

PAPER



Cite this: *Environ. Sci.: Water Res. Technol.*, 2018, **4**, 513

Copper current collectors reduce long-term fouling of air cathodes in microbial fuel cells†

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Long-term operation of wastewater-fed, microbial fuel cells (MFCs) with cathodes made of activated carbon and stainless steel (SS) current collectors can result in decreased performance due to cathode fouling. Copper has good antimicrobial properties, and it is more electrically conductive than SS. To demonstrate that a copper current collector could produce a more fouling resistant cathode, MFCs with air cathodes using either SS or copper current collectors were operated using domestic wastewater for 27 weeks. The reduction in biofouling over time was shown by less biofilm formation on the copper cathode surface compared to SS cathodes, due to the antimicrobial properties of copper. Maximum power densities from 17–27 weeks were $440 \pm 38 \text{ mW m}^{-2}$ using copper and $370 \pm 21 \text{ mW m}^{-2}$ using SS cathodes. The main difference in the microbial community was a nitrifying community on the SS cathodes, which was not present on the copper cathodes.

Received 24th November 2017,
Accepted 2nd February 2018

DOI: 10.1039/c7ew00518k

rsc.li/es-water

Water impact

Long-term operation of microbial fuel cells (MFCs) can result in decreased performance due to cathode fouling. Here, copper was examined as an alternative to stainless steel as the current collector in an activated carbon cathode, to produce a more fouling-resistant cathode. It was shown that MFCs with copper current collector cathodes maintained better long-term performance than those using stainless steel.

1. Introduction

Microbial fuel cells (MFCs) can be used to remove organic matter from wastewater and simultaneously generate electricity, and thus they have great potential for treating wastewater economically and without the use of energy derived from fossil fuels.^{1–3} Single-chamber, air-cathode MFCs are the most promising design for practical applications since they use passive oxygen transfer to the cathode as an electron acceptor, and avoid the need for a membrane.⁴ Recent innovations in electrode materials, architecture, and solution chemistry have reduced the cost of MFC materials, and improved power densities over time.^{5–12} However, long-term, sustainable operation of wastewater-fed MFCs still remains a challenge, particularly due to fouling of the air cathodes, as these can rap-

idly foul when the MFCs are fed wastewaters, resulting in reduced oxygen reduction potentials and power densities. Both external fouling (*i.e.*, the growth of biofilm) and internal fouling (*i.e.*, adsorption of humic acids and deposition of salts) can contribute to fouling over the long term.^{13–16}

Different methods have been proposed to reduce cathode fouling or restore performance, such as physically removing the cathode biofilm or chemically cleaning the cathode.^{17–21} However, it was shown that physically removing the biofilm has only a small impact in recovering the original power densities,¹⁹ indicating that internal cathode biofouling may be a more critical issue.²² Chemical cleaning strategies are widely used for fouling control in biological systems.^{23–25} However, it has been reported that use of strong acids (*e.g.*, HCl) decreased the performance of the MFCs further after cleaning.¹⁷ It is therefore important to find better ways to prevent the occurrence of fouling, by using anti-fouling materials compatible with mechanically and electrochemically stable air cathodes. Previous approaches have included using silver nanoparticles instead of Pt as the cathode catalyst,²⁶ coating an additional polymer layer on the catalyst layer surface,²⁷ adding vanillin to the binding materials as an antimicrobial additive,²⁸ and incorporating quaternary ammonium compounds into the catalyst layer on activated carbon air cathodes.²⁹ However, silver is a precious metal and the other

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ew00518k

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compounds added to the cathode could leach into the liquid over time. Therefore, other alternatives or methods that could be used in conjunction with these chemical additions are needed for long-term stability.

Copper is known to have anti-microbial properties, and it is highly electrically conductive.^{30–32} While the use of copper as an anode should be avoided due to its potential for corrosion,³³ copper and other metals on the cathode should be protected from corrosion due to the more favorable reaction of oxygen reduction than corrosion (cathodic protection). In addition to anti-microbial properties, copper is more electrically conductive than other current collectors that have been used with activated carbon catalysts, such as stainless steel or nickel.^{3,34–36} The better conductivity of copper, however, might not necessarily lead to improved cathode performance as addition of copper particles to an activated carbon cathode to improve conductivity did not improve performance.³⁷ However, impact of copper was only examined in short-term tests using small cathodes, where the benefits of copper might not have been helpful.

In this study, we examined the impact of using a copper mesh current collector on biofouling in a long-term study of approximately half a year (27 weeks). MFCs with either stainless steel- or copper-based air cathodes were constructed and operated using domestic wastewater as the feed. Power production in both types of MFCs was monitored and compared over time.

2. Experimental

2.1 Cathode fabrication

Cathodes were prepared using a hot-pressing method as previously described.³⁸ The catalyst layer (CL) was prepared by mixing activated carbon (AC, Norit SX plus, Norit Americas Inc., TX, USA) with a 60% PTFE emulsion (Sigma Aldrich, MO, USA) at a mass ratio of AC:PTFE (6:1). Two different current collector (CC) materials were used: stainless steel (SS) mesh (42 × 42, type 304, McMaster-Carr, IL, USA), or copper (Cu) mesh (40 × 40, McMaster-Carr, Elmhurst, IL, USA). A hydrophobic polyvinylidene fluoride (PVDF) membrane (0.45 μm, Millipore, MA, USA) diffusion layer (DL), an AC/PTFE CL, and the CC were pressed at 3×10^7 Pa for at least 15 s at 60 °C until the membrane surface became dry.^{38,39} The pressed cathodes were then taken out and dried in a fume hood for later use.

2.2 MFC construction and operation

A total of six MFC reactors were prepared (SS or Cu cathodes, each in triplicate). The MFCs were single-chamber, cubic-shaped MFC reactors containing a cylindrical anode chamber 4 cm long and 3 cm in diameter.⁴ The graphite fiber brush anode (2.5 cm in both diameter and length) was heat treated at 450 °C in air for 30 min before use, and was placed horizontally in the middle of MFC chambers. Reactors were initially inoculated and operated in batch mode using primary clarifier effluent from the Penn State University Wastewater Treatment Plant, and the anode and cathode were connected with a 1000 Ω resistor in the circuit for each reactor. The

MFCs were emptied and refilled with fresh primary clarifier effluent every 24 h for 14 d until the reactors reached a steady state based on power output, and data were collected.

Voltage (U) across the external resistor in the MFC circuit was measured at 20 min intervals using a data acquisition system (2700, Keithley Instrument, OH, USA) connected to a personal computer. Current ($I = U/R$) and power ($P = IU$) were calculated as previously described,² with the current and power normalized by the projected surface area of the cathode (7 cm²). Power density curves (ESI,† Fig. S1) were obtained by varying external circuit resistance using the single cycle polarization method, with a single resistor used for a full batch cycle. An Ag/AgCl reference electrode (BASi) was placed in the middle of the MFC chamber to obtain anode potentials (reported *versus* Ag/AgCl electrode, +210 mV *vs.* a standard hydrogen electrode), with the cathode potential calculated using the anode potential and the whole cell voltage.

2.3 Chemical analyses

The chemical oxygen demand (COD) of wastewater samples were analyzed using a standard method (HACH COD Kits, Method 5220, HACH, Loveland, CO, USA).⁴⁰ Soluble COD (sCOD) samples were first filtered through syringe filters (0.45 μm pore size, PVDF, 20 mm diameter, Restek Corporation, PA, USA) prior to COD analysis.

To determine the amount of biofilm on cathode surfaces, a round piece of cathode with a diameter of 5 mm (0.196 cm²) was punched out from the cathodes and soaked in 300 μL of an extraction reagent (B-PER II bacterial protein extraction reagent, Pierce, Thermo Fisher Scientific, MA, USA) to solubilize the proteins, following the manufacturer's instructions. The protein concentration was then determined by the bicinchoninic acid method (Pierce BCA Protein Assay Kit, Thermo Fisher Scientific, MA, USA) using a Microplate Reader (Bio-Rad 680, Bio-Rad Laboratories, CA, USA) and bovine serum albumin (BSA) standards supplied with the kit.

The total concentration of copper in MFC effluents was examined by using digestion method as previously described.⁴¹ The samples were digested with a mix of acids (nitric, hydrochloric, and hydrofluoric) in an open glass dish and was heated to dryness on a hot plate. The residue was then dissolved in a dilute nitric acid solution, and the copper concentration was determined using an ICP-MS (Thermo X Series II ICP-MS, Thermo Fisher Scientific, MA, USA) with high-purity argon (99.99%) in a directly coupled on-line configuration.

For all data, arithmetic mean values and standard deviations were calculated for triplicate samples. Statistical differences between sample means were tested using the Welch's *t*-test for unpaired samples. The *p*-value was used to evaluate significance, with differences defined as significantly different for $p \leq 0.05$.

2.4 Surface analysis of copper mesh

To determine the oxidation states of copper electrode surfaces, X-ray photoelectron spectroscopy (XPS) experiments

were performed using a Physical Electronics VersaProbe II instrument (Physical Electronics, MN, USA) equipped with a monochromatic Al $K\alpha$ X-ray source ($h\nu = 1486.7$ eV) and a concentric hemispherical analyzer. Charge neutralization was performed using both low energy electrons (<5 eV) and argon ions. The binding energy axis was calibrated using sputter cleaned Cu foil (Cu $2p_{3/2} = 932.7$ eV, Cu $2p_{3/2} = 75.1$ eV). Peaks were charge referenced to CH_x band in the carbon 1 s spectra at 284.8 eV. Measurements were made at a takeoff angle of 45° with respect to the sample surface plane. This resulted in a typical sampling depth of 3–6 nm (95% of the signal originated from this depth or shallower). Quantification was done using instrumental relative sensitivity factors (RSFs) that account for the X-ray cross section and inelastic mean free path of the electrons.

2.5 Antimicrobial tests

The relative toxicity of three different copper species (Cu, CuO, or Cu₂O powders, prepared at 540 mg Cu L⁻¹ concentrations; Sigma Aldrich, MO, USA) was evaluated using fresh primary clarifier effluent sample from the wastewater treatment plant. A control was prepared by using wastewater without any copper addition. Samples were incubated at 37 °C on a shaker table. Aliquots (100 μ L) were taken in duplicate at $t = 0, 0.5, 1, 2$, and 3 h for each of the conditions assayed, and diluted in order to obtain suitable plate counts (10–100 colonies). Following dilution, 100 μ L of the sample was used to inoculate nutrient agar plates for each samples, incubated at 37 °C for 24 hours. The colonies were counted, and the results were expressed as colony forming units per mL (CFU mL⁻¹) of sample (Fig. S3†).

2.6 Microbial community analyses

After 27 weeks of MFC operation, microbial communities on the electrodes were examined using biofilm scraped off from the cathode and anode surfaces with a clean pipet tip. DNA was extracted from the biofilm using the MO Bio PowerSoil DNA extraction kit (QIAGEN, Germany) following the manufacturer's protocols. PCR was performed on the isolated DNA using the 515F/805R primer set. Amplicon sequences were obtained using Illumina MiSeq and were classified using the Ribosomal Database Project (RDP) at a 95% confidence interval. Relative abundance of each genus was estimated by normalizing the number of reads assigned to each genus against the total reads obtained for that sample. The heatmap was generated using R version 2.11.0 using the heatmap function. Fifteen most abundant classified genera per sample were represented in the heatmap.

3. Results and discussion

3.1 MFC power production over time

The power production by the MFCs varied due to changes in sCOD (Fig. 1a), and therefore it was differences in power between the MFCs with the two types of cathodes which showed

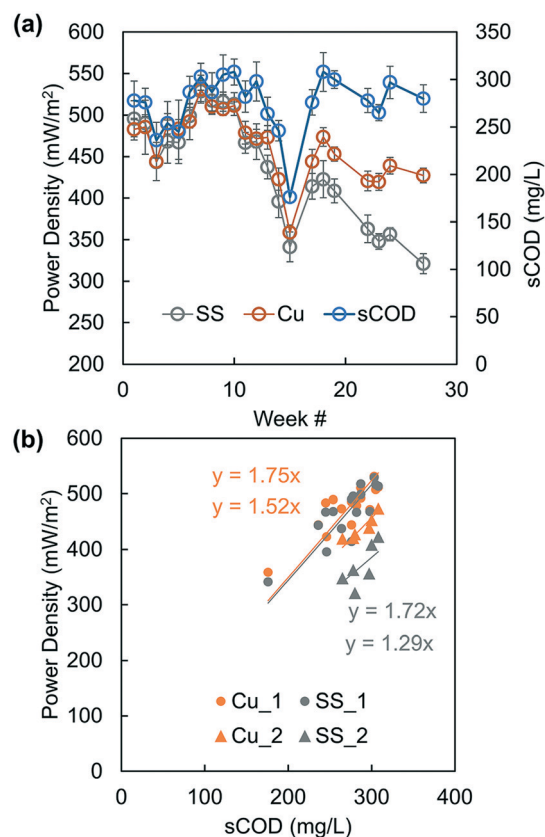


Fig. 1 (a) Maximum power densities generated from SS and Cu MFCs, and sCOD values of MFC influent (wastewater) monitored over a 27 week test period. (b) Relationship between power densities and influent sCOD values before week 15 (group 1) and after week 15 (group 2).

the changes in performance over time. The power densities produced by the MFCs with the SS or Cu cathodes were initially (first 10 weeks) very similar to each other, taking into account the variability of the sCOD (Fig. 1a). Although the output power densities depended on the sCOD values of the influent wastewater (Fig. 1b), the difference between the maximum power densities of the SS reactors (494 ± 27 mW m⁻²) and the Cu reactors (490 ± 23 mW m⁻²) during the first ten weeks were not significantly different (p -value = 0.36).

It was evident from the changes in the power densities produced at similar sCOD values (Fig. 1b) that the performance of the SS cathodes declined more rapidly than the copper cathodes in long-term operation. Comparison of the slope of the group 2 data (after week 15) with that of group 1 data (before week 15) (Fig. 1b), Cu reactors decreased by 13% (from 1.75 to 1.52), while the SS reactors decreased by 25% (from 1.72 to 1.29).

The performance of the SS reactors and the Cu in terms of power production clearly diverged after week 15, which was when the sCOD value of the MFC influent was significantly lower compared to other periods (Fig. 1a). After that, the performance of the SS reactors gradually declined until week 27. During this period, the maximum power densities of the MFCs with Cu cathodes (440 ± 38 mW m⁻²) was $19 \pm 6\%$

higher (p -value = 0.032) than the maximum power densities of the SS reactors ($370 \pm 21 \text{ mW m}^{-2}$).

3.2 Analysis of the cathodes based on protein and copper composition

After 27 weeks of operation, it was evident based on visual examination of the cathodes that thicker biofilms grew on the surface of the SS cathodes than on the Cu cathodes (Fig. 2a). The protein measurements using biofilm scraped from the SS and Cu cathodes after 27 weeks of MFC operation also supported this observation. The protein density of the SS cathode biofilm (9.5 g m^{-2}) was approximately 2.5 times higher (p -value = 0.015) than that of the Cu cathode biofilm (3.9 g m^{-2}) (Fig. 2b).

Analysis of copper concentrations in the MFC influent showed that copper was present at very low concentrations in the wastewater samples at $20 \pm 3.0 \mu\text{g L}^{-1}$. Tests on the MFC effluent at the end of week 26 showed that the concentration was lower in the MFCs with SS cathodes, at $7.4 \pm 0.9 \mu\text{g L}^{-1}$. However, the copper concentration increased after operation of MFCs using the Cu cathodes, to $35 \pm 9.0 \mu\text{g L}^{-1}$. In either case, dissolved copper concentrations in both types of reactors fell below the US Environmental Protection Agency (EPA) maximum contaminant level goals (MCLG) for copper, which is $1300 \mu\text{g L}^{-1}$.

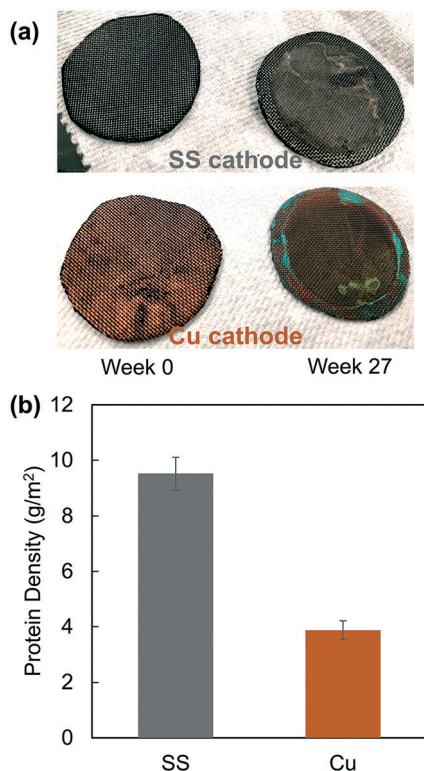


Fig. 2 (a) Photographs of the SS and Cu cathodes after 27 weeks of MFC operation. (b) Mass of biofilms on the SS and Cu cathodes based on the mass of protein extracted from the biofilm, normalized to the projected cathode area.

Changes in the oxidation state of the solid copper mesh were found over time (Table 1). As expected, elemental copper (Cu^0) was the major valence state at week 0, although the second major valence state changed from Cu^+ before cathode fabrication to Cu^{2+} after cathode fabrication. Larger changes were observed after 2 weeks, where Cu^{2+} and Cu^+ became the major copper valence states, with the corresponding copper species of $\text{Cu}(\text{OH})_2$ and Cu_2O . At week 8, most surface copper was oxidized to Cu^{2+} and the only apparent copper species identified was $\text{Cu}_3(\text{PO}_4)_2$. This indicates that long-term operation of Cu cathodes will oxidize Cu^0 to its most oxidized state.

Antimicrobial tests indicated that all copper species had antimicrobial activities, but Cu^0 or Cu_2O powder showed lower viable numbers than the samples that had CuO powder (Fig. S3†).

3.3 Microbial community analysis

The microbial communities on the different electrodes were examined to see if the use of the different metals produced large changes in the cathode communities. As expected, the microbial communities found on anodes from the reactors with the different cathodes (SS and Cu) anodes were quite similar, and the communities that develop on the anode should not be appreciably impacted by the cathode material (Fig. 3a). The three major genera on the anodes were *Geobacter*, *Shewanella*, and *Azoarcus*, which are commonly found in typical MFC anodic biofilms.^{42,43}

In contrast, the microbial communities found on cathodes made with the SS or Cu mesh differed substantially (Fig. 3b). The most distinctive feature in the microbial communities in the SS cathode biofilm was the high abundance of nitrifiers including *Nitrosomonas* and *Nitrospira*. These nitrifiers were not as abundant on the Cu cathode surface. However, the biofilm of the Cu cathode contained a greater relative abundance of denitrifiers including *Dechloromonas*, *Arenimonas*, and *Zoogloea*. It is well known that both nitrification and denitrification can occur on cathodes in MFCs.^{44,45} Also, genera that play a role in nitrification (*Nitrosomonas* and *Nitrospira*) and denitrification (*Dechloromonas*) were reported to be present on carbon-based cathodes in MFCs.^{42,46} It is not clear why in the current study nitrifiers were mainly enriched on the SS cathode and denitrifiers on Cu cathode. It is possible that nitrifiers are less tolerant to the presence of trace concentrations of copper, and thus they grew in the absence of copper on the SS cathode, but this would need to be specifically addressed in a future study. Interestingly, *Dechloromonas* and *Zoogloea* are known to be Cu-tolerant genera present in microbial communities in activated sludge.⁴⁷ It may be possible that nitrifiers were inhibited in the Cu cathode, and denitrifiers were inhibited in the SS cathode. Alternatively, denitrifiers may prefer using Cu cathode as their electron donors. Future studies should evaluate the tolerance of these genera to SS and Cu materials, and the capability of denitrifiers of utilizing SS and Cu cathodes as their electron donors.

Table 1 Major copper valance and corresponding copper species of the cathodes analyzed using XPS at different time point throughout the course of MFC operation. Copper valance and species are listed in the order of abundance

Time	Major copper valance	Major copper species
Week 0 (before cathode fabrication)	Cu ⁰ , Cu ⁺	Cu ⁰ , Cu ₂ O
Week 0 (after cathode fabrication)	Cu ⁰ , Cu ²⁺	Cu ⁰ , CuO
Week 2	Cu ²⁺ , Cu ⁺	Cu(OH) ₂ and Cu ₂ O
Week 9	Cu ²⁺	Cu ₃ (PO ₄) ₂

3.4 Implications for using copper cathodes in MFCs

The results using the copper or SS cathodes over 27 weeks of operation with domestic wastewater as a feedstock clearly showed that the use of copper cathodes maintained higher power densities over time (Fig. 1). Differences in power production were only noticeable after 15 weeks of operation

when presumably fouling of the cathodes became a factor in MFC performance. A comparison of the biofilm densities (based on protein) on the cathodes after 27 weeks demonstrated greater biofouling on the SS cathodes compared to the Cu cathodes (Fig. 2b). The decrease in fouling on the Cu cathodes can be attributed to the antimicrobial properties of copper.^{30,31} The significant improvement of the long-term performance in Cu cathodes suggests that copper not only reduced biofilm growth but also hindered inner fouling, which is known to be a more important contributor to long-term fouling of MFC cathodes.²²

The antimicrobial impact of copper on the cathodes did not impact the MFC anodes. The copper cathode surface showed less biofilm growth compared to the SS cathode (Fig. 2), and the microbial community on the Cu cathode was different from that on the SS cathode (Fig. 3). In the SS cathodes, the major genera consisted of nitrifying bacteria, which were absent in the Cu cathodes. The dominant genera in the Cu cathode (*Dechloromonas*, *Arenimonas*, and *Zoogloea*) were absent in the SS cathode, and are more likely resistant to

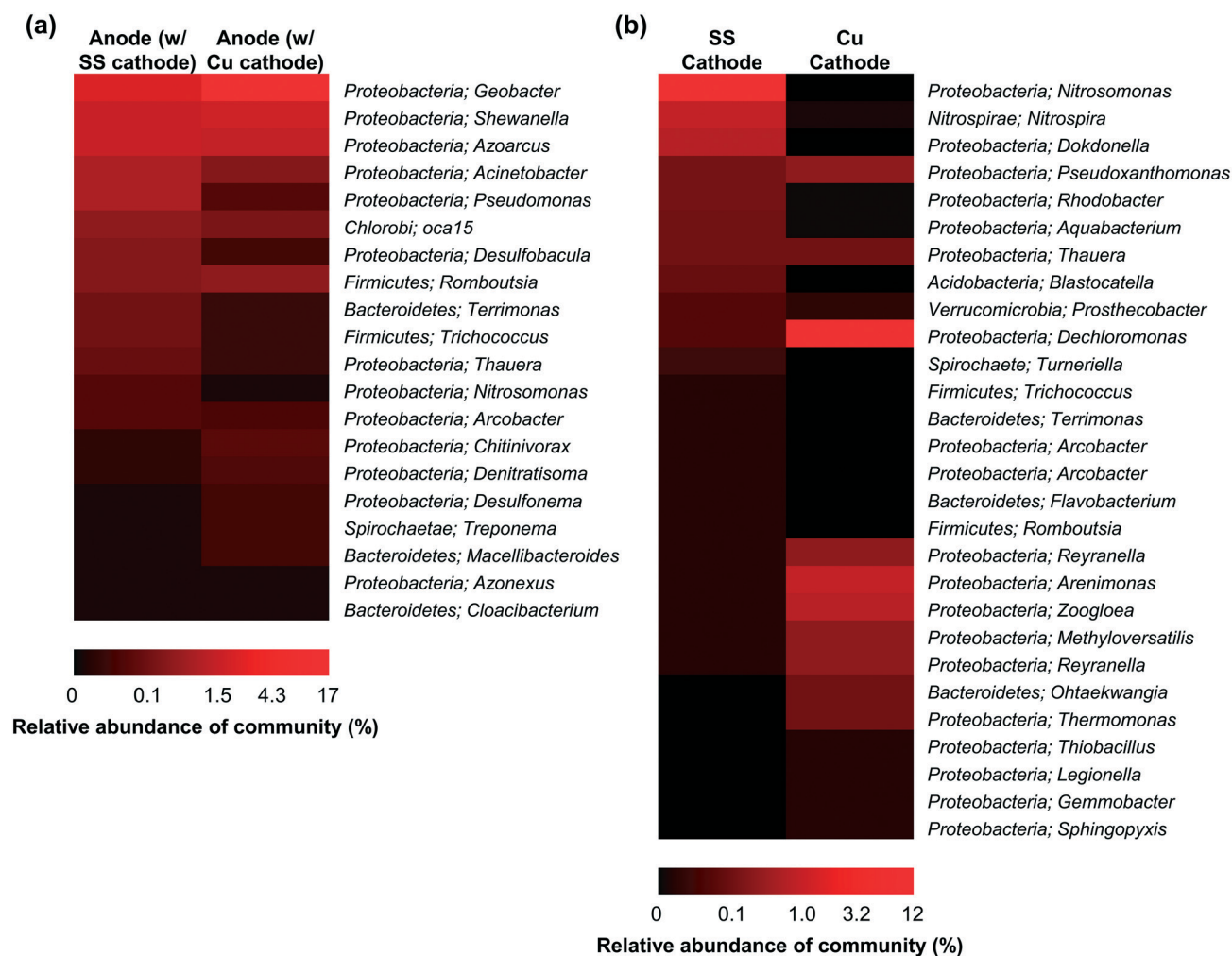


Fig. 3 Comparison of microbial communities in biofilm scraped from (a) graphite fiber, brush anodes in MFC with either SS or Cu cathodes; and (b) SS or Cu mesh cathodes. The heatmap was created using 15 most abundant classified genera selected from each sample. The color intensity of scale demonstrates the relative abundance of each genus.

copper than what were found in the SS cathode.⁴⁷ In contrast, the microbial community in the anodic biofilms were similar, with *Geobacter*, *Shewanella*, and *Azoarcus* identified as the major genera with both types of cathodes.

One of the concerns with using copper was its stability over time. Copper can corrode in water, which could impact its physical stability and electrical conductivity. However, there were only minor losses of copper over time, based on the measured effluent copper concentrations of only $35 \pm 9.0 \mu\text{g L}^{-1}$, compared to $20 \pm 3.0 \mu\text{g L}^{-1}$ in the influent wastewater. After 27 weeks of operation, the Cu mesh cathode was mechanically stable, and although the valence state of the surface of the copper changed over time, this change did not adversely impact performance. Antimicrobial tests using wastewater samples indicated that the oxidized copper species (CuO or Cu_2O) that became more prevalent than the elemental copper (Cu^0) in tests after a long-term operation (Table 1), had antimicrobial properties at a similar level to Cu_2O , but at a lesser degree to CuO (Fig. S3†).

These results suggest that copper may be more suitable as a current collector in MFC cathodes than SS, particularly for larger cathodes that would be needed for scaled-up MFCs.^{14,48} Although copper has a higher electrical conductivity than SS, there was no difference in the initial performance of the MFCs with the Cu cathodes than the SS cathodes. However, the small size of the cathodes would mean that differences in conductivity would likely not be important at this scale. Simulations on the impact of cathode conductivity at larger sizes has shown that electrical conductivity can be a major factor in cathode performance.⁴⁹ When treating domestic wastewater, power densities can be limited by the anode when sCODs are very low.¹⁴ Although relatively low strength domestic wastewater was used here, it was still shown over many weeks following substantial cathode fouling that the MFCs with the Cu cathodes maintained better performance than those with SS, and thus the cathodes were an important factor in overall performance and power generation. Copper cathodes may therefore be very beneficial for improved long-term performance of MFCs treating domestic and other types of wastewaters.

4. Conclusions

Operation of domestic wastewater-fed MFCs for 27 weeks showed that using a copper current collector produced a more fouling resistant cathode than a stainless steel cathode. Long-term maximum power densities using copper were $19 \pm 6\%$ higher than those with stainless steel. The reduction in biofouling over time was shown by less biofilm formation on the cathode surface, suggesting the antimicrobial properties of copper was the key factor for the improvement. The use of copper as a current collector in MFC cathodes may be particularly useful for larger cathodes that would be needed for scaled-up MFCs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was funded by the Environmental Security Technology Certification Program via cooperative research agreement W9132T-16-2-0014 with the US Army Engineer Research and Development Center.

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