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Electrochemical generation of hydrogen peroxide from dissolved oxygen in acidic solutions

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Abstract

Hydrogen peroxide (H_2O_2) was electro-generated in a parallel-plate electrolyzer by reduction of dissolved oxygen (DO) in acidic solutions containing dilute supporting electrolyte. Operational parameters such as cathodic potential, oxygen purity and mass flow rate, cathode surface area, pH, temperature, and inert supporting electrolyte concentration were systematically investigated as to improve the Faradic current efficiency of H_2O_2 generation. Results indicate that significant self-decomposition of H_2O_2 only occurs at high pH (>9) and elevated temperatures ($>23^\circ\text{C}$). Results also indicate that the optimal conditions for H_2O_2 generation are cathodic potential of -0.5 V vs. saturated calomel electrode (SCE), oxygen mass flow rate of $8.2 \times 10^{-2}\text{ mol/min}$, and pH 2. Under the optimal conditions, the average current density and average current efficiency are 6.4 A/m^2 and 81%, respectively. However, when air is applied at the optimal flow rate of oxygen, the average current density markedly decreases to 2.1 A/m^2 , while the average current efficiency slightly increases to 90%. The limiting current density is 6.4 A/m^2 , which is independent of cathode geometry and surface area. H_2O_2 generation is favored at low temperatures. In the concentration range studied (0.01–0.25 M), the inert supporting electrolyte (NaClO_4) affects the total potential drop of the electrolyzer, but does not affect the net generation rate of H_2O_2 . © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Hydrogen peroxide (H_2O_2) is an environmentally friendly chemical because it leaves no hazardous residuals but oxygen and water after reaction. It has been widely applied to the synthesis of organic compounds, bleaching of paper pulp, treatment of wastewater, and destruction of hazardous organic wastes. In the environmental field, H_2O_2 is used as a supplement of oxygen source to enhance the bioremediation of contaminated aquifers [1,2]. Moreover, H_2O_2 coupled with ozone or UV radiation can effectively decompose aqueous organic contaminants [3–6]. The most common environmental application of H_2O_2 is the

Fenton's reagent, an aqueous mixture of H_2O_2 and Fe^{2+} . Under an acidic condition, the reaction between H_2O_2 and Fe^{2+} generates hydroxyl radicals that are strong enough to non-selectively oxidize most organic as well as some inorganic compounds. The Fenton's reagent has recently been applied to in-situ remediation of contaminated soils and groundwaters [7–9].

H_2O_2 is usually produced by electrochemical methods, such as electrolysis of inorganic chemicals ($\text{H}_2\text{S}_2\text{O}_8$, KHSO_4 and NH_4HSO_4) and autoxidation of organic compounds (alkylhydroanthraquinones and isopropyl alcohol) [10]. The electrolysis of inorganics requires excessive energy and the autoxidation of organics requires non-aqueous solvents for catalyst cycle [11]. H_2O_2 may also be directly generated from water, hydrogen, and oxygen using thermal, photochemical and electrical discharge processes. However, these processes require specific operational conditions such

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as high temperature, combustion, UV radiation plus mercury vapor, or high voltage. In recent years, small scale, on-site H_2O_2 production processes have gained increasing attention because of the cost and the hazards associated with the transport and handling of commercial concentrated H_2O_2 [11]. If H_2O_2 can be generated on-site in an economic and safe way, its field application will be largely simplified. For example, it would be attractive to use the on-site generated H_2O_2 , coupled with ozone, UV, or Fe^{2+} , for the detoxification of effluents from electro-kinetics, pump and treat, soil washing, and soil flushing processes.

Most electro-generation of H_2O_2 experiments are conducted in alkaline solutions with a high electrolyte concentration for the purpose of bleaching paper pulp [12–19]. In concentrated alkaline solutions, HO_2^- is formed ($\text{p}K_{\text{a}, \text{H}_2\text{O}_2} = 11.62$ at 25°C) which will be immediately repelled by the cathode upon its generation. Because the reduction of HO_2^- to OH^- is minimized, a high current efficiency (about 80–95%) can usually be achieved. However, if H_2O_2 is generated in alkaline solutions, a substantial amount of acid will be consumed for pH adjustment if an acidic condition is required. The Fenton's reagent, which is most commonly applied in organic synthesis and effluent treatment, has an optimal pH range of 2.5–3.5. Moreover, a high electrolyte concentration not only increases the treatment cost, but also introduces additional pollutants. Therefore, it is desirable to generate H_2O_2 in acidic solutions only containing dilute supporting electrolyte.

It has been reported that H_2O_2 can be electrochemically generated by reduction of dissolved oxygen (DO) in acidic solutions. The H_2O_2 so generated can be coupled with Fe^{2+} to produce the Fenton's reagent for either degradation or synthesis of organic compounds [20–28]. In order to differentiate this process from conventional Fenton process that uses commercial H_2O_2 , the term “electro-Fenton process” is applied. The major advantages of the electro-Fenton process include: (1) H_2O_2 can be continuously generated on-site whenever needed, which eliminates acquisition, shipment and storage; (2) A dilute H_2O_2 solution enhances safety during material handling; (3) The production process can be simply conducted at ambient pressure and temperature; (4) Fe^{2+} can be electrochemically regenerated at the cathode, which minimizes the quantity of iron sludge; and (5) Oxygen or air sparging enhances the mixing of reaction solution. The disadvantage is that H_2O_2 will accumulate at the cathode-solution interface and may be partially decomposed. Protons at a high concentration may also compete for electrons, leading to hydrogen gas evolution. Both effects will reduce the current efficiency of H_2O_2 production. Therefore, in acidic solutions, cathodic potential and solution pH are two essential factors controlling the current efficiency.

Though the electro-generation of H_2O_2 in acidic solutions has been studied by a few researchers, there exist conflicting results. Sudoh et al. [21] investigated the decomposition of aqueous phenol by electro-generated Fenton's reagent. They found that the highest current efficiency (85%) was obtained at a cathodic potential of -0.6 V vs. a saturated Ag/AgCl electrode (SSE) and pH 3. Tzedakis et al. [23] reported that the electrolysis of an oxygen-saturated H_2SO_4 solution (0.6 M) using a stirred mercury pool electrode yielded a current efficiency of 55% at a cathodic potential of -0.30 V vs. SCE. Chu [27] used the electro-Fenton process to remove aqueous chlorophenols at a cathodic potential of -0.6 V vs. SCE, and reported that the current efficiency increased with decreasing pH. Hsiao and Nobe [25] investigated the oxidative hydroxylation of phenol and chlorobenzene using electro-generated Fenton's reagent. They reported that the optimal cathodic potential was -0.55 V vs. SCE, and the generation of H_2O_2 was favored at low pH values.

The primary objective of the present study is to improve the Faradic current efficiency of H_2O_2 generation in acidic solutions. It is also expected that the results will clarify existing discrepancies among various studies of its kind. Influential parameters such as cathodic potential, oxygen purity and mass flow rates, cathode surface area, solution pH, temperature, and inert supporting electrolyte concentration were systematically examined. Considering that a high electrolyte concentration is usually not feasible for effluent treatment by the electro-generated H_2O_2 , the inert supporting electrolyte, i.e., NaClO_4 , was used only at a low concentration.

2. Experimental

Fig. 1 shows the schematic diagram of the reaction system. An acrylic parallel-plate electrolyzer was employed for the electro-generation of H_2O_2 . The cathodic and anodic compartments had a volume of 4.50 and 3.15 l, respectively. During the experiments, 4.0 l of catholyte and 3.0 l of anolyte were used and both were completely mixed by a magnetic stir plate. A cation exchange membrane (Neosepta CMX, Electrosynthesis Company, Lancaster, NY) was used to separate the two compartments. This membrane prohibits the penetration of anions and H_2O_2 molecules, but allows cations to freely penetrate through it. As a result, H_2O_2 generated at the cathode will be confined in the catholyte, avoiding its decomposition at the anode. Moreover, protons generated at the anode will be electrically driven to the catholyte, partially supplementing the protons consumed for H_2O_2 synthesis. Sodium perchlorate (NaClO_4) was used as an inert supporting electrolyte (or background ionic strength). Both cathode and anode

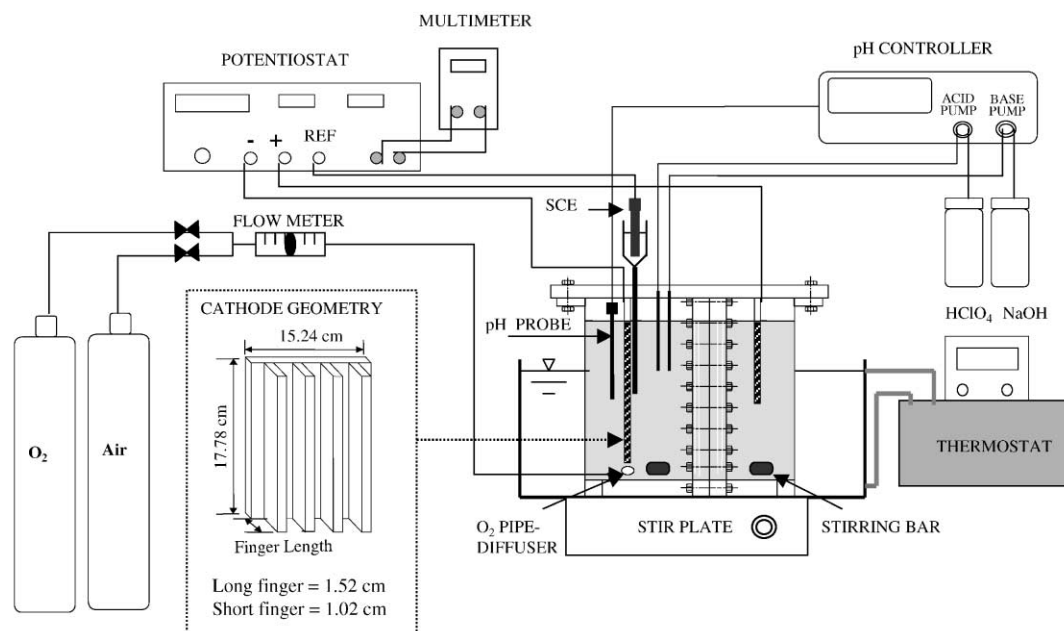


Fig. 1. Schematic diagram of reaction system.

were made of corrosion-resistant graphite (Grade 2020, Carbon of America, Bay City, MI). Sudoh et al. [16] reported that graphite was the best cathode material for the electro-generation of H_2O_2 in alkaline solutions, while metal cathodes such as copper, stainless steel, lead and nickel were likely to decompose H_2O_2 . Three cathode geometries (Fig. 1), i.e., plain plate ($17.78 \text{ cm} \times 15.24 \text{ cm}$, or $7 \text{ in} \times 6 \text{ in}$), plate with protruded short “fingers” ($17.78 \text{ cm} \times 15.24 \text{ cm} \times 1.02 \text{ cm}$, or $7 \text{ in} \times 6 \text{ in} \times 0.4 \text{ in}$) and plate with protruded long “fingers” ($17.78 \text{ cm} \times 15.24 \text{ cm} \times 1.52 \text{ cm}$, or $7 \text{ in} \times 6 \text{ in} \times 0.6 \text{ in}$) were employed to investigate the effect of cathode surface area. Unless otherwise stated, all experiments were conducted using the long-finger plate. A graphite plain plate ($8.89 \text{ cm} \times 15.24 \text{ cm}$, or $3.5 \text{ in} \times 6 \text{ in}$) was used as the anode. Copper wires were connected to both electrodes through Teflon screws. The connections were carefully sealed with silicon to prevent copper electro-corrosion. Compressed oxygen gas (99.6%) and air were used as DO sources. The gas was sparged into the catholyte through a porous pipe-diffuser placed right under the cathode. The catholyte was pre-saturated with DO by purging pure oxygen gas or air for 15 min before electrolysis was initiated. The catholyte pH was controlled by a pH-stat (Model pH-40, New Brunswick Scientific Co., Edison, NJ), HClO_4 (1 M) and NaOH (1 M) solutions. A high performance combination pH probe (Cat. No. 376490, Corning Inc., Corning, NY) was placed behind the cathode to avoid the interference from the electrical field. The solution

temperature was controlled by a thermostat (Model EX-200, Brookfield Engineering Laboratories, Inc., Stoughton, MA) and a water bath.

Polarization curves were obtained by cyclic voltammetry using a three-electrode bi-potentiostat (Model AFRDE4, Pine Instrument Co., Grove City, PA). A saturated calomel electrode (SCE) was used as the reference electrode. The SCE was inserted into a Luggin capillary filled with saturated KCl solution. By placing the tip of the Luggin capillary in contact with the cathode surface, the cathodic potential can be accurately controlled against the SCE. The cathodic potential of the parallel-plate electrolyzer was swept from 0 to -0.8 V (vs. SCE) at a linear rate of 33.3 mV/s . Transient current response was recorded by a Hewlett Packard X-Y recorder (Model 7001A, Moseley Division, Pasadena, CA). The electro-generation of H_2O_2 experiments were carried out under either constant potential or constant current mode. Usually, constant potential mode is used to derive fundamental electrochemical information in laboratory scale experiments, while constant current mode is commonly used in industrial electrolysis because it is technically much easier to control the current than the potential [29].

In this study, the factors significantly affecting the limiting current of H_2O_2 generation, including cathodic potential, oxygen purity and mass flow rate, and cathode surface area were investigated using the constant potential mode. Under this mode, the electrical current was monitored on-line by a digital multimeter (Model

22-183A, Tanday Co., Fort Worth, Texas). The effect of pH was studied using both constant potential and constant current modes. The effects of temperature and inert supporting electrolyte concentration were investigated by the constant current mode. A regulated DC power supply (Model WP-705B, Vector-Vid Inc., Horsham, PA) was employed to provide constant current. The concentration of H_2O_2 was determined by the titanate sulfate [$\text{Ti}(\text{SO}_4)_2$] method [16]. A diode array spectrophotometer (Model 8452A, Hewlett Packard) was used to measure the light absorbance of the Ti^{4+} – H_2O_2 orange complex at 410 nm. The DO concentration was determined by an oxygen electrode (Model 97-08-99, Orion Research Inc., Beverly, MA). A pH meter was used to record the DO concentration in the range of 0–14 mg/l. When the concentration exceeded the upper response limit, dilution was made with deoxygenated distilled water.

3. Results and discussion

3.1. Stability of hydrogen peroxide

In a thoroughly clean container without the presence of any catalysts, H_2O_2 is very stable at any concentration. However, the presence of a trace amount of metal ions in the solution or on the container surface will lead to the decomposition of H_2O_2 . In practice, stabilizing agents such as sodium stannate, 8-hydroxyquinoline and sodium pyrophosphate are commonly used to stabilize H_2O_2 for long-term storage [10]. The self-decomposition rate of H_2O_2 is primarily influenced by pH and temperature. Sudoh et al. [16] attributed the low current efficiency (6.88%) of H_2O_2 generation in alkaline solutions at 30°C to a high self-decomposition rate of H_2O_2 . Solution pH influences the chemical speciation of both H_2O_2 and trace metals. The trace metals that can catalytically initiate the self-decomposition of H_2O_2 may be introduced from acid and base used for pH adjustment, from container surfaces, and even from distilled water. At low pH, H_2O_2 and free metal ions predominate. At high pH, HO_2^- and metal-hydroxo complexes are the major species. Therefore, it is necessary to investigate the effects of pH and temperature on the self-decomposition of H_2O_2 .

The H_2O_2 solution with an initial concentration of 150 mg/l was prepared by diluting a commercial grade H_2O_2 solution (31.5% by weight) with distilled water. A series of plastic bottles (250 ml) were washed with 1 M HClO_4 solution, and then filled with the H_2O_2 solution. The pH was adjusted by reagent grade HClO_4 or NaOH to cover the range of 1–13. The effect of temperature was investigated at 10°C, 23°C and 50°C. At selected time intervals, the concentration of H_2O_2 was determined. Fig. 2 shows the self-decomposition of H_2O_2 at various

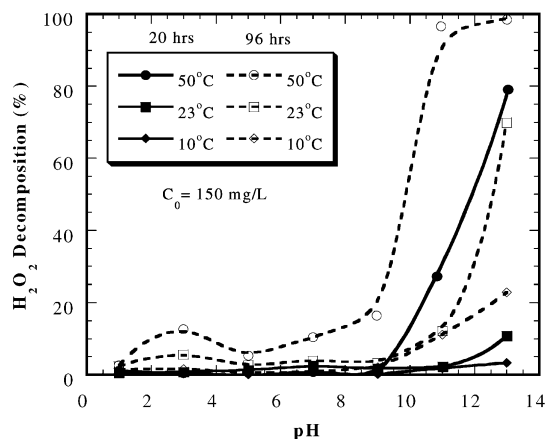
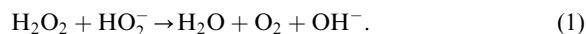


Fig. 2. Stability of hydrogen peroxide.

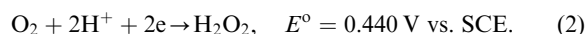
pH values, temperatures and reaction times. Results indicate that H_2O_2 is relatively stable at $\text{pH} < 9$. However, above $\text{pH} 9$, H_2O_2 decomposes markedly with increasing pH, temperature and reaction time. There is complete H_2O_2 decomposition at $\text{pH} 13$ and temperature 50°C after 96 h. According to Schumb et al. [10], even with the purest H_2O_2 and at elevated temperatures, the decomposition of H_2O_2 in the liquid phase is not a homogeneous autodecomposition process of the H_2O_2 itself. Generally, increasing temperature increases the reaction rate. The self-decomposition of H_2O_2 at high pH and elevated temperatures are attributed in part to the catalytic effect of the container walls and the reagent impurities. Another aspect is the anion, HO_2^- . The role of HO_2^- in the base catalyzed H_2O_2 decomposition was suggested by Abel [30] following the reaction:



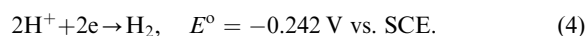
However, a low temperature (e.g., 10°C) suppresses H_2O_2 self-decomposition, even at high pH. It is also noted that in the acidic region, the highest self-decomposition rate appears at $\text{pH} 3$. It is known that $\text{pH} 3$ is the optimal value for the Fenton's reagent. The possible presence of trace metals in the solution or on the bottle surfaces may catalytically stress the decomposition of H_2O_2 at $\text{pH} 3$. It is noted that the electrolysis was conducted in acidic conditions, i.e., $\text{pH} \leq 4.0$, and the electrolysis time was 2 h. Therefore, based on the results shown in Fig. 2, it is clear that the self-decomposition of H_2O_2 would be insignificant.

3.2. Optimal cathodic potential

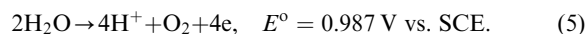
In acidic solutions, the dissolved oxygen is electrochemically reduced to H_2O_2 at the cathode



Two side reactions simultaneously occur at the cathode: (1) the reduction of H_2O_2 to H_2O due to the accumulation of H_2O_2 at the cathode-solution interface, and (2) the hydrogen gas evolution. These reactions are shown as follows:



At the anode, the oxidation of H_2O releases oxygen gas and protons



The protons so generated will be driven to the catholyte electro-statically and partially supplement the protons consumption during the synthesis of H_2O_2 .

Polarization curves reflect transient current response with respect to cathodic potential (E_c) applied. Results in Fig. 3 indicate that at $-E_c < 0.15 \text{ V}$, the current density (i) increases rapidly with increasing $-E_c$. However, a “plateau” appears in the range of -0.15 to -0.5 V . This “plateau” represents the limiting current region for the electro-generation of H_2O_2 (Reaction 2). When the $-E_c$ continues to increase above 0.5 V , the i quickly rises again. It implies a significant reduction of H_2O_2 to H_2O (Reaction 3) and an enhanced H_2 evolution (Reaction 4). Pure oxygen gas provides a higher DO concentration than air, thereby yielding a higher i . Fig. 3 also shows that the initial equilibrium potential, E_0 , is -0.075 V at $i = 0$. If a constant potential of -0.5 V is applied, the initial overpotential is calculated as -0.425 V . As electrolysis proceeds, the overpotential becomes more negative since the E_0

continuously increases with increasing H_2O_2 concentration.

In the limiting current region, H_2O_2 generation is controlled by the mass transfer of DO through the cathode-solution diffusion layer, rather than by the electron transfer between DO and cathode. Since the DO concentration at the cathode surface rapidly approaches zero after electrolysis starts, the limiting current under a steady-state condition can be expressed by the following equation for macroscopic electrodes [29]:

$$I_L = k_m n F A_c C^*, \quad (6)$$

where I_L represents the limiting current (A), k_m is the mass transfer coefficient (m/s), n is the stoichiometric number of electrons transferred, F is the Faraday's constant ($96,490 \text{ C/mol}$), A_c is the effective cathode surface area (m^2), and C^* is the DO concentration in bulk solution (M). The mass transfer coefficient, k_m , can be determined by Eq. (7):

$$k_m = D/\delta \quad (7)$$

where D represents the diffusion coefficient of oxygen (m^2/s) and δ is the thickness of diffusion layer (m). Fig. 3 shows that the maximum limiting current is approximately located in the range of $0.4\text{--}0.5 \text{ V}$ ($-E_c$).

Current efficiency (η), defined as the ratio of the electricity consumed by the electrode reaction of interest over the total electricity passed through the circuit, can be calculated by Eq. (8):

$$\eta = \frac{n F C_{\text{H}_2\text{O}_2} V}{\int_0^t I dt} \times 100\%, \quad (8)$$

where $C_{\text{H}_2\text{O}_2}$ represents H_2O_2 concentration in bulk solution (M) and V is the catholyte volume (L). By definition, the η actually represents an overall current efficiency over a certain period of electrolysis time.

The effect of cathodic potential was investigated from $0.2\text{--}0.9 \text{ V}$ ($-E_c$). Figs. 4a–c shows the time-dependent changes of H_2O_2 concentration, current density and current efficiency at various applied potentials, respectively. Results indicate that at $0.2 \leq -E_c \leq 0.5 \text{ V}$, the H_2O_2 concentration increases linearly with reaction time (Fig. 4a). The slope represents a constant net generation rate of H_2O_2 (γ_n) throughout the whole electrolysis course. Correspondingly, Fig. 4b shows that i stabilize quickly after the electrolysis is initiated. A steady-state condition is rapidly reached because a constant DO concentration is maintained in the solution. Fig. 4c indicates a slight decrease of η during electrolysis because the reduction of H_2O_2 to H_2O is gradually promoted by the accumulation of H_2O_2 . Results further indicate that at $-E_c > 0.5 \text{ V}$, both γ_n and η decrease notably with reaction time (Figs. 4a and c). It implies that a high $-E_c$ stresses the reduction of H_2O_2 as well as the evolution of H_2 . Fig. 4b shows that at 0.6 V , the i

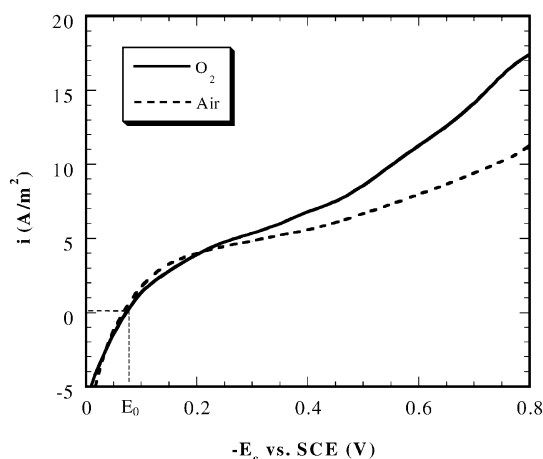


Fig. 3. Polarization curves of pure oxygen and air sparging. Experimental conditions: completely mixing, sweeping rate = 33.3 mV/s ; $\text{pH} = 2$; $T = 23^\circ\text{C}$; $Q_{\text{O}_2} = 8.2 \times 10^{-2} \text{ mol/min}$; $Q_{\text{air}} = 8.2 \times 10^{-2} \text{ mol/min}$; ionic strength = 0.05 M NaClO_4 ; long-finger plate cathode.

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