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Characterization and optimization of cathodic conditions for H_2O_2 synthesis in microbial electrochemical cells

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HIGHLIGHTS

- H_2O_2 conversion efficiency increased by 65% using O_2 diffusion.
- The maximum H_2O_2 production rate was 141 mg H_2O_2/L-h.
- O_2 diffusion to the cathode would be rate-limiting for H_2O_2 production.

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ABSTRACT

Cathode potential and O_2 supply methods were investigated to improve H_2O_2 synthesis in an electrochemical cell, and optimal cathode conditions were applied for microbial electrochemical cells (MECs). Using aqueous O_2 for the cathode significantly improved current density, but H_2O_2 conversion efficiency was negligible at 0.3–12%. Current density decreased for passive O_2 diffusion to the cathode, but H_2O_2 conversion efficiency increased by 65%. An MEC equipped with a gas diffusion cathode was operated with acetate medium and domestic wastewater, which presented relatively high H_2O_2 conversion efficiency from 36% to 47%, although cathode overpotential was fluctuated. Due to different current densities, the maximum H_2O_2 production rate was 141 mg H_2O_2/L-h in the MEC fed with acetate medium, but it became low at 6 mg H_2O_2/L-h in the MEC fed with the wastewater. Our study clearly indicates that improving anodic current density and mitigating membrane fouling would be key parameters for large-scale H_2O_2-MECs.

1. Introduction

H_2O_2 is a powerful oxidant that can be used for advanced oxidation, odor control, sludge pre-treatment, and membrane cleaning (Eskicioglu et al., 2008; Jo et al., 2011; Hijnen et al., 2012). H_2O_2, however, is not cheap, which limits its wide application to water and wastewater treatment. High concentration of H_2O_2 over 50% has been typically used in field, and hence the transport and storage of concentrated H_2O_2 is another limitation for the H_2O_2 application.

Microbial electrochemical cells (MECs), that include microbial fuel cells and microbial electrolysis cells, are able to produce H_2O_2 from organic wastewater by using two electrons reduction of O_2 into H_2O_2 on the cathode in MECs (Rozendal et al., 2009), which can address the existing challenges of H_2O_2 costs and handling in sustainable manners. Several works proved H_2O_2 synthesis using MECs (Rozendal et al., 2009; Fu et al., 2010; Chen et al., 2014; Arends et al., 2014; Modin and Fukushi, 2013), but H_2O_2 production is not consistent. Different cathode conditions (e.g., cathode potential or O_2 supply method) seem to affect H_2O_2 yield and production rate in previous works. Rozendal et al. (2009) reported relatively high concentration of H_2O_2 close to 1300 mg/L at applied voltage 0.5 V (the conversion efficiency from coulombs to H_2O_2 84%); the cathode potential in this work would be close to −0.7 V (vs. SCE). Arends et al. (2014) also reported high H_2O_2 concentration of 26,000 mg/L at cathode potential fixed at −0.23 V (vs. Ag/AgCl) (H_2O_2 conversion 40%). In comparison, other studies have reported very low H_2O_2 concentration, ranging from 79 to 196 mg/L (H_2O_2 conversion 69–70%) in MECs in which cathode potential was −0.25–0.3 V (vs. SCE) (Fu et al., 2010; Chen et al., 2014). Current density would mainly account for H_2O_2 concentration, but H_2O_2 conversion efficiency (from coulombs to H_2O_2) can also affect H_2O_2 concentration. In fact, H_2O_2 is not stable in a cathode chamber of MECs. H_2O_2 decomposition

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to O_2 and H_2O in liquid phase can decrease H_2O_2 yield (Choudhary and Gaikwad, 2003). At the same time, the H_2O_2 reduction to H_2O on the cathode, that is thermodynamically more favorable than O_2 reduction to H_2O_2 on the cathode, can reduce H_2O_2 yield in MECs. The standard potential (E°) for H_2O_2 reduction to H_2O is 1.76 V vs. SHE, while E° for O_2 reduction to H_2O_2 is 0.7 V. H_2O_2 yield will be smaller as current density increases in MECs due to cathode polarization that can more drive H_2O_2 reduction to H_2O on the cathode (Fu et al., 2010; Song and Zhang, 2008). Unfortunately, cathode polarization seems essential to improve H_2O_2 formation kinetics for engineering H_2O_2-MECs. In the mode of microbial fuel cells, H_2O_2 production rate is too small (Rozendal et al., 2009; Fu et al., 2010; Chen et al., 2014) so that the application of H_2O_2-MECs to water and wastewater treatment will be seriously limited. Several works provided external power for MECs to improve H_2O_2 production rate, and showed the improvement of H_2O_2 production rate by 54–79 mg H_2O_2/L-h (Rozendal et al., 2009; Arends et al., 2014), which is 5–14 times faster than the H_2O_2 rate in microbial fuel cell mode (6.6–10 mg H_2O_2/L-h) (Fu et al., 2010; Chen et al., 2014). For the success of H_2O_2-MECs, cathode potential should be optimized to meet fast kinetics and high yield for H_2O_2, but there is limited information on the relationship between cathode potential, and H_2O_2 kinetics and yield.

In addition to cathode potential conditions, O_2 supply methods (the supply of aqueous O_2 vs. O_2 gas to the cathode) should be also rectified for successful application of H_2O_2-MECs. Passive O_2 diffusion from air to gas diffusion cathode can save operating costs substantially, but the mass transport of O_2 to the cathode would be limited under passive O_2 diffusion conditions, especially for cathode-polarized conditions leading to high current density. For instance, Rozendal et al. (2009) reported high H_2O_2 production rate of 79 mg H_2O_2/L-h using passive diffusion of O_2 gas to a cathode, but other works using O_2 gas diffusion showed H_2O_2 production rate as low as 6 mg H_2O_2/L-h (Chen et al., 2014; Modin and Fukushi, 2013). Sluggish kinetics on the anode (like kinetically poor anode-respiring bacteria) or large ohmic resistances can lower current density and H_2O_2 formation rate, but mass transport limitation for O_2 to the cathode cannot be ruled out for low H_2O_2 production rate in MECs utilizing passive O_2 diffusion. For instance, Arends et al. (2014) using aqueous O_2 as an oxidant to the cathode recently reported 54 mg H_2O_2/L-h, which is much faster than H_2O_2 production rate in recent studies using passive O_2 diffusion to the cathode (Chen et al., 2014; Modin and Fukushi, 2013), but less than the rate from the literature (Rozendal et al., 2009). Despite the significance of O_2 supply methods for commercialization of H_2O_2-MECs, there are no studies of comparing aqueous and gaseous O_2 for H_2O_2 synthesis.

In this work, cathode potential was optimized for H_2O_2 production rate and yield with electrochemical cells using aqueous O_2 as electron acceptor to cathodes. Then, O_2 supply methods (passive O_2 gas diffusion vs. direct aeration to catholytes) were compared at fixed cathode potential. Finally, performance of a H_2O_2-MEC using selected cathode potential and O_2 provision means was assessed using acetate medium and domestic wastewater as substrate.

2. Methods

2.1. Reactors configuration

Two dual-chamber electrochemical cells were constructed in the engineering machine shop at the University of Waterloo for experiments: cell #1 and cell #2 were exploited in abiotic and biotic experiments, respectively. The electrochemical cell #1 consists of an anode and a cathode chamber, which are partitioned by a membrane. Both chambers are made from cylindrical plexiglass and the working volumes of the anode and the cathode are 35 and 25 mL, respectively. A graphite plate (Isomolded Graphite Plate 203101, Fuel Cell Earth) was selected as the anode. For the cathode, a graphite cathode (GC) (Isomolded Graphite Plate 203101, Fuel Cell Earth, USA) and a gas diffusion cathode (GDC) (GDS2230 carbon fiber, Fuel Cell Earth, USA) were compared to optimize H_2O_2 production. Both anode and cathode had the projected surface area of 17.4 cm^2. Cation exchange membrane (CEM) (CMI-7000, Membranes International Inc., USA) with the projected surface area of 17.4 cm^2 was used as the membrane. An Ag/AgCl reference electrode (MF-2052, Bioanalytical System Inc. (BASi, USA) was located ~0.5 cm apart from the cathode to control cathode potential ($E_{cathode}$) using a potentiostat (BioLogic, VSP, Gamble Technologies, Canada); here, we reported $E_{cathode}$ vs. Ag/AgCl reference electrode.

The cell #2 was operated as microbial electrochemical cell (MEC) fabricated with cylindrical plexiglass. The MEC comprises an anode and a cathode chamber whose working volumes are 289 and 70 mL, respectively. High density carbon fibers (2293-A, 24A Carbon Fiber, fiber Glast Development Corp., Ohio, USA) connected with a stainless steel frame (current collector) was used as an anode module with approximate surface area of 4480 cm^2 (An and Lee, 2013; Dhar and Lee, 2014). The anode module was designed to improve the biofilm density of anode-respiring bacteria (ARB) per membrane surface area that determines MEC footprint in dual-chamber configuration. The carbon fibers were pretreated with nitric acid (1 N), acetone (1 N), and ethanol (1 N) prior to use (Lee et al., 2009). The GDC (GD2230, Fuel Cell Earth, USA) with the projected area of 33 cm^2 was used as the cathode in the MEC in which O_2 in the air passively diffuses to the cathode. The distance between the anode and the cathode was 2 cm. The CEM (CMI-7000, Membranes International Inc., USA) with the surface area of 33 cm^2 was employed as the membrane. An Ag/AgCl reference electrode (MF-2052, Bioanalytical System Inc.) was placed ~0.5 cm apart from the anode module to fix anode potential (E_{anode}) at −0.4 V using the potentiostat during tests.

2.2. Inoculation and operation

The electrochemical cell #1 was operated for abiotic experiments (no microorganisms on the anode) in which the effect of various parameters ($E_{cathode}$, cathode material, and aeration method) on H_2O_2 production was investigated. The anode and the cathode chambers in cell #1 were filled with tap water and the cell #1 was operated in batch mode. For the first set of the abiotic experiments, the GC and the GDC for H_2O_2 production were compared under identical $E_{cathode}$ and aeration method. The cathode chamber was aerated with an air blower (DW-12, Tetron Product, Taiwan) at a flow rate of 860 mL/min, and the $E_{cathode}$ was changed at −0.4, −0.6, and −0.8 V. In the second set of the abiotic experiments in which the GDC only was used as the cathode, oxygen molecules passively diffused to the GDC, and $E_{cathode}$ was varied at −0.4, −0.6, and −0.8 V. For each experimental run in the abiotic experiments, cell #1 was operated for 180 min, and 0.5 mL sample was collected from the cathode chamber every 30 min for H_2O_2 quantification. Current, electrode potential, and cell voltage were monitored using EC-Lab software in a personal computer connected with the potentiostat.

The H_2O_2-generating MEC was inoculated with 10 mL of the effluent from an existing MEC that had been operated with acetate medium (25 mM acetate medium) for over 6 months. The composition of the medium was (per L of 18.2 MΩ cm MilliQ water) 2050 mg/L CH_3COONa, 2274 mg KH_2PO_4, 11,678 mg $Na_2HPO_4{\cdot}12H_2O$, 37 mg NH_4Cl, 25 mg $MgCl_2{\cdot}6H_2O$, 6 mg $MnCl_2{\cdot}4H_2O$, 0.1 mg $CuSO_4{\cdot}5H_2O$, 0.1 mg $Na_2WO_4{\cdot}2H_2O$, 0.1 mg $NaHSeO_3$, 0.01 mg $CaCl_2{\cdot}2H_2O$, 0.5 mg $ZnCl_2$, 0.1 mg $AlK(SO_4)_2$,