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“Floating” cathode for efficient H₂O₂ electrogeneration applied to degradation of ibuprofen as a model pollutant

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Abstract

The performance of the Electro-Fenton (EF) process for contaminant degradation depends on the rate of H₂O₂ production at the cathode via 2-electron dissolved O₂ reduction. However, the low solubility of O₂ ($\approx 1 \times 10^{-3}$ mol dm⁻³) limits H₂O₂ production. Herein, a novel and practical strategy that enables the synergistic utilization of O₂ from the bulk electrolyte and ambient air for efficient H₂O₂ production is proposed. Compared with a conventional “submerged” cathode, the H₂O₂ concentration obtained using the “floating” cathode is 4.3 and 1.5 times higher using porous graphite felt (GF) and reticulated vitreous carbon (RVC) foam electrodes, respectively. This surprising enhancement results from the formation of a three-phase interface inside the porous cathode, where the O₂ from ambient air is also utilized for H₂O₂ production. The contribution of O₂ from ambient air varies depending on the cathode material and is calculated to be 76.7% for the GF cathode and 35.6% for the RVC foam cathode. The effects of pH, current, and mixing on H₂O₂ production are evaluated. Finally, the EF process enhanced by the “floating” cathode degraded 78.3% of the anti-inflammatory drug ibuprofen after 120 min compared to only 25.4% using a conventional “submerged” electrode, without any increase in the cost.

Keywords

Air cathode; Electro-Fenton; Graphite felt; Hydrogen peroxide; Oxygen reduction reaction

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1. Introduction

The Electro-Fenton (EF) process is an important advanced oxidation process (AOP) for removal of pollutants from contaminated media that has attracted increasing attention in recent years [1-5]. In this process, H_2O_2 is continuously electrogenerated in situ on the cathode via a 2-electron O_2 reduction reaction (ORR, Eq. 1) [6], while Fe^{2+} is added externally and is regenerated at the cathode (Eq. 2) [7,8]. Highly oxidative hydroxyl radicals ($\cdot\text{OH}$) are then produced by the reaction between H_2O_2 and Fe^{2+} (Eq. 3) [3,9].

The EF performance for degradation of pollutants is dependent on the rate of production of H_2O_2 [1,10,11]. Conventional cathode materials, such as graphite [12], carbon felt (CF) [13], graphite felt (GF) [14,15], RVC foam [16-18], and activated carbon fiber [19] have been widely studied in connection with the EF process. New types of cathodes, such as carbon black/polytetrafluoroethylene (PTFE)/GF [20], acetylene black/PTFE [21,22], graphene/CF [23,24], CNTs/graphite [25], and CNTs/polypyrrole/graphite [26] are still under development with varying advantages and limitations in achieving higher H_2O_2 production. However, H_2O_2 generation processes that rely on 2-electron ORR are limited by low O_2 solubility in the aqueous phase ($\approx 1 \times 10^{-3} \text{ mol dm}^{-3}$) [27]. Typically, O_2 is supplied to the cathode surface by aeration or using an external pure oxygen source. Since the O_2 utilization efficiency is extremely low ($< 0.1\%$), a significant energy loss occurs, especially when upscaling the process [10,28]. Meanwhile, the O_2 concentration in the atmosphere is $45 \times 10^{-3} \text{ mol dm}^{-3}$ (101 kPa) [27], 45 times higher than in aqueous solution. Direct utilization of O_2 from the air for H_2O_2 electrogeneration should significantly improve the performance of the EF process.

To facilitate the mass transport of O_2 to the cathode, methods such as pressurized reactors, Venturi-based jet aerators [28], gas diffusion electrodes (GDEs) [10], reactors equipped with rotating cathodes [11], and stacked electrosynthesis reactors [29] have been developed. Among these, gas diffusion electrodes (composed of a diffusion layer, a current collector layer, and a catalyst layer) have been recognized as an efficient cathode for H_2O_2 generation with high current efficiency [30,31]. In this system, the pumped air or oxygen can pass directly through the diffusion layer and reach the electrode/electrolyte interface, overcoming the limitation of low O_2 solubility. PTFE and Poly(vinylidene fluoride) (PVDF) [32,33] have been used as a binder with powdered carbon materials (carbon black [15], acetylene black

[22], activated carbon [33]) to form many pores to act as gas channels. However, wider and larger-scale applications of GDEs are still a challenge because of the complexity of the cathode structure, possible flooding during extended use [34] and energy consumption for air/O₂ pumping.

In this work, the concept of a “floating” cathode, in which one side of a porous cathode is open to the air, and the other side is submerged in the aqueous solution, is proposed and tested. This novel approach enables the formation of a three-phase boundary (gaseous O₂, aqueous electrolyte, and solid cathode), thus allowing synergistic utilization of O₂ from both ambient air and the electrolyte. Compared with a GDE, construction of a hydrophobic gas diffusion layer as well as an air/O₂ pumping system are avoided, making this approach energy-efficient and cost-effective. In this study, we compare the performance of the floating cathode with that of a fully “submerged” cathode. The effects of pH, current, and mixing on H₂O₂ production are analyzed. Finally, the performance of the EF process for degradation of the anti-inflammatory drug ibuprofen (IBP) is evaluated.

2. Methods and Materials

Ferrous sulfate and ibuprofen (2-(4-(2-methyl propyl)phenyl)propanoic acid, C₁₃H₁₈O₂) were obtained from Fisher Scientific. Sodium sulfate (anhydrous, 99%) and titanium sulfate (99.9%) were purchased from Aladdin Chemical Reagent Co. Ltd. Deionized water (18.2 MΩ cm) obtained from a Millipore Milli-Q system was used in all the experiments.

Experiments were conducted using a batch reactor (180 dm³) with the cathode either fully submerged or floating. A Ti/mixed metal oxide (MMO, 3N International) electrode that consists of IrO₂ and Ta₂O₅ coating (1.9 μm thickness) on titanium mesh (3.6 cm in diameter by 1.8 mm thick) was used as the anode. O₂ was provided by the oxygen evolution reaction (OER) occurring at the anode and was then electroreduced at the cathode. GF (Fuel cell store, USA) and RVC foam (45 pores per inch (PPI), KR Reynolds Ltd.) were used as cathode materials, and were cut into pieces 2 cm x 3 cm and 3 cm x 3.5 cm, respectively (thickness: 3.2 mm and 6 mm, respectively). The anode and cathode were arranged horizontally in the batch reactor 3 cm apart. 50 × 10⁻³ mol dm⁻³ Na₂SO₄ was used as the electrolyte. A constant current (30 mA, 50 mA, 100 mA, 150 mA) was provided by an Agilent E3612A power supply. The cell voltages corresponding to these currents are 1.4 V, 2.0 V, 3.4 V and 4.1 V, respectively.

At preset intervals, 3 cm³ solution was sampled and measured at 405 nm using a Shimadzu UV-Vis spectrometer after coloration with TiSO₄ for H₂O₂ determination [35]. The methods used for IBP concentration and total organic carbon (TOC) measurement are the same as in our previous work [36]. The faradic current efficiency (CE) is calculated using Eq. 4, where n is the number of electrons required for O₂ reduction to H₂O₂, F is the Faraday constant (96485.3 C mol⁻¹), $c_{\text{H}_2\text{O}_2}$ is the H₂O₂ concentration (mol dm⁻³), V is the solution volume (L), I is the current (A), and t is the time (s) [11]. The theoretical production of O₂ (OTP) was calculated using Eq. 5, where I is the current (A), t is the time (s), F is the Faraday constant, n is the number of electrons of oxygen evolution reaction ($n = 4$), V_t is the molar gas volume at 25 °C (24.5 L mol⁻¹). The O₂ utilization efficiency (OUE) was calculated

using Eq. 6, where $n(O_2, OTP)$ is the amount of O_2 theoretical production in moles, $n(O_2, 2e^- \text{ reduction})$ is the amount of O_2 that is used for H_2O_2 production, which is the same value of H_2O_2 production in moles [37].

$$CE = \frac{nFc_{H_2O_2}V}{\int_0^t Idt} \times 100\% \quad 4$$

$$OTP = \frac{\int_0^t Idt}{nF} \times V_t \quad 5$$

$$OUE = \frac{n(O_2, 2e^- \text{ reduction})}{n(O_2, OTP)} \times 100\% \quad 6$$

3. Results and Discussion

3.1 H_2O_2 production using “floating” and “submerged” cathodes

H_2O_2 is produced by the reduction of dissolved O_2 in a conventional EF process. H_2O_2 concentrations measured in the setup (Figure 1a) with GF and RVC foam “floating” cathodes were up to 61.7 mg dm^{-3} and 37.8 mg dm^{-3} , respectively, after 50 min (Figure 1b and 1c). These concentrations were significantly higher (4.3 times and 1.5 times, respectively) than those measured for the “submerged” cathode (the CE was calculated and shown in Figure 1d). Only dissolved O_2 from the electrolyte was utilized by the “submerged” cathode, while synergistic utilization of O_2 from the electrolyte and ambient air is achieved by the “floating” cathode.

The OUE under “submerged” conditions is 9.8% for the GF cathode and 16.6% for the RVC foam cathode, which is within the range reported in the literature [37]. In the “floating” cathode reactor, the contribution of O_2 from ambient air is calculated to be 76.7% and 35.6% for GF and RVC foam, respectively, illustrating that the ambient air was effectively utilized for H_2O_2 synthesis. Moreover, the GF electrode performs significantly better than the RVC foam electrode under floating conditions. The experimental conditions can be further developed and enhanced to achieve higher values of CE compared with those reported in the literature [38,39].

3.2 Effect of pH, current, and mixing

The effects of operating parameters on H_2O_2 production using a fully “submerged” cathode are well documented [19,20,23,40]. Herein, the effect of pH, current, and mixing on H_2O_2

production using a “floating” cathode are evaluated (Figure 2). Compared with the control experiment, a low current of 30 mA does not enable H_2O_2 production. It is expected that H_2O_2 production will increase with increasing current. Interestingly, the H_2O_2 concentration after 50 min at 100 mA and 150 mA is 61.7 mg dm^{-3} and 10.4 mg dm^{-3} , respectively, indicating that increasing the current does not necessarily increase H_2O_2 production. In other words, there is an optimum value for the current to maximise H_2O_2 production, beyond which production decreases. This is because H_2O_2 electrogeneration changes from a current limited process to one limited by dissolved oxygen (DO) mass-transfer [41]. Another important reason is the severe decomposition and/or activation of H_2O_2 via several pathways (Eq. 7-Eq. 9) [1,6].

Solution pH also has a significant influence on H_2O_2 production due to the participation of protons in 2-electron ORR [42]. The results in Figure 2b show that H_2O_2 yield was highest at a pH of 7 and then dropped as the pH decreased, especially at a pH of 2.11. The results demonstrate that a pH of 7 is the optimal condition for H_2O_2 electrogeneration using a “floating” cathode, which is consistent with the literature [15,43]. At a pH of 2.11, the H^+ concentration is significantly higher than at a pH of 3.08, the H_2 evolution reaction (HER) can thus compete with 2-electron O_2 reduction, resulting in a severely decreased yield of H_2O_2 .

The effects of mixing are also investigated (Figure 2c). The stirring rate is extremely important for the utilization of O_2 from ambient air. The inset in Figure 2c shows that under “submerged” conditions, changing the stirring rate from 200 rpm to 350 rpm does not result in any significant change in H_2O_2 production, which implies that 200 rpm is sufficient for effective dissolved O_2 mass transfer to the cathode. In contrast, under “floating” conditions, the three-phase interface is significant for the dissolution of ambient air, and a stirring rate of 200 rpm is possibly inefficient to utilize O_2 from ambient air, even when a three-phase interface is present.

3.3 Ibuprofen degradation via the EF process with a “floating” cathode

At this point, the EF process enabled by the “floating” cathode was applied to the degradation of organic pollutants. IBP was selected as a model pollutant because it is resistant to conventional water treatment processes and is frequently detected in surface water and waste water [36,44]. The IBP removal efficiency, TOC removal efficiency, and OH generation assessment are shown in Figure 3. Results show that IBP degradation is more effective using the EF process with a “floating” cathode than with a “submerged” cathode, as 74.9% and 24.7%, respectively, of IBP is removed after 10 min. The time required for 100% removal is 60 min and 120 min for EF with a “floating” cathode and “submerged” cathode, respectively. Moreover, after 120 min, the TOC removal efficiency of the two systems is 78.3% and 25.4%, respectively, implying that EF assisted by the “floating” cathode is more efficient. Compared with the literature [44,45], the IBP removal kinetics could be further improved by several methods, such as adjusting the cathode area. This result is consistent with the enhanced H_2O_2 yield using a “floating” cathode shown in Figure 1b, where 61.7 mg dm^{-3} H_2O_2 was generated, 4.3 times the yield obtained using the “submerged” cathode. OH is responsible for IBP removal and TOC removal. Furthermore, by using benzoic acid as trapping reagent, we found a higher spectral peak value, implying that more OH is generated in the EF process enabled by the “floating” cathode.

4. Conclusions

Compared with the conventional “submerged” cathode, H_2O_2 production using a “floating” cathode is highly efficient. Both the dissolved O_2 generated from the anode and the O_2 in ambient air are utilized for H_2O_2 production, due to the facile strategy of using a 3-phase interface. This practical method can be further developed and enhanced to achieve significantly higher H_2O_2 production rates. Compared with a “submerged” cathode, the EF process enabled by a “floating” cathode is confirmed to be more efficient for ibuprofen degradation.

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Highlights

- (1) The H_2O_2 yield obtained using a “floating” cathode is 61.7 mg/L compared with 14.4 mg/L using a “submerged” cathode.
- (2) O_2 from the anode and ambient air are both utilized for H_2O_2 production.
- (3) The effects of electrolyte pH, applied current, and mixing on H_2O_2 production were evaluated.
- (4) The Electro-Fenton process enabled by a “floating” cathode is effective for ibuprofen degradation.

Figure 1.

(a) A schematic of the setup and two cathode arrangements. (b)-(c) Enhanced H_2O_2 production was obtained using a "floating" cathode compared to a fully "submerged" cathode: (b) GF, (c) RVC foam, and (d) CE for "submerged" cathode and "floating" cathode. Conditions: 180 cm^3 , 100 mA , $50 \times 10^{-3} \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$, 350 rpm , $\text{pH } 7$.

Figure 2.

Effect of (a) current, (b) pH, and (c) stirring on H_2O_2 production using a "floating" GF cathode. Inset: effect of stirring rates of 200 rpm and 350 rpm on H_2O_2 production using a GF cathode under "submerged" conditions. Conditions: 180 cm^3 , $50 \times 10^{-3}\text{ mol dm}^{-3}$ Na_2SO_4 , 100 mA (for b and c), 350 rpm (for a and b), pH 7 (for a and c).

Figure 3.

(a) Profile of IBP concentration in EF process enabled by “floating” and “submerged” GF cathodes; conditions: 180 cm^3 , 100 mA , $50 \times 10^{-3} \text{ mol dm}^{-3} \text{ N}_2\text{SO}_4$, 350 rpm , $c(\text{IBP}) = 40 \text{ mg dm}^{-3}$, $c(\text{Fe}^{2+}) = 40 \text{ mg dm}^{-3}$, $\text{pH } 3$. (b) Profile of fluorescence intensity at different emission wavelengths in $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system. The internal figure shows the change of peak values vs. time; conditions: $c(\text{Fe}^{2+}) = 40 \text{ mg dm}^{-3}$, $\text{pH } 3$, 350 rpm , excitation wavelength: 303 nm .