Bioresource Technology 172 (2014) 429–432

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Short Communication

Percarbonate as a naturally buffering catholyte for microbial fuel cells

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HIGHLIGHTS

- The new percarbonate catholyte provides good performance in MFCs.
- Percarbonate provides natural buffering capacity.
- Percarbonate prevents biofouling and safe to use.

ARTICLE INFO

Article history:
Received 13 June 2014
Received in revised form 29 August 2014
Accepted 4 September 2014
Available online 16 September 2014

Keywords:
Percarbonate
Microbial fuel cell
Bioelectrochemical system
Cathode
Catholyte

ABSTRACT

Sustainable cathode development has been a challenge for the emerging microbial fuel cell (MFC) technology. This study presents a simple catholyte called sodium percarbonate to serve as a new type of electron acceptor for MFCs. Lab scale comparisons showed sodium percarbonate cathode obtained comparable power density (9.6 W/m^3) with traditional air–cathode and potassium ferricyanide, but percarbonate showed multiple additional benefits that no other catholyte had demonstrated. Percarbonate has a sustaining natural buffering capacity that can counter pH fluctuations seen in many other systems, and the peroxide produced prevents bio-fouling problems associated with air–cathodes. It is also safer to use and has the lowest cost among popular cathode options based on per mole of electron transferred, which makes it a good candidate for modular system scale up.

1. Introduction

The development of microbial fuel cell technology platform has led to major advances in sustainable wastewater treatment, environmental remediation, energy and chemical production, and many other areas (Li et al., 2014; Logan and Rabaey, 2012; Wang and Ren, 2013). With over a decade of research, a wide range of systems with different functions have been developed, but one main challenge on microbial fuel cell scale up for wastewater treatment and other applications is the cathode reaction, especially when oxygen is used as the terminal electron acceptor. While oxygen in air is free thus ideal for larger scale applications, oxygen reduction reaction (ORR) is a complicated 3-phase reaction and generally requires high cost metal catalysts and materials. Early lab scale MFC studies avoided ORR by using ferricyanide, permanganate, or persulfate as the catholytes (Li et al., 2009; Ren et al., 2007; You et al., 2006), which provide stable and relatively high cathode potential, but these chemicals cannot be used in engineering applications, because they are expensive and can be toxic that requires complicated procedure for hazardous waste disposal. While there have been great development in air–cathode, which reduced or replaced platinum with cheaper alternative catalysts or used catalyst-free cathodes such as activated carbon and carbon nanotubes, the system performance generally is lower due to the slowed ORR kinetics (Cheng et al., 2006; HaoYu et al., 2007; Wang et al., 2011; You et al., 2006; Zhao et al., 2006). Current single chamber air–cathode designs use multiple layers of coating or pressing with the attempt to maximize air diffusion yet prevent solution loss from the system, but it is a double-edged sword that either low ORR kinetics or significant water leak due to static pressure were reported, especially in larger scale reactors. (Cheng et al., 2006; Zhang et al., 2012, 2011b) Another main obstacle of MFC air–cathode reaction is the catholyte pH increase due to the loss of protons for water production. For example, Nam et al. (2010) reported that without using buffer, the pH could increase to 8.5 in a single cycle, and other studies even produced caustic base solution (pH > 12) in two chamber systems (Nam et al., 2010; Rabaey et al., 2010). To keep a neutral pH, most studies use buffer solution to temporarily mitigate the problem, but it is not applicable in larger scale systems due to the very high cost applications.

In this study, we present a new low-cost catholyte called sodium percarbonate for solving these challenges. Sodium percarbonate is one type of oxygen releasing compounds (ORC) also

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http://dx.doi.org/10.1016/j.biortech.2014.09.014

known as solid state peroxide, because the molecular structure of the chemical is hydrogen peroxide bound to sodium carbonate. Hydrogen peroxide use as a catholyte has been investigated in an MFC with results showing improvements over pure oxygen, but the peroxide itself is not stable therefore cannot last for sustained reactions (Tartakovsky and Guiot, 2006). When sodium percarbonate is added to water, hydrogen peroxide is released quickly into solution according to Eq. (1):

$$2Na_2CO_3 \cdot 3H_2O2 \rightarrow 2Na_2CO_3 + 3H_2O_2 \qquad (1)$$

Hydrogen peroxide then reacts with the cathode and receives electrons transferred from the anode. The end product after the reaction is water and sodium carbonate species, which has been known as a pH buffer and can be discharged to the environment safely. We compared sodium percarbonate MFC performance with traditional air–cathode and ferricyanide MFCs and found that percarbonate not only can serve as a low-cost and safe catholyte for MFCs without using catalysts, it also provides excellent buffer capacity for pH stabilization and serves as an anti-foulant for biofouling control.

2. Methods

2.1. MFC reactor design

Traditional cubic two-chamber MFC reactors were used, with each reactor consisting of two polycarbonate blocks that were clamped together to form one anode chamber and one cathode chamber, with the effective volume of 23 mL and 27 mL, respectively (Wang et al., 2011). A graphite brush was used as the anode electrode (Golden Brush, CA) for all reactors. For sodium percarbonate and potassium ferricyanide studies, a 9 cm^2 piece of activated carbon cloth (ACC) (Chemviron Carbon, UK) was used as the cathode material. For the air–cathode reactor, the cathode was made with PTFE diffusion layers described by (Cheng et al., 2006). Cation exchange membrane (CEM) separators were used between the anode and cathode chambers. A 3 cm distance was held between the membrane and cathode for two-chamber MFCs and between the anode and cathode for the single chamber MFC. The anolyte contained per liter: 1.6 g $NaCH_3COO$, 0.62 g NH_4Cl, 4.9 g NaH_2PO_4–H_2O, 9.2 g Na_2HPO_4, 0.3 g KCL, and 10 mL trace metals and 10 mL vitamin solution (Wang et al., 2011). The sodium percarbonate catholyte contained per liter: 5 g/L $2Na_2CO_3$–$3H_2O_2$, 4.9 g/L NaH_2PO_4–H_2O, 9.2 g/L Na_2HPO_4 (16.1 mS/cm), the potassium ferricyanide catholyte contained 8.2 g/L $K_3Fe(CN)_6$, 4.9 g NaH_2PO_4–H_2O, 9.2 g Na_2HPO_4 (20.1 mS/cm) and the catholyte for the air cathode was 4.9 g NaH_2PO_4–H_2O, 9.2 g Na_2HPO_4 (12.0 mS/cm). The anode electrode was inoculated with activated sludge from the Broomfield Wastewater Treatment facility (Broomfield, CO).

2.2. Reactor operation, analysis and calculations

All three reactors were initially acclimated using potassium ferricyanide as the catholyte. After three repeatable batch voltage profiles for each reactor reached greater than 500 mV at 1000 Ω external resistance with less than 20 mV difference between the three reactors (Huggins et al., 2014), the membranes and the cathode electrodes were replaced with their respective cathodes/catholyte and new membranes were inserted. Dissolved oxygen (DO) measurements were recorded using a DO probe (HACH, CO). Cathode potentials were recorded using a Gamry potentiostat with an Ag/AgCl reference electrode inserted into the cathode chamber. Voltage data was recorded using a data recording system (model 2300, Keithley Instruments, OH). Power density was determined by linear sweep voltammetry (LSV) with the scan rate of 0.1 mV/s using the potentiostat.

Internal resistance was measured using electrochemical impedance spectroscopy (EIS) with the cathode electrode as the working electrode, the anode as the counter electrode, and an Ag/AgCl electrode next to the working electrode as a reference. pH was measured in both the anode and cathode chambers before and after the experiments.

Buffer capacity was determined outside of the MFC in a 50 mL beaker (Luo et al., 2012). 1 M HNO_3 acid solution was used to adjust the pH, while being monitored by a pH probe (HACH, CO). 1 g/L, 5 g/L, and 10 g/L sodium percarbonate concentrations were investigated over three time points 1, 24, and 48 h. Buffer capacity was calculated as:

$$\beta = \frac{\Delta B}{\Delta \mathrm{pH}}$$

where β is buffer capacity, ΔB is gram equivalent of strong acid, ΔpH is change in pH.

3. Results and discussion

3.1. Power output, cathode potential, internal resistance, and voltage output comparison

Initially the results voltage profile for the three reactors fluctuated as the microbes recovered from opening the reactor to replace the membrane and the cathode. After a 1–2 day re-acclimation period the voltage profile for all three reactors were stabilized. Under a 1000 Ω resistance, the maximum voltage obtained for the ferricyanide, platinum air–cathode, and percarbonate cathode was 560 mV, 530 mV, and 520 mV, respectively. Fig. 1 shows the power density curves obtained from the reactors, which demonstrates that the ferricyanide cathode had the highest power density 13.8 W/m^3 (416 mW/m^2), the sodium percarbonate cathode obtained 9.6 W/m^3 (289 mW/m^2), and the air cathode produced the lowest power with 8.2 W/m^3 (246 mW/m^2) (Fig. 1). The cathode potential data largely correlate with the power output, with ferricyanide showed the highest potential of 350 mV followed by the air cathode (250 mV) and percarbonate (200 mV, data not shown). Interestingly, despite having the lowest cathode potential, the percarbonate reactor showed comparable power output with the Pt-coated air cathode. One possible explanation for this is that sodium carbonate has a pKa value of 10.3, and carbonate species in the electrolyte have been demonstrated to improve hydroxide transfer to the cathode electrode (Popat et al., 2012). Additionally, because the electrode is given directly hydrogen peroxide, the

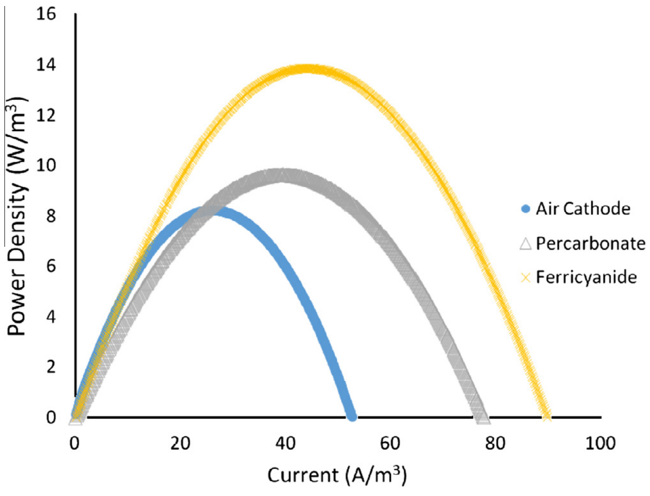

Fig. 1. Volumetric power density curves of the three cathode or catholytes.