Published in final edited form as:

Electrochim Acta. 2018 July 1; 277: 185–196. doi:10.1016/j.electacta.2018.04.174.

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.

Keywords

Batch cell; Electro-Fenton; Flow-through cell; Hydrogen peroxide; Oxygen reduction reaction

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

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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 to 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 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 H₂O₂ accumulation than conventional system (72 vs. 65% at 1 h) was obtained. Although the jet aerator stands as a promising O₂ supply approach, the system is not practical for in situ water treatment.

In traditional EF systems, O₂ is externally injected to produce a high concentration of H₂O₂ [16]. Development of a system with continuous, in situ H₂O₂ generation, could be used for the treatment of contaminated groundwater while avoiding additional costs and safety concerns of H₂O₂ handling, installing external O₂ injectors and pH adjustments [20-22]. Principally, the EF process utilizes water electrolysis products (Eq. 3 and Eq. 4) where O₂ and H⁺ are continuously generated at the anode (Eq. 3).

Compared with externally injected O₂ gas, the electrochemical system can be optimized to transfer the anodic O₂ to the cathode vicinity, while H⁺ generated on the anode can develop a localized acidic environment for 2 electron O₂ reduction reaction (2e⁻ ORR) to H₂O₂. In our previous work, a three-electrode flow-through system (anode→cathode→cathode) was designed for Pd-catalyzed H₂O₂ generation to support EF reaction [23-25]. In the Pd-catalyzed system, H₂ and O₂ from water electrolysis are used for the synthesis of H₂O₂. 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, 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 μ m) and Ti/mixed metal oxide (MMO, 3N International) mesh were used as electrode materials. Physical characteristics of RVC foam are shown in Table S1. The Ti/MMO electrode consists of IrO₂ and Ta₂O₅ 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 Figure S1. Na₂SO₄

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 Figure 1. RVC foam electrode was cut into 2 cm × 3 cm × 2.5 mm. The effects of solution pH, dissolved oxygen (DO) and current intensity on H₂O₂ 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 Figure 1 were connected by a salt bridge, which was filled with K₂SO₄ 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 Figure 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 O₂ and H⁺, cathode 1 generate H₂O₂ via dissolved O₂ 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 (Figure 1(d)) or RVC foam (Figure 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.

In the 3-electrode system with two cathodes, the current was split by the rheostat, allowing the current to pass through two cathodes. Two RVC foam cathodes were used to increase O₂ utilization within the column. Electrode and sampling port locations are shown in Figure 1. In Section 3.4, Pd/Al₂O₃ catalysts were dispersed in the undivided batch reactor. This experiment was designed to utilize H₂ from water electrolysis for H₂O₂ production further. At regular time intervals, three mL of solution was sampled from port 3 or port 4 and filtered through a 0.45 μm micropore filter membrane for analysis of pH, DO and H₂O₂. Detailed experimental conditions are shown in Table 1.

2.4 Analytical methods

pH and DO were measured by a pH meter and a DO meter (Thermo Scientific). H₂O₂ was measured at 405 nm on a Shimadzu UV-Vis spectrometer after coloration with TiSO₄ [18].

The current efficiency (CE) of H_2O_2 generation, defined as the ratio of the electricity consumed by the electrode reaction over the total electricity passed through the circuit, was calculated by Eq. 5 [3].

$$CE = \frac{nFC_{H_2O_2}V}{\int_0^t Idt} \times 100 \% \quad (5)$$

Where n is the number of electrons transferred for O_2 reduction to H_2O_2 , F is the Faraday constant ($96,486 \text{ C mol}^{-1}$), $C_{H_2O_2}$ is the concentration of H_2O_2 (mol L^{-1}), V is the electrolyte volume (L), I is the applied current intensity (A), and t is the reaction time (s).

3 Results and Discussion

3.1 Anodic O_2 generation in undivided batch cell: comparison of Ti/MMO and graphite anode

Anode materials can be active or non-active electrodes. Active anodes present low oxygen evolution overpotential, are good electrocatalysts for the oxygen evolution reaction (OER) [36-38]. The OER directly determines the DO and thus significantly influences the generation of H_2O_2 . Here we compare the performance of the graphite plate and Ti/MMO electrode since they are commercially available and are widely used for industrial applications [39,40].

The profiles of DO and H_2O_2 concentrations are presented in Figure 2. Experiments were operated in 50 mM Na_2SO_4 electrolyte under current of 100 mA and stirring rate of 350 rpm. DO concentration in the electrolyte significantly differ. DO concentration increased almost instantaneously with Ti/MMO anode and reached a steady-state concentration of 7.5 mg/L in 8 minutes. On the contrary, using graphite anode decreased DO concentration to 2.43 mg/L after 20 min of electrolysis. Results clearly demonstrate that Ti/MMO is more active than graphite for O_2 generation and can thus be used as the anode to support H_2O_2 production.

The electrogeneration of H_2O_2 influences the DO concentration. In Figure 2(b), the yield of H_2O_2 at 40 min by Ti/MMO anode is nearly four times higher than by graphite anode. This further illustrates that sufficient O_2 supplied by the anode is the prerequisite of a high yield of H_2O_2 electrogeneration. In the case of graphite anodes, the DO contributing to the H_2O_2 electrogeneration mostly originates from the initial solution.

3.2 Batch cell

3.2.1 pH distribution—The pH profile in undivided and divided batch cell is shown in Figure 3. The catholyte pH in the divided cell increased to 11.82, while the anolyte pH decreased to 2.96. In the undivided cell without stirring, the pH in the anode vicinity (1.5 cm) dropped to 3.44 after 15 min, and the pH in the cathode vicinity (1.5 cm) increased to 11.59 after 15 min. Once the electrolyte was stirred, a constant pH, equivalent to the initial value was reached.

3.2.2 DO mass transfer—DO mass transfer to the cathode is a limiting factor in all systems for direct H₂O₂ electrogeneration [16]. In the undivided batch cell, stirring enhances the O₂ mass transfer from the anode vicinity to RVC foam cathode vicinity. Therefore, the influence of stirring on DO in the undivided batch cell was assessed (Figure 4(a)). A current of 100 mA was applied to the undivided and divided cells leading to an increase in DO from 4.21 mg/L to 11.74 mg/L and to 12.63 mg/L in the undivided and divided cells, respectively. The DO increase was caused by O₂ generated from the anode, not from the air even with stirring (Figure S2). A higher stirring rate results in lower DO, which suggests the efficient utilization of O₂. Therefore, 350 rpm was selected for further experiments. In the divided batch cell (Figure 4(b)), the DO in the catholyte decreased to 2.86 mg/L after 35 min. While in the anolyte, the DO increased to 12.63 mg/L. The maximum DO in the divided cell is just slightly higher than DO in the undivided cell without stirring (12.63 mg/L and 11.74 mg/L, respectively), demonstrating that only with stirring, DO could be transferred and utilized by RVC foam cathode.

3.2.3 Influence of current intensity on H₂O₂ generation—The oxygen reduction reaction plays a vital role in environmental remediation and energy conversion technologies. Oxygen is reduced on the cathode via two different pathways: One is a 4 electron pathway (Eq. 6 and Eq. 7), in which O₂ is reduced to H₂O or OH⁻. The second is a 2 electron pathway (Eq. 2 and Eq. 8), in which O₂ is partially reduced to H₂O₂ or OOH⁻, in acid and alkaline electrolyte, respectively [41,42].

Figure 5(a) shows H₂O₂ concentration in the batch cell under 50 mA, 100 mA, 150 mA, and 200 mA. With increasing current, the H₂O₂ concentration increased initially and then dramatically decreased. H₂O₂ concentration at 40 min under 100 mA is nearly 9 times higher than 200 mA (4.53 mg/L and 0.53 mg/L, respectively). H₂O₂ was electrogenerated by 2e⁻ ORR via mechanism presented in Figure 5(b). However, it will undergo several decomposition and activation pathways as shown in Eq's. 9-11. Disproportion occurs at the RVC foam surface and inside, as well as in the bulk electrolyte; this route has no relation with the current [43]. Cathodic reduction and anodic oxidation of H₂O₂ is closely related to current intensity, in which higher currents cause severe consumption by these two pathways. In our previous work [44], anodic oxidation and cathodic reduction were investigated in a decoupling manner, and results showed that the anodic oxidation and cathodic reduction of H₂O₂ were severe especially under high currents. Therefore, for the undivided cell tested here, we can reasonably assume that a current of 100 mA achieves a balance between generation and electro-induced decomposition of H₂O₂.

3.2.4 Influence of initial pH—The pH plays a significant role for H_2O_2 generation (Figure 6). H_2O_2 concentration reached 9.66 mg/L at pH 2, nearly 2 times the concentration when pH is 7. The concentration of H_2O_2 under pH 3 is higher than under pH 7 for the first 30 min but lower after 30 min. Under acidic conditions, enough protons are available for 2e ORR to produce H_2O_2 . In alkaline solutions (pH of 11 and 13), a very low concentration of H_2O_2 was measured. The impacts of alkaline conditions include self-decomposition of H_2O_2 and inhibition of 2e ORR to H_2O_2 . As Qiang et al. [3] suggested, 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. This is because at high pH, HO_2^- are the primary species, and it could catalyze H_2O_2 decomposition via Eq. 12.

Even though decomposition occurs, the very low concentration of H_2O_2 at pH 11 and 13 indicates that alkaline conditions inhibited 2e ORR on RVC foam cathode, as reported in the literature [13,45]. Many suggested that acidic oxygen-containing functional groups at the carbon cathodes play an essential role for 2e ORR [46,47]. Under pH of 11 and 13, the RVC acidic functional groups were neutralized by OH^- , causing the decrease in 2e ORR activity. CE shown in Figure 6(b) was calculated in accordance with H_2O_2 concentration. The highest CE (2.2%) was achieved at pH 2 under 100 mA. The relatively low CE obtained in the undivided batch cell is partial because the O_2 was supplied by the anode surface, compared with literature using pure O_2 , the O_2 could thus be a limiting step [48,49]. Furthermore, the relatively low CE was also caused by side reactions includes H_2O_2 disproportion (Eq. 9), cathodic oxidation (Eq. 10), anodic oxidation (Eq. 11) and H_2 evolution reaction (HER, Eq. 4).

3.2.5 Influence of mixing: facilitated O_2 mass transfer at high stirring rate—

H_2O_2 concentration profiles are reported in Figure 7. Under 350 rpm stirring rate, H_2O_2 concentration is much higher than at 0 rpm or 200 rpm. Enhanced O_2 mass transfer towards the cathode is achieved only at high mixing rates (Figure 4). Visual evaluation of bubbles behavior could serve as an indicator of O_2 mass transfer rates. In the batch cell, Ti/MMO anode and RVC foam cathode were separated horizontally (Figure 5(b)), O_2 bubbles float upward along the Ti/MMO surface without mixing (Figure 7(b)). This causes aggregation

bubbles at the anode, limited O₂ dissolution and mass transfer to the cathode. Under high mixing rates, small bubbles successfully detach from the anode surface and remain in solution for a more extended period; smaller and uniform O₂ bubbles contribute to better O₂ dissolution and oxygen mass transfer to the RVC foam cathode vicinity, which was well recognized in the field of micro-nano bubbles [50,51].

3.3 Flow-through cell

3.3.1 pH distribution—The pH influences both 2e ORR and EF [2,12,52]. Therefore, we investigated the pH distribution in 2-electrode and 3-electrode flow-through cells. Results are shown in Table 2 while steady-state pH is plotted in Figure 8. In both 2-electrode and 3-electrode systems, the pH in the cathode vicinity decreased. Our flow-through cell is designed with the anode to cathode sequence, which generates a localized acidic environment needed for both ORR and EF [53,54]. The electrode sequence automatically controls pH in the cathode vicinity by H⁺ generated at the anode (Eq. 3).

In the 2-electrode system (Figure 8(a)), the pH of inlet flow after the anode (Port 2) was 3.65, 2.90, 2.77, and 2.58 under a constant current of 10 mA, 50 mA, 100 mA, and 200 mA, respectively. In the 3-electrode system (Figure 8(b)), the pH was 2.80, 2.68, and 2.44 under 60 mA, 120 mA, and 250 mA, respectively. Even under relatively low currents (10 mA), a localized acidic pH (3.65) could be created under flow conditions. Our observations on localized pH were in accordance with results reported in the literature [55]. We also observed that the distance between the sampling port and electrode do not influence pH measurement, as shown in Figure S3. Bubbles formation and transport (Figure S4) also facilitated the transport of H⁺ and OH⁻.

3.3.2 DO mass transfer—In the flow-through cell, the arrangement of anode followed by RVC foam cathode achieves the required O₂ mass transfer. Therefore, the influence of such configurations on the change of DO before and after the cathode was investigated. As Figure 9 shows, DO before RVC foam cathode increased from 3.96 mg/L to 9.81 mg/L in the first 30 min under a constant flow rate of 3 mL/min. At 30 to 60 min, the DO was relatively stable, which indicates that the Ti/MMO anode successfully increased DO in the electrolyte. The decrease of DO after RVC foam cathode in Figure 9 reflects consumption of O₂ generated at the anode for production of H₂O₂.

3.3.3 Influence of flow rate and current on H₂O₂ generation—The flow rate affects H₂O₂ production due to its influence on the transport of O₂ and H⁺ (Figure 1(c)). Using the setup shown in Figure 1, we evaluated the impact of flow rate on H₂O₂ production under different currents (Figure 10(a, b, c)). Figure 10(d) shows DO content before and after the cathode under a flow rate of 15 mL/min. Samples were collected after RVC foam cathode (port 3).

Figure 10(d) shows that under a flow rate of 15 mL/min, O₂ is better utilized at the cathode than the flow rate of 3 mL/min (average DO during 10 to 60 min: 6.22 mg/L < 7.39 mg/L). Both flow rate and current significantly influence the H₂O₂ concentration and H₂O₂ accumulation (Figure 10 a-c). Under 120 mA and flow rate of 3 mL/min, a stable H₂O₂ concentration of 2.27 mg/L was obtained within 20 to 60 min, compared to 1.99 mg/L, 0.96

mg/L and 0.55 mg/L under flow rates of 15 mL/min, 30 mL/min, and 60 mL/min, respectively. Higher flow rate could facilitate the O₂ mass transfer, but the retention time for H₂O₂ production via 2e⁻ ORR decreases. The similar performance under flow rates of 3 mL/min and 15 mL/min possibly indicate that the O₂ mass transfer under 15 mL/min was better, but the retention time is shorter than 3 mL/min. Increasing the current to 250 mA, significantly decreased the yield of H₂O₂ under 3 mL/min (a 66.1% decrease compared with 120 mA). We assume that under high current, H₂O₂ was partially electroreduced to H₂O or disproportionate to H₂O and O₂, as illustrated in Section 3.2.3.1. However, 1.68 mg/L was obtained after 60 min under 15 mL/min, which should be ascribed to the fast transport of H₂O₂ molecules that avoid further electroreduction on the RVC foam cathode. A current of 60 mA was not enough for effective production of H₂O₂. Under higher flow rates, such as 30 mL/min and 60 mL/min, little H₂O₂ was detected. Under flow rates of 3 mL/min and 15 mL/min, 1.17 mg/L and 0.75 mg/L H₂O₂ were obtained after 60 min, respectively, also confirming the flow rate of 15 mL/min achieves better O₂ mass transfer.

Moreover, the accumulative H₂O₂ production was calculated and plotted in the internal figure. It shows that the highest accumulative amount (1.87 mg) at 60 min was obtained under 120 mA and 60 mL/min. This value is 1.42 times higher than 1.32 mg under 250 mA and 15 mL/min, 2.75 times higher than 0.68 mg under 60 mA and 15 mL/min. This illustrates that considering the H₂O₂ accumulation, 120 mA and 60 mL/min are the best conditions for a high H₂O₂ yield. Regarding application, the operation of flow-through cell under high flow rates means the system could treat a larger volume of contaminated groundwater in time. DO change along the column was shown in Figure S5. Previous researchers also successfully achieved in situ H₂O₂ production in flow-through cell under different conditions. Drogui et al. used a 2-electrode column cell with carbon felt as cathode and Ti/RuO₂ as anode, O₂ was supplied by water oxidation, 15.2 mg/L H₂O₂ was obtained at 90 min under a constant flow rate of 140 L/h and current of 2000 mA [33]. Qian et al. reported a novel designed gravity-feed flow system using anthraquinonyl-modified RVC cathode, the system achieved a fractional current conversion of nearly 0.9 at a volume flow rate of 0.006 mL/s. The gravity-feed mode makes the H₂O₂ production in a continuous manner. However, the O₂ generated on anode was not used [34].

Interestingly, we observed that bubbles formation and entrapment under RVC foam lower the active cathode area (Figure 11). At higher flow rates, the bubbles easily detached from the cathode but the retention time decreased. In conclusion, we found for a 3-electrode system, the flow rate influenced O₂ mass transfer and H₂O₂ transportation as well, and the current affected both H₂O₂ generation and decomposition. The O₂ mass transfer is limited in comparison to the batch cell, which should be improved in future work.

3.3.4 The influence of a secondary RVC foam cathode—In the 3-electrode system, the cathode 2 was used to neutralize the acid electrolyte. What if we change it to RVC foam? In this part, 2 RVC foam cathodes (Figure 1(c)) were used to investigate H₂O₂ generation. Influence of flow rate and current was shown in Figure 12. Samples were taken after the secondary RVC foam cathode (port 4). Generally, flow rate functions on H₂O₂ concentration in a similar way as the system with one foam cathode. Under 250 mA, 1.94 mg/L and 1.60 mg/L H₂O₂ were obtained under flow rates of 3 mL/min and 15 mL/min after

60 min, respectively, which accumulates to 0.30 mg and 1.24 mg, respectively. This result also indicates that in a flow-through cell with 2 RVC foam cathodes, the flow rate of 15 mL/min achieve better O_2 mass transfer, even if the retention time is shorter than the flow rate of 3 mL/min. Under 120 mA, higher H_2O_2 concentration under flow rate of 3 mL/min was obtained than 15 mL/min (1.18 mg/L > 0.81 mg/L). However, the accumulated H_2O_2 under 15 mL/min is higher than 3 mL/min, due to the larger volume flow through the cell. Under 60 mA, 0.27 mg/L and 0.52 mg/L H_2O_2 were obtained under flow rates of 3 mL/min and 15 mL/min at 60 min, respectively, which indicates the effective O_2 mass transfer is especially significant under low current. Another important phenomenon is that the concentration of H_2O_2 is lower than in a system with 1 foam cathode. This is interesting because we designed this part to enhance the H_2O_2 generation. This is possible because the secondary RVC foam cathode cannot receive enough O_2 for H_2O_2 generation due to bubbles accumulation; therefore, it functions as the catalysis for H_2O_2 electroreduction.

Compared with a system with 1 foam cathode, the current of 120 mA performs the best for all flow rates, while it is 250 mA in a system with 2 foam cathodes. Sufficient O_2 supply is important for a system with 2 foam cathode, so the current of 250 mA could generate more O_2 , which is favorable for the second cathode. Although 250 mA caused severe decomposition of H_2O_2 , it also produced sufficient O_2 compared with other cases. Internal figures show the highest yield at 60 min was 1.24 mg, obtained under 250 mA and 30 mL/min. Methods that can enhance the O_2 dissolution and mass transfer to the cathode after the first RVC foam cathode could increase the overall H_2O_2 production in a 3-electrode flow-through cell with 2 RVC foam cathodes. Considering the energy consumption for H_2O_2 production, H_2O_2 concentration and accumulation vs. the ratio of current to flow rate are calculated and shown in Table S2. Results illustrate that the optimal conditions for H_2O_2 accumulation are current of 120 mA and flow rate of 60 mL/min in a 3-electrode system with 1 RVC foam cathode.

Profile of CE shown in Figure 12(d) was in accordance with H_2O_2 accumulation. CE of 4.92% was achieved in a system with 1 foam cathode (120 mA, 60 mL/min), while the optimal CE was 1.13% in a system with 2 foam cathodes (60 mA, 15 mL/min). As discussed earlier, the relatively low CE is partial because O_2 was supplied by Ti/MMO anode, compared providing pure O_2 in the literature [10, 27], the O_2 supply could thus be a limiting step. Second, the O_2 mass transfer was not effective under low flow rate. Furthermore, the relatively low CE was also influenced by side reactions that include H_2O_2 disproportion (Eq. 9), cathodic reduction (Eq. 10), anodic oxidation (Eq. 11) and H_2 evolution reaction (HER, Eq. 4). H_2O_2 generation rates in batch and flow-through cells are compared with literature and are summarized in Table 3.

3.3.5 Comparison of 2-electrode and 3-electrode system—Comparison between 3-electrode and 2-electrode systems was conducted by the setup shown in Figure 1(c) and Figure 1(d). A current of 120 mA and a flow rate of 3 mL/min were selected for the 3-electrode system, while currents of 120 mA and 60 mA, the flow rate of 3 mL/min were selected for the 2-electrode system. Results in Figure 13 shows the current of 120 mA and 60 mA in 2-electrode system produce less H_2O_2 than 3-electrode system (1.50 mg/L, 0.70 mg/L, and 2.27 mg/L at 60 min, respectively). Compared with the 3-electrode system under

a total current of 120 mA (each cathode shares 60 mA), in the 2-electrode system, a current of 60 mA generated less O₂ available for H₂O₂ production, while a current of 120 mA causes non-negligible H₂O₂ decomposition (see Section 3.2.4)

3.4 Strategy for enhancement of H₂O₂ generation

RVC foam cathode shows potential to be applied to Fenton-based groundwater remediation technologies. However, H₂ from water electrolysis was not utilized for H₂O₂ generation, which could mean the inefficient use of electricity. Thus, the utilization of H₂ is one strategy to enhance the yield of H₂O₂. Yuan et al. [18] used Pd/C catalysts to directly synthesize H₂O₂ from H₂ and O₂ in water electrolysis system. Herein, we proposed a strategy that couples two mechanisms: one pathway is 2e⁻ ORR on RVC foam cathode, another pathway is Pd-catalyzed H₂O₂ synthesis from O₂ and H₂ (Eq. 13). A preliminary result is shown in Figure 14.

In the coupled system, H₂O₂ concentration reached 7.24 mg/L at 40 min, higher than 3.27 mg/L by RVC foam cathode and 5.85 mg/L by the Pd-catalyzed system. This verified our hypothesis that coupled process could make full use of O₂ and H₂, thus generating more H₂O₂. What should be noted is that H₂O₂ concentration in a combined system is lower than the sum of the individual system. This is because of both systems use O₂ as reactants. Based on this strategy, systematic work is undertaken to improve the performance of our system further.

4 Conclusions

This study evaluates the significant role of anodic O₂ mass transfer and acidic conditions on H₂O₂ electrogeneration via 2e⁻ ORR. The main advantage of the batch cell is the effective O₂ mass transfer while the main advantage of the flow-through cell is the automatic formation and control of the required localized low pH conditions. In batch conditions, low pH (pH=2) and high mixing (350 rpm stirring rate) are preferred for H₂O₂ generation, while a maximum current can achieve effective 2e⁻ ORR and low decomposition of H₂O₂ as well. In flow-through conditions, both flow rate and current significantly influence H₂O₂ concentration and H₂O₂ accumulation. The best current intensity is different for a system with one and two RVC foam cathode due to enhanced oxygen formation. The disadvantage of the flow-through cell is the bubbles accumulation which hinders the effective O₂ mass transfer. Finally, we propose a strategy that includes utilization of H₂ from water electrolysis for higher yield of H₂O₂.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgment

This work was financially supported by the US National Institute of Environmental Health Sciences (NIEHS, Grant No. P42ES017198) and National Natural Science Foundation of China (Grant No. 91434134, 51421063). The content is solely the responsibility of the authors and does not necessarily represent the official views of the NIEHS, the National Institutes of Health and the National Natural Science Foundation of China.

References

- [1]. Chen L, Ma J, Li X, Zhang J, Fang J, Guan Y, Xie P, Strong enhancement on Fenton oxidation by addition of hydroxylamine to accelerate the ferric and ferrous iron cycles, *Environmental Science and Technology*. 45 (2011) 3925–3930. doi:10.1021/es2002748. [PubMed: 21469678]
- [2]. Pignatello JJ, Oliveros E, MacKay A, Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry, *Critical Reviews in Environmental Science and Technology*. 36 (2006) 1–84. doi:10.1080/10643380500326564.
- [3]. Qiang ZM, Chang JH, Huang CP, Electrochemical generation of hydrogen peroxide from dissolved oxygen in acidic solutions, *Water Research*. 36 (2002) 85–94. doi:10.1016/S0043-1354(01)00235-4. [PubMed: 11766820]
- [4]. Oturan MA, Peiroten J, Chartrin P, Acher AJ, Complete destruction of p-Nitrophenol in aqueous medium by electro-fenton method, *Environmental Science and Technology*. 34 (2000) 3474–3479. doi:10.1021/es990901b.
- [5]. Brillas E, Mur E, Casado J, Iron(II) Catalysis of the Mineralization of Aniline Using a Carbon-PTFE O₂ - Fed Cathode, *Journal of The Electrochemical Society* . 143 (1996) L49–L53. doi:10.1149/1.1836528.
- [6]. Zhou W, Gao J, Kou K, Meng X, Wang Y, Ding Y, Xu Y, Zhao H, Wu S, Qin Y, Highly efficient H₂O₂ electrogeneration from O₂ reduction by pulsed current: Facilitated release of H₂ O₂ from porous cathode to bulk, *Journal of the Taiwan Institute of Chemical Engineers*. 12 (2017) 59–0. doi:10.1016/j.jtice.2017.10.041.
- [7]. Salari D, Niaei A, Khataee A, Zarei M, Electrochemical treatment of dye solution containing C.I. Basic Yellow 2 by the peroxi-coagulation method and modeling of experimental results by artificial neural networks, *Journal of Electroanalytical Chemistry*. 629 (2009) 117–125. doi:10.1016/j.jelechem.2009.02.002.
- [8]. Zhou W, Ding Y, Gao J, Kou K, Wang Y, Meng X, Wu S, Qin Y, Green electrochemical modification of RVC foam electrode and improved H₂O₂ electrogeneration by applying pulsed current for pollutant removal, *Environmental Science and Pollution Research*. (2017) 1–11. doi:10.1007/s11356-017-0810-8.
- [9]. Zarei M, Salari D, Niaei A, Khataee A, Peroxi-coagulation degradation of CI Basic Yellow 2 based on carbon-PTFE and carbon nanotube-PTFE electrodes as cathode, *Electrochimica Acta*. 54 (2009) 6651–6660. doi:10.1016/j.electacta.2009.06.060.
- [10]. Ozcan A, Sahin Y, Savas Koparal A, Oturan MA, Carbon sponge as a new cathode material for the electro-Fenton process: Comparison with carbon felt cathode and application to degradation of synthetic dye basic blue 3 in aqueous medium, *Journal of Electroanalytical Chemistry*. 616 (2008) 71–78. doi:10.1016/j.jelechem.2008.01.002.
- [11]. Zhou L, Hu Z, Zhang C, Bi Z, Jin T, Zhou M, Electrogeneration of hydrogen peroxide for electro-Fenton system by oxygen reduction using chemically modified graphite felt cathode, *Separation and Purification Technology*. 111 (2013) 131–136. doi:10.1016/j.seppur.2013.03.038.
- [12]. Liu Y, Chen S, Quan X, Yu H, Zhao H, Zhang Y, Efficient Mineralization of Perfluorooctanoate by Electro-Fenton with H₂O₂ Electro-generated on Hierarchically Porous Carbon, *Environmental Science and Technology*. 49 (2015) 13528–13533. doi:10.1021/acs.est.5b03147. [PubMed: 26465252]
- [13]. Sirés I, Brillas E, Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: A review, *Environment International*. 40 (2012) 212–229. doi:10.1016/j.envint.2011.07.012. [PubMed: 21862133]

- [14]. Sirés I, Brillas E, Oturan MA, Rodrigo MA, Panizza M, Electrochemical advanced oxidation processes: Today and tomorrow. A review, *Environmental Science and Pollution Research*. 21 (2014) 8336–8367. doi:10.1007/s11356-014-2783-1. [PubMed: 24687788]
- [15]. Scialdone O, Guarisco C, Galia A, Filardo G, Silvestri G, Amatore C, Sella C, Thouin L, Anodic abatement of organic pollutants in water in micro reactors, *Journal of Electroanalytical Chemistry*. 638 (2010) 293–296. doi:10.1016/j.jelechem.2009.10.031.
- [16]. Yu F, Zhou M, Yu X, Cost-effective electro-Fenton using modified graphite felt that dramatically enhanced on H₂O₂ electro-generation without external aeration, *Electrochimica Acta*. 163 (2015) 182–189. doi:10.1016/j.electacta.2015.02.166.
- [17]. Yu F, Zhou M, Zhou L, Peng R, A Novel Electro-Fenton Process with H₂O₂ Generation in a Rotating Disk Reactor for Organic Pollutant Degradation, *Environmental Science and Technology Letters*. 1 (2014) 320–324. doi:10.1021/ez500178p.
- [18]. Yuan S, Fan Y, Zhang Y, Tong M, Liao P, Pd-catalytic in situ generation of H₂O₂ from H₂ and O₂ produced by water electrolysis for the efficient electro-fenton degradation of rhodamine B., *Environmental Science & Technology*. 45 (2011) 8514–20. doi:10.1021/es2022939. [PubMed: 21866953]
- [19]. Perez JF, Llanos J, Saez C, Lopez C, Canizares P, Rodrigo MA, Electrochemical jet-cell for the in-situ generation of hydrogen peroxide, *Electrochemistry Communications*. 71 (2016) 65–68. doi:10.1016/j.elecom.2016.08.007.
- [20]. Daughton CG, Ternes TA, Pharmaceuticals and personal care products in the environment: Agents of subtle change?, *Environmental Health Perspectives*. 107 (1999) 907–938. doi:10.1289/ehp.99107s6907. [PubMed: 10592150]
- [21]. Schwarzenbach RP, Escher BI, Fenner K, Hofstetter TB, Johnson CA, von Gunten U, Wehrli B, The challenge of micropollutants in aquatic systems., *Science (New York, N.Y.)*. 313 (2006) 1072–7. doi:10.1126/science.1127291.
- [22]. Wang A, Qu J, Ru J, Liu H, Ge J, Mineralization of an azo dye Acid Red 14 by electro-Fenton's reagent using an activated carbon fiber cathode, *Dyes and Pigments*. 65 (2005) 227–233. doi:10.1016/j.dyepig.2004.07.019.
- [23]. Rajic L, Fallahpour N, Podlaha E, Alshawabkeh A, The influence of cathode material on electrochemical degradation of trichloroethylene in aqueous solution, *Chemosphere*. 147 (2016) 98–104. doi:10.1016/j.chemosphere.2015.12.095. [PubMed: 26761603]
- [24]. Rajic L, Fallahpour N, Yuan S, Alshawabkeh AN, Electrochemical transformation of trichloroethylene in aqueous solution by electrode polarity reversal, *Water Research*. 67 (2014) 267–275. doi:10.1016/j.watres.2014.09.017. [PubMed: 25282093]
- [25]. Gent DB, Wani AH, Davis JL, Alshawabkeh A, Electrolytic redox and electrochemical generated alkaline hydrolysis of hexahydro-1,3,5-trinitro-1,3,5 triazine (RDX) in sand columns, *Environmental Science and Technology*. 43 (2009) 6301–6307. doi:10.1021/es803567s. [PubMed: 19746729]
- [26]. Wang CT, Hu JL, Chou WL, Kuo YM, Removal of color from real dyeing wastewater by Electro-Fenton technology using a three-dimensional graphite cathode, *Journal of Hazardous Materials*. 152 (2008) 601–606. doi:10.1016/j.jhazmat.2007.07.023. [PubMed: 17707581]
- [27]. Zhang G, Yang F, Gao M, Fang X, Liu L, Electro-Fenton degradation of azo dye using polypyrrole/anthraquinonedisulphonate composite film modified graphite cathode in acidic aqueous solutions, *Electrochimica Acta*. 53 (2008) 5155–5161. doi:10.1016/j.electacta.2008.01.008.
- [28]. Khataee AR, Vatanpour V, Amani Ghadim AR, Decolorization of C.I. Acid Blue 9 solution by UV/Nano-TiO₂, Fenton, Fenton-like, electro-Fenton and electrocoagulation processes: A comparative study, *Journal of Hazardous Materials*. 161 (2009) 1225–1233. doi:10.1016/j.jhazmat.2008.04.075. [PubMed: 18524478]
- [29]. Nava JL, Recéndiz A, González LG, Carreño G, Martínez F, PORTUGALIAE ELECTROCHIMICA ACTA Mass Transport and Potential Studies in a Flow-through Porous Electrode Reactor. A Comparative Study of Reticulated Vitreous Carbon and Graphite Felt Used as Cathode, *Portugaliae Electrochimica Acta*. 27 (2009) 381–396. doi:10.4152/pea.200903381.

- [30]. Xie YB, Li XZ, Interactive oxidation of photoelectrocatalysis and electro-Fenton for azo dye degradation using TiO₂-Ti mesh and reticulated vitreous carbon electrodes, *Materials Chemistry and Physics*. 95 (2006) 39–50. doi:10.1016/j.matchemphys.2005.05.048.
- [31]. Gong Y, Li J, Zhang Y, Zhang M, Tian X, Wang A, Partial degradation of levofloxacin for biodegradability improvement by electro-Fenton process using an activated carbon fiber felt cathode, *Journal of Hazardous Materials*. 304 (2016) 320–328. doi:10.1016/j.jhazmat.2015.10.064. [PubMed: 26561756]
- [32]. Özcan A, ahin Y, Koparal AS, Oturan MA, A comparative study on the efficiency of electro-Fenton process in the removal of prothion from water, *Applied Catalysis B: Environmental*. 89 (2009) 620–626. doi:10.1016/j.apcatb.2009.01.022.
- [33]. Drogui P, Elmaleh S, Rumeau M, Bernard C, Rambaud A, Oxidising and disinfecting by hydrogen peroxide produced in a two-electrode cell, *Water Research*. 35 (2001) 3235–3241. doi:10.1016/S0043-1354(01)00021-5. [PubMed: 11487121]
- [34]. Li Q, Batchelor-Mcauley C, Lawrence NS, Hartshorne RS, V Jones CJ, Compton RG, A flow system for hydrogen peroxide production at reticulated vitreous carbon via electroreduction of oxygen, *Journal of Solid State Electrochemistry*. 18 (2014) 1215–1221. doi:10.1007/s10008-013-2250-9.
- [35]. Liu H, Wang C, Li X, Xuan X, Jiang C, Cui HN, A novel electro-Fenton process for water treatment: Reaction-controlled pH adjustment and performance assessment, *Environmental Science and Technology*. 41 (2007) 2937–2942. doi:10.1021/es0622195. [PubMed: 17533861]
- [36]. Martínez-Huitle CA, Andrade LS, Electrocatalysis in wastewater treatment: Recent mechanism advances, *Quimica Nova*. 34 (2011) 850–858. doi:10.1590/S0100-40422011000500021.
- [37]. Di Blasi A, D'Urso C, Baglio V, Antonucci V, Arico AS*, R. Ornelas, F. Matteucci, G. Orozco, D. Beltran, Y. Meas, L.G. Arriaga, Preparation and evaluation of RuO₂–IrO₂, IrO₂–Pt and IrO₂–Ta₂O₅ catalysts for the oxygen evolution reaction in an SPE electrolyzer, *Journal of Applied Electrochemistry*. 39 (2009) 191–196. doi:10.1007/s10800-008-9651-y.
- [38]. Ren Z, Quan S, Gao J, Li W, Zhu Y, Liu Y, Chai B, Wang Y, The electrocatalytic activity of IrO₂–Ta₂O₅ anode materials and electrolyzed oxidizing water preparation and sterilization effect, *RSC Adv*. 5 (2015) 8778–8786. doi:10.1039/C4RA14671A.
- [39]. Da Pozzo A, Di Palma L, Merli C, Petrucci E, An experimental comparison of a graphite electrode and a gas diffusion electrode for the cathodic production of hydrogen peroxide, *Journal of Applied Electrochemistry*. 35 (2005) 413–419. doi:10.1007/s10800-005-0800-2.
- [40]. Petersen MA, Sale TC, Reardon KF, Electrolytic trichloroethene degradation using mixed metal oxide coated titanium mesh electrodes, *Chemosphere*. 67 (2007) 1573–1581. doi:10.1016/j.chemosphere.2006.11.056. [PubMed: 17234239]
- [41]. Yu L, Pan X, Cao X, Hu P, Bao X, Oxygen reduction reaction mechanism on nitrogen-doped graphene: A density functional theory study, *Journal of Catalysis*. 282 (2011) 183–190. doi:10.1016/j.jcat.2011.06.015.
- [42]. Yeager E, Electrocatalysts for O₂ reduction, *Electrochimica Acta*. 29 (1984) 1527–1537. doi:10.1016/0013-4686(84)85006-9.
- [43]. Sánchez-Sánchez CM, Bard AJ, Hydrogen peroxide production in the oxygen reduction reaction at different electrocatalysts as quantified by scanning electrochemical microscopy, *Analytical Chemistry*. 81 (2009) 8094–8100. doi:10.1021/ac901291v. [PubMed: 19725556]
- [44]. Zhou W, Gao J, Ding Y, Zhao H, Meng X, Wang Y, Kou K, Xu Y, Wu S, Qin Y, Drastic Enhancement of H₂O₂ Electro-generation by Pulsed Current for Ibuprofen Degradation: Strategy Based on Decoupling Study on H₂O₂ Decomposition Pathways, *Chemical Engineering Journal*. (2017). doi:10.1016/j.cej.2017.12.152.
- [45]. Zhang C, Fan FRF, Bard AJ, Electrochemistry of oxygen in concentrated NaOH solutions: Solubility, diffusion coefficients, and superoxide formation, *Journal of the American Chemical Society*. 131 (2009) 177–181. doi:10.1021/ja8064254. [PubMed: 19063634]
- [46]. Yue ZR, Jiang W, Wang L, Gardner SD, Pittman CU, Surface characterization of electrochemically oxidized carbon fibers, *Carbon*. 37 (1999) 1785–1796. doi:10.1016/S0008-6223(99)00047-0.

- [47]. Tang X, Guo K, Li H, Du Z, Tian J, Electrochemical treatment of graphite to enhance electron transfer from bacteria to electrodes, *Bioresource Technology*. 102 (2011) 3558–3560. doi:10.1016/j.biortech.2010.09.022. [PubMed: 20888221]
- [48]. Plakas KV, Karabelas AJ, Sklari SD, Zaspalis VT, Toward the development of a novel electro-fenton system for eliminating toxic organic substances from water. Part 1. in situ generation of hydrogen peroxide, in: *Industrial and Engineering Chemistry Research*, 2013: pp. 13948–13956. doi:10.1021/ie400613k.
- [49]. Scialdone O, Galia A, Gattuso C, Sabatino S, Schiavo B, Effect of air pressure on the electro-generation of H_2O_2 and the abatement of organic pollutants in water by electro-Fenton process, *Electrochimica Acta*. 182 (2015) 775–780. doi:10.1016/j.electacta.2015.09.109.
- [50]. Agarwal A, Ng WJ, Liu Y, Principle and applications of microbubble and nanobubble technology for water treatment, *Chemosphere*. 84 (2011) 1175–1180. doi:10.1016/j.chemosphere.2011.05.054. [PubMed: 21689840]
- [51]. Bredwell MD, Worden RM, Mass-transfer properties of microbubbles. 1. Experimental studies, *Biotechnology Progress*. 14 (1998) 31–38. doi:10.1021/bp970133x. [PubMed: 9496668]
- [52]. Zhou W, Gao J, Zhao H, Meng X, Wu S, The role of quinone cycle in $Fe^{2+} - H_2O_2$ system in the regeneration of Fe^{2+} , *Environmental Technology*. 3330 (2016) 1–10. doi:10.1080/09593330.2016.1240241.
- [53]. Yuan S, Gou N, Alshawabkeh AN, Gu AZ, Efficient degradation of contaminants of emerging concerns by a new electro-Fenton process with Ti/MMO cathode, *Chemosphere*. 93 (2013) 2796–2804. doi:10.1016/j.chemosphere.2013.09.051. [PubMed: 24125716]
- [54]. Zhou W, Zhao H, Gao J, Meng X, Wu S, Qin Y, Influence of Reagents Addition Strategy on Fenton Oxidation of Rhodamine B: Control of Competitive Reaction of $\cdot OH$, *RSC Adv.* (2016). doi:10.1039/C6RA20242J.
- [55]. Qian A, Yuan S, Zhang P, Tong M, A new mechanism in electrochemical process for arsenic oxidation: Production of H_2O_2 from anodic O_2 reduction on the cathode under automatically developed alkaline conditions, *Environmental Science and Technology*. 49 (2015) 5689–5696. doi:10.1021/acs.est.5b00808. [PubMed: 25853500]

Figure 1.

A schematic of the electrochemical batch cell and flow-through cell. (a) undivided batch cell; (b) divided batch cell; (c) 2-electrode flow-through cell; (d) 3-electrode flow-through cell with one RVC foam cathode; (e) 3-electrode flow-through cell with two RVC foam cathodes. In batch cell, A is Ti/MMO or graphite plate, C is Ti/MMO or RVC foam. In flow-through cell, A is Ti/MMO anode; C, C1, and C3 is RVC foam cathode; C2 is Ti/MMO cathode. Pd/Al₂O₃ catalysts shown in (a) were only used in section 3.4.

Figure 2.

Comparison of Ti/MMO and graphite anodes in undivided batch cell. (a) Profile of dissolved oxygen; (b) Change of H₂O₂ concentration (Ti/MMO electrode was used in Figure 2(a) since it doesn't consume O₂, RVC foam was used in Figure 2(b), 180 mL, 350 rpm, initial pH of 7, 100 mA (current density: 166.7 A/m²), 50 mM Na₂SO₄, room temperature).

Figure 3.

Profile of pH value in (a) divided batch cell with two compartments and (b) undivided batch cell (Anode: Ti/MMO, cathode: Ti/MMO, 180 mL, 350 rpm for (a), initial pH of 7, 100 mA, 50 mM Na₂SO₄, room temperature).

Figure 4. Profile of DO in (a) undivided batch cell and (b) divided batch cell (Anode: Ti/MMO, cathode: RVC foam, 180 mL, 350 rpm for (b), initial pH: 7, 100 mA, 50 mM Na_2SO_4 , room temperature).

Figure 5.

(a) Profile of H_2O_2 concentration at different current intensity in the batch cell; (b) Illustration of H_2O_2 electrogeneration from anodic O_2 (Anode: Ti/MMO, cathode: RVC foam, 180 mL, 350 rpm, initial pH of 7, 50 mM Na_2SO_4 , room temperature).

Figure 6.

(a) Profile of H_2O_2 concentration at different initial pH value in the batch cell; (b) A summary of current efficiency for H_2O_2 under different initial pH and current intensity (Anode: Ti/MMO, cathode: RVC foam, 180 mL, 350 rpm, 100 mA, 50 mM Na_2SO_4 , room temperature).

Figure 7.

(a) Influence of stirring rate on H_2O_2 concentration in the batch cell; (b) The behavior of O_2 bubbles after generation on the anode surface (Anode: Ti/MMO, cathode: RVC foam, 180 mL, 100 mA, initial pH of 7, 50 mM Na_2SO_4 , room temperature).

Figure 8.

Steady-state pH distribution in flow-through cell with (a) two electrode and (b) three electrode (Anode: Ti/MMO, cathode 1 and 2: Ti/MMO, flow rate: 3 mL/min, initial pH of 7, feed solution: 50 mM Na₂SO₄, room temperature).

Figure 9.

Profile of DO before and after RVC foam cathode in flow-through cell (Anode: Ti/MMO, cathode 1: RVC foam, cathode 2: Ti/MMO, 120 mA (60 mA for cathode 1 and 2), flow rate: 3 mL/min, initial pH of 7, feed solution: 50 mM Na₂SO₄, room temperature).

Figure 10.

Influence of flow rate on H_2O_2 concentration in 3-electrode flow-through cell with 1 RVC foam cathode under different current intensity: (a) 60 mA; (b) 120 mA; (c) 250 mA. (d) Profile of DO sampled from port 2 and 3 (Anode: Ti/MMO, cathode 1: RVC foam, cathode 2: Ti/MMO, initial pH of 7, feed solution: 50 mM Na_2SO_4 , room temperature, sampling position: port 3).

Figure 11. Photos of oxygen bubble accumulated under the cathode surface (Anode: Ti/MMO, cathode 1: RVC foam, cathode 2: Ti/MMO, initial pH of 7, 120 mA, feed solution: 50 mM Na₂SO₄, room temperature).

Figure 12.

Influence of flow rate on H_2O_2 concentration in 3-electrode flow-through cell with 2 RVC foam cathodes under different current intensity: (a) 60 mA; (b) 120 mA; (c) 250 mA. (d) A summary of current efficiency for 1 and 2 RVC foam under different flow rates and current intensities (Anode: Ti/MMO, cathode 1 and 2: RVC foam, initial pH of 7, feed solution: 50 mM Na_2SO_4 , room temperature, sampling position: port 4).

Figure 13.

Profile of H₂O₂ concentration in 2-electrode and 3-electrode flow-through cell (Anode: Ti/MMO, cathode: RVC foam (for 2-electrode cell), cathode 1: RVC foam (for 3-electrode cell), cathode 2: Ti/MMO (for 3-electrode cell), initial pH of 7, feed solution: 50 mM Na₂SO₄, room temperature, sampling position: port 3 for 3-electrode cell, port 2 for 2-electrode cell).

Figure 14.

Profile of H_2O_2 concentration from coupled process in the batch cell (Anode: Ti/MMO, cathode: Ti/MMO or RVC foam (for Pd/ Al_2O_3 system, Ti/MMO was used as cathode), 180 mL, 350 rpm, 100 mA, initial pH of 7, 2g Pd/ Al_2O_3 catalysts).

Table 1

Experimental conditions (influent pH of 7)

Electrode Arrangement	Current on A (mA)	Current on C/C1 (mA)	Current on C2/C3 (mA)	Flow rate (mL/min)
T-R-T ¹	60	30	30	3, 15, 30, 60
T-R-T	120	60	60	3, 15, 30, 60
T-R-T	250	125	125	3, 15, 30, 60
T-R-R ²	60	30	30	3, 15, 30, 60
T-R-R	120	60	60	3, 15, 30, 60
T-R-R	250	125	125	3, 15, 30, 60
T-R ³	60	60	-	3
T-R	120	120	-	3

Note:

¹T-R-T means the electrode sequence: Ti/MMO-RVC foam-Ti/MMO.²T-R-R means the electrode sequence: Ti/MMO-RVC foam-RVC foam.³T-R means the electrode sequence: Ti/MMO-RVC foam.

Table 2

Profile of pH at different sampling port under different current in 2 and 3 electrode systems.

System	Current (mA)	Time (min)	Sampling position		
			Port 2	Port 3	Port 4
2-electrode	200	5	2.63	11.77	-
		10	2.58	11.65	-
	100	5	2.96	11.38	-
		10	2.77	11.41	-
	50	5	3.07	11.76	-
		10	2.90	11.36	-
	10	5	3.98	10.57	-
		10	3.65	10.86	-
3-electrode	250	5	2.55	11.13	11.74
		10	2.44	10.85	11.47
	120	5	2.64	11.34	11.51
		10	2.68	11.40	11.55
	60	5	2.96	10.79	11.3
		10	2.80	11.23	11.53

Table 3Comparison of H₂O₂ production rate with literature.

Cathode	pH	Current density (A/m ²)	t (min)	O ₂ flow rate (L/min)	[H ₂ O ₂] (mg/h/cm ²)	Reactor	Ref.
GDE ^a	3	204	300	0.14	1.94	batch	[7]
Graphite felt	3	132	300	0.14	0.11	batch	[7], [9]
Carbon felt	3	161	180	0.1	0.62	batch	[10]
Graphite felt	6.4	-0.65 ^b	120	0.4	0.44	batch	[11]
Graphite felt	3	50	60	0	0.58	batch	[17]
ACF	3	250	180	0.1	0.55	batch	[22]
Graphite	3	-0.65 ^c	120	0.33	1.00	batch	[27]
RVC foam	2	167	70	0	0.25	batch	This work
RVC foam	7	59	60	0	0.18	flow-through	This work

Note:

^a-GDE means gas diffusion electrodes^b-the bias potential of the cathode (volts) (vs. the saturated calomel electrode (SCE))^c-the bias potential of the cathode (vs. SCE)