Poly(allilamine hydrochloride) (PAH^+, $M_W \approx 15,000$, product number 283215), poly(acrylic acid) (PAA^-, $M_W \approx 100,000$, product number 523925), and Prussian blue soluble (Product number 03899) from Sigma–Aldrich (Oakville, ON, Canada), were used as the polycation, polyanion, and sensing dye, respectively, in the LbL ESA process.

L-ascorbic acid from Aldrich, (catalog number 25,556-4), was used as the reducing agent for the Prussian blue to Prussian white reaction. Glacial acetic acid from Anachemia and Sodium acetate trihydrate 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

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