



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.

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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 $2.78 \pm 0.08 \text{ W m}^{-2}$, 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 $0.73 \pm 0.01 \text{ W m}^{-2}$, 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.

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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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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 $1.6 \pm 0.1 \text{ W m}^{-2}$ to $2.6 \pm 0.05 \text{ W m}^{-2}$ 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 $0.8 \pm 0.03 \text{ W m}^{-2}$) 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 synthesized 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 N₂ 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 $3 \times 10^7 \text{ Pa}$ 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 (Na₂HPO₄, 4.58 g L⁻¹; NaH₂PO₄·H₂O, 2.45 g L⁻¹; NH₄Cl, 0.31 g L⁻¹; KCl, 0.13 g L⁻¹; pH 7.0; conductivity of $\sigma = 6.2 \text{ mS cm}^{-1}$) 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 (Na₂HPO₄, 4.58 g L⁻¹; NaH₂PO₄·H₂O, 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 cm²), 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 AlKα source, 1486 eV) scan was conducted on the cathode to identify the elements present initially and after eight

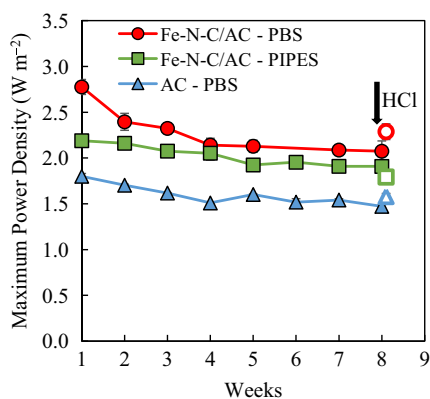


Fig. 1. Maximum power production over time using Fe-N-C/AC catalyst in PBS and PIPES and plain AC in PBS. After the eight weeks the cathodes were treated with hydrochloric acid (arrow) and tested again for the maximum power density (open symbols).

weeks of operation with a high generation energy, and short dwell time. CASA XPS software was used for the elemental analysis.

3. Results and discussion

3.1. MFC performance in PBS or PIPES over time

MFCs with the MOF catalyst and 50 mM PBS initially (week 1) produced $2.78 \pm 0.08 \text{ W m}^{-2}$, which was 54% higher than the power initially generated by the plain AC catalyst in the same buffer ($1.80 \pm 0.03 \text{ W m}^{-2}$) (Fig. 1). This initial increase was consistent with that previously reported for these MOF AC-treated cathodes in MFCs. The behaviour of the MOF catalyst was also examined in an organic buffer lacking phosphate to avoid possible ligation of phosphorus with iron. The power generation in the first week using the PIPES buffer was $2.19 \pm 0.01 \text{ W m}^{-2}$, which was 21% lower of that obtained using PBS (Fig. S1). This impact of the buffer on MFCs performance was different from that previously shown by Nam et al. (2010) using PBS, PIPES or other buffers in single-chambered MFCs with a different architecture (bottles, with relatively small cathodes compared to the anode size) and Pt catalysts. It is likely that differences in the buffers were due to the different catalysts and the much higher internal resistances, and therefore lower power densities, which may have precluded observing an impact of the buffer.

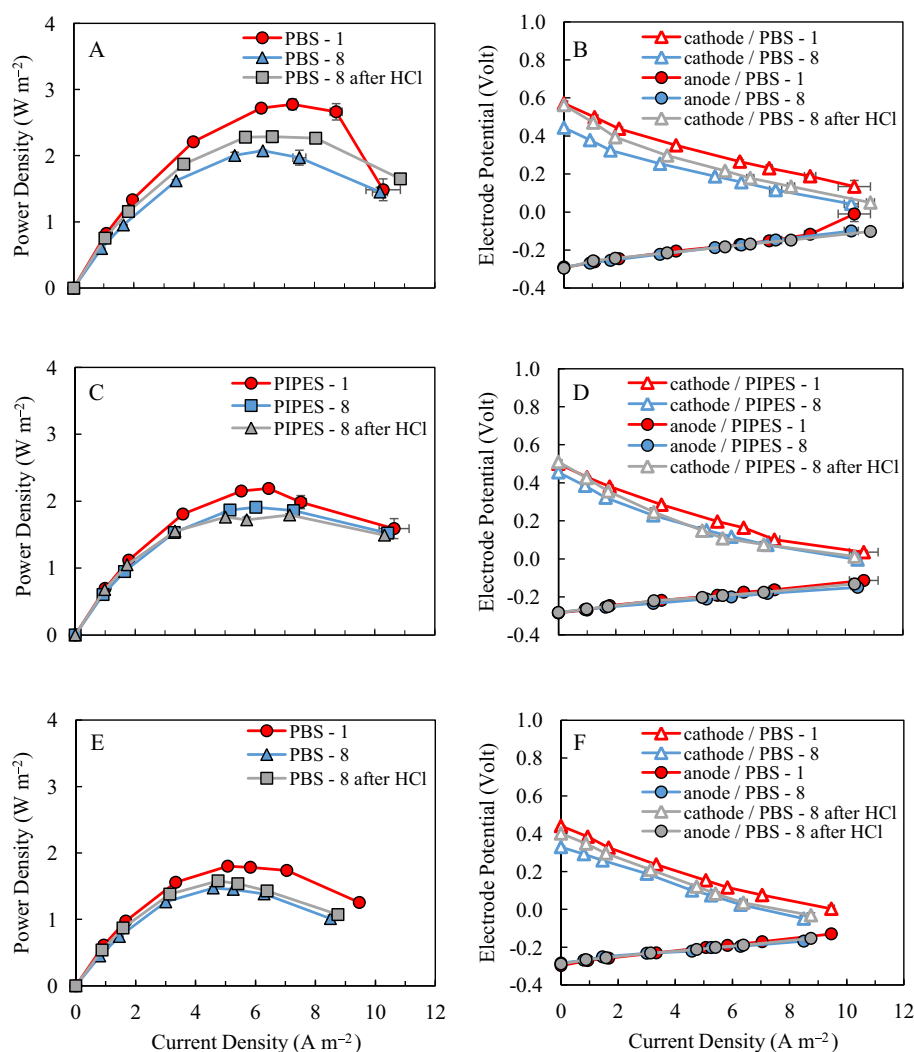


Fig. 2. Comparison of power density curves of (A) Fe-N-C/AC catalyst in 50 mM PBS and corresponding electrode potentials (B). Power density curves of (C) Fe-N-C/AC catalyst in 50 mM PIPES and corresponding electrode potentials (D). Power density curves of (E) AC catalyst in 50 mM PBS and corresponding electrode potentials (F) during the 1st, 8th week and after the acid cleaning.

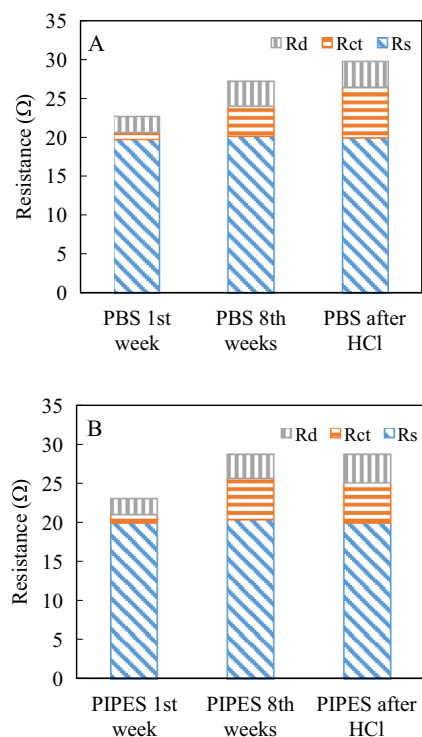


Fig. 3. Component analysis of internal resistance for the Fe-N-C/AC catalyst under both new and used conditions in (A) PBS and (B) PIPES.

The maximum power density of Fe-N-C/AC cathodes in PBS decreased by 23% in the first four weeks to $2.14 \pm 0.07 \text{ W m}^{-2}$ and then remained constant through the rest of the experiment with a final maximum power density of $2.07 \pm 0.01 \text{ W m}^{-2}$ ($F_{\text{test}} = 3.00$; $\alpha = 0.05$). The power generation using the MOF-AC cathodes in the PIPES buffer was lower but relatively more stable than results with PBS, decreasing by only 13% over the eight weeks to a final maximum power density of $1.91 \pm 0.03 \text{ W m}^{-2}$. This final power density with PIPES buffer was only slightly lower than that of $2.07 \pm 0.01 \text{ W m}^{-2}$ obtained with PBS in the last week. The performance obtained with the plain AC cathodes also declined slowly over time, with an 18% decrease in power over eight weeks, from $1.80 \pm 0.03 \text{ W m}^{-2}$ to $1.47 \pm 0.02 \text{ W m}^{-2}$. The relatively rapid decrease in the MOF-AC catalyst indicated that the high initial power density of the MOF catalyst could not be maintained over time. As a rapid decrease in power was not observed in tests with the plain AC catalyst or using the PIPES media with the MOF-AC catalyst, it was concluded that the rapid initial decrease was due to the interactions of the inorganic phosphate salts with the iron catalyst. However, despite this rapid decrease in power, relatively stable power generation was obtained in weeks 4–8 (average $2.11 \pm 0.03 \text{ W m}^{-2}$) at a power density that was 38% higher than that of plain AC over weeks 4 to 8 and 41% greater at week 8.

To examine if the decrease in the maximum power densities could be restored, after eight weeks of operation the cathodes were cleaned by gently removing the biofilm and soaking them in weak hydrochloric acid (Zhang et al., 2014). The acid cleaning partially

restored the performance of the MOF cathodes tested in PBS to $2.29 \pm 0.09 \text{ W m}^{-2}$ (82% of the initial value) compared to the last value of $2.07 \pm 0.01 \text{ W m}^{-2}$. However, the performance of the MFCs with the MOF cathodes in PIPES was negatively affected by the cleaning procedure, as cleaning resulted in slightly lower power density value of $1.79 \pm 0.02 \text{ W m}^{-2}$ compared to $1.91 \pm 0.03 \text{ W m}^{-2}$ before the acid cleaning. The recovery for plain AC was 88% of the initial value, with $1.58 \pm 0.03 \text{ W m}^{-2}$ after eight weeks with cleaning, compared to the initial power density of $1.47 \pm 0.02 \text{ W m}^{-2}$. These results showing improved performance with the PBS electrolyte were consistent with previous results, where 85% of performance was restored by acid cleaning, although those tests compared power after 17 months to 1 month (Zhang et al., 2014).

To demonstrate that the changes in power generation were due to the cathode performance, the electrode potentials were examined during polarization tests (Fig. 2). The cathode potential of the MOF catalyst at its maximum power in PBS was $0.23 \pm 0.01 \text{ V}$ in the first week, with a decrease to 0.16 V after eight weeks. In PIPES the cathode shifted from 0.16 V to 0.12 V , while with plain AC it decreased from 0.15 V to 0.10 V (Fig 2B, D and F). In all tests, the anode potentials were stable and constant over time (Fig 2B, D and F). These changes in the cathode potentials to more negative potentials for both cathodes when using PBS, with no changes in the anode potentials over time, demonstrated that the reductions in power production were due to changes in the cathodes and not the anodes.

The cathode potentials at open circuit voltage (OCV) of the MOF catalyst in PBS dropped from $0.57 \pm 0.01 \text{ V}$ at week 1 to 0.44 V at week 8. This suggested a reduction in the catalyst conductivity, which could be due to deposition of salts on the solution side of the cathode (Winfield et al., 2011). In contrast, the cathode potential at OCV in PIPES was relatively stable over time and decreased only slightly from $0.50 \pm 0.01 \text{ V}$ to 0.47 V . Acid cleaning partially restored the initial cathode potentials. The initial OCVs of the MOF cathodes tested in PBS were recovered after acid cleaning (from 0.44 to $0.52 \pm 0.02 \text{ V}$) while cathode potentials at OCV in PIPES showed no change, suggesting that cathode potential drop was due to the deposition of phosphate salts on the cathodes which could be reversed by acid treatment. The salts precipitation could potentially lower the cathode performance by affecting the conductivity of the catalyst. Although the acid treatment was effective in restoring the initial open circuit potentials, it did not completely restore cathode performance at higher current densities indicating other irreversible changes in the oxygen reduction reaction, as observed for the plain AC catalyst following cleaning.

3.2. Electrochemical analysis

EIS was performed on new and used cathodes in an abiotic electrochemical cell to evaluate changes in performance of the cathodes in the absence of bacteria (Fig. S2). The new MOF cathodes showed the same solution resistance of $R_s = 19.9 \Omega$, and a similar charge transfer resistance in both PBS ($R_{ct} = 0.90 \Omega$) and PIPES ($R_{ct} = 0.99 \Omega$). After eight weeks operation, the charge transfer resistance of the MOF cathode increased to $R_{ct} = 3.85 \Omega$ (PBS) and $R_{ct} = 5.24 \Omega$ (PIPES), mainly due to the deterioration of the catalyst,

Table 1
Elemental composition of Fe-N-C/AC cathodes under new, used, and cleaned conditions.

Sample	C [%]	O [%]	N [%]	Fe [%]
Fe-N-C/AC 1st week	73.1	8.4	0.3	5.6
Fe-N-C/AC 8th week	57.6	24.2	6.4	–
Fe-N-C/AC 8th week after HCl cleaning	78.1	4.8	1.0	–

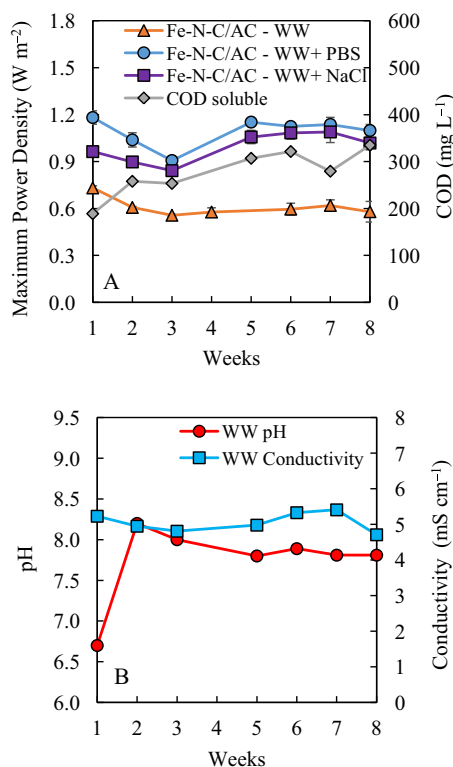


Fig. 4. (A) Maximum power production and COD level over time using Fe-N-C/AC catalyst in wastewater, wastewater added with PBS and wastewater added with sodium chloride (same conductivity of wastewater with PBS). (B) Wastewater pH and conductivity after the addition of NaCl.

consistent with the lower performance of the cathodes at the end of the experiment (Fig. 3).

Cleaning the cathodes with hydrochloric acid did not restore the initial charge transfer resistance, which suggested an alternative cleaning method or another type of chemical treatment might be needed to fully restore cathode performance. The R_{ct} after the acid cleaning procedure was 5.02 Ω in PIPES and 6.48 Ω in PBS, which were higher than the resistance registered before the treatment (3.85 Ω).

3.3. Surface characterization

SEM images (Fig. S3) clearly showed the effectiveness of the cathode cleaning procedure on removing material from the cathode. After eight weeks of operation the catalyst on the solution side of the cathode was completely covered by the microorganisms but the cleaning procedure was effective in restoring the initial appearance of the solution side of the cathode. XPS analysis of new cathodes confirmed the addition of iron due to the MOF treatment of the AC cathodes, based on Fe peaks in the new cathodes. However, after eight weeks operation no iron peaks were detected in the catalyst (Table 1). The loss of iron from the MOF catalyst likely explains the large decrease in the power density performance in the initial weeks of operation. Moreover, the iron content of the new samples was four times higher than previously reported (Yang and Logan, 2016), showing a large variability on the effectiveness of the immobilization. Based on the methods used here to add the MOF to the carbon, there is no obvious way that additional MOF could be added to the cathode to restore the original performance. The continued improved performance of the cathode compared to the plain AC control suggest that sufficient residual

nitrogen, or changes to the AC (pore sizes or surface area) during MOF addition favourably improved the ORR kinetics.

3.4. MFCs performance in wastewater over time

To better examine the longevity of the MOF catalyst in more complex medium, the performance of the Fe-N-C/AC modified cathodes was evaluated in MFCs fed with domestic wastewater (Fig. 4A). The initial maximum power density of the MOF-AC cathodes in raw wastewater was 0.73 ± 0.01 W m⁻², consistent with power densities previously obtained using new MOF cathodes and domestic wastewater (Yang and Logan, 2016). After an initial decrease in power production after week 1 (from 0.73 ± 0.01 W m⁻² to 0.61 ± 0.01 W m⁻²), there was no observable change in the maximum power densities due to the high variability of the different wastewater samples (Fig. 4B). While the maximum power density decreased by 25% from the initial value (0.73 ± 0.01 W m⁻²) to that obtained after eight weeks (0.58 ± 0.07 W m⁻²) (Fig. 5A), the decline in power was not associated with changes in cathode potentials in this case, as the anode potentials changed likely due to the use of the different wastewater samples, particularly at high current densities (Fig. 5B). The average power density for the raw wastewater reactors was 0.61 ± 0.05 W m⁻² over either weeks, which was 53% higher than that previously reported (0.40 ± 0.03 W m⁻²) for new Pt based carbon cloth (Pt/C) cathodes and domestic wastewater from the same treatment plant (Yang and Logan, 2016).

To further evaluate if phosphate salts in solution could affect the performance of the catalyst, MFCs were tested using wastewater amended with phosphate (50 mM PB) (Fig. 4). Adding salts to the wastewater increased the solution conductivity and consequently the power densities. The initial power density using wastewater with PBS was 1.18 ± 0.04 W m⁻². The power generation decreased to 0.91 ± 0.03 W m⁻² at week 3 followed by increases to 1.15 ± 0.01 W m⁻² in week 5. The last four weeks showed relatively stable values of the maximum power densities with a final value of 1.10 ± 0.04 W m⁻² at week 8. The increases

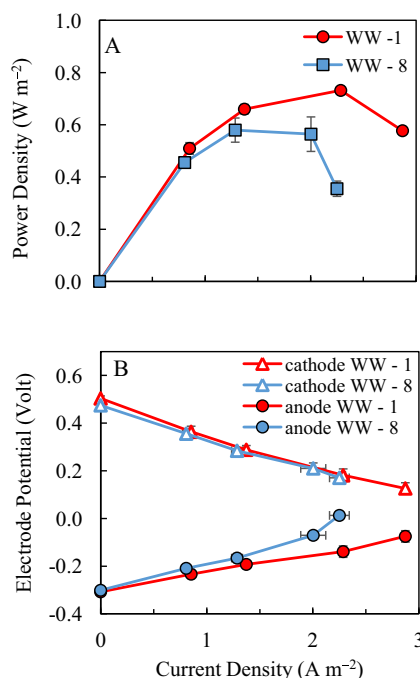


Fig. 5. Comparison of (A) power density curves and (B) corresponding electrode potentials for MFCs using Fe-N-C/AC catalyst in wastewater in 1st and 8th week.

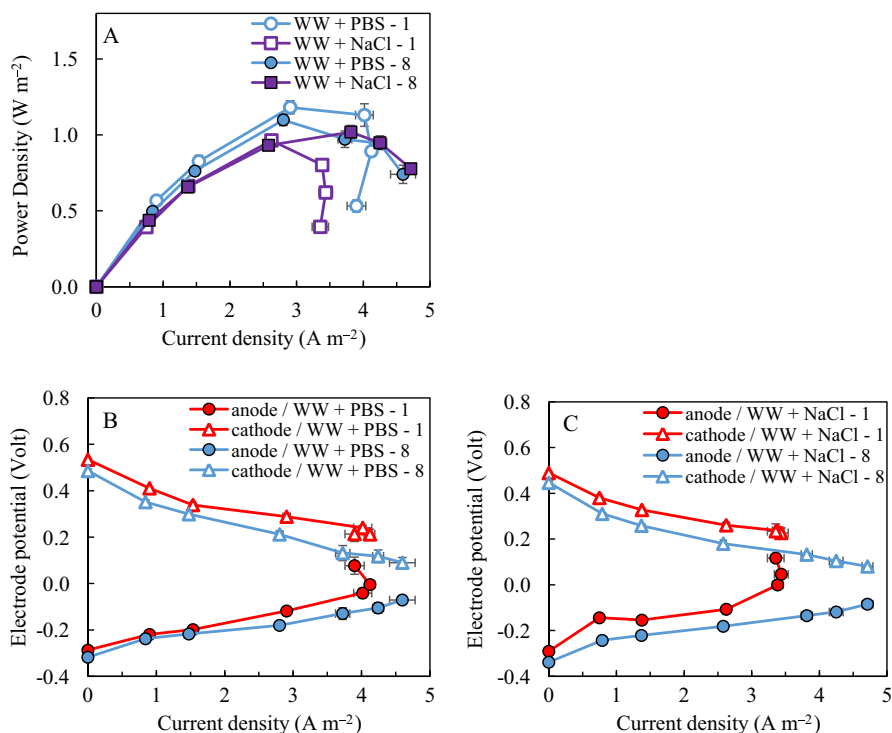


Fig. 6. Comparison of power density curves (A) and corresponding electrode potentials (B, C) for MFCs using cathodes with Fe-N-C/AC catalyst in wastewater added with PBS and NaCl in 1st and 8th week.

and decreases in maximum power densities generally followed the same trend as the changes conductivity of the solution. The variability of the wastewater parameters (Fig. 4B) caused small changes in both the anode and the cathode potentials and affected the final power output (Fig. 6 and Fig. S4).

The control reactors with wastewater amended with NaCl showed the same behavior of the wastewater amended with PBS over time. The initial power generation was $0.96 \pm 0.03 \text{ W m}^{-2}$ with a decrease to $0.84 \pm 0.03 \text{ W m}^{-2}$ at week 3, before increasing to $1.06 \pm 0.04 \text{ W m}^{-2}$ in the fifth week. In the last three weeks, the power density generated by the MFCs was stable and comparable with the values obtained with wastewater amended with PBS, with the maximum power density at week 8 of $1.02 \pm 0.04 \text{ W m}^{-2}$. The anode and the cathode potentials of the controls reactors showed the same variability of the reactors with wastewater amended with PBS (Fig. 6 and Fig. S4). The small decrease of the cathode potential after eight weeks could not be concluded to be due to deterioration of the catalyst due to the larger changes in power associated with changes in batches of wastewater. Thus, the addition of phosphate into the wastewater did not allow evaluation of the impact of the phosphate on power generation with the wastewater over time due to changes in COD, pH and conductivity.

4. Conclusions

Power densities generated using MOF catalyst cathodes and phosphate buffer decreased over time, but they were still 41% greater than plain AC after 8 weeks, consistent with a loss of iron from the framework. Power with wastewater also declined over time, but it remained higher than the plain AC and 53% higher than maximum power densities previously reported for Pt catalysed cathodes. These results show that the performance of MFC AC cathodes can decrease over time, but because power remains higher than untreated AC cathodes, MOF treatment is useful for improving

MFC power generation from solutions or wastewaters containing phosphate.

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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.2017.02.105>.

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