Anion-exchange membrane-separated electrochemical cells enable the use of sacrificial anodes for hydrogen peroxide detection with enhanced dynamic ranges

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ABSTRACT

Conventionally, both a working and counter electrode are housed in a single cell to form an electrochemical device for quantification of various analytes. For reductive sensing of hydrogen peroxide, however, analyte losses due to oxidation and catalytic decomposition on the counter electrode are significant, rendering such devices unsuitable for continuous monitoring of analyte concentration changes over time. Further, only chemically inert materials such as platinum can be used to construct the counter electrode, where their high cost limits potential applications. To circumvent such issues, an anion-exchange membrane was employed to fabricate a two-chamber device housing each electrode in each individual chamber, to physically prevent the counter electrode from interfering with working electrode analysis. Such a design enables the use of sacrificial anodes as the counter electrodes, thereby significantly expanding the linear range of detection, improving sensitivity, and reducing device cost.

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1. Introduction

Quantitative detection of hydrogen peroxide (H_2O_2) is of great interest due to the ubiquitous presence of H_2O_2 in biological and environmental systems, as well as its use in many industries including pulp and paper [1], healthcare [2] and environmental remediation [3]. Relative to other analytical methods for H_2O_2 detection (direct absorption measurement [4], colorimetric methods [5], and chemiluminescence [6]), electrochemical methods are preferable due to their instantaneous signal generation and capability of continuously monitoring H_2O_2 levels over time [2]. Further, electrochemical sensors can be mass-produced and are thus cost-effective for wide adoption in diverse applications.

To date, constant-potential amperometry has been the most reported electrochemical method for H_2O_2 detection since H_2O_2 carries no charge, but is a redox active compound [7–26]; consequently, H_2O_2 detection requires two collaborative electrodes: a working electrode (WE) and a counter electrode (CE), both closely positioned in a single chamber in which the WE carries out the H_2O_2 redox reaction for signal generation, while the CE accepts (or donates) electrons from water electrolysis to maintain system charge conservation (Scheme 1a). Herein, the WE could be either an anode or a cathode (for oxidative or reductive sensing of the analyte, respectively). Most of the current studies of H_2O_2 sensing are based on reduction H_2O_2 on a WE and they were all conducted in a single chamber device. The single-chamber device is simple and straightforward to construct, thus being widely adopted in experimental research; however, analyte (*i.e.,* H_2O_2) redox reactions on a CE surface may affect WE signal generation (Scheme 1a). To minimize such interference, chemically inert materials such as platinum (or occasionally gold or graphite) are commonly used to fabricate CEs [7,9,10,13,15,16,20,27–30]. Nevertheless, in addition to the oxidation of H_2O_2 on the CE surfaces at polarized potentials (Fig. S5), platinum itself is not inert but catalytically reactive towards H_2O_2 decomposition [31,32]. Platinum reactivity accelerates H_2O_2 decomposition, resulting in significant loss of H_2O_2 during measurement, thereby seriously limiting accuracy during continuous monitoring of H_2O_2 concentrations over time (*i.e.,* in dynamic sampling systems) [33–37]. Reactivity at CE surfaces is particularly problematic when H_2O_2 concentrations are low (*e.g.,* mM levels). Further, due to its extreme rarity, platinum is very expensive, limiting its suitability for large-scale and/or routine use. Additionally, other technical issues, such as pH change induced by electrode reactions and oxygen bubbles generated on CE surfaces further undermine sensor performance during continuous monitoring of H_2O_2 within dynamic systems. As
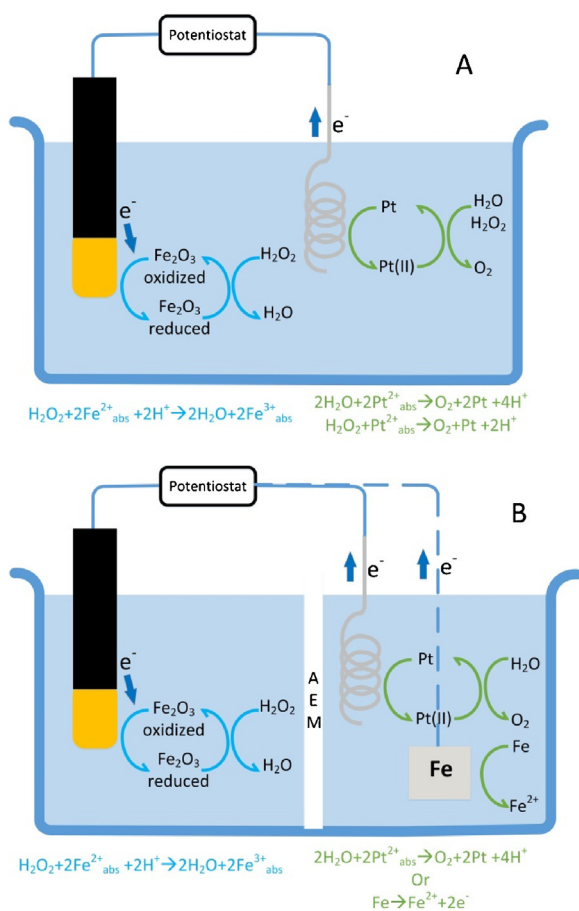
Scheme 1. Schematic configuration and electrode reactions within a single and a two-chambered H_2O_2 sensing system. The conventional reductive H_2O_2 sensing system (A) with a Fe_2O_3 nanoparticles-graphite-chitosan doped WE (cathode) and a platinum coil CE (anode) in the same chamber; an anion-exchange membrane (AEM)-separated two-chamber H_2O_2 sensing system (B) used in this study with the same WE. A scenario where iron is used as the CE is also depicted in (B).

with platinum, graphite was also considered to be a non-reactive CE material, but it is oxidizable, resulting in inferior reproducibility and a narrow dynamic range, rendering it even less favorable than platinum for H_2O_2 sensing [38]. Consequently, it would be highly desirable to develop electrochemical sensors without CE interference towards the WE, facilitating improved sensitivity and dynamic ranges, suitable for continuous H_2O_2 monitoring.

2. Experimental Section

2.1. Preparation of the working electrode

The working electrode was fabricated with a chitosan-trapped Fe_2O_3 nanoparticle (20–40 nm, US Research Nanomaterials) functionalized graphite bar. The detailed study on the comparison of two iron oxides nanoparticles (Fe_2O_3 and Fe_3O_4 NPs) with paraffin oil-based carbon paste electrodes (CPEs) and the preparation of chitosan-trapped Fe_2O_3 NPs can be found in the SI (supplementary information, Figs. S1–S4). Graphite powder was used to facilitate the electron transfer between the catalyst (*i.e.*, Fe_2O_3 NPs) and the substrate electrode. A solution of 0.5% chitosan in 1% acetic acid was used for attaching the catalytic iron oxide NPs to the substrate electrode. The functionalized electrodes were evaluated by cyclic voltammetry, which is detailed in the electrochemistry section.

2.2. Construction of a two-chamber H_2O_2 sensing system

A two-chamber device (Fig. S9) separated by an anion-exchange membrane (AEM, AMI-7001, Membrane International Inc.) was assembled for the amperometric detection of H_2O_2. The CE and the WE chambers were made of two polypropylene housing of common laboratory syringe filters. The anode (CE) was a platinum coil (0.25 mm diameter, Lot #39383, Alfa Aesar, VWR) or a metal foil (stainless steel, Lot # 117985, McMaster-Carr; Reynolds aluminum foil) and the cathode (WE) is a Fe_2O_3 NPs-graphite-chitosan doped graphite bar. The CE was connected to the external circuit through a hole on the polypropylene packing material with a male-to-male jumper wire. The two syringe filter packages were taped to the AEM using a double-sided tape (Scotch® Exterior Mounting Tape, Staples). The edges of the assembled device were then sealed by a silicone sealant (GE SE2182 24C, Home Depot). A slot was cut on top of the cathodic chamber to allow the entrance of the graphite WE and an RE (reference electrode, Ag/AgCl, RE-5B, BASi).

2.3. Comparison of the conventional single-chamber device and the two-chamber device

The H_2O_2 sensing in a single chamber and in an AEM-based two-chamber system was compared. A platinum coil (13 cm, 7 mm diameter) was used in both cases as the CE. The WEs were graphite bars doped with 40 μl of Fe_2O_3 NPs-graphite-chitosan suspension. Single chamber tests were conducted in a 50 ml beaker with a Ag/AgCl RE and 30 ml of $1 \times$ PBS (phosphate buffer saline, pH = 7.4) [39] as the electrolyte. The WE was poised at −0.4 V vs Ag/AgCl RE and various amounts of 3% or 30% H_2O_2 were sequentially injected after the background current leveled off. Transfer of liquid was made by using Eppendorf™ Research plus™ adjustable pipettes (0.1 to 2.5 μL and 0.5 to 10 μL).

When the two-chamber device was used, the WE and CE chambers were filled with 10 ml $1 \times$ PBS. A modified graphite bar electrode and a Ag/AgCl RE were inserted into the WE chamber while a platinum coil or a piece of stainless steel (1-inch square, folded) or aluminum foil (1-inch square, folded) is inserted into the CE chamber. The WE was again poised at −0.4 V vs Ag/AgCl RE and H_2O_2 was sequentially injected into the WE chamber. All electrolytes were stirred with a VWR magnetic stirrer.

2.4. Electrochemical analyses

Cyclic voltammetry was conducted on a Gamry 750 potentiostat. A three-electrode system was used with a specific CPE or a Fe_2O_3 NPs-graphite-chitosan doped graphite electrode, a Ag/AgCl electrode, and a graphite bar (6.35 mm square, McMaster-Carr) or a platinum coil (13 cm long, 7 mm diameter) as the WE, the RE, and the CE, respectively. During the initial comparison of the two iron oxide NPs, sodium chloride solution (0.9% in distilled water) was the electrolyte (Figs. S1–S4) while $1 \times$ PBS was used in the rest of the study [39].

Chronoamperometric tests were conducted with the same potentiostat during the titration tests for calibration curves (Fig. S7). The tests were run in the aforementioned three-electrode mode. In cases where the two-chamber device was used, the WE and the RE were placed in the same chamber. The WE potential was poised at −0.4 V vs Ag/AgCl RE. In all cases with the two-chamber cell, the electrolytes were mixed with mini-stir bars (2 mm × 7 mm) on a VWR magnetic stirrer. When a beaker was used, a bigger stir bar (8 mm × 13 mm) was used. More details are available in the SI.