Bioresource Technology 233 (2017) 399–405

Contents lists available at ScienceDirect

Bioresource Technology

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

Assessment of a metal–organic framework catalyst in air cathode microbial fuel cells over time with different buffers and solutions

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HIGHLIGHTS

- Metal organic framework (MOF) catalysts greatly increased power using acetate.
- MOF cathodes had a larger percent decrease in power after 4 weeks than AC.
- Power after 8 weeks with MOF cathodes was still 41% higher than plain AC.
- Power with wastewater after 8 weeks was 53% higher than reported for Pt/C.
- Power using wastewater was more affected by changes in composition than time.

ARTICLE INFO

Article history:
Received 14 January 2017
Received in revised form 17 February 2017
Accepted 22 February 2017
Available online 27 February 2017

Keywords:
Air cathode
Fe–N–C/AC catalyst
MFC
MOF
Power density

ABSTRACT

Metal–organic framework (MOF) on activated carbon (AC) enhanced the performance of cathodes but longevity needs to be considered in the presence of metal chelators or ligands, such as phosphate, present in wastewaters. MOF catalysts on AC initially produced 2.78 ± 0.08 W m^{-2}, but power decreased by 26% after eight weeks in microbial fuel cells using a 50 mM phosphate buffer (PBS) and acetate due to decreased cathode performance. However, power was still 41% larger than that of the control AC (no MOF). Power generation using domestic wastewater was initially 0.73 ± 0.01 W m^{-2}, and decreased by 21% over time, with power 53% larger than previous reports, although changes in wastewater composition were a factor in performance. Adding phosphate salts to the wastewater did not affect the catalyst performance over time. While MOF catalysts are therefore initially adversely affected by chelators, performance remains enhanced compared to plain AC.

1. Introduction

Microbial fuel cells (MFCs) are devices that use bacteria to directly produce electricity from biodegradable organic matter. In an MFC, exoelectrogenic bacteria on the anode oxidize the organic matter in solution and release electrons to the anode. The electrons are conveyed through an external circuit to the cathode, where oxygen reduction reaction takes place (Logan et al., 2006; Logan, 2008; Lovley, 2006). MFCs were originally constructed using cathodes containing precious metal catalysts like platinum, due to its high catalytic activity (Cetinkaya et al., 2015; Rozendal et al., 2008). However, these cathodes are expensive and they are rapidly deactivated due to poisoning or loss of Pt from the cathode (Li et al., 2016; Zhang et al., 2014). The discovery that activated carbon (AC) had an oxygen reduction catalytic activity similar to Pt in MFCs, and much greater longevity, enabled the development of relatively inexpensive MFC cathodes that could have relatively stable performance over several months (Pant et al., 2010; Zhang et al., 2014; Zhang et al., 2013, Watson et al., 2013).

In order to further improve MFC cathode performance, different procedures have been used to modify the AC to increase the kinetics of the oxygen reduction reaction, and consequently increase power (Mustakeem, 2015). The most successful approaches to improve the catalytic activity have been based on adding high concentrations of nitrogen into the catalyst (Feng et al., 2011; Shi et al., 2012). Even greater performance has been obtained using less nitrogen in a metal–organic framework (MOF) (Bezerra et al., 2008; Yang and Logan, 2016). MOFs are extended crystalline structures wherein metal cations or clusters of cations are connected to organic ions or molecules (Kreno et al., 2012). Several metals and many organic molecules can be used, and each combination provides unique characteristics of porosity and chemical structure. MOFs have been implemented as electrochemically active materi-

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http://dx.doi.org/10.1016/j.biortech.2017.02.105
0960-8524/

als for different energy conversion applications (Corma et al., 2010; Jiang et al., 2011). Jasinski (1964) discovered that cobalt phthalocyanine can catalyse the oxygen reduction reaction (ORR), and Xiao et al. (2013) studied the structure of this material. The addition of inexpensive metal (iron) and an organic ligand containing nitrogen (1,10–phenanthroline) at high temperatures was used to generate this MOF on AC, which improved the ORR and MFC cathode performance, increasing power densities from 1.6 ± 0.1 W m^{-2} to 2.6 ± 0.05 W m^{-2} with the MOF catalyst (Yang and Logan, 2016). Most of the studies using nitrogen–amended or MOF modified cathodes have been conducted with acetate in phosphate buffer solutions, rather than with actual wastewaters (Pan et al., 2016). In one study, it was shown that power was doubled (from 0.4 ± 0.03 to 0.8 ± 0.03 W m^{-2}) using domestic wastewater (Yang and Logan, 2016). However, these increases in performance were only examined using new cathodes, and thus it was not known if improved performance could be retained over time.

In this study, the longevity of MOF catalyst added onto AC (Fe–N–C/AC) and plain AC cathodes (control) were examined over eight weeks using acetate and two different buffers, or domestic wastewater. One concern with using a phosphate as a buffer, or with wastewater, is that phosphate in these solutions could cause the deactivation of the catalytic activity of iron through the formation of iron–phosphate complexes or through precipitation of salts on the catalyst. To examine the potential impact of phosphate on iron, the performance of MFCs over time with an inorganic phosphate buffer solution (PBS) was compared to that obtained using an organic buffer (piperazine–N,N′–bis(2–ethanesulfonic acid), PIPES) that did not contain phosphate. In addition, MFCs were also examined using domestic wastewater, which contain a complex organic matter as the fuel and inorganic and organic forms of phosphorus. Additional experiments were conducted with phosphate salts added to the wastewater to evaluate if the presence of higher concentrations of inorganic phosphorus would affect power generation over time.

2. Materials and methods

2.1. Catalyst synthesis and cathode fabrication

Cathodes with the Fe–N–C/AC catalyst were synthetized as previously described (Yang and Logan, 2016). Briefly, 6 g of AC powder (Norit SX plus, Norit Americas Inc., TX) was dispersed in water containing 1 g of iron chloride (anhydrous, Sigma Aldrich, USA) and 1 g of 1,10–phenanthroline (Sigma Aldrich, USA) at 60 °C. The mixture was stirred until dryness under a fume hood at 60 °C, and then pyrolyzed at 800 °C for 15 min in an N_2 atmosphere. The resulting powder was dispersed in 10 mM hydrochloric acid (HCl), filtered, and dried at room temperature for 48 h. AC–based cathodes were fabricated by placing the catalyst layer between stainless steel mesh (42 mesh size, type 304, McMaster–Carr, USA) and the hydrophobic PVDF membrane diffusion layer (0.45 μm, MILLIPORE, USA). The material was then rinsed with ethanol, pressed at 3×10^7 Pa for at least 15 s at 60 °C (Model 4388, CARVER, INC., USA), and dried in a fume hood at room temperature. The AC catalyst layer was prepared by mixing and then drying 6 g of the AC catalyst and 0.67 mL of a 60% PTFE (polytetrafluoroethylene) emulsion (Sigma Aldrich, USA) in ethanol on a hot plate at 60 °C.

2.2. MFC construction and operation

MFCs were single–chamber, cubic reactors constructed from a polycarbonate block 4 cm in length, with an inside cylindrical chamber having a diameter of 3 cm (Zhang et al., 2011). The anodes were graphite fiber brushes (2.5 cm in both diameter and length), heat treated at 450 °C in air for 30 min, and placed horizontally in the middle of MFC chambers (Logan et al., 2007; Vargas et al., 2013; Shi et al., 2012). Anodes were fully pre–acclimated in MFCs for over four months at a fixed external resistance of 1000 Ω, at a constant temperature (30 °C). The medium contained 1 g L^{-1} sodium acetate dissolved in 50 mM PBS (Na_2HPO_4, 4.58 g L^{-1}; $NaH_2PO_4{\cdot}H_2O$, 2.45 g L^{-1}; NH_4Cl, 0.31 g L^{-1}; KCl, 0.13 g L^{-1}; pH 7.0; conductivity of $\sigma = 6.2$ mS cm^{-1}) or a PIPES buffer (15.12 g L^{-1}, pH adjusted to 7 using NaOH) that was amended with 12.5 mL L^{-1} minerals and 5 mL L^{-1} vitamins (Cheng et al., 2009). Previous studies have suggested that the conductivity of the solution is more important to performance than the buffer concentration (Nam et al., 2010). Therefore, NaCl was added to adjust the conductivity of the PIPES buffer to match that of the PBS solution (6.2 mS cm^{-1}).

Domestic wastewater was collected once a week from the primary clarifier of the Pennsylvania State University Waste Water Treatment Plant, and stored at 4 °C prior to use. For some tests, wastewater was amended with the same phosphate concentration used for acetate fuelled MFCs (Na_2HPO_4, 4.58 g L^{-1}; $NaH_2PO_4{\cdot}H_2O$, 2.45 g L^{-1}). Control reactors were operated with NaCl amended wastewater with the same conductivity as that of phosphate amended wastewater. All reactors were operated in batch mode at 30 °C.

Single cycle polarization tests were conducted by varying the external resistance from 1000, 500, 200, 100, 75, 50, to 20 Ω at a 20 min interval after open circuiting for 2 h with a total test duration of 4 h, in a constant temperature room (30 °C) (Yang et al., 2015). The voltage drop (U) across an external resistor was recorded by a computer based data acquisition system (2700, Keithley Instrument, OH). Current densities (i) and power densities (P) were normalized to the exposed projected cathode area (A = 7 cm^2), and calculated as $i = U/RA$ and $P = iU/A$, where R is the external resistance. The high conductivity combined with low COD of the solutions with wastewater and salts led to power overshoot in single cycle polarization tests, so the multiple cycle polarization test was used for power tests in wastewater to avoid power overshoot (Watson and Logan, 2011). The external resistance was gradually changed from 1000 to 50 Ω and the reactors were operated for at least two fed–batch cycles at each resistance to allow the biofilm to adapt and ensure reproducible power output. At each cycle, the voltages were measured for 1 h after the MFC produced the peak voltage and were averaged for the final reported value.

2.3. Electrochemical analysis

The ohmic and charge transfer resistances were measured using electrochemical impedance spectroscopy (EIS). A potentiostat (VMP3 Multichannel Workstation, Biologic Science Instruments, USA) was used for all measurements, with all electrochemical tests conducted in a constant temperature room (30 °C). EIS was performed under open circuit voltage (OCV) conditions over a frequency range of 100 kHz to 100 mHz with sinusoidal perturbation of 10 mV amplitude. Ohmic resistance was obtained from a Nyquist plot as the first x–intercept (lower value of x) at high frequency range, while the diameter of the fitted semicircle was the charge transfer resistance (Sekar and Ramasamy, 2013).

2.4. Surface characterization

Environmental scanning electron microscopic (ESEM) images were produced using a FEI Quanta 200 instrument (FEI company, Hillsboro, OR, USA). A quick XPS (Axis Ultra XPS, Kratos Analytical, UK, monochrome AlKa source, 1486 eV) scan was conducted on the cathode to identify the elements present initially and after eight