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Temperature response and durability characterization of an optical fiber sensor for the detection of hydrogen peroxide

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

[a] Department of Mechanical Engineering, University of Victoria (UVic), Victoria, BC, Canada
[b] Institute for Integrated Energy Systems (IESVic), University of Victoria (UVic), Victoria, BC, Canada
[c] Escuela de Física, Universidad Nacional de Colombia, Medellín, Colombia

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ABSTRACT

Hydrogen peroxide is a precursor to damage mechanisms in numerous applications; its monitoring is important and challenging. The effect of temperature on the performance and durability of a recently developed optical fiber sensors sensitive to the presence of hydrogen peroxide in low concentrations is investigated. The sensors are fabricated by immobilizing Prussian blue within a multilayer of electrostatically self-assembled polyelectrolytes. The sensing principle of this optical electrode relies on the change in the intensity of the reflected light when Prussian white is oxidized back to the blue state due to the presence of hydrogen peroxide. The amplitude of the intensity of the reflected light is found to vary with temperature in a quadratic fashion, but the characteristic response time which correlates with concentration remains constant. Thus the sensing device retains its abilities to determine and quantify the concentration of hydrogen peroxide in a liquid solution. Additionally, the degradation of these fiber sensors when subjected to high temperature is examined. Four optical fiber sensing devices were subjected to different testing conditions and a characterization protocol that included: measurement of the intensity of the cyanide stretch (2150 cm^{-1}) via Raman micro spectroscopy; imaging with scanning electron microscopy; and measurement of the presence of iron ions using energy dispersive X-ray spectroscopy. The results show a gradual degradation of the sensing device as a result of progressive desorption of the polyelectrolyte multilayer structure that leads to leaching of the Prussian reagent. This degradation mechanism does not compromise the functionality of the device which is found sufficiently robust for multiple tests at high temperature. The simplicity of this sensing system combined with its relative robustness and reusability make it a good a good candidate for minimally intrusive and localized monitoring of hydrogen peroxide formation in operating PEMFCs.

1. Introduction

Hydrogen peroxide (H_2O_2) is generated as a by-product in the electrochemical reactions occurring in polymer electrolyte membrane fuel cells (PEMFC) [1], and has been linked to chemical degradation that causes premature failure in PEMFCs. Reactive oxygen species (ROS) such as hydroxyl (HO·) and hydroperoxyl (HOO·) radicals can be formed upon the decomposition of H_2O_2, and the rate of this decomposition increases in the presence of cations like Fe^{2+} due to theFenton reaction [2,3]. These ROS induce degradation of polymers due to their high reactivity [4]. In the case of PEMFCs, degradation is associated with the attack of the C-F bonds in the side chains and the main backbone of the perfluorosulfonated polymer, and results in low ionic conductivity and thinning of the membrane [5]. The quantification of this degradation mode has typically been done by measuring the released fluorine ions (F^-) in the condensates at the exhaust of PEMFCs [6].

It should be noted that there is some debate on the role that H_2O_2 plays in the chemical degradation of PEMFCs, and other mechanisms that promote radical formation have been proposed [7,8]. Regardless of possible alternative mechanisms, multiple *ex situ* and *in situ* tests have shown an increase in F^- ions release as a consequence of the presence of H_2O_2 [5,6,9–11].

The presence of H_2O_2 in PEMFCs has been detected using methods based on *ex situ* measurements in membranes that have been removed from operational fuel cells [12] and in fuel cells exhaust gases [13,14] using techniques such as ion chromatography, Fourier

* Corresponding author. Department of Mechanical Engineering, University of Victoria (UVic), Victoria, BC, Canada.
E-mail addresses: jfbotero@uvic.ca, jfbotero@unal.edu.co, jfbotero@gmail.com (J.F. Botero-Cadavid), ndjilali@uvic.ca (N. Djilali).

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transform infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR).

In addition to the exhaust gas and membrane methods, *in situ* detection of H_2O_2 in PEMFCs has been achieved using electrochemical techniques. Liu and Zuckerbrod reported the presence of H_2O_2 inside PEMFC membranes while in operation using an electrochemical amperometric measurement, consisting of a measurement of the current between a working and a reference electrode at constant potential. The H_2O_2 detected in the PEMFC ranged from 3 to 25 ppm (≈90–735 μmol L^{-1}) [15]. This technique, although having the advantage of better signal-to-noise ratio and simpler instrumentation required compared to other electrochemical techniques such as potentiometric and conductometric techniques [16], can still be affected by the electromagnetic fields (EMF) generated by the electrical currents in a PEMFC. Furthermore, in an acidic environment such as the catalyst layer of a PEMFC, Pt can catalyze the formation of H_2O_2 [17,18]. Thus, the Pt wire used as a working electrode could itself be inducing the formation of H_2O_2 rather than simply detecting the by-product of the operating PEMFC.

The use of optical fiber sensors for the detection and quantification of H_2O_2 has recently been demonstrated [19]. These sensors are well-suited to the detection of H_2O_2 by-products in PEMFCs because: (1) optical signals are immune to interference due to electric currents in a PEMFC; (2) silica glass fibers are not adversely affected by the electrochemical reactions that take place in the PEMFC; (3) optical fibers are relatively small, which enable minimally invasive distributed measurements, and; (4) immobilization techniques for chemical reagents that are sensitive to H_2O_2, using the electrostatic self-assembly (ESA) of polyelectrolytes, have been demonstrated on optical fibers allowing H_2O_2 to be detected in acidic media. These techniques use the Prussian blue/Prussian white (PB/PW) system, where the organometallic compound PB is chemically reduced to PW by the immersion of the fiber in ascorbic acid, and is oxidized back to PB by the action of H_2O_2. Fiber optic devices based on this system provide reusable sensing systems for the detection of H_2O_2 [19–21].

The PB/PW fiber optics sensors presented in [19] were demonstrated at room temperature. Heat transfer and temperature variations play a key role in the operation and durability of PEMFCs [22,23] which typically operate at temperatures that range from 60 °C to 90 °C. It is therefore essential that *in situ* sensors for this application operate reliably across this range. The focus of this work is, therefore, to characterize the performance of PB/PW-based fiber optic sensors for H_2O_2 over this temperature range. The key performance parameters that are assessed in this study are: (1) verification of the ability of the PB/PW system to detect H_2O_2 at typical operational temperatures of a PEMFC; (2) characterization of the response of the sensing device to changes in the temperature, and (3) quantification of the degradation experienced by the sensitive coating, which limits the lifetime of the sensing device in continuous operation.

2. Materials and Methods

2.1. Sensing film deposition

The fabrication of a multilayer structure for immobilizing PB on the tip of an optical fiber using the layer-by-layer (LbL) ESA of polyelectrolytes follows the procedure described in [19]. Briefly, pigtails of multimode optical fibers SFS105/125Y and SFS200/225Y from Thorlabs (Newton, NJ) are cleaved, and then cleansed using a 3:1 solution of H_2SO_4 (>98%) and H_2O_2 (30 wt%) for 30 min. This promotes the attachment of hydroxide anions (OH^-) onto the fiber surface. The fibers are then dried at 80 °C for 60 min. to ensure that the surfaces remained negatively charged [24,25].

The fibers are then immersed for 20 min. in a polycation solution of poly(allylamine hydrochloride) (PAH^+, $M_W \approx 15{,}000$, product number 283215) and Prussian blue soluble (product number 03899) with concentrations of 2.0 mg mL^{-1} and 2.5 mg mL^{-1}, respectively. A thin film of this positively charged polyelectrolyte is adsorbed by the glass surface and held by electrostatic forces. The non-adsorbed excess material is removed by three consecutive immersions in distilled water, each for 1 min. The first bilayer is completed by immersing the fibers for 20 min. in a polyanion solution of poly(acrylic acid)(PAA^-, $M_W \approx 100{,}000$, product number 523925) with a concentration of 2.0 mg mL^{-1}. A total of 17 bilayers were deposited with these solutions at pH 4.0, and finally two capping bilayers of similar solutions at pH 5.5 but without PB were deposited onto the multilayered structure. The fibers were finally annealed for 2 h at 100 °C and stored at room temperature for one week before the initial tests.

All solutions were prepared using acetate buffer solution (ABS) at pH 4.0 as solvent and the pH values were adjusted using aliquots of aqueous solutions of NaOH and HCl as required. All products were from Sigma-Aldrich (Oakville, ON, Canada), used without further purification.

2.2. Liquid test solutions preparation

A pH 4.0 solution of 0.04 mol L^{-1} of L-ascorbic acid (Product number 283215, Sigma-Aldrich) using ABS as solvent was used as reducing agent for the sensing film. The oxidative stages of the redox reactions were performed using solutions of 100×10^{-6} mole L^{-1} H_2O_2, prepared by adding 30 μL of 0.01 mM H_2O_2 to 3 mL of ABS at pH 4.0. Each H_2O_2 test solution was prepared immediately before immersing the optical fiber with the multilayered sensing structure in it regardless of the temperature of the test.

2.3. Test for temperature response

The systematic testing of the sensor involving both changes in temperature and concentration was experimentally impractical at this stage of development, but prior to the temperature response experiments, the fiber response to concentration was checked and a log-linear behavior was obtained consistent with the results reported in [19].

The experimental setup to test the response to temperature is shown in Fig. 1. The white light source (HL-2000-FHSA, OceanOptics, Dunedin, FL) was connected to the arm 1 of a bifurcated optical fiber (BIF200-UV-VIS, OceanOptics). Light was carried to the common arm that is connected to the sensing probe in one of the optical fibers SFS105/125Y. The reflected light was carried back through the common arm and into arm 2, where the spectrum was measured using an optical fiber spectrometer (USB2000, OceanOptics). Spectra from the sensing probe were recorded at a sampling rate of 0.5 Hz using the software SpectraSuite (OceanOptics). The software was set to display the intensity at each wavelength in counts per second (cps) at a sweeping rate of 500 ms, and to present the trendline of light intensity, determined by integrating the cps over a range of wavelengths from 370 to 1050 nm.

The temperature at which the tests were performed was controlled by placing the sensing probe inside an environmental chamber (TestEquity, Model 123H, Moorpark, CA). High density polyethylene (HDPE) containers were filled with either 3.0 mL of ABS at a pH 4.0 or 3.0 mL of ascorbic acid solution at pH 4.0 and placed inside the environmental chamber. The temperature of the solutions was monitored with a K-type thermocouple in a control bottle with 3.0 mL of ABS. Measurements were made at the time of the immersion of the probe. The uncertainty in these measurements is ±0.1 °C. Fig. 1 also shows how the sensing probe is held in