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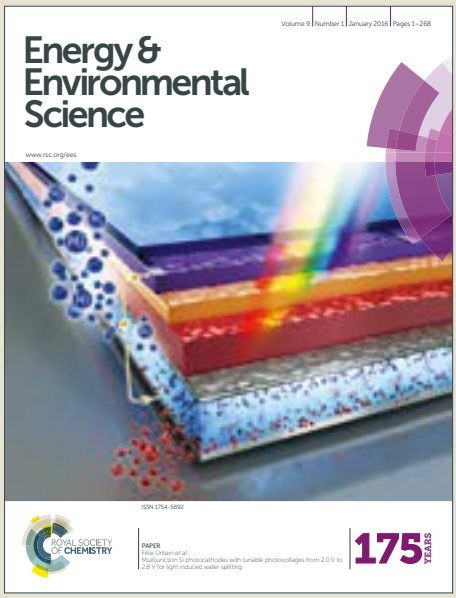

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The impact of new cathode materials relative to baseline performance of microbial fuel cells all with the same architecture and solution chemistry

Wulin Yang[a], Kyoung-Yeol Kim[a], Pascal E. Saikaly[b], and Bruce E. Logan[a*]

[a]Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States
[b]Biological and Environmental Sciences and Engineering Division, Water Desalination and Reuse Research Center, King Abdullah University of Science and Technology, Thuwal 23955–6900, Saudi Arabia
*Corresponding Author. Telephone: +1 814 863 7908. Fax: +1 814 863 7304.
E-mail: blogan@psu.edu

Abstract

Differences in microbial fuel cell (MFC) architectures, materials, and solution chemistries, have previously hindered direct comparisons of improvements in power production due to new cathode materials. However, one common reactor design has now been used in many different laboratories around the world under similar operating conditions based on using: a graphite fiber brush anode, a platinum cathode catalyst, a single-chamber cube-shaped (4-cm) MFC with a 3-cm diameter anolyte chamber, 50 mM phosphate buffer, and an acetate fuel. Analysis of several publications over 10 years from a single laboratory showed that even under such identical operational conditions, maximum power densities varied by 15%, with an average of 1.36 ± 0.20 W m^{-2} (n=24), normalized to cathode projected area (34 W m^{-3} liquid volume). In other laboratories, maximum power was significantly less, with an average of 0.91 ± 0.26 W m^{-2} (n=10), despite identical conditions. One likely reason for the differences in power is cathode age. Power production with Pt catalyst cathodes significantly declined after one month of operation or more to 0.87 ± 0.31 W

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m^{-2} (n=18) based on studies where cathode aging was examined, while in many studies the age of the cathode was not reported. Using these studies as a performance baseline, we review the claims of improvements in power generation due to new anode or cathode materials, or changes in solution conductivities and substrates.

Introduction

Microbial fuel cells (MFCs) that use certain bacteria, referred to as exoelectrogens, to produce electricity from organic matter have been widely investigated since the early 21st century as a possible method for wastewater treatment with net energy production.[1-5] Increased power production from <1 mW m^{-2} of electrode (anode or cathode) have improved over the years to a range of ~1-4 W/m^2,[6-8] due to many improvements that include: improving the architecture, by moving from two-chamber bottles with salt bridges to single chamber reactors without membranes;[9-11] improved anodes, with new 3-D materials such as graphite brushes and felt or cloth replacing graphite rods;[12-19] improved cathodes, with power production and longevity of improved compared to platinum cathodes;[20-28] decreased ohmic resistance due to closer-spaced electrodes and increased solution conductivities;[27, 29-31] and improved cultivation of exoelectrogenic microorganisms and use of substrates more amenable to current generation, through the use of relatively high concentrations of acetate as a fuel compared to dilute organic matter in many domestic wastewaters.[32-34] In the early development of MFCs, several materials and operational parameters were often simultaneously changed, making it difficult to specifically identify the factors that led to improved power compared to previous reports in the literature. As the development of these systems matured, greater attention has been given to specific impacts of the

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individual components, but often in systems fundamentally different from each other, for example by using different size electrodes or electrode spacing.[35, 36]

Over the last decade, many researchers around the world have started to use a similar reactor design for experiments,[37-42] based on a cube-shaped reactor first reported in papers in 2004.[9] The original design contained a carbon paper anode separated by 4 cm from a Pt-catalyzed carbon cloth cathode, in a 4-cm cube drilled to produce an anolyte chamber 3-cm in diameter. The power density was evaluated using glucose, with 0.26 mW/m^2 (6.6 W/m^3 based on liquid volume) produced with a Nafion membrane hot-pressed to the cathode. Power was shown to increase by removing the membrane,[9] while adding a diffusion layer on the air-side of the cathode to prevent leakage,[43-46] using acetate as a fuel more suitable for exoelectrogens such as *Geobacter sulfurreducens*[33, 47] or *Geobacter anodireducens,* since these two species were not distinguishable based on based on full-length (1457 bp) 16S rRNA gene sequencing and the primers used in that study.[48, 49] It was also demonstrated that replacing the flat anode with a graphite fiber brush anode that helped to avoid power decreases due to oxygen crossover when the anode was placed near the cathode.[12, 50, 51] Over the past ten years, this basic cube design has been used by researchers around the world, usually with solution conditions of 50 mM phosphate buffer solution (PBS) as the electrolyte and medium, and acetate as the fuel. Much of this research has focused on improving the cathode performance, as the cathode limits power production as long as the anode bacteria have sufficient substrate, and are not cultivated under conditions that impact anode performance due to the presence of dissolved oxygen or other electron acceptors (e.g. nitrate) or inhibitors.[52-55] For the first time, it is now possible to directly compare results from one laboratory to another due to the use of the same reactor and test conditions. The mean values of maximum power densities reported were used for our analysis, excluding the variations among replicates in each study. Our preliminary analysis of

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the "baseline" performance of MFCs in these studies showed that even under apparently identical conditions, and even in the same laboratory, the maximum power densities of these systems differed. Therefore, we collected and compared results from a larger number of studies to quantify these differences, and determine if we could find critical differences in performance among these systems that might help explain the reasons for power differences.

Benchmarking Maximum Power Densities using a Pt Cathode and Brush Anode

A total of 35 studies were used to compare power generation using the 4-cm cube reactors, all with 2.5 cm brush anodes and Pt catalyst cathodes. With the same operation conditions using a 50 mM PBS, and 1 g L^{-1} acetate, the maximum power densities reported in 24 of these studies from the same laboratory (Penn State University, PSU) was 1.36 ± 0.20 W m^{-2}, with a range of 1.02 to 1.68 W m^{-2} (Figure 1A). This suggests that even when the researchers were all trained in the same laboratory using the same protocols and supplies, there was a standard deviation of 15% in the maximum power density obtained in polarization tests. While these variations are unexpectedly large, such differences have been observed for other types of biological tests. For example, five-day biochemical oxygen demand tests conducted at the same laboratory have shown a ±5% variation, but this increases to ±15% based on comparisons among different researchers in different laboratories. [56]

The maximum power densities reported by non-PSU laboratories (others) using the same test conditions was slightly different from this result of the PSU laboratory (PSU), with an average of 1.03 ± 0.46 W m^{-2} based on 11 different studies, with a wider range of 0.57 to 2.20 W m^{-2} (Figure 1B). One of these non-PSU studies is noteworthy as the baseline power density was 2.20 ± 0.05 W m^{-2}, which was well above the range of all other studies[57]. The reason for this is not known. If

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this study is omitted, the average for other laboratories would decrease to 0.91 ± 0.26 W m^{-2} (n=10; range of 0.57 to 1.21 W m^{-2}) for platinum cathodes (Figure 1B), which was significantly lower than that obtained at PSU laboratory ($p<0.01$).

The significantly lower (on average) power densities obtained in these non-PSU laboratories suggested that there might be other factors involved that reactor design and materials. For example, it is now well known that the performance of Pt catalyst cathodes decreases rapidly over time.[58, 59] Studies have shown that platinum can be poisoned by phosphate or sulfur species, which are in the medium used for most MFC tests.[60] It is also possible the binding of the Pt particles to the carbon cloth becomes impaired over time resulting in loss of the catalyst particles over time. A comparison of 18 studies in the PSU laboratory where polarization data were reported after one month or more of operation supported this decrease in power with Pt catalyst cathodes, with an average of 0.87 ± 0.31 W m^{-2} (n=18) (Figure 1A). There were only two studies from non-PSU laboratories where we identified cathode polarization data obtained after more than one month, but for these two studies the maximum power densities were 0.92 ± 0.04 W m^{-2}, which was not significantly different from the data reported in other non-PSU studies for their baseline studies of power generation. Therefore, we speculate that one factor that may complicate comparisons between laboratories, and account for generally lower power at other laboratories, is the use of "old" cathodes. If a reactor is started up until there are reproducible cycles of power generation, a new cathode should be used for the first set of polarization data. Otherwise, it is likely that tests done a few weeks to a month after acclimation with the original cathode would result in lower maximum power densities than that possible with a fresh catalyst material.

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Evaluation of Alternative Cathodes

There are now a large number of studies where alternatives to Pt cathodes have been studied, with most of these papers looking at activated carbon as an alternative cathode catalyst, although not all of these studies have controls using Pt catalyst cathodes. We expected that the performance of activated carbon cathodes would be comparable to that of new platinum cathodes as many laboratories have now reported good results with this material.[61] Our analysis of the maximum power densities from the PSU laboratory using alternative cathode catalysts (all with activated carbon as a base material, with different treatments) showed an average of 1.42 ± 0.11 W m^{-2} (n=15), with a range of 1.22 to 1.61 W m^{-2} (Figure 1A). In the majority of these studies, when the alternative catalyst was compared to the Pt control, the alternative cathode resulted in higher power production. However, when all of these studies are compared grouped together on the basis of using a Pt or an alternative catalyst, there was no significant difference in power production for the alternative catalysts (1.42 ± 0.11 W m^{-2}) compared to that of the Pt catalysts (1.36 ± 0.20 W m^{-2}; p=0.13 at 95% confidence interval except as noted).

In studies conducted in non-PSU laboratories, the alternative cathodes showed an average maximum power density of 1.19 ± 0.45 W m^{-2} (n=11), which was not significantly improved compared to the Pt control tests reported by these laboratories (p=0.42). Note that we have not included data in this comparison any studies that did not include a Pt control test. For tests in non-PSU laboratories, 73% of the studies showed improved performance relative to the Pt controls. However, these results for alternative cathodes reported by non-PSU laboratories were not significantly different from the results obtained from the PSU lab using Pt or alternative materials (P=0.24 for Pt, P=0.11 for alternative). We speculate that age of the cathodes made using alternative materials may be less of a factor in comparison of power densities using polarization

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data. In the PSU lab tests, after one month the maximum power densities averaged 1.22 ± 0.16 W m^{-2}, which was significantly higher than that of Pt cathodes (0.87 ± 0.31 W m^{-2}) after one month (n=16, p=0.0002). For non-PSU laboratories, the average was 0.86 W m^{-2} (n=2; for 0.6 and 1.12 W m^{-2}) for alternative cathodes operated for more than 1 month.

Our analysis of these data on alternative cathode catalysts and materials suggests that claims of improved power production based on comparison of laboratory data—when compared to only literature values— cannot be supported. Polarization tests with new cathodes need to be conducted in side-by-side tests, or even with the same reactors by switching cathodes, with new Pt catalyst cathodes as controls. Furthermore, even for tests in the same laboratory, there should be some consistency in maximum power densities (~15% based on our experience), but in several cases we observed much larger changes in "baseline" conditions. For example, in one study using a 4-cm cube reactor, 0.80 ± 0.04 W m^{-2} for an alternative cathode (iron/polyindole) the authors claimed greatly improved power compared to the Pt control which produced 0.65 ± 0.03 W m^{-2}.[62] However, in another study by the same group the Pt control produced 0.95 ± 0.01 W m^{-2}.[63] This 46% change in the Pt control is very large, suggesting that the iron/polyindole cathode did not significantly produce more power than a Pt control. In another study by a different group, the Pt control produced 1.71 W m^{-2},[64] with the alternative cathode producing 2.08 W m^{-2}. However, two years later the same group reported that a different alternative cathode produced 1.16 W m^{-2}, which was higher than their Pt control in this same study, but in this case the control only produced 0.86 W m^{-2} (26% decrease).[65] Although the reactors were identical (6 cm diameter and 8 cm long, compared to the 3-cm diameter, 4 cm long reactor in our other comparisons), the later study used a brush anode rather than a flat, carbon felt anode.[64, 65] Based on our analysis of the anode type in 4-cm cube reactors (see below), the use of a brush anode would not be expected to greatly reduce

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power output of the Pt controls. A third group of researchers from the same lab using the 4-cm cube reactors claimed that the alternative cathodes improved performance based on obtaining maximum power densities of 0.95, 1.08 1.39 and 1.42 W m^{-2}. While these are better than their Pt controls (range of 0.64 to 0.88 W m^{-2}), these values for the controls are comparable to or less than Pt controls obtained by PSU and some other labs.[25, 66-68] Results showing greater power with alternatives than a Pt control, that fall within the expected range, would indicate improved performance. There are several results shown in Figure 1B that do indicate improved power relative to Pt controls as they fall within the expected range for the Pt controls.

An excellent approach to evaluate new cathode catalysts is to use abiotic, three-electrode systems as they can reduce the impacts of other factors on cathode performance, such as mass transfer limitations or biofouling.[69] With defined electrolyte and counter electrode potentials, electrochemical techniques such as linear sweep voltammetry, rotating disk electrodes, and electrochemical impedance spectra can help identify catalytic activities separate from these other factors. In addition, it may not be possible to test the actual cathode structure (i.e. a catalyst on a stainless steel mesh current collector) in some specialized devices such as a rotating disc electrode. There can still be differences in electrochemical techniques adopted among laboratories for these tests, such as using slow or fast LSVs, different rates of stirring or no stirring, or conducting tests using chronoamperometry. We recommend that both abiotic electrochemical tests, as well as MFC tests, be conducted with any new cathode material.

Effect of Anode Type on Power Output

In the original study of graphite fiber brush anodes it was demonstrated that power was improved with brush anodes (2.40 mW m^{-2}) relative to flat carbon cloth anodes (1.07 W m^{-2}) in

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4-cm cube MFCs, but the tests were conducted using a 200 mM PBS electrolyte, and ammonia gas-treated anodes.[12] Other tests comparing performance using 50 mM or 200 mM PBS were made using a different type of reactor (bottle brush reactors). To see if published studies since then supported claims that brush anodes could produce more power than other types of anodes in 50 mM PBS, we examined studies where brush or other anodes were tested in 4-cm cube MFCs with Pt catalyst cathodes. In these brush anode tests, anodes were heat-treated in a muffle furnace to improve their performance.[50] Brush anodes produced an average maximum power density of 1.11 ± 0.45 W m^{-2}, compared to 0.79 ± 0.19 W m^{-2} for cloth anodes and 0.51 ± 0.00 W m^{-2} for felt anodes (Figure 2). The brush anodes performed better than the cloth anodes ($p<0.01$) but based on this comparison the power densities were not significantly different from the felt anodes ($p=0.07$). No significant difference is shown between the cloth anodes and felt anodes ($p=0.06$).

There are also studies where brush or felt anodes were used with alternative cathodes in 4-cm cube reactors with 50 mM PBS. In these tests with non-Pt cathodes, felt anodes produced a maximum power density of 1.30 ± 0.27 W m^{-2} (n=9), which was higher than 1.15 ± 0.44 W m^{-2} (n=12) for brush anodes. However, eight of the nine studies using felt anodes were conducted without a Pt cathode control, making it difficult to draw the conclusion that felt anode performed better than brush anode. In one study conducted by PSU researchers, the highest power density produced with felt anodes of three different thicknesses was 1.05 W m^{-2} (1.27 thick felt anode). However, this was less than the 1.36 ± 0.20 W m^{-2} average for the PSU studies using brush anodes, and this best result was only comparable to the lowest value with brush anodes (1.02 W m^{-2}) (Figure 1A).[70] Thus, we conclude that brush anodes appear to provide better performance on average than felt anodes, but further direct comparisons will be needed to fully justify that claim.

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Impact of Solution Conductivity on Power Output

The use of a solution with higher conductivity (higher ionic strength) should improve power production due to a reduced ohmic resistance, as long as bacteria are not adversely impacted by higher salt concentrations. The first report that power was increased with solution conductivity used MFCs with flat anodes in 4-cm cube reactors, with conductivity increased using NaCl.[71] When several studies using brush anodes were compared on the basis of solution conductivity using 50 and 100 mM PBS (Pt cathodes), no significant difference ($p=0.98$) was observed in maximum power among these studies (Figure 3). This outcome of no significant difference between 50 and 100 mM PBS among all studies was likely due to differences between laboratories being larger than differences specifically due to solution conductivity, as in most of these studies conductivity was not the main focus of the experiments. Based on tests conducted in the same laboratory (PSU), but by different researchers, power was increased with conductivity, with 1.35 W m^{-2} using 50 mM PBS, 2.11 W m^{-2} in 100 mM PBS and 3.20 W m^{-2} in 200 mM PBS.[38, 72] In one study using alternative cathodes, side-by-side tests showed that power increased from 2.60 W m^{-2} in 50 mM PBS, to 4.70 W m^{-2} in 200 mM PBS.[27]

Changes in solution conductivity over time due to media storage, or incorrect preparation of media can impact conclusions regarding other study parameters. The effect of solution conductivity on ohmic resistance is easily quantified using electrochemical impedance spectroscopy (EIS). As the ionic strength is increased, ohmic resistance decreases as shown by the intercept of the EIS curve with the x-axis in the high frequency range. For example, the ohmic resistance decreased from 18.3 Ω in 50 mM PBS, to 10.4 Ω in 100 mM and 6.8 Ω in 200 mM PBS in tests with a brush anode and an activated carbon cathode (Figure 4). Tests using the solutions using 50 or 200 mM PBS using the same conditions as those for Figure 4 showed that power was

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increased by a factor of 1.8 due only to solution conductivity. However, this increase in power due to conductivity was about the same as that reported in a different study on improved power using an alternative cathode material (iron and nitrogen doped activated carbon) relative to the plain activated carbon control.[26] EIS data reported in that study showed that the ohmic resistance was reduced in tests with the alternative cathode compared to the activated carbon cathode control by a factor of 1.9. Thus, conductivity alone could have been the main factor for the improved performance. Solution conductivity should always be reported and carefully monitored with a conductivity meter in all tests as it is a factor that can greatly impact power production.

Errors in media preparation can easily result in changes in solution conductivity, especially due to the amount of hydration of the buffer salts used to prepare the medium. For example, 50 mM buffer is often made using 4.58 g L^{-1} of Na_2HPO_4 and 2.45 g L^{-1} of $NaH_2PO_4 \cdot H_2O$.[73] However, others have used 10.9 g L^{-1} of $Na_2HPO_4 \cdot 12H_2O$ and 3.04 g L^{-1} of $NaH_2PO_4 \cdot 2H_2O$.[74] Thus, accidental use of a less hydrated buffer salt at the higher mass concentration could easily lead to conclusions of improved power due to materials that were really due to buffer concentration. Repeated addition of sodium acetate to the same solution can also increase conductivity and voltage or power over time.[23] This conductivity change can be avoided by using fresh buffer on successive cycles, or adding acetic acid rather than the salt.

Impact of Microbial Community on Performance

The anode materials, operating conditions, and inoculum source can affect the performance of an acetate-fed MFC, but *Geobacter* is usually the predominant genus on the anode when there is good power generation. For example, Vargas et al.[75] showed that *Geobacter* spp. were predominant on brush anodes in cube-type air-cathode MFCs fed acetate (1 g/L, 50 mM PBS),

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with improved performance and a higher abundance of *Geobacter* spp. on a brush anode (57 ± 4%) compared to a carbon-cloth anode (27 ± 5%). In H-type MFCs fed with acetate and graphite anodes, Picot et al.[76] found anodes modified with positively charged groups (4-benzyltriphenylphophonium) increased power output and had a biofilm dominated with *Geobacter* spp., whereas *Geobacte*r spp. were not detected on the poorer performing graphite anodes modified with negatively charged groups (4-benzylcarboxylic acid diazonium). Inocula from many different sources (primary clarifier effluent, primary anaerobic digester effluent, anaerobic bog sediment) and geographical locations (USA and Saudi Arabia), used in acetate-fed air-cathode MFCs operated using graphite fiber brush anodes and Pt cathodes, were always found to be dominated by the genus *Geobacter*, with sequences closely related to *G. sulfurreducens*.[75, 77-79] In one study where three-electrode reactor operated under potentiostatic control were inoculated with different sources from a wastewater treatment plant (primary wastewater, primary sludge, activated sludge or secondary sludge), better performance was characterized by a strong dominance of *Geobacteraceae*.[80] In tests with a different type of inoculum (soils from separate geographic locations), all reactors had the same electrochemical performance and all were colonized primarily by a single *Geobacter* spp. (*Geobacter psychrophilus*).[81] Taken together, these results all show the electrochemically driven selection of a single phylotype in different microbial electrochemical systems, with good performance linked to the abundance of different *Geobacter* spp.

The method used to analyze the microbial community does not seem to be as important as other factors, such as substrate, materials, and inoculum source, for characterizing the microbial communities. For example, Vargas et al.[75] used a more traditional pyrosequencing-based approach, while Picot et al.[76] used fluorescent *in situ* hybridization with *Geobacter* specific probes, but both studies found a predominance of *Geobacter* spp. Analysis of communities using a different

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approach based on flow-cytometry and 16S rRNA gene sequencing also found an abundance of a single phylotype (*G. sulfurreducens*) on an electrode of an acetate-fed, three-electrode reactor operated under potentiostatic control.[82] Flow cytometry-based studies have also shown that pH and inoculum source can impact the microbial community, but the best performing MFCs were always dominated by *G. sulfurreducens*, while low-performing biofilms had a higher microbial diversity.[83] Even with full-length 16S rRNA gene sequencing, it is sometimes not possible to distinguish organisms at the species level. For example, *Geobacter anodireduces* isolated from an MFC could not be distinguished as different species from *G. sulfurreducens* based on full-length (1457 bp) 16S rRNA gene sequencing due to their high 16S rRNA gene sequence similarity (98%), but the two exoelectrogens were shown to be different on the basis of their other characteristics.[48, 49]

Another factor that could affect the microbial communities in acetate-fed MFCs is the duration of operation. Microbial communities in acetate-fed MFCs are mainly characterized after only few weeks or months of operation, and longer periods of operation could affect the anodic microbial community structure and abundance of *Geobacter* spp. [84] Based on 16S rRNA gene cloning and sequencing, the anode biofilm community of acetate-fed two-chambered MFC operated for over 1 year was dominated by *Betaproteobacteria* (48.8%) followed by *Deltaproteobacteria* (31.7%), with predominance of *Geobacter* spp.[85] The predominance of *Betaproteobacteria*, which consists of aerobic and facultative bacteria, was possibly due to oxygen intrusion to the anode from the continuously aerated cathode. In another study, *Pelobacter propionicus* was the dominant bacteria (63% of the anodic community) detected in acetate-fed air-cathode MFCs with brush anode and operated for more than 1 year.[86] While *Geobacter* spp. was not detected in this study, when the authors changed the operation from MFC to microbial electrolysis cell (MEC) operating by

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replacing and sealing off the cathode from air, the proportion of *Geobacter* spp. with sequences closely related to *G. sulfurreducens* increased to 38%.

These studies on the microbial communities on MFC anodes show that *Geobacter* spp. predominate on the anode, although many factors can impact the relative abundance of different *Geobacter* spp. Most studies on brush have shown a predominance of *Geobacter* spp. with sequences most closely related to *G. sulfurreducens*. We infer from such studies that the presence of *Geobacter* is important for producing high-power densities in these studies. Also, using a bacterial inoculum enriched in *Geobacter*, such as media or biofilms from existing MFCs, can decrease startup time and increase power production of newly inoculated air-cathode MFCs.[87-90] Thus, members of the genus *Geobacter* appear to be ubiquitous in nature, and they become dominant on anodes operated under the highly-selective conditions in acetate-fed, brush anode and air-cathode MFCs.

MFC Performance with Glucose versus Acetate

Acetate and glucose have most commonly been used as single substrate fuels in MFCs,[32] particularly in studies examining the impact of the cathode on power production.[33, 40, 59, 91, 92] The use of a defined medium provides consistent solution chemistry for evaluating the cathode performance, which could be obscured by changes in wastewater composition over time.[93] The anodes of MFCs that produce high power usually contain a high proportion of *Geobacter* species, usually *G. sulfurreducens*, which is only able to use simple volatile fatty acids such as acetate and lactate, but not glucose. Thus, glucose must first be fermented by other microorganisms in order to enable these exoelectrogens to produce current. In tests from a number of different laboratories where Pt catalyst cathodes were used, the average maximum power density was 0.86 ± 0.26 W m^{-}

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^{2} with glucose substrate, compared to 1.21 ± 0.55 W m^{-2} (n=7) among several different laboratories using acetate (Figure 5). When alternative cathodes were tested using glucose as the substrate, the power densities in different studies averaged 1.08 ± 0.45 W m^{-2}, which was not significantly different (p=0.55) than 1.24 ± 0.40 W m^{-2} calculated using alternative cathodes with acetate (Figure 5). Thus, there seemed to be no noticeable increase in power using acetate compared to glucose, but concentrations of the fuel could impact the concentrations of acetate available for power generation, and thus result in different maximum power densities in polarization tests. Because glucose must first be fermented to acetate, polarization tests need to be done under conditions where acetate concentrations in the medium have increased, and therefore polarization tests should be not conducted beginning of a fed batch test as often done when acetate is used as the fuel in an MFC.

Outlook

A comparison of MFC results under conditions intended to be identical shows that there is a wide variation in maximum power densities, even when using identical materials. Part of this variability could be due to other factors that impact comparisons of performance between different laboratories. For example, the method used to collect polarization data can be important. It has been shown that rapid voltage scans using a potentiostat show apparent increases in maximum power densities compared to steady state values at a fixed resistance.[94] For fed-batch tests, a slow scan rate should be set when a potentiostat is used to obtain polarization data. When using fixed resistors in the external circuit, the best results are obtained by using a single resistor for the whole cycle, with multiple cycles used with different resistors (multiple cycle tests).[94] Resistors can be changed over a single cycle, but sufficient time must be allowed at each resistance to enable pseudo-steady states (single cycle method). Acclimation to a high external resistance, followed by

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polarization tests using much lower resistances, can also lead to power overshoot (a doubling back of the power density curve as resistance is lowered) and underestimation of maximum power densities possible if the MFCs are acclimated under lower resistances.[95, 96]

These results show that improved cathode performance with alternative materials is often unsupported by lack of data with Pt controls, or power densities using Pt controls that are less than those expected based on tests by others. Power densities with Pt catalyst cathodes, in 50 mM PBS with 4-cm cube reactors and brush anodes, should typically average around 1.38 W m^{-2}. In cases where values are significantly below this value, new reactors should be started up using effluent from a well performing MFC, and power densities in this range confirmed using new Pt catalyst cathodes. At this point, alternative cathode materials can be tested with confidence to examine their performance. Meanwhile, electrochemical half-cell can be used to further characterize the catalytic activity and kinetics of alternative catalysts. A comparison of new materials, solutions, or microorganisms under conditions similar to previous studies will help in understanding the factors that impact performance of MFCs for electricity generation using single substrates as well as wastewaters.

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Associated content

Supporting information available: copies of a spreadsheet of the data used to make the comparisons, with references. This material is available free of charge via the internet.

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Broader Context

Microbial fuel cells (MFCs) have been widely studied for more than a decade as a sustainable strategy for generating electricity from organic matter in wastewater while accomplishing wastewater treatment. Power densities have improved through the use of different electrode materials, architectures (varied electrode sizes, spacing and liquid volume), and solution (electrolyte) chemistry. However, power densities reported after changing one part of the MFC, such as the cathode, can be higher or lower than those reported by others. In order to determine more accurately how specific changes in MFC materials and solution chemistry impact power production, we reviewed power densities reported by many groups around the world that all used an MFC with the same architecture. We show that even under exactly the same baseline materials and operating conditions, there are substantial variations in power densities reported by different researchers even within the same laboratory. Our analysis suggests that claimed improvements in power production must be substantiated by more than a 15% increase relative to control experiments conducted at the same time, and not through comparison to values reported in the literature.

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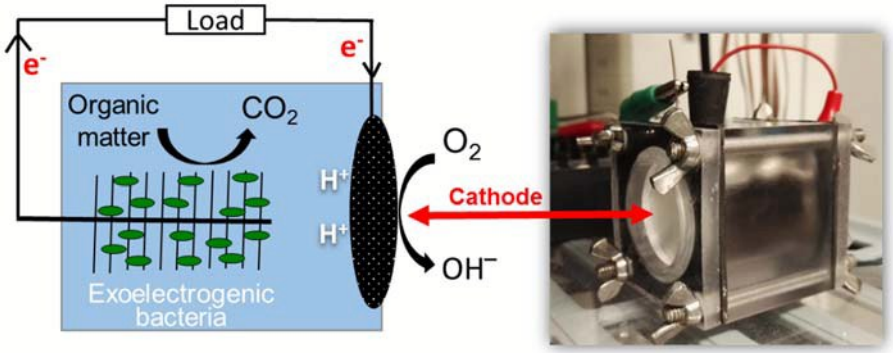

A review of the literature using cube-type microbial fuel cell reveals the extent in variability of power production.

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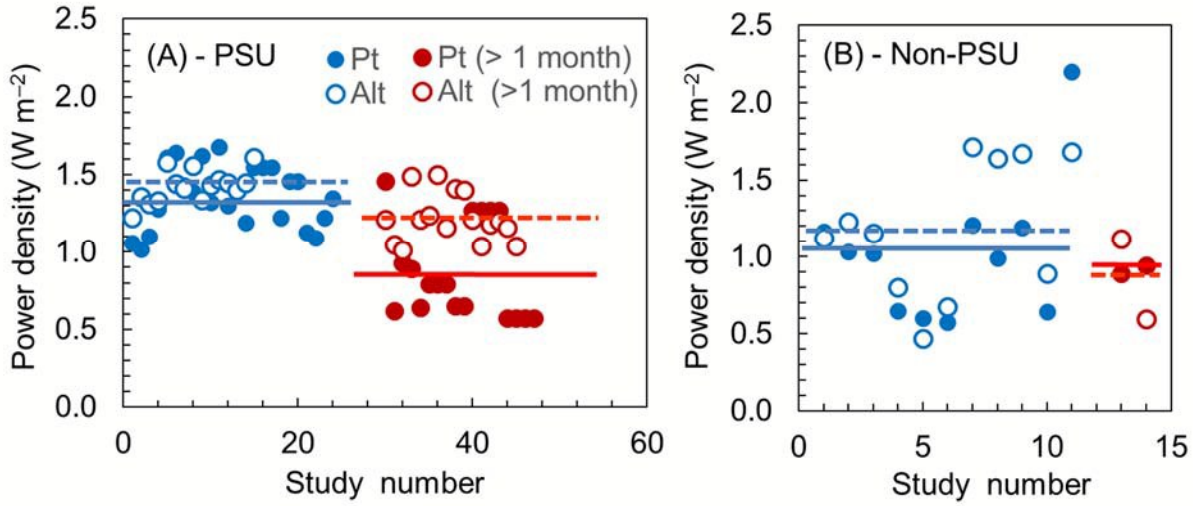
534 **Figures**



535

536 **Figure 1.** (A) Power density values for Pt control and alternative cathodes in short term (blue) and
537 long term (>1 month; red) tests from the same laboratory (PSU). (B) Power density values for Pt
538 control and alternative cathodes from other groups. (Solid lines, average power densities for
539 platinum cathodes; dashed lines, average power densities for alternative cathodes).

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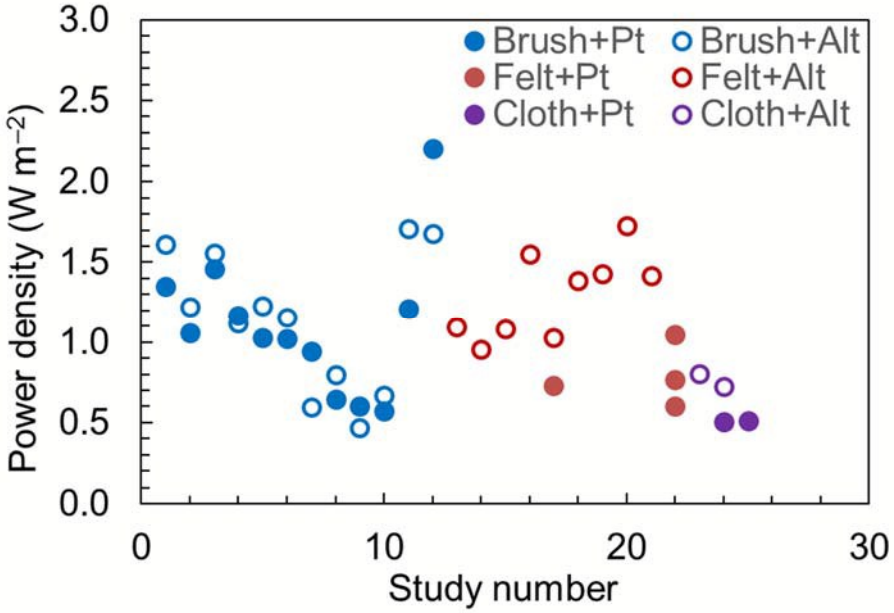

542

543 **Figure 2.** Power densities for Pt (control) and alternative cathode catalysts with different types of
544 anodes (brush, carbon felt and carbon cloth).

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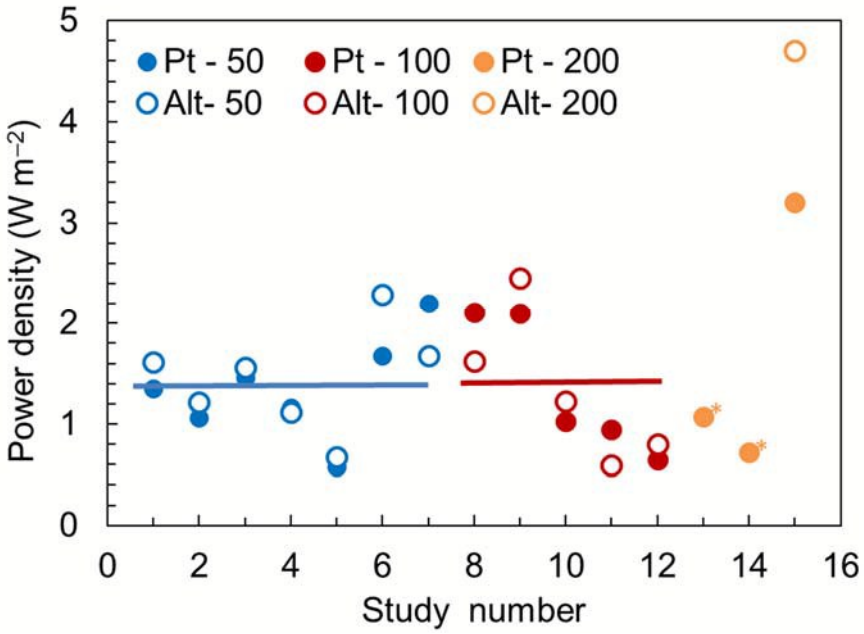

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548 **Figure 3.** Power densities for Pt (control) and alternative cathode catalysts in 50, 100 and 200 mM
549 PBS (*, not brush anode). (Solid lines, average power densities for platinum cathodes.)

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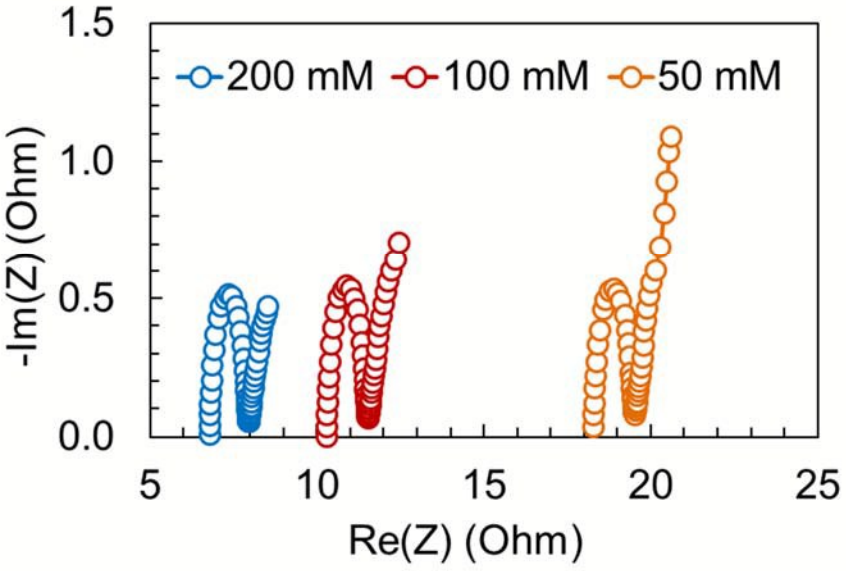

551

552 **Figure 4.** Electrochemical impedance spectroscopy (EIS) curves for activated carbon cathode in
553 50, 100 and 200 mM PBS.

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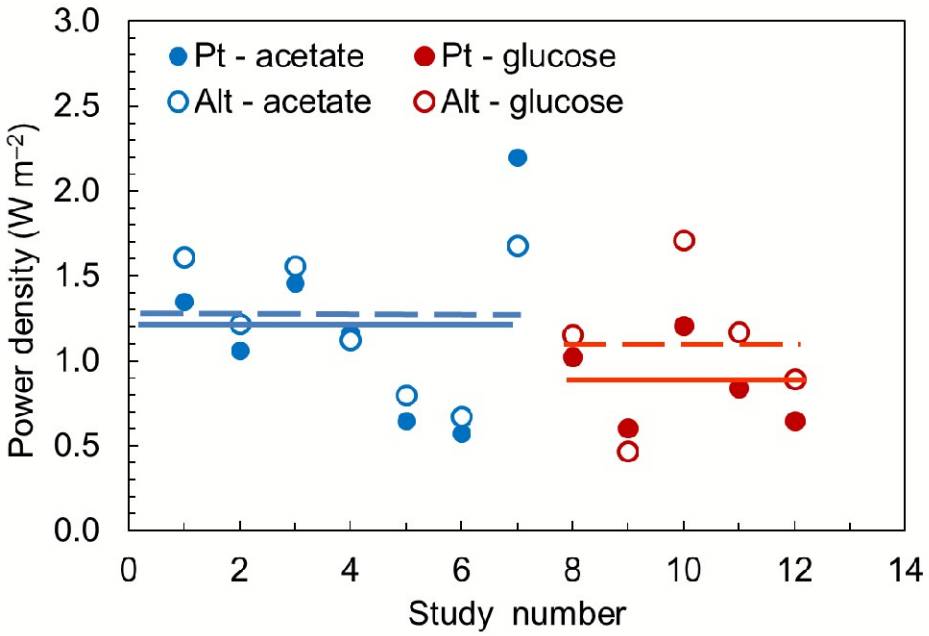

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557 **Figure 5.** Power density values for Pt control and alternative cathodes fed with acetate and glucose.
558 (Solid lines, average power densities for platinum cathodes; dashed lines, average power densities
559 for alternative cathodes).

560