



Sacrificing power for more cost-effective treatment: A techno-economic approach for engineering microbial fuel cells



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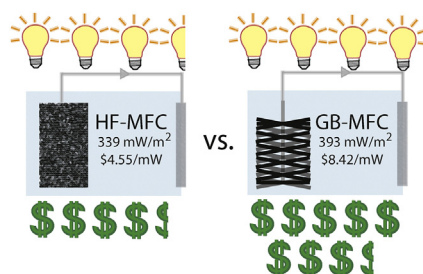
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HIGHLIGHTS

- Power density correlated with the anode specific surface area.
- Power density did not correlate with anode conductivity or internal resistance.
- No statistical difference between MFCs' electrochemical or biological properties.
- Inexpensive anode materials are cost-effective despite having non-ideal properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Microbial fuel cells (MFCs) are a promising energy-positive wastewater treatment technology, however, the system's cost-effectiveness has been overlooked. In this study, two new anode materials – hard felt (HF) and carbon foam (CF) – were evaluated against the standard graphite brush (GB) to determine if using inexpensive materials with less than ideal properties can achieve more cost-effective treatment than high-cost, high-performing materials. Using domestic wastewater as the substrate, power densities for the GB, HF and CF-MFCs were 393, 339 and 291 mW m^{-2} normalized by cathodic surface area, respectively. Higher power densities correlated with larger anodic surface areas and anodic current densities but not with electrical conductivity. Cyclic voltammetry revealed that redox systems used for extracellular electron transport in the GB, HF and CF-MFCs were similar (-0.143 ± 0.046 , -0.158 ± 0.004 and -0.100 ± 0.014 V vs. Ag/AgCl) and that the electrochemical kinetics of the MFCs showed no correlation with their respective electrical conductivity. 16S rRNA sequencing showed the GB, HF and CF microbial community compositions were not statistically different while organic removal rates were nearly identical for all MFCs. The HF-MFC generated a power output to electrode cost ($\text{W } \$^{-1}$) 1.9 times greater than the GB-MFC, despite producing 14% less power and 15% less anodic current, while having 2.6 times less anodic surface area, 2.1 times larger charge transfer resistance and an electrical conductivity three orders of magnitude lower. The results demonstrate that inexpensive materials are capable of achieving more cost-effective treatment than high-performing materials despite generating lower power when treating real wastewater.

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1. Introduction

Microbial fuel cells (MFCs) are bioelectrochemical systems capable of converting organic compounds in wastewater directly into electricity. The first generation of MFCs generated low power densities, required media to be replenished frequently and used toxic materials, making the process unsustainable (Cohen, 1931; Potter, 1911). Over the past decade, power densities have increased by orders of magnitude reaching 3320 W m^{-3} in miniature MFCs (<1 mL) (Ren et al., 2015), and up to 30 W m^{-3} in larger-scale MFCs (>2 L) (Ge et al., 2013). These power densities provide a valuable baseline understanding of the MFC's capabilities but the majority of data were generated using synthetic media, overestimating the system's capabilities when treating real wastewater. If MFCs are to be implemented for real wastewater treatment, the system's true limitations must be acknowledged and the cost-effectiveness must also be improved.

Although performance has increased significantly since the inception of the first MFC, the amount of power that can be generated from wastewater is limited. Domestic wastewater is more difficult to treat than synthetic media due to the low electrical conductivity ($<5 \text{ mS cm}^{-1}$) (Liu et al., 2005), circumneutral pH (He et al., 2008; Rozendal et al., 2006), and the presence of complex organics. These limitations result in higher electrolyte resistances (He et al., 2006), unfavorable cathodic thermodynamics (Stoll et al., 2016), and sluggish kinetics (Zhao et al., 2005). Ultimately, these factors lead to lower than expected power outputs and longer retention times, both of which increase the capital costs.

It has been suggested that using bioelectrochemical systems to treat wastewater will only become economically viable and competitive against other energy positive treatment processes [e.g. anaerobic digestion (AD)] if revenue from the products can be increased (Rozendal et al., 2008). However, the average cost for electricity is \$0.11 per kWh (EPA, 2015) in the U.S. and with the reported liter-scale MFCs generating volumetric power outputs below 30 W m^{-3} (Ren et al., 2015; Ge et al., 2013), potential revenue from electricity production is only \$0.08 per m^3 per day, indicating that recovering energy using MFCs is not cost-attractive from an energy production standpoint. Furthermore, capital costs of MFCs have been estimated at \$8 per kg COD (chemical oxygen demand) removed versus \$0.01 per kg COD for AD (Rozendal et al., 2008). Low revenue combined with high capital costs results in prohibitive life cycle costs, especially when compared to other competing technologies. These considerations raise the question of whether or not increasing power output is the most sensible method for MFCs to achieve cost-effectiveness as an energy-positive wastewater treatment technology.

For example, using crumpled graphene instead of activated carbon anode electrode increased power density by 112% from 1.7 to 3.6 W m^{-3} (Xiao et al., 2012). However, graphene is still extremely expensive, with commercially available products costing more than \$30 per cm^2 . If output is normalized by cost, the unit power generated is orders of magnitude lower than liter-scale MFCs. This is compounded by the fact that there is no method to manufacture large graphene sheets. While new breakthroughs in graphene development have been achieved that claim to reduce production costs by 99% (Bointon et al., 2015), anodes would still be thousands of dollars per m^2 . While new materials research will be absolutely crucial for the development and improvement of future and existing technologies, increases in power output need to be economically justified.

Researchers have realized the prohibitive cost of MFC components and progress has been made to reduce the overall system cost while maintaining similar power outputs. Nafion membranes (\sim \$1000 per m^2) are an essential part of hydrogen fuel cells and

were initially thought to be necessary for MFCs. However, once it was realized that cations other than H^+ (e.g., Ca^{2+} , Mg^{2+} , Na^+) were responsible for satisfying electroneutrality within the system (Rozendal et al., 2006), Nafion membranes were quickly replaced with other low cost separators (Fan et al., 2007) without adversely affecting performance. Additionally, the single chamber MFC configuration omits the membrane entirely, greatly reducing system costs while increasing performance.

More recently, low-cost platinum-free cathodes and carbon brush anodes have been developed. Xia et al. developed an activated carbon cathode catalyst pyrolyzed with iron ethylenediaminetetraacetic acid that generated power outputs comparable to Pt cathodes ($1580 \pm 80 \text{ mW m}^{-2}$) (Xia et al., 2013). Zhang et al. also achieved similar power densities (1580 mW m^{-2}) when using an activated carbon/carbon black mixture spread over stainless steel mesh (Zhang et al., 2014). Both studies used a single chamber configuration and both found the non-Pt cathode catalysts to be less susceptible to degradation over long periods of time (<4.5 months), decreasing 0 and 7%, respectively (Xia et al., 2013; Zhang et al., 2014). In contrast, power densities in single chamber MFCs with Pt-based cathodes diminished by more than 50% over the same amount of time. Baudler et al. grew biofilms on copper anodes with no adverse effects and suggested that copper foil could be implemented at \$0.53 per m^2 (Baudler et al., 2015). The authors note that the thickness of the foil at this price was 11 μm , which would require mechanical stabilization, thus increasing costs. With most feasibility studies still using synthetic media to provide a baseline understanding of performance, more research is needed to understand how material characteristics, such as the electrical conductivity and specific surface area, affect MFC performance when treating real wastewater.

In this study, it was hypothesized that using inexpensive anode materials with non-ideal properties would reduce power output but achieve much more cost-effective wastewater treatment. To test this, we evaluated the standard graphite brush (GB) with high electrical conductivity and surface area against two other carbon materials with lower conductivity and surface area, hard felt (HF) and carbon foam (CF), in their ability to treat real domestic wastewater. In addition to their properties, we chose to evaluate the HF and CF materials because they could be manufactured on a large scale, which newer anode materials could not be. The power output, polarization curves, biodegradation rates, zeta potential, specific surface area and electrochemical impedance spectroscopy (EIS) were measured to understand how the material properties affected overall performance. Cyclic voltammetry (CV) and 16S rRNA sequencing were also conducted to elucidate if the material properties altered extracellular electron transport (EET) and microbial community composition. Electrode costs were estimated and the power output normalized by cost was calculated.

2. Materials and methods

2.1. Reactor configurations, inoculation and operation

2.1.1. Reactor configuration

MFC reactors used a single chamber configuration with a 20 mL working volume. Anodes were a graphite brush with titanium core (GB, Mill Rose, USA), hard carbon felt (HF) (Anshan Sinocarb Carbon Fibers Co., Ltd. China) or carbon foam (CF) material (The Institute of Coal Chemistry, Chinese Academy of Sciences, China). The GB anodes were 6 cm in diameter with a 7 cm brush length (15 cm overall). HF and CF anodes were disk shaped with a 3 cm diameter and 1.5 cm thickness. All anodes were soaked in acetone for 24 h then heated at $450 \text{ }^\circ\text{C}$ for 15 min to remove impurities. Anode-cathode spacing was 1.5 cm and was measured from the cathode

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