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Amperometric detection of hydrogen peroxide at a Prussian Blue-modified FTO electrode

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Abstract

This research focuses on the use of a Prussian Blue (PB)-modified optically transparent electrode for sensing hydrogen peroxide (H_2O_2). The PB thin films were deposited galvanostatically onto F-doped tin oxide (FTO) glass substrates. Then a reliable and reproducible detection was achieved by exerting a constant bias of −0.2 V (versus Ag/AgCl/saturated KCl) at the PB-modified FTO electrode immersed in an H_2O_2 solution containing 0.1 M KCl, pH 2. The dynamic range of detection was found to lie between 50 μM and 50 mM, and the sensitivity was ca. 58.1 mA/cm^2 M. But it was also observed that the dissolved oxygen interfered the H_2O_2 sensing. Better sensing results could be obtained if the solution was pre-purged with N_2. To sum up, this study possesses the potential to eliminate the use of costly platinum or glassy carbon in a PB-based H_2O_2 sensor and may provide the basis for optical sensing.

Keywords: FTO; Hydrogen peroxide; Modified electrode; Prussian Blue; H_2O_2 sensor

1. Introduction

Detection of hydrogen peroxide (H_2O_2) has been an important topic for sensor research for decades. The relevant techniques have been applied to industrial, environmental, clinical, and food analyses [1–3]. Among them, amperometric detection is one of the promising approaches to achieve accurate, specific, economical, and rapid H_2O_2 monitoring. To date, a multitude of commercial electrochemical biosensors are based on oxidase-modified electrodes, which react with bio-substrates and yield H_2O_2, and thus sensing H_2O_2-induced currents in practice. An elaborate review about the fundamentals and applications of peroxidase-modified electrodes could be found in the paper by Ruzgas et al. [4]. In the earlier days, amperometric detection of H_2O_2 was usually performed at either platinum (Pt) or platinized surface [5,6]. Yet, the trend has been employing chemically modified electrodes to detect H_2O_2 since two decades ago.

Cox and Jaworski reported that a glassy carbon (GC) electrode modified by a thin film composed of palladium and iridium could catalyze the reduction of H_2O_2 [7]. In contrast to the reduction of H_2O_2, Taha and Wang modified a GC electrode by a thin film of oxymanganese species, which catalyzed the oxidation of H_2O_2 [8]. Also, Khoo et al. monitored a fermentation process by detecting the oxidation of H_2O_2 at a GC electrode modified by an oxycobalt film [9]. Besides the above-mentioned modified layers, transition metal hexacyanoferrates (MHCF) as well as Prussian Blue (PB) analogs have been considered as another class of interesting materials for H_2O_2 electrocatalysis for years. Table 1 summarizes a partial list of literature reporting the performances of amperometric H_2O_2 detection based on PB and its analogs [10–17].

As far as the electrochemistry of PB is concerned, it is known that PB features multiple redox states. With a high formal potential of ca. 0.87 V versus SCE, PB can be oxidized to yield Berlin green (BG) reversibly when using a

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Table 1
A partial list of literature reporting amperometric H_2O_2 detection based on Prussian Blue and its analogs

Electrode configuration[a]	Operating potential	Sensitivity (mA/cm^2 M)	Dynamic range (M)	References
PB/FTO[b]	−0.20 V vs. Ag/AgCl	58.1	5×10^{-5} to 5×10^{-2}	This work
PB/GC[c]	0.18 V vs. Ag/AgCl	1000	1×10^{-6} to 1×10^{-2}	[10]
PB/GC[d]	−0.05 V vs. Ag/AgCl	600	1×10^{-7} to 1×10^{-4}	[11]
CrHCF/GC[c]	0.00 V vs. Ag/AgCl	1152	3×10^{-8} to 1.3×10^{-3}	[12]
PB/SPE[b]	0.00 V vs. Ag/AgCl	137	4×10^{-7} to 1×10^{-4}	[13]
PB/graphite[e]	0.45 V vs. SCE	0.7	NA	[14]
PB/CPE[e]	−0.20 V vs. Ag/AgCl	0.9	NA	[15]
PB/GC[d]	−0.05 V vs. Ag/AgCl	300	NA	[16]
Nano-PB/GC[d]	0.05 V vs. Ag/AgCl	60	1×10^{-8} to 1×10^{-2}	[17]

SPE: screen printing electrode; CPE: carbon paste electrode.
[a] Different detection systems were compared.
[b] Static electrochemical cell.
[c] Rotating disk electrode (RDE) system.
[d] Flow-injection system.
[e] Continuously stirred electrochemical cell.

K^+-containing electrolyte [18,19]. On the other hand, PB can be reversibly reduced to Prussian white (PW or Everitt's salt, ES). The formal potential of PB/PW redox system is ca. 0.20 V versus SCE [18,19]. Among the redox states of PB, it is the PW state to reduce H_2O_2 and to act as an electron-transfer mediator between the electrode and H_2O_2, which can be initially present in solution or be produced from an enzyme-catalyzed reaction. In the middle of 1980s, Itaya et al. first discovered that an electrodeposited PB thin film is an excellent catalyst for both O_2 and H_2O_2 electrochemical reductions [20]. Recently, Karyakin et al. further demonstrated that the catalytic ability of PB is even better than that of bare platinum [10]. Also, a lot of H_2O_2 sensors based on a PB-modified GC electrode [10,11,16,17,20,21] or a PB-modified Pt electrode [22,23] have been successfully investigated. In addition, other metal hexacyanoferrates have been investigated as electrocatalysts for H_2O_2. For example, Lin et al. modified a glassy carbon electrode by cobalt(II) hexacyanoferrate and chromium(III) hexacyanoferrate, and fabricated amperometric H_2O_2 sensors, accordingly [12].

The fact mentioned in the above paragraph convinces us that a PB-based H_2O_2 sensor may be commercially viable. Nonetheless, the cost of a Pt or GC electrode is on the hard side. Therefore, the aim of this work is to develop a low-cost, easy-operating, and high-sensitive H_2O_2 sensing process based on a PB-modified optically transparent electrode (OTE), in which the F-doped tin oxide (FTO) glass serves as the OTE. Although, there are many researchers reporting H_2O_2 sensing based on PB-modified electrodes, there is no reported literature, to our best knowledge, using a PB-modified OTE to detect H_2O_2. Moreover, FTO glasses are superior to ordinary glassy carbon or platinum electrode from the cost consideration. Besides, FTO glasses can allow optical sensing [24]. In this paper, a reproducible and reliable H_2O_2 sensing process at the PB-modified FTO electrode (denoted as PB/FTO) using the amperometric method will be presented. PB/FTO electrode stability, H_2O_2 catalytic mechanisms, detection limits and reproducibility of H_2O_2 sensing, and oxygen interference will also be discussed thoroughly.

2. Experimental

2.1. Materials and apparatus

The main chemicals used in this work were $FeCl_3$, $K_3Fe(CN)_6$, KCl, HCl, and high-purity N_2 gas (99.9%). All of them were ACS reagent grade and not further purified. Deionized water (DIW) was used throughout. F-doped SnO_2 (FTO) coated glass substrates ($R_{sh} = 20\ \Omega$/sq. and 2 mm in thickness) were obtained from a local supplier (Sinonar Corporation, Hsinchu, Taiwan). Before using, FTO glass substrates were washed ultrasonically with 0.1 M HCl for 5 min and with DIW for another 5 min. After an extra DIW rinse, the substrates were dried in air. When preparing an FTO electrode, a piece of copper tape (3M Company), serving as the bus bar, was applied to the FTO-coated surface of a glass substrate, and then a insulating tape was applied to the same surface to define an electrode area of 3.0 cm × 1.0 cm.

All of the electrochemical experiments were performed in a three-electrode cell ($V = 50$ mL) without or with a magnetic stirring. A home-made Ag/AgCl/saturated KCl reference electrode and a Pt planar auxiliary electrode were used. Electrode potentials or currents were controlled using a potentiostat/galvanostat (Autolab, model PGSTAT30), which also collected electrochemical responses. All of the experiments were done at room temperature.

2.2. Electrodeposition of the PB thin films on the FTO glass substrates

Prussian Blue thin films were electrodeposited galvanostatically onto the FTO glass substrates: a cathodic bias with a constant current density of 20 μA/cm^2 was exerted to the FTO substrate immersed in the aqueous solution of 10 mM $K_3Fe(CN)_6$, 10 mM $FeCl_3$, and 10 mM HCl for 300 s.

An insoluble form of PB was thus electrodeposited by the chosen method [19,20]. The as-prepared PB-modified FTO (PB/FTO) electrodes films were washed with DIW and then were dried in air for at least 24 h prior to use. For quality controls, the charge capacities of PB thin films were measured based on chronoamperometry, in which a potential step, switched from +0.70 to −0.20 V (versus Ag/AgCl/saturated KCl), was applied to a PB/FTO electrode in 0.1 M KCl aqueous solution (pH 2, adjusted with HCl) for 30 s. Also, the PB/FTO electrode was characterized using cyclic voltammetry (CV) in the same electrolyte at a scan rate of 5 mV/s.

2.3. Linear sweep voltammetry for the PB/FTO electrode in the presence of H_2O_2

To search for an ideal electrocatalytic condition for H_2O_2, linear sweep voltammetry (LSV) was performed to PB/FTO electrodes in contact with the following aqueous solutions: (1) 10 mM H_2O_2, pH 5; (2) 10 mM H_2O_2, pH 2; and (3) 10 mM H_2O_2 + 0.1 M KCl, pH 2. The solution pH values were adjusted with HCl. For each run, the electrode potential was scanned linearly from 0.75 to −0.50 V (vs. Ag/AgCl/saturated KCl) at a scan rate of 30 mV/s.

2.4. Sampled-current voltammetry for H_2O_2 catalytic reduction

By the potential step method, sampled-current voltammograms (steady-state currents versus electrode potentials) for H_2O_2 reduction at the PB/FTO electrode were determined. Electrolytic solution composed of 10 mM H_2O_2 and 0.1 M KCl (pH 2) was either stationary or stirred during the measurements. Before stepping to each desired potential for steady-state current measurement (sampling time = 100 s), the PB/FTO electrode was pre-equilibrated at 0.70 V (versus Ag/AgCl/saturated KCl) for 30 s. By judging from the sampled-current voltammogram obtained in the stationary electrolyte, the H_2O_2 sensing potential was determined to be −0.20 V (versus Ag/AgCl/saturated KCl).

2.5. Amperometric detection of H_2O_2 at the PB/FTO electrode

The amperometric detection was carried out by applying −0.20 V (versus Ag/AgCl/saturated KCl) at a PB/FTO electrode in contact with non-stirred solutions of different H_2O_2 concentrations. All of the H_2O_2 solutions contained 0.1 M KCl and a trace amount of HCl (to adjust pH to 2). The electrode was pre-equilibrated at 0.70 V for 30 s before each run of the detection, and the steady current readings at −0.20 V were acquired after 100 s. To investigate the effect of dissolved oxygen on the detection, the amperometric experiments without (as described above) and with 5 min high-purity N_2 (99.9%) purging were compared.

3. Results and discussions

3.1. Electrochemical characteristics of the PB-modified FTO electrode

Fig. 1 shows the cyclic voltammogram of a PB/FTO electrode cycled in an electrolyte of 0.1 M KCl (pH 2) and reveals the existence of two redox systems—PB/PW and BG/PB. It can be found that their redox potentials are in the vicinity of 0.20 and 0.90 V (versus Ag/AgCl/saturated KCl), respectively. This is consistent with the CV of a PB-modified GC electrode reported by Itaya et al. [20]. In the present study, we focused on the PB/PW redox system because of the high reducing ability of PW. In Fig. 1, a reduction current of ca. −70 μA is present when the PB electrode is biased to the PW state, and this current is presumably produced by the reduction of dissolved oxygen catalyzed by PW [20]. To be sure, it is the PW to have the capability for reducing H_2O_2 and to act as an electron-transfer mediator. The PB/PW redox process in the presence of K^+ ions can be expressed as follows [20]:

$$Fe_4^{III}\left[Fe^{II}(CN)_6\right]_3 + 4K^+ + 4e^- \leftrightarrow K_4Fe_4^{II}\left[Fe^{II}(CN)_6\right]_3 \quad (1)$$

where $Fe_4[Fe(CN)_6]_3$ and $K_4Fe_4[Fe(CN)_6]_3$ are PB and PW, respectively. Since PB has been known as a zeolite analog with channel diameters of ca. 3.2 Å, hydrated K^+ ions are small enough to reversibly insert into and extract from the PB lattice and to result in very high PB/PW redox reversibility [25]. Therefore, we chose K^+ ions for maintaining the electrode stability during the H_2O_2 detection. In addition to the electrochemical reversibility, high reproducibility of PB electrodeposition was confirmed. All of the electrodeposited PB films were tested by potential step experiments in the presence of 0.1 M KCl, pH 2 prior to use for quality control (see Section 2.2). We found that the passed charges of PB films (electrode area = 3.0 cm × 1.0 cm) were within 29.0 and 32.9 mC, and the coefficient of variation was

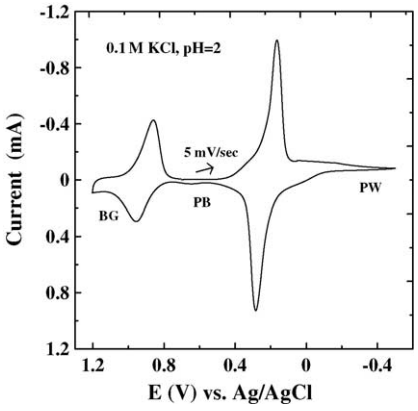

Fig. 1. Cyclic voltammogram of a PB/FTO electrode in 0.1 M KCl, pH 2. Scan rate = 5 mV/s.

ca. 3.96% ($N = 30$). This means the electrode-to-electrode variation could be neglected when performing the H_2O_2 sensing.

3.2. Determination of the H_2O_2 sensing conditions at the PB/FTO electrode

To achieve reliable H_2O_2 detection at the PB/FTO electrode, the effects of supporting electrolytes and stirring on the electrocatalytic reaction were investigated. Fig. 2 compares cathodic linear sweep voltammograms (LSVs) of the PB/FTO electrodes immersed in the following three aqueous solutions: (1) 10 mM H_2O_2, pH 5; (2) 10 mM H_2O_2, pH 2; (3) 10 mM H_2O_2, 0.1 M KCl, pH 2. (For solutions (2) and (3), the pH values were adjusted using HCl.) It can be seen that solution (3) gives a higher reductive response than solution (2) does, whereas solution (1) has no significant signal. It is noticed that only solution (3) results in an observable cathodic peak in response to the PB-to-PW conversion, which is necessary for the H_2O_2 electrocatalysis. When the electrode potential was biased negatively beyond −0.2 V, the PW-driven H_2O_2 reduction took place in solution (3), giving a net catalytic current of H_2O_2 reduction; whereas PB was still under conversion to PW in solution (2). Accordingly, in the potential region between −0.2 and −0.4 V, the H_2O_2 electrocatalytic current was observed in solution (3), but the PB reduction current was detected in solution (2). This explains why the current in solution (3) was smaller than that in solution (2) in the above-mentioned potential region. Moreover, the addition of 0.1 M KCl effectively lowers the overpotential required for the PB-mediated H_2O_2 reduction. The results can be explained by Eq. (1) and the following formula reported in literature [20]:

$$K_4Fe_4^{II}\left[Fe^{II}(CN)_6\right]_3 + 2H_2O_2 + 4H^+ \rightarrow Fe_4^{II}\left[Fe^{II}(CN)_6\right]_3 + 4H_2O + 4K^+ \quad (2)$$

It can be seen in the above formula that protons act as a reactant and participate in the PW-driven H_2O_2 reduction. In addition, Eq. (1) elucidates that the existence of K^+ ions can facilitate the PB-to-PW conversion. Since both the acidity and K^+ ions play significant roles, H_2O_2 solutions were added with 0.1 M KCl and a trace amount of HCl (for adjusting pH to 2) prior to analyses.

Fig. 3 compares the sampled-current voltammograms (steady-state currents versus electrode potentials) of the PB/FTO electrodes immersed in the stationary and stirred H_2O_2 solutions (10 mM H_2O_2, 0.1 M KCl, pH 2). It can be seen that stirring results in several-fold higher current response by increasing convective mass transfer of H_2O_2 from bulk solution to electrode surface. On the other hand, stirring does not yield a limiting current, which is crucial for a reliable amperometric H_2O_2 sensing, and may involve more dissolved oxygen to interfere H_2O_2 sensing (see Section 3.5). However, for the stationary case, a limiting current is achieved when the PB/FTO electrode is biased to ca. −0.20 V versus Ag/AgCl/saturated KCl. The limiting current observed in the stationary condition implies that it was the PB thin film, not the H_2O_2, that plays the role of the limiting reagent in the present system. The Nernstian current–potential behavior can thus reflect the PB/PW redox characteristics. According to the above considerations, we decided to use a stationary environment to sense H_2O_2 by compromising sensitivity in exchange for reliability. And the sensing potential was thus set to −0.20 V versus Ag/AgCl/saturated KCl. The sensing results will be given and discussed in Section 3.4.

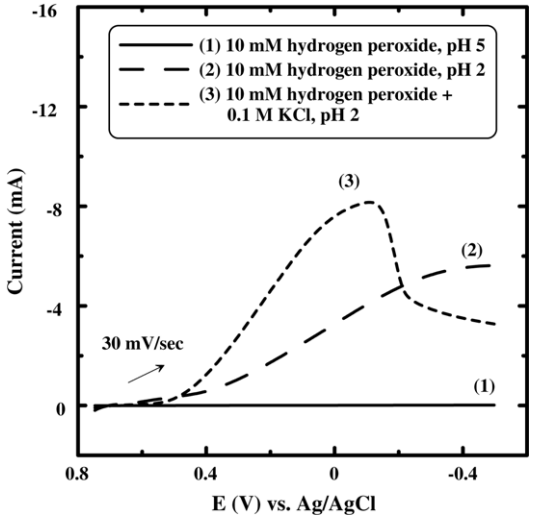

Fig. 2. Linear sweep voltammograms of PB/FTO electrodes in: (1) 10 mM H_2O_2, pH 5; (2) 10 mM H_2O_2, pH 2; and (3) 10 mM H_2O_2, 0.1 M KCl, pH 2. Scan rate = 30 mV/s.

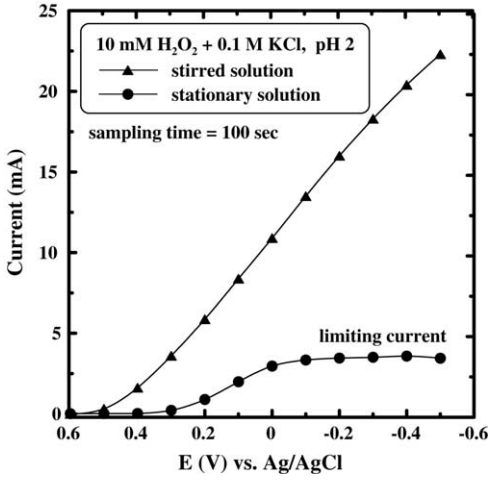

Fig. 3. Sampled-current voltammograms (steady-state currents vs. electrode potentials) of the PB/FTO electrodes immersed in the stationary and stirred H_2O_2 solutions (10 mM H_2O_2, 0.1 M KCl, pH 2). Sampling time = 100 s. Before each run, the PB/FTO electrode was re-equilibrated at 0.70 V (vs. Ag/AgCl/saturated KCl) for 30 s.

3.3. Electrode kinetics of the PB-catalyzed H_2O_2 reduction

By combining Eqs. (1) and (2), we obtain the following formula:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (3)$$

This means that the overall reaction at the PB/FTO electrode is simply H_2O_2 reduction in the acidic environment. To further understand the electrode kinetics, the sampled-current voltammogram for the stationary H_2O_2 reduction at the PB/FTO electrode (see Fig. 3) is re-plotted in Fig. 4. Fig. 4 presents the sampled-current voltammograms in the form of E versus $\log[(I_L - I)/I]$, where E is the electrode potential, I the sampling current, and I_L the limiting current. Fig. 4 is known as a wave-slope plot and can be fitted by the following equation in the case of totally irreversible kinetics:

$$E = E_{1/2} + \frac{2.303RT}{\alpha n F} \log\left[\frac{I_L - I}{I}\right] \quad (4)$$

where $E_{1/2}$ is the half-wave potential, n the number of electrons transferred during the H_2O_2 reduction, α the transfer coefficient, F the Faraday constant, and RT remains its physical meaning. By fitting, we obtain

$$E_{1/2} = 122.4\,\text{mV}$$

$$\frac{2.303RT}{\alpha n F} = 154.5\,\text{mV}$$

The half-wave potential estimated here is more negative by ca. 77 mV when compared to the redox potential of the PB/PW redox system in the absence of H_2O_2 (see Fig. 1). This verifies that the PB-to-PW reduction takes place ahead of the H_2O_2 reduction and is in accordance with Eq. (2). Meanwhile, the second fitting parameter describes that the transfer coefficient, α, for the overall electrode process is equal to ca. 0.19 if two-electron-transfer reaction (3) takes place in one step at 25 °C. (The value of F/RT is 38.92 V^{-1} at 25 °C.) But, the overall electrode process involves reactions (1) and (2). Therefore, the transfer coefficient estimated here might be less reliable.

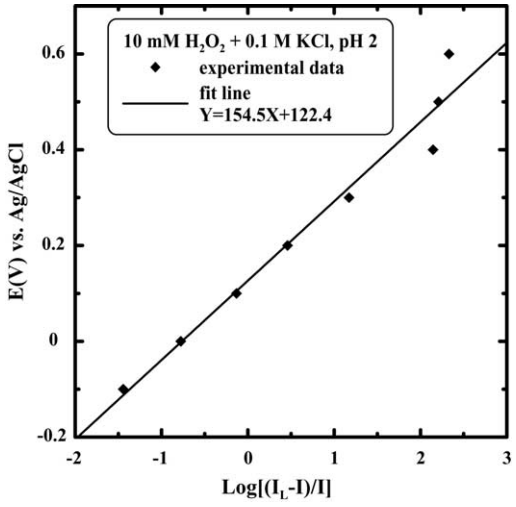

Fig. 4. The wave-slope plot presenting the stationary sampled-current voltammogram of Fig. 3 in the form of E vs. $\log[(I_L - I)/I]$, where E is the electrode potential, I the sampling current, and I_L the limiting current.

3.4. Amperometric detection of H_2O_2

Fig. 5 demonstrates the successful H_2O_2 detection at the PB/FTO electrode. The calibration curve, plotting steady-state currents versus H_2O_2 concentrations, is highly linear (ca. $R^2 = 0.9997$) and features a detection sensitivity of ca. 58.1 mA/cm^2 M. The highly linear correlation could be attributed to first-order chemical kinetics or linear diffusion. Experiments were performed with the same electrode and the numbers in Fig. 5 represent the detection sequence (we operated from 100 μM to 20 mM and then reversed the detection sequence). Obviously, detection sequence does not alter the calibration curve. Yet, the PB film was slightly degraded after 16-round detection by judging from the decrease of current response. To more precisely evaluate the run-to-run deviation of H_2O_2 response, a PB/FTO electrode was used to continuously detect 10 mM H_2O_2 (in the presence of 0.1 M KCl, pH 2) 40 times, and the results are presented in Fig. 6. (Before each run, the PB/FTO electrode was re-equilibrated at 0.70 V versus Ag/AgCl/saturated KCl for 30 s.) It reveals that the sensing current suffered from an early decay but then became steady after 10 runs of detection. When compared to the fresh PB film, 17% of charge capacity was lost after 40 runs of H_2O_2 sensing. On average, charge capacity loss was

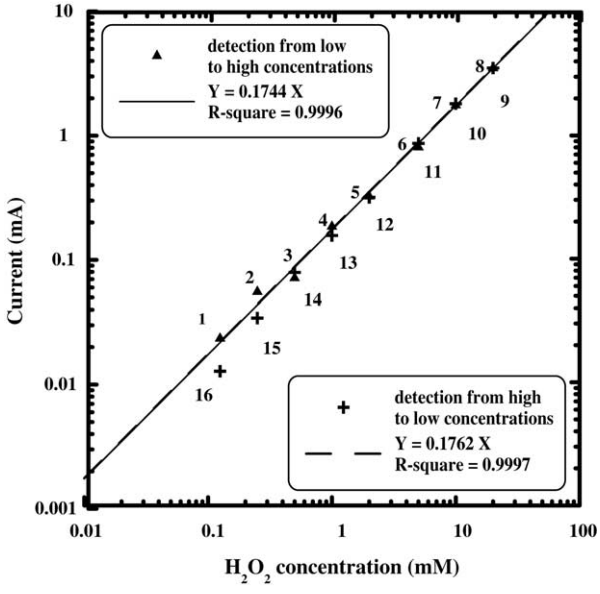

Fig. 5. Calibration curves demonstrating the H_2O_2 detection at the PB/FTO electrode in the presence of 0.1 M KCl, pH 2. Numbers in the figure represent the sensing sequence. The sensing potential was −0.20 V vs. Ag/AgCl/saturated KCl. Sampling time = 100 s. Before each run, the PB/FTO electrode was re-equilibrated at 0.70 V for 30 s.

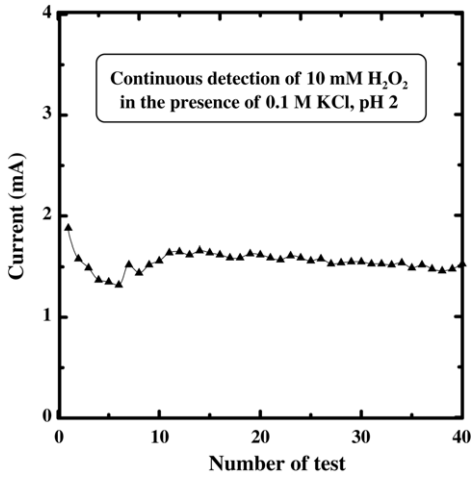

Fig. 6. Forty-round continuous detection of 10 mM H_2O_2 in the presence of 0.1 M KCl, pH 2. Detection method is the same as that described in Fig. 5.

smaller than 0.5% per run. The degradation could be due to the decomposition of PW to Fe^{2+} and $Fe(CN)_6^{4-}$ ions, and it was reported that the stability of the PB-modified electrode could be improved by drying the PB films at 100 °C for 1 h before using [21].

To evaluate the detection limits, a wide-range H_2O_2 detection (concentrations ranged from 1 μM to 60 mM) was performed, and the results are plotted in Fig. 7. On the basis of the calibration curve in Fig. 7, the high and low detection limits are estimated to be 50 mM and 50 μM, respectively. That is, when the concentration is out of the limits, the current response will be no longer proportional to the bulk concentration of H_2O_2 and becomes unreliable. Accordingly, the dynamic range (linear detection range) is almost across three orders. The high detection limit is presumably caused by the depletion of PW when catalyzing highly concentrated H_2O_2; nonetheless, sample dilution can resolve this kind of problem. Thus, the practical sensing issue is to lower the detection limit. In the present case, the limitation on the low detection limit might be attributed to the interference of dissolved oxygen, which oxidized PW to PB and then led to a background signal. Besides, this could be an intrinsic issue for the static, macro-electrode system. Table 1 clearly shows that not only higher sensitivity but wider dynamic range could be obtained in convective, stirred systems, as compared to those of static detections. Especially, it was reported recently that a nano-structured PB-modified electrode coupled with the flow injection system could effectively boost the dynamic range of H_2O_2 detection to six orders (10^{-8} to 10^{-2} M) [17]. Hence, proper convective source, electrode miniaturization, and analyte enrichment can be useful strategies for improving the present system's detection limits.

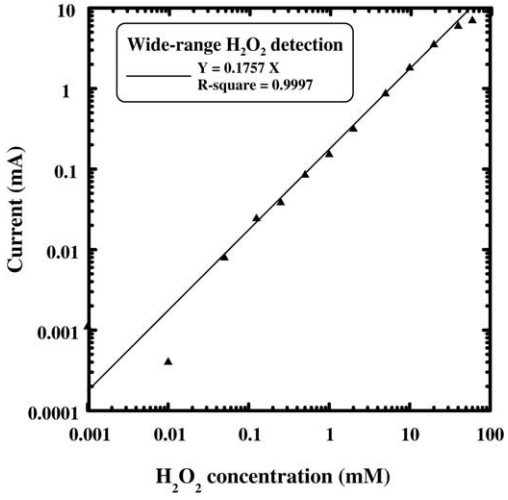

Fig. 7. A wide-range H_2O_2 detection (concentrations ranged from 1 μM to 60 mM) for estimation of detection limits. Detection method is the same as that described in Fig. 5.

3.5. Effects of the dissolved oxygen

It was reported that the dissolved oxygen in the bulk solution would be reduced to water when the potential of a PB-modified electrode was lower than 0.2 V (versus SCE) [20]. This implies that the dissolved oxygen and H_2O_2 are competing for the reductive electrons transferred from the PW. Therefore, the H_2O_2 detection interferes with the dissolved oxygen if the analyte concentration is relatively low. To illustrate how the dissolved oxygen affects the H_2O_2 sensing, Fig. 8 compares the low-concentration calibration curves (0–0.25 mM) obtained before and after 5 min N_2 purging to investigate how the dissolved oxygen from the ambient affects the H_2O_2 detection. It is obvious that sensing currents obtained without N_2 purging are slightly higher than those obtained with N_2 purging. The data support that the dissolved oxygen from the ambient atmosphere contributes additive

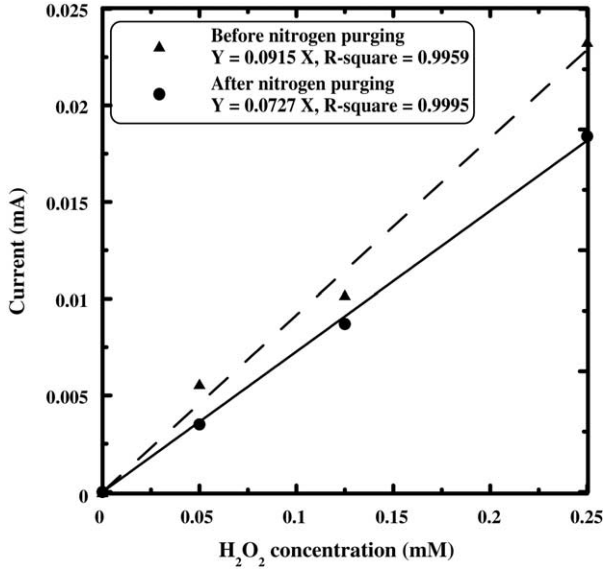

Fig. 8. The interference of dissolved oxygen. The calibration curves of H_2O_2 detection before and after 5 min N_2 purging are compared. Detection method is the same as that described in Fig. 5.

current responses for the amperometric H_2O_2 detection. On the other hand, the N_2-purged current is more linearly dependent on the H_2O_2 concentration ($R^2 = 0.9995$) than that without N_2 purging ($R^2 = 0.9959$). So we infer that removal of dissolved oxygen might widen the dynamic range of the H_2O_2 detection. However, as far as some biosensor applications are concerned, the presence of oxygen is necessary. For example, a PB-based glucose sensor [10] is known to function based on the following principle:

$$\text{Glucose} + O_2 \xrightarrow{\text{GOD}} \text{Gluconic acid} + H_2O_2 \quad (5)$$

And it is the dissolved oxygen that reacts with glucose and glucose oxidase (GOD) to yield H_2O_2 for PB-mediated amperometric detection. Thus, one should consider if the N_2 purging is appropriate treatment before performing H_2O_2 sensing.

4. Conclusions

On the basis of the above results and discussions, a reliable and reproducible amperometric detection of H_2O_2 at the PB/FTO electrode has been verified. In conclusions, we summarize the major findings of this work as follows:

1. H_2O_2 catalytic reduction occurs after the formation of PW and requires low-pH environment, for example, pH 2. Besides, the existence of K^+ ions (0.1 M KCl) effectively reduces the catalytic overpotential and enlarges the catalytic current.
2. Reliable and reproducible amperometric detection can be achieved by applying a constant potential of −0.20 V (versus Ag/AgCl/saturated KCl) at the PB/FTO electrode in contact with a stationary H_2O_2 solution in the presence of 0.1 M KCl, pH 2.
3. The detection current responds to the bulk solution of H_2O_2 linearly when the concentration ranges between 50 μM and 50 mM. The sensitivity within this dynamic range is estimated to be ca. 58.1 mA/cm^2 M.
4. Dissolved oxygen is to affect the reductive H_2O_2 detection at the PB/FTO electrode and to contribute additive current responses. N_2 purging can minimize the interference of dissolved oxygen.

In addition to the above findings, we believe that this work also provides the opportunities for reducing the cost of a PB-based sensor and helps for the design of optical sensing devices.

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