

Development of Electrochemical Hydrogen Peroxide Sensor for In situ Real-time Monitoring of Radiolysis Products in Aqueous Solutions

Wansik Cha*

Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, 34057, Korea

*Corresponding author: wscha@kaeri.re.kr

***Keywords :** Radiolysis, hydrogen peroxide, electrochemical sensor, amperometry, gas-permeable membrane

1. Introduction

Water radiolysis plays an important role in governing the dissolution behavior of spent nuclear fuel within the near-field environment of a geological repository. As groundwater contacts the fuel matrix, ionizing radiation—primarily alpha, and to a lesser extent beta and gamma radiation from the decaying fuel—decomposes water molecules into a series of reactive species, including radical species ($\cdot\text{OH}$, $\cdot\text{OH}_2$, e_{aq}^- , $\cdot\text{H}$) and molecular products (H_3O^+ , H_2 , H_2O_2 , O_2). Among these, oxidants such as H_2O_2 , O_2 , $\cdot\text{OH}$ can locally oxidize U(IV) to more soluble U(VI) species, significantly enhancing fuel matrix dissolution and radionuclide release rates, leading to so-called oxidative dissolution. Thus, quantitative characterization of radiolysis products—is essential for kinetic investigations of dissolution rates and for elucidating the associated oxidation mechanisms.

Hydrogen peroxide (H_2O_2) is regarded as the most significant radiolytic oxidant, due to its relatively long lifetime, high diffusivity, and strong oxidizing capacity toward UO_2 . Quantitative analysis of H_2O_2 and its formation/decomposition kinetics are therefore essential for accurately modeling near-field redox conditions and predicting long-term dissolution behavior. Thus, we previously examined analytical performances of spectroscopic and electrochemical methods for H_2O_2 determination and utilized them to estimate H_2O_2 stability in various aqueous solutions [1,2].

In this study, electrochemical sensors were further developed for in situ real-time monitoring of H_2O_2 in aqueous solutions. Fig. 1 illustrates the simplified sensing mechanism of the sensor, which is a type of amperometric sensor measuring oxidative current from the Pt working electrode during the surface oxidation of H_2O_2 present in the sample solution. In fact, such strategy of amperometric H_2O_2 detection was inspired by the nitric oxide sensor previously reported in the literature [3]. The basic amperometric performances, such as the limit and range of detection, response time and selectivity, were examined and optimized. Since the application of gas-permeable membrane (GPM) was shown to effectively improve the sensor's selectivity against various ionic species in aqueous samples [3], the dependence of the sensor performance on the GPM properties including its porosity was evaluated in detail. The permeability of H_2O_2 , that is the key concept of the

proposed electrochemical H_2O_2 sensor, was additionally investigated using the two spectroscopic H_2O_2 determination methods, i.e., ferrous oxidation-xylenol orange (FOX) assay and the luminol chemiluminescence (LM-CL)-based method.

2. Methods and Results

2.1 Amperometric Detection of H_2O_2

An amperometric sensor for H_2O_2 detection was developed by adopting the nitric oxide sensor configuration [3]. As shown in Fig. 1 the sensor was equipped with a non-coated Teflon GPM, a Pt working electrode at the sensor tip, and a chlorinated Ag wire serving as a combined reference-counter electrode. Current changes upon sample addition were monitored using a potentiostat (SP-200, Biologic) based on pre-calibration data obtained using standard H_2O_2 solutions (Sigma-Aldrich).

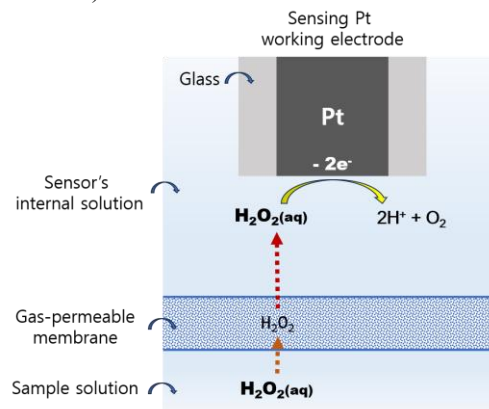


Fig. 1. Schematic presentation of the electrochemical detection mechanism; the proposed H_2O_2 sensor equipped with a gas-permeable membrane (GPM).

2.2 FOX Assay for H_2O_2 Determination

The FOX assay method was employed to spectrophotometrically determine H_2O_2 concentrations based on the color change (or absorption spectra) of Fe-xylenol orange (XO) complexes. In this method, Fe^{2+} -XO complexes were prepared in working solutions at pH 3, then mixed with H_2O_2 -containing samples to allow quantitative oxidation of Fe^{2+} to Fe^{3+} . Detailed analytical procedure were provided in our previous study [1]. The FOX assay exhibited an analytical dynamic range up to

approximately 200 μM depending on the composition of the XO-Fe(II) working solution.

2.3 LM-CL-based Determination of H_2O_2

The LM-CL method exploits the chemiluminescence reaction caused by luminol and a metallic catalyst (e.g., Cu^{2+} , Co^{2+}). Luminol emits a blue light (425 nm) at pH 10–11 in response to oxidizing agents such as hydrogen peroxide. In our previous study, the analytical sensitivity was achieved for the analytical dynamic range up to $\sim 200 \mu\text{M}$ and limit of detection $< 1 \mu\text{M}$ by a batch-wise CL detection using conventional cuvette cells and an intensified charge-coupled device (ICCD) [1].

2.4 Amperometric Responses of the H_2O_2 Sensor

The H_2O_2 sensor developed in this study has a two-electrode system in a compact plastic (polyethylene) housing. Therefore, its sensing area (see Fig. 1) can be directly immersed into aqueous sample solutions so as to enable in situ and real-time H_2O_2 determination without any sample pre-treatment and other reagent preparation. Such amperometric sensors measure oxidation currents (nA-level) of H_2O_2 from the Pt working electrode (see Fig. 1) which was pre-polarized at an anodic potential (e.g., +0.6 V vs. Ag/AgCl). Fig. 2 shows the typical amperometric calibration curves of the H_2O_2 sensor obtained by using a standard H_2O_2 solution. The result clearly demonstrates the fully reversible and quantitative amperometric responses according to the H_2O_2 concentration in the sample solutions.

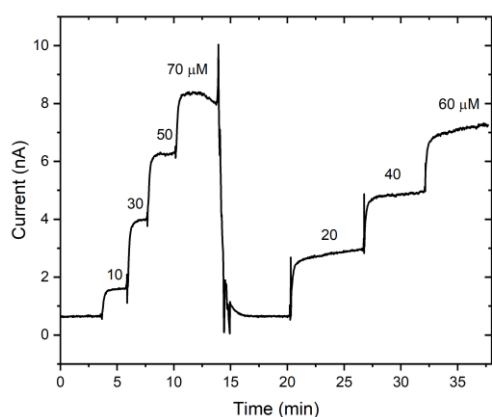


Fig. 2. The real-time amperometric monitoring profile of the H_2O_2 sensor developed in this study. A series of aliquots of a standard H_2O_2 stock solution (10 mM) were added into an aqueous solution (DI water). The testing solution was replaced with a new blank solution to demonstrate the reversibility of the sensor responses.

2.5 GPM Permeability Tests Using Spectroscopic H_2O_2 Analysis

The quantitative amperometric responses of the sensor as shown in Fig. 2 strongly indicate that the permeability of H_2O_2 through the GPM. Therefore, the H_2O_2 permeability was further examined using a diffusion cell

having two liquid cell chambers that are separated by a mounted permeable membrane. During the permeability test, H_2O_2 is allowed to permeate through the GPM from the solution of known H_2O_2 concentration in one chamber to the blank solution in the other chamber. Then, the H_2O_2 concentration change in the blank solution was monitored by using either the FOX assay or LM-CL method. Such permeability test results (data not shown) provided additional evidences that dissolved H_2O_2 in the sample solution phase permeates in the form of vapor or $\text{H}_2\text{O}_2(\text{g})$ through the GPM and redissolves in the internal solution phase to be detected on the surface of Pt electrode (see Fig. 1).

2.6 Sensor Performance Depending on GPM Permeability

As the permeability of H_2O_2 through the GPM was confirmed, a few H_2O_2 sensors having GPMs of different porosity (or pore size) were prepared and tested to monitor their H_2O_2 sensing performance, such as the limit and range of detection, response time and selectivity. Such test results were further used to optimize the sensor performance for quantifying H_2O_2 concentrations; more details will be provided in the presentation.

3. Conclusions

A new type of electrochemical H_2O_2 sensor was developed by modifying the configuration of an amperometric nitric oxide sensor. The proposed H_2O_2 sensor exhibited reversible and quantitative amperometric responses to the H_2O_2 concentration in aqueous sample solutions, thus, enabling in situ and real-time monitoring of H_2O_2 by using the sensor. The permeability of H_2O_2 through GPM was independently confirmed by applying a diffusion cell test and spectroscopic H_2O_2 determination methods. It is further shown that the sensors performance is also dependent on the permeability (or porosity) of GPM.

ACKNOWLEDGMENTS

This study was supported by the KAERI Institutional Program (Project No. 79704-26)

REFERENCES

- [1] W. Cha and Y. Kim, Evaluation of Spectroscopic Methods for Determination of Hydrogen Peroxide as a Radiolysis Product, Fall Meeting of the Korean Radioactive waste Society (KNS), November 2-3, 2023, Jeju, Korea.
- [2] W. Cha and J. Nam, Monitoring Temperature-dependent Stability of Hydrogen Peroxide as a Radiolysis Product in Various Aqueous Solutions, Spring Meeting of the Korean Nuclear Society (KNS), May 22-23, 2025, Jeju, Korea.
- [3] W. Cha and M. E. Meyerhoff, Enhancing the Selectivity of Amperometric Nitric Oxide Sensor over Ammonia and Nitrite by Modifying Gas-Permeable Membrane with Teflon AF®, Chemical Analysis (Warsaw), Vol.51, p. 949, 2006