



Short communication

In situ Fenton-enhanced cathodic reaction for sustainable increased electricity generation in microbial fuel cells

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ABSTRACT

This study reports that Fenton's reaction is capable of facilitating cathodic reaction and thus increasing the current output in microbial fuel cells (MFCs). The hydroxyl radicals ($\bullet\text{OH}$) produced via Fenton's reaction are demonstrated to be vital to the enhancement of electricity generation in MFCs. In a two-chamber MFC employing expanded polytetrafluoroethylene (e-PTFE) laminated cloth as a separator, the power output is enhanced approximately four times with Fenton's reaction. However, the enhancement lasts only a short time period due to the rapid consumption of Fenton's reagents. To overcome this problem, a Fe@Fe₂O₃/carbon felt (CF) composite cathode is made, which results in a greater and, more importantly, sustainable power output. In the composite cathode, Fe@Fe₂O₃ functions as a controllably releasing Fenton iron reagent and CF functions as an air-fed cathode to electro-generate H₂O₂. This newly developed MFC with a Fenton system can ensure a continuous high power output, and also provides a potential solution to the simultaneous electricity generation and degradation of recalcitrant contaminants.

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1. Introduction

Microbial fuel cells (MFCs) are a promising technology for simultaneous electricity production and wastewater treatment [1–3]. In the anode chamber, microorganisms oxidize organic substrates, releasing electrons and protons. The electrons are subsequently conducted over an external resistor towards the cathode and the protons migrate through a membrane to the cathode compartment, where the electrons and protons are consumed to reduce electron acceptors. Due to its inexhaustible availability and high redox potential, oxygen has been generally regarded as the best electron acceptor for cathodic reaction in MFCs. However, the cathodic oxygen reduction reaction (ORR) can proceed through a two-electron pathway with the formation of H₂O₂ [4–8], which prevents the system from delivering its all energy and constrains the performance of MFCs.

Under acidic condition, H₂O₂ can react with ferrous ions (Fe²⁺) to generate hydroxyl radicals ($\bullet\text{OH}$) via Fenton's reaction [9,10]. The produced $\bullet\text{OH}$ is a very powerful oxidizer with a redox potential of 2.83 V ($\bullet\text{OH} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}$). Thus, the presence of $\bullet\text{OH}$ in the cathode compartment would promote cathodic reaction. However, Fenton's reaction has rarely been used in fuel cells because $\bullet\text{OH}$ can result in degradation of a membrane [11]. Similar to many other

chemical oxidizers (such as ferricyanide, permanganate), $\bullet\text{OH}$ is not self-sustaining because Fenton's reaction requires a periodical replenishment of the exhausted reagents (Fe²⁺ and H₂O₂), which also limits its application.

For the first time, this study provided direct evidences that Fenton's reaction can facilitate cathodic reaction and thus improve the electricity generation of an MFC. Instead of conventional ion exchange membranes, we used an expanded polytetrafluoroethylene (e-PTFE) laminated cloth as a separator in a two-chamber MFC to prevent membrane degradation. A Fe@Fe₂O₃/carbon felt (CF) composite cathode was made and functioned as the cathode in the MFCs. Fe²⁺ leached from Fe@Fe₂O₃ and H₂O₂ formed by two-electron reduction of dissolved O₂ established an *in situ* Fenton's reaction, which was able to enhance MFC performance over a longer period.

2. Experimental procedure

2.1. Preparation of Fe@Fe₂O₃/CF composite cathode

The carbon felt (CF, 4.5 cm × 4.5 cm, Liaoyang, China) used for the composite cathode was washed for 24 h in 4 M HCl to eliminate potentially catalytic foreign compounds from the CF's surface, and the washing process was repeated four times [12]. In the following texts, we refer to such pretreated, non-catalyzed CF as NCF. The preparation of the Fe@Fe₂O₃/NCF composite cathode followed the method described elsewhere [13], with slight modifications. To

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prepare a ferric solution and a NaBH_4 solution, 0.9 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1.8 g NaBH_4 were dissolved in 100 and 40 mL distilled water, respectively. After the ultrasonic treatment of the NCF in the ferric solution for 20 min, the NaBH_4 solution was slowly added to reduce ferric ions into metallic iron on the NCF. The composite electrode was rinsed with deionized water thoroughly and dried in nitrogen for use. The Fe loaded onto the NCF was determined by weight method [13] and kept at a concentration of 0.2 g L^{-1} of $\text{Fe@Fe}_2\text{O}_3$ in the final solution.

2.2. MFC configuration and operation

The MFC reactor consisted of two identical chambers separated by GORE-TEX[®] cloth (Zhejiang, China), which is an e-PTFE laminated compound fabric. Each cell chamber is made of plexiglass and has an effective volume of 75 mL. CF (4.5 cm × 9.0 cm) was used as anodic electrode. The anode chamber was inoculated and operated similarly to our previous work [14], and was continuously fed with brewery wastewater by a peristaltic pump at 3.1 mL h^{-1} . The corresponding volumetric loading rate was $4.25 \text{ g COD L}^{-1} \text{ d}^{-1}$, which ensured substrate sufficiency.

In the first experiment to explore the role of Fenton's reaction in improving MFC performance, NCF was used as the cathode electrode and the cathodic electrolyte was 2% NaCl solution at pH 3.0 (adjusted by diluted HCl). The Fenton reagents were added in two different sequences: (1) an initial addition of $0.2 \text{ g L}^{-1} \text{ Fe}^{2+}$ followed by $1.0 \text{ g L}^{-1} \text{ H}_2\text{O}_2$; (2) an initial addition of $1.0 \text{ g L}^{-1} \text{ H}_2\text{O}_2$ followed by a co-addition of $0.2 \text{ g L}^{-1} \text{ Fe}^{2+}$ and 20 mM 2-propanol. The long-term operation of the MFC was performed with a $\text{Fe@Fe}_2\text{O}_3/\text{NCF}$ composite cathode, along with the MFCs using NCF and NCF in the presence of Fe^{2+} in the solution (denoted as $\text{Fe}^{2+}/\text{NCF}$) as the cathode electrodes. For better comparison with a benchmark system, a control experiment was carried out with a MFC using NCF in the presence of $\text{Fe}(\text{CN})_6^{3-}$ solution (20 mmol L^{-1} , pH 7.0) (denoted as $\text{Fe}(\text{CN})_6^{3-}/\text{NCF}$). The cathodic compartment was continuously sparged with air (300 mL min^{-1}) by using a fish pump (Harbin, China). All MFC experiments were conducted at a controlled temperature of 30°C and atmospheric pressure.

2.3. Power measurement and chemical analysis

Connected to a 1000Ω external resistor, the cell voltage output of the MFC was continuously monitored by a 16-channel voltage collection instrument (AD8223, China). Polarization and power density curves were obtained by varying the external resistance (R_{EX}) from 5 to 5000Ω when the voltage output approached steady-state. The power densities were normalized to the projected surface area of the cathode (20.25 cm^2).

The concentration of total iron ions (Fe^{2+} and Fe^{3+}) in the solution was determined using 1,10-phenanthroline colorimetric assay [15]. The concentration of H_2O_2 was determined by a H_2O_2 colorimeter (LOVIBOND-ET8600, Germany) at 528 nm.

3. Results and discussion

3.1. Evidences of enhanced current output by Fenton's reaction

The current outputs under two different situations were plotted in Fig. 1. In the first case (Fig. 1a), data showed that the initial addition of $0.2 \text{ g L}^{-1} \text{ Fe}^{2+}$ increased the current from 0.29 to 0.36 mA within 15 min. The sequent addition of $1.0 \text{ g L}^{-1} \text{ H}_2\text{O}_2$ quickly boosted the current output to 0.60 mA. The first current increase resulting from Fe^{2+} was due to its reaction with H_2O_2 that was *in situ* generated from the two-electron reduction of dissolved O_2 , producing $\bullet\text{OH}$ through Fenton's reaction. The sequent addition

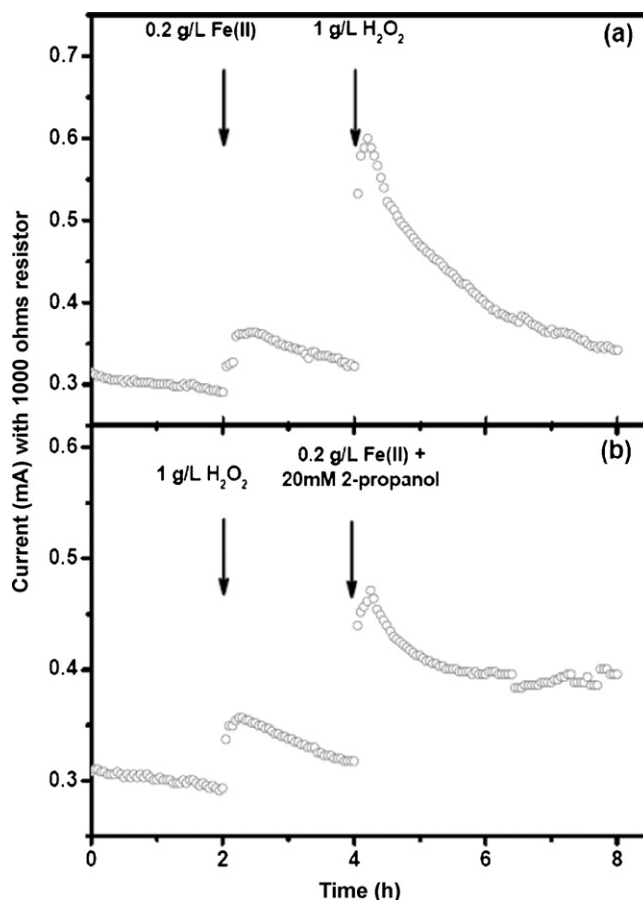


Fig. 1. The current output (mA) at an external resistance of 1000Ω . (a) The cathodic electrolyte firstly added with $0.2 \text{ g L}^{-1} \text{ Fe}^{2+}$ followed by the addition of $1 \text{ g L}^{-1} \text{ H}_2\text{O}_2$; (b) the cathodic electrolyte firstly added with $1 \text{ g L}^{-1} \text{ H}_2\text{O}_2$ followed by the co-addition of $0.2 \text{ g L}^{-1} \text{ Fe}^{2+}$ and 20 mM 2-propanol.

of H_2O_2 intensified the Fenton's reaction and increased the production of $\bullet\text{OH}$, which explained the rapid current increase after H_2O_2 amendment. Meanwhile, obvious gas bubbles and red iron oxides precipitation were observed in the cathode chamber. In the second case (Fig. 1b), the initial addition of H_2O_2 also enhanced the current from 0.29 to 0.36 mA, which was a consequence of H_2O_2 's more efficient cathode oxygenation, in comparison with air [16]. The following co-addition of $0.2 \text{ g L}^{-1} \text{ Fe}^{2+}$ and 20 mM 2-propanol resulted in a current increase from 0.32 to 0.46 mA, which was 40.8% less than the second current increase in the previous case. 2-Propanol, as a scavenger of $\bullet\text{OH}$ radicals [17], would reduce the amount of $\bullet\text{OH}$ radicals. The presence of 2-propanol decreased the contribution of Fenton's reaction to the improvement of current output, suggesting that the active species to enhance current output were the $\bullet\text{OH}$ radicals from Fenton's reaction.

This study demonstrated that Fenton's reaction can effectively improve the current output in MFCs and the principal active species was the highly oxidizing agent of $\bullet\text{OH}$ radicals. However, the enhanced performance by Fenton's reaction declined quickly due to the rapid consumption of the reagents required for Fenton's reaction.

3.2. Sustainable increased electricity generation using $\text{Fe@Fe}_2\text{O}_3/\text{NCF}$ composite cathode

In an attempt to approach sustainable increased power output with Fenton's reaction, a $\text{Fe@Fe}_2\text{O}_3/\text{NCF}$ composite cathode was made. Previous study has demonstrated the use of

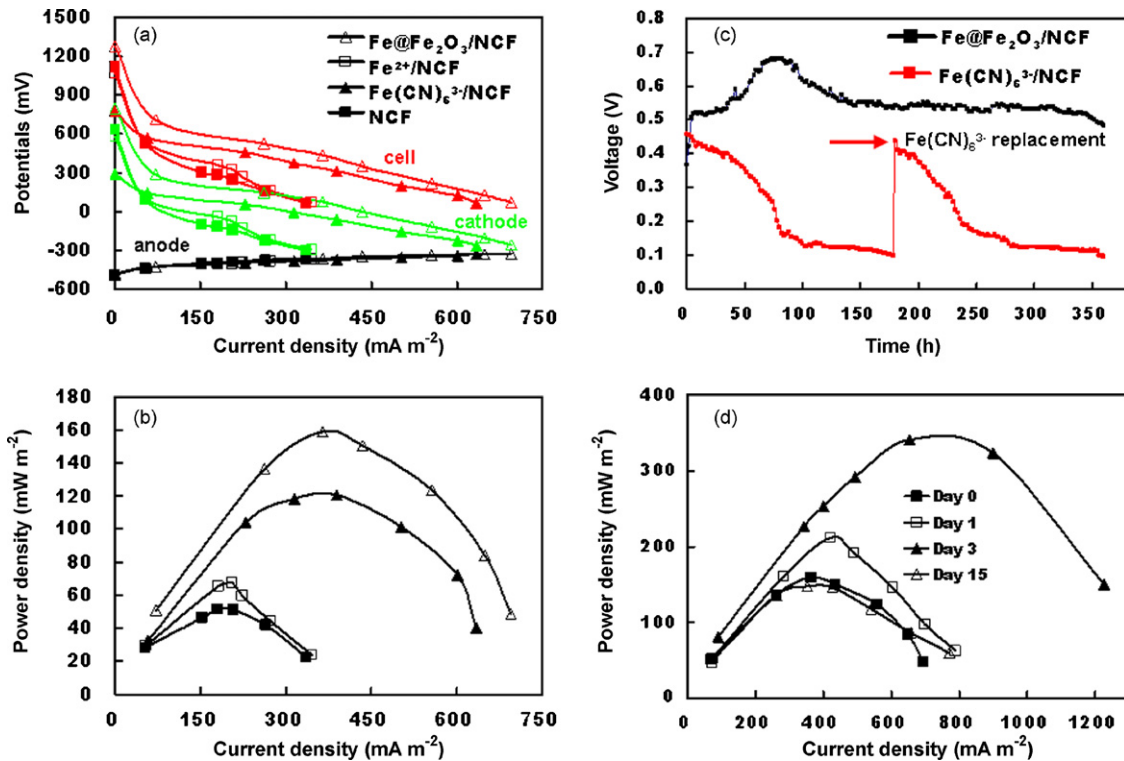


Fig. 2. (a) Electrode potentials (red symbols: cell potential, green symbols: cathode potential, black symbols: anode potential) for the MFCs using NCF, Fe²⁺/NCF, Fe(CN)₆³⁻/NCF and Fe@Fe₂O₃/NCF; (b) power density (normalized to the cathode projected surface area) as a function of current density (same legends as Fig. 2a); (c) the voltage output versus time for the MFCs using Fe@Fe₂O₃/NCF and Fe(CN)₆³⁻/NCF over 15-d operation (at an external resistance of 1000 Ω); (d) The performance of the MFC using Fe@Fe₂O₃/NCF over 15-d operation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fe@Fe₂O₃/ACF (active carbon felt) in a heterogeneous electro-Fenton system, in which the iron reagent leached from Fe@Fe₂O₃ (Fe + 2H⁺ → Fe²⁺ + H₂O) can react with *in situ* electro-generated H₂O₂ [13,18].

Polarization and power density curves for the MFCs using NCF, Fe²⁺/NCF, Fe(CN)₆³⁻/NCF and Fe@Fe₂O₃/NCF were compared and presented in Fig. 2a and b. It was clear that Fe@Fe₂O₃/NCF generated higher voltage output and power density than other MFCs, which was a consequence of the difference in cathode potentials since the anode potentials of all MFCs were similar (Fig. 2a). Fe@Fe₂O₃/NCF produced an open circuit voltage of 1.28 V and a maximum power density of 159.2 mW m⁻², which was comparable to those previous two-chamber MFCs using Co-tetra-methyl phenylporphyrin (CoTMPP), iron phthalocyanine (FePc), lead dioxide as ORR catalyst [19,20]. The better performance of Fe@Fe₂O₃/NCF than Fe²⁺/NCF may be due to the following two reasons: (1) the *in situ* reaction between Fe²⁺ leached from Fe@Fe₂O₃ and H₂O₂ generated from the NCF is more kinetically favorable than the reaction between H₂O₂ from the NCF and Fe²⁺ in the bulk solution; (2) the zerovalent iron in Fe@Fe₂O₃/NCF would react with dissolved O₂ to form the reactive intermediates of HO₂•/O₂⁻, H₂O₂, •OH, which would promote cathode reaction [17]. Over the long-term operation, data (Fig. 2c) showed that Fe@Fe₂O₃/NCF was more capable of producing sustainable power output than Fe(CN)₆³⁻/NCF, which only maintained 21% of initial value even undergoing a replacement of catholyte. The Fe@Fe₂O₃/NCF electrode approached a maximum power density of 341.4 mW m⁻² after 3-d, and the performance did not deteriorate, even after 15-d (Fig. 2c and d). The sustainable increased power generation in the MFC was a consequence of the slow release of iron reagents from Fe@Fe₂O₃ that allowed the continuous generation of •OH via Fenton's reaction.

The improvement of power production in this MFC was mainly due to the high redox potential of •OH from Fenton's reaction. As a

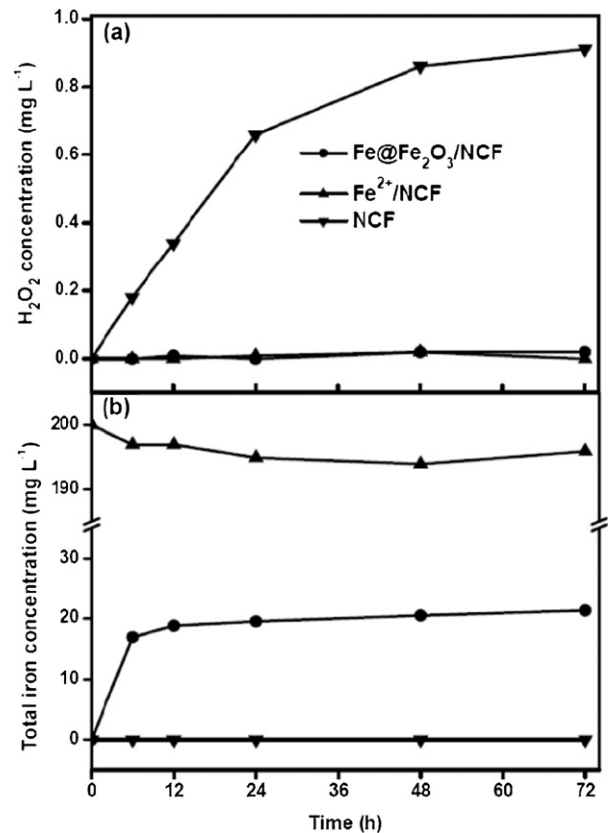


Fig. 3. The concentrations of H₂O₂ (a) and total iron ions (Fe²⁺ and Fe³⁺) (b) versus time in the MFCs using NCF, Fe²⁺/NCF and Fe@Fe₂O₃/NCF.

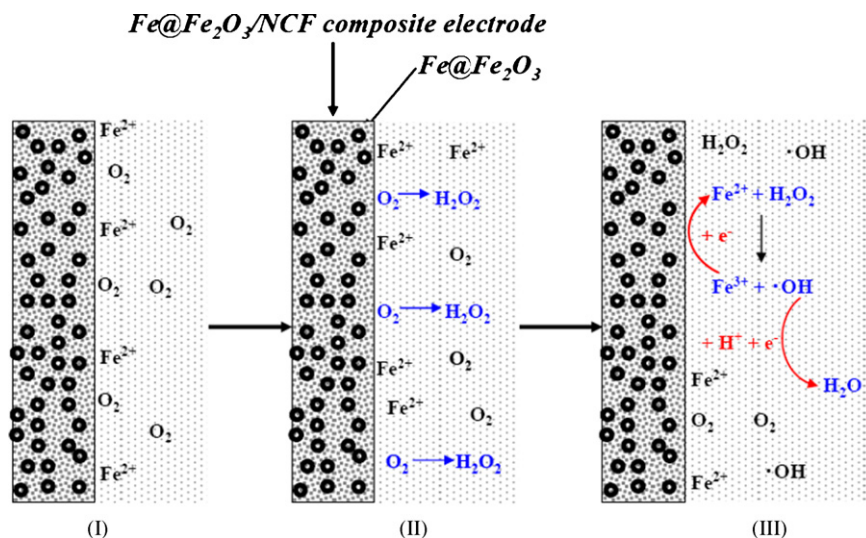


Fig. 4. The proposed pathway of *in situ* Fenton's reaction on Fe@Fe₂O₃/NCF.

highly oxidizing agent of persistent organic contaminants, •OH can react with organic pollutants and thus lead to their degradation [21–23]. Thus, such an MFC configuration provides the possibility for simultaneous electricity generation and bio-refractory pollutant degradation.

To maintain an optimal pH for Fenton's reaction, the addition of hydrochloric acid is required, which requires an extra investment. Previous study demonstrated that low catholyte pH in MFC can be maintained without the need of acid dosage by using bipolar membrane [24]. In further work, we may consider using a bipolar membrane to sustain pH stability and thus reduce the acid addition.

3.3. Proposed mechanism

During MFC operation, the concentrations of H₂O₂ and the total iron ions (Fe²⁺ and Fe³⁺) in the cathodic compartment were monitored (Fig. 3). As shown in Fig. 3a, within 72 h, H₂O₂ accumulated to a maximum value of 0.91 mg L⁻¹ in the NCF, while for Fe²⁺/NCF and Fe@Fe₂O₃/NCF, the concentrations of H₂O₂ were close to the detection limit. This suggested that: (1) H₂O₂ accumulated in the cathode chamber via the two-electron reduction of dissolved O₂ in the MFCs; (2) in the presence of iron agents, the consumption rate of H₂O₂ due to Fenton's reaction was much faster than its production rate. Demonstrated by Fig. 3b, the concentration of total iron ions for Fe@Fe₂O₃/NCF reached a range from 18.9 to 21.4 mg L⁻¹ after 6 h, indicating the presence of iron reagents in Fe@Fe₂O₃/NCF.

Based on the above results, we proposed a potential pathway for sustainable Fenton's reaction on Fe@Fe₂O₃/NCF (Fig. 4). First, oxygen was adsorbed on the surface of carbon felt and the corrosion of Fe@Fe₂O₃ resulted in Fe²⁺ formation. Next, the oxygen reduction via two-electron reaction led to *in situ* H₂O₂ production. Finally, the leached Fe²⁺ reacted with *in situ* formed H₂O₂, producing •OH and Fe³⁺. •OH then reacted with the cathode to form H₂O, and Fe³⁺ can be reduced to regenerate Fe²⁺.

4. Conclusion

This study demonstrated that the •OH produced from Fenton's reaction can significantly increase the current production in MFCs. Although Fenton's reaction is not normally self-sustainable, this work successfully established a relatively sustainable Fenton's reaction by using a Fe@Fe₂O₃/NCF composite cathode,

which produced a maximum power density of 341.4 mW m⁻². This MFC configuration provides a promising approach for continuous high power output and degradation of recalcitrant contaminants.

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