Short Communication

Time behavior and capacitance analysis of nano-Fe₃O₄ added microbial fuel cells

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Highlights
• Kinetic dynamics is dominant over thermodynamics on performance after Fe addition.
• Maximum capacitance of 574.6 C m⁻² is obtained at an optimal interval of 20 min.
• Fe₃O₄/Fe(II) may be the solid mediator for extracellular electron transfer.

Abstract
The addition of nano Fe₃O₄ is beneficial to boost the transient charge storage of the anode accompanying with the enhancement of power performance in microbial fuel cells (MFCs) in our previous study. Here we found that both the anodic open circuit potential and the current increased when comparing the AcFeM (Fe₃O₄ added activated carbon anode) with the AcM (activated carbon anode), indicating that the Fe₃O₄ dynamically accelerated the anodic electron transfer although it thermodynamically limited the anode potential. The net storage capacity initially increased followed by a decrease with the maximum capacitance of 574.6 C m⁻² (AcFeM) and 459 C m⁻² (AcM) under 20 min of open circuit interval. The Fe₃O₄/Fe(II) possibly stored charges temporarily as a solid-state electron shuttle.

1. Introduction
Microbial fuel cell (MFC), one of emerging-energies, appears as a promising technology for power generation from organic or inorganic pollutants (Logan and Regan, 2006). The anodic performance, mainly limited by the inefficient extracellular electron transfer (EET) between the anode and the exoelectrogenic bacteria (most are dissimilatory metal reducing bacteria, DIRB), needs to be improved when the feasibility of commercial application is considered.

It has been reported that iron(III) oxide is reduced as the natural terminal electron acceptor of DIRB (Nakamura et al., 2009) and conducive to boost the EET (Lower et al., 2001) with advantages of good biocompatibility, environmental stability and low cost. Magnetite (Fe₃O₄) with the spatial structure of Fd₃m has exhibited a unique electric property due to its transfer of electrons between Fe(II) and Fe(III) in octahedral sites (Zhang et al., 2008) and the higher conductivity (σ = 2 × 10⁴ S m⁻¹) than most of other metal oxides (Li et al., 2012), making it as a good material for electrochemical capacitors (Chen et al., 2009). It is interesting that the addition of Fe₃O₄ to the anode not only enhanced the power output...
but also increased the anodic capacitance (Peng et al., 2012). This would be a good amendment for the anodic stability to avoid power overshoot (Peng et al., 2013b). However, limited information is given to the storage capacity and the mechanism in our previous study.

In the present work, a composite anode (AcFeM) made of activated carbon powder (AC, SPC-01, Xinsen Carbon Co. Ltd., Fujian, China)/nano Fe₃O₄ (self-prepared)/stainless steel mesh (SSM, type 304L, 80 × 80 mesh, 0.2 mm in thickness, Anping County Shengze Screen Co., Ltd, Hebei, China) was assembled by roll-press technique. Fe₃O₄ was utilized mainly as a promoter for EET and capacitance, and the SSM was the matrix and current collector. The charge storage at different charge–discharge interval was investigated with comparison between AcFeM and AcM (AC with SSM) anodes. And the possible mechanism was analyzed from the physicochemical and electrochemical perspectives.

2. Methods

2.1. Fabrication of MFCs anodes

Prior to use, the SSM was ultrasonically cleaned to remove the grease using acetone and ethanol for 10 min each, followed by rinsing with distilled water and drying at 60 °C. AC powder, Fe₃O₄ powder and polytetrafluoroethylene (PTFE; 60 wt.%; Horizon LID, Shanghai, China) emulsion were mixed with a mass ratio of 18:1:1 in ethanol under ultrasonic bath for 20 min to create a highly dispersed mixture as previously reported (Peng et al., 2012). This mixture was then heated at 80 °C until it resembled an ointment in appearance, and then was roll-pressed into a flexible film (0.2 mm in thickness). Finally, the film was roll-pressed onto the SSM. The AcM anode was prepared according to the same procedure without Fe₃O₄ addition. Anodes were cut into circles with the same diameter of 4 cm, and then dried at 70 °C for ethanol evaporation before using.

2.2. Operation and measurements

Single chambered MFCs with anodes and cathodes placed on the opposite sides of cylindrical membrane-less reactors (4 cm long by 3 cm in diameter; net volume of 28 mL; 7 cm² project area) were operated in parallel under batch mode. The prepared electrodes were used as anodes with the AcM as the positive control. Air–cathode was made of carbon mesh (10 wt.% wet proof, Jilin Carbon Plant Co. Ltd., China) with four PTFE diffusion layers on the air side and 0.5 mg cm⁻² platinum loaded as catalyst on the water-facing side according to Wang et al. (2012). Electrodes were connected to the external resistance (1 kΩ expected as noted) with titanium wires. MFCs were initially inoculated using the effluent from MFCs operated under the similar condition. The medium was 50 mM phosphate buffer solution (PBS, conductivity of 6.82 mS cm⁻¹) with sodium acetate (1 g L⁻¹) as the electron donor according to our previous report (Peng et al., 2013a). The medium was refreshed to form a complete cycle when the voltage decreased below 20 mV. Electrochemical tests were performed when similar voltage was produced over three consecutive cycles.

The in situ bio–electrochemical measurements were performed in MFCs, with anodes as the working electrode, air–cathodes as the counter electrode and an Ag/AgCl reference electrode placed close to the anode. Anodic capacitance test was conducted at a poised anode potential of −0.4 V (versus Ag/AgCl) using a multichannel potentiostat (CHI1000B, CH Instruments Inc., China) based on charge–discharge experiment with different charge and discharge periods: open circuit intervals of 5, 10, 20, 30 and 60 min accompanied with 10, 20, 40, 60 and 120 min of connected circuit respectively. Cyclic voltammetry (CV) of biotic anode was conducted under acetate depletion condition by a potentiostat (CHI660D, CH Instruments Inc., China) with a sweep rate of 0.1 mV s⁻¹ over the potential range of −0.8 to 0 V (versus Ag/AgCl). Abiotic tests were performed by soaking anodes in 50 mM PBS for 48 h to allow the electrolyte to impregnate the pores inside AC particles. All the measurements were carried out in a 30 ± 0.5 °C temperature-controlled biochemical incubator in duplicate.

3. Results and discussion

3.1. Time behavior of open-circuit potential and closed-circuit current

With the external circuit interruption conducted periodically, five repeats were performed to analyze the variations of biotic anode potentials and currents (Figs. 1 and S1 in supporting information). With the addition of Fe₃O₄, a negative effect was observed that the anodic open circuit potential (OCP) became more positive in all tests in Figs. 1 and S1. This can be interpreted by the change of redox environment with and without Fe₃O₄. The OCP of the carbon anode was considered to be determined by the redox potential

![Fig. 1. The current density and OCP (inset) behaviors with charge–discharge period of 60–120 min.](image-url)
of NADH/NAD\(^+\) (Wang et al., 2011). Whereas, the redox potential of Fe\(_2\)O\(_3\)/Fe(II) (Weber et al., 2006) is more positive, which thermodynamically made the anodic OCP more positive. The difference of OCP before and after Fe\(_2\)O\(_3\) addition was 3–5 mV, with a value comparable with the potential difference between Fe\(_2\)O\(_3\)/Fe(II) and NADH/NAD\(^+\) (6 mV).

A transient peak current far more over those at steady state was observed for both AcM and AcFeM anodes, suggesting that electrons gathered from the metabolism at open circuit condition were released to the cathode as soon as the external circuit was connected (Figs. 1 and S1). The higher temporary current produced, the more charge stored during intermittent period.

Either temporary or stable current showed in Figs. 1 and S1 was increased after the addition of Fe\(_2\)O\(_3\), which can be attributed to the kinetic acceleration of electron transfer at the interface of the cell membrane and the electrode. In case of 10 min of interval, the peak and steady current density increased by 42% and 16% from 2.67 and 1.43 A m\(^{-2}\) (AcM) to 3.80 and 1.76 A m\(^{-2}\) (AcFeM). Correspondingly, cumulative charge (Q\(_{c}\)) and produced charge (Q\(_{p}\)) (Table S1) increased by 26% and 23% from 193.2, 321.8 to 574.6 C m\(^{-2}\) (AcFeM), with respective values 30–63% and 32–63% higher than those (1490 ± 22345/15, 1296 = 19440/15 C m\(^{-2}\)) of AC pasted graphite plate anodes (Deeke et al., 2012), probably due to the differences in inoculation and electrode materials.

However, the net charges stored in intermittent operation initially increased with the increase of the interruption time from 5 min until reaching a maximum at an interval of 20 min, with values decreased as AcFeM (from 193.2, 321.8 to 574.6 C m\(^{-2}\)) > AcM (from 144.7, 217.3 to 459 C m\(^{-2}\)) > AcFeM (from 537.5 to 437.6 C m\(^{-2}\)) at the interval of 20 min for MFCs with and without Fe\(_2\)O\(_3\) (Fig. S3). As described above, the biofilm attached on the anode is analogous an electrochemical capacitor where the transient charges from oxidative/reductive enzymes store on the cell membrane and in the cytoplasm. With the growth of the biofilm, the biotic capacitance increased following the order: AcFeM (2.4 F cm\(^{-2}\)) > AcM (1.8 F cm\(^{-2}\)). The AcM anode exhibited a rectangular CV curves without obvious oxidative peaks, which was the characteristic of double-layer capacitance (Ren et al., 2012). However, for the Fe\(_2\)O\(_3\) added anode, redox peaks was clearly observed with quadrilateral-shape region (Fig. S3) as a pseudo-capacitance behavior, probably due to the oxidation/reduction of Fe\(_2\)O\(_3\) (Wang et al., 2011) and their adsorption capacity on AC surface. Since the redox potential (–0.314 V) (Weber et al., 2006) of Fe\(_2\)O\(_3\)/Fe(II) is higher than that of NADH/NAD\(^+\) (–0.320 V) (Wang et al., 2011) but lower than that of cytochrome c (–0.212 V) (Li et al., 2011), the magnetite can be reduced by DIRB to Fe(II) accompanied with Fe\(_2\)O\(_3\) formation through anaerobic bio-oxidation of soluble Fe(II), where Fe\(_2\)O\(_3\) acts as a solid-state electron shuttle with the ability to store charges temporarily. Thus, the capacitance of AcFeM can be from following three aspects: pore structure of carbon, capacitor-like behavior of anodic biofilm and the redox couple of Fe\(_2\)O\(_3\)/Fe(II) at the interface of biofilm and the anode (Fig. 3).

### 4. Conclusion

Both anodic open-circuit potential and current density increased when Fe\(_2\)O\(_3\) was added into the anode, indicating a dynamical acceleration of extracellular electron transfer accompanied with a thermodynamical inhibition on potential. The anodic transient storage capacities reached maximum values of 574.6 and 459 C m\(^{-2}\) at the interval of 20 min for MFCs with and without Fe\(_2\)O\(_3\). The capacitance was from pores of the electrode, anodic biofilm and the redox couple of Fe\(_2\)O\(_3\)/Fe(II) as an electron shuttle. These results showed more information about anodic electron transfer and storage.
Acknowledgements

This research was supported by National Natural Science Foundation of China (NSFC, Nos. 21107053 and 51208352), Tianjin Research Program of Application Foundation and Advanced Technology (Nos. 13JCQNJC08000 and 13JCQNJC09100), National Science & Technology Program of China on Water Pollution Control and Treatment (2012ZX07501002) and the scholarship for excellent PhD student from Shanghai Tongji Gao Tingyao Environmental Science & Technology Development Foundation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2013.07.037.

References