



Rates of H₂O₂ electrogeneration by reduction of anodic O₂ at RVC foam cathodes in batch and flow-through cells

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ABSTRACT

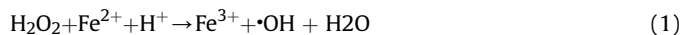
The Electro-Fenton process for in-situ H₂O₂ electrogeneration is impacted by low O₂ utilization efficiency (<0.1%) and the need of acid for pH adjustment. An electrochemical flow-through cell can develop localized acidic conditions, coupled with simultaneous formation and utilization of O₂ to enhance H₂O₂ formation. Multiple electrode configurations using reticulated vitreous carbon (RVC) foam and Ti/mixed metal oxides (MMO) are proposed to identify the optimum conditions for H₂O₂ formation in batch and flow-through cells. A pH of 2.75 ± 0.25 is developed locally in the flow-through cell that supports effective O₂ reduction. Up to 9.66 mg/L H₂O₂ is generated in a 180 mL batch cell under 100 mA, at pH 2, and mixing at 350 rpm. In flow-through conditions, both flow rate and current significantly influence H₂O₂ production. A current of 120 mA produced 2.27 mg/L H₂O₂ under a flow rate of 3 mL/min in a 3-electrode cell with one RVC foam cathode at 60 min. The low current of 60 mA does not enable effective H₂O₂ production, while the high current of 250 mA produced less H₂O₂ due to parasitic reactions competing with O₂ reduction. Higher flow rates decrease the retention time, but also increase the O₂ mass transfer. Furthermore, 3-electrode flow-through cell with two RVC foam cathodes was not effective for H₂O₂ production due to the limited O₂ supply for the secondary cathode. Finally, a coupled process that uses both O₂ and H₂ from water electrolysis is proposed to improve the H₂O₂ yield further.

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1. Introduction

The Fenton process (dissolved Fe²⁺ and H₂O₂), first reported by Fenton over 100 years ago [1], generates highly reactive, nonselective hydroxyl radicals (Eq. (1)). Although the Fenton process has been applied for treatment of wastewater, the reaction is optimum under a narrow pH range (2.0–4.0) which often requires adjustments of pH [2]. The production, transportation, and storage of H₂O₂ are expensive [3]. Due to these drawbacks, an in situ, electrochemically-induced production of H₂O₂ via two-electron reduction of O₂ (Eq. (2)) has gained significant interest in the past

two decades [4–7].



The efficiency of H₂O₂ generation, one of the most vital parameters of the electro-Fenton (EF) process, is highly dependent on the type of cathode materials [8–11], O₂ flow rate and the solution pH [12–15]. The conventional EF process requires a high flow rate of external O₂ supply and external adjustment of pH, which increase the operation cost of the treatment [16]. Additionally, the O₂/air utilization efficiency is extremely low (<0.1%) [17]. Yuan et al. [18] presented a novel EF system with automatic pH adjustment. In this system, two compartments were connected by a salt bridge, a pH of 3–3.5 can be automatically generated in one compartment for effective H₂O₂ catalytic generation from H₂ and O₂ by palladium/activated carbon catalysts. However, the system utilizes costly palladium/activated carbon catalysts and is affected by

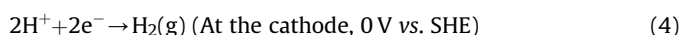
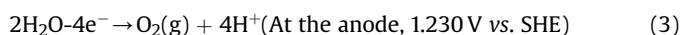
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energy loss due to the use of salt bridge (divided electrochemical cell). Perez et al. [19] designed a conceptual cell which incorporates a venturi-based jet aerator to supply atmospheric oxygen to a carbon felt cathode without additional energy consumption. A higher current efficiency towards H_2O_2 accumulation than conventional system (72 vs. 65% at 1 h) was obtained. Although the jet aerator stands as a promising O_2 supply approach, the system is not practical for in situ water treatment.

In traditional EF systems, O_2 is externally injected to produce a high concentration of H_2O_2 [16]. Development of a system with continuous, in situ H_2O_2 generation, could be used for the treatment of contaminated groundwater while avoiding additional costs and safety concerns of H_2O_2 handling, installing external O_2 injectors and pH adjustments [20–22]. Principally, the EF process utilizes water electrolysis products (Eq. (3) and (4)) where O_2 and H^+ are continuously generated at the anode (Eq. (3)).



Compared with externally injected O_2 gas, the electrochemical system can be optimized to transfer the anodic O_2 to the cathode vicinity, while H^+ generated on the anode can develop a localized acidic environment for 2 electron O_2 reduction reaction (2e ORR) to H_2O_2 . In our previous work, a three-electrode flow-through system (anode \rightarrow cathode \rightarrow cathode) was designed for Pd-catalyzed H_2O_2 generation to support EF reaction [23–25]. In the Pd-catalyzed system, H_2 and O_2 from water electrolysis are used for the synthesis of H_2O_2 . Moreover, automatic control of low pH in Pd vicinity and neutral pH is feasible in the treated solution. One downside is that the system employs Pd catalyst, which can be costly for full-scale groundwater treatment systems.

Carbonaceous materials such as graphite [26,27], graphite felt [28], reticulated vitreous carbon (RVC) foam [29,30], activated carbon fiber (ACF) [31], and carbon sponge [32] are the most commonly used cathode materials for H_2O_2 production via 2 electron O_2 reduction. However, there are limited studies on the application of direct H_2O_2 electrogeneration in a flow-through cell. A 2-electrode flow-through system that uses carbon felt cathode and a dimensionally stabilized anode to produce H_2O_2 was proposed [33]. This system could partially remove dissolved organic carbon (DOC) in solutions of phenol, salicylic acid, benzoic acid and humic acid. However, only a flow rate of 140 L/h was applied. An RVC electrode modified with anthraquinone groups in a gravity-feed system was used [34] to generate H_2O_2 , but the O_2 produced from water electrolysis was not utilized. Thus the system did not support efficient H_2O_2 generation. Furthermore, H_2O_2 electrogeneration and EF process for water treatment require acidic conditions. Thus a 3-electrode flow-through cell where localized acidic conditions could be automatically developed would be favorable. Understanding and optimizing parameters required for electrochemically-generated H_2O_2 will lead to efficient in situ EF treatment for contaminated groundwater.

The primary goal of this study is to evaluate the parameters affecting the electrochemically-induced H_2O_2 production and pH distribution in batch and flow-through electrochemical cell without external O_2 injection. The comparison between the batch cell and flow-through cell highlights the significant role of acidic conditions and O_2 mass transfer on H_2O_2 production. We used RVC foam cathode due to its sufficient porosity and active area while Ti/MMO was used as anode material with low oxygen overpotential and as the most stable electrode material in large-scale industrial applications. We tested the influence of anode material, current intensity, pH, and stirring rate in a batch cell, while the impacts of

the flow rate, current intensity, and arrangement of the electrodes were investigated in a flow-through cell.

2. Experimental

2.1. Materials and chemicals

Sodium sulfate (anhydrous, $\geq 99\%$) and titanium sulfate (99.9%) were purchased from Sigma-Aldrich. H_2O_2 (30% solution) was purchased from Fisher Scientific. Deionized water (18.2 M Ω cm) obtained from a Millipore Milli-Q system was used in all experiments. Solution pH was adjusted by sulfuric acid (98%, JT Baker) and sodium hydroxide (Fisher Scientific).

Graphite plate (Shanxi Kaida Chemical Ltd., 2 cm \times 3 cm \times 2 mm), RVC foam (45 PPI, Purity > 99.99%, Duocel[®], specific surface area of 27.9 cm²/cm³, pore diameter of 563 μm) and Ti/mixed metal oxide (MMO, 3 N International) mesh were used as electrode materials. Physical characteristics of RVC foam are shown in Table S1. The Ti/MMO electrode consists of IrO_2 and Ta_2O_5 coating on titanium mesh with dimensions of 3.6 cm diameter by 1.8 mm thickness (surface area of 6 cm²). Holes with 0.5 cm diameter were drilled on RVC foam cathode to support uniform flow through the cell and prevent accumulation of gas bubbles in the cathode vicinity. Digital photos of electrodes are shown in Fig. S1. Na_2SO_4 solution with 50 mM concentration was used as electrolyte in batch and flow-through cell [16,19].

2.2. Batch experiments for mechanistic study

A glass beaker with 200 mL total volume containing two parallel, vertical electrodes (RVC cathode and Ti/MMO anode) was used in batch operations. The schematic diagram of the batch cell and flow-through cell are shown in Fig. 1. RVC foam electrode was cut into 2 cm \times 3 cm \times 2.5 mm. The effects of solution pH, dissolved oxygen (DO) and current intensity on H_2O_2 generation were evaluated. Three mL samples were taken at set intervals and filtered through a 0.45 μm micropore filter membrane before analysis. Constant currents were applied by an Agilent E3612A DC power supply. The two compartments of the divided cell shown in Fig. 1 were connected by a salt bridge, which was filled with K_2SO_4 and agar. Salt bridge was used to connect anodic and cathodic compartments in previous studies [18,35].

2.3. Column experiments

The electrochemical flow-through cell with 2 and 3 electrodes are shown in Fig. 1. A vertical acrylic column was used as an electrochemical flow-through column (230 mL). An RVC foam electrode, 3.6 cm in diameter was used as a cathode. While the anode supplies O_2 and H^+ , cathode 1 generate H_2O_2 via dissolved O_2 reduction. Cathode 2 in the 3-electrode system shares the current with Cathode 1 and neutralizes the effluent. A uniform flow distribution is important for the mass transport; the holes on the Ti/MMO mesh are small, which contribute to the uniform flow distribution in the flow-through reactor.

For the 2-electrode system, a piece of Ti/MMO mesh and RVC foam were installed in an upward sequence as the anode and the cathode with a distance of 3.5 cm. For the 3-electrode system, another piece of Ti/MMO mesh (Fig. 1(d)) or RVC foam (Fig. 1(e)) used as the cathode was installed on the top of the central RVC foam electrode with a distance of 3.5 cm. The flow rate was regulated by a peristaltic pump (Cole-Parmer, Masterflex C/L). Flow rates of 3 mL/min, 15 mL/min, 30 mL/min, and 60 mL/min were used, and the superficial velocity was calculated to be 0.29 cm/min, 1.47 cm/min, 2.95 cm/min, and 5.90 cm/min, respectively.

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