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Short communication

Recycled tire crumb rubber anodes for sustainable power production in microbial fuel cells

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ABSTRACT

One of the greatest challenges facing microbial fuel cells (MFCs) in large scale applications is the high cost of electrode material. We demonstrate here that recycled tire crumb rubber coated with graphite paint can be used instead of fine carbon materials as the MFC anode. The tire particles showed satisfactory conductivity after 2–4 layers of coating. The specific surface area of the coated rubber was over an order of magnitude greater than similar sized graphite granules. Power production in single chamber tire-anode air-cathode MFCs reached a maximum power density of 421 mW m^{-2}, with a coulombic efficiency (CE) of 25.1%. The control graphite granule MFC achieved higher power density (528 mW m^{-2}) but lower CE (15.6%). The light weight of tire particle could reduce clogging and maintenance cost but posts challenges in conductive connection. The use of recycled material as the MFC anodes brings a new perspective to MFC design and application and carries significant economic and environmental benefit potentials.

1. Introduction

Microbial fuel cells (MFCs) are an emerging bioelectrochemical technology that produces electrical energy from organic matter catalyzed by exoelectrogenic bacteria on the anode [1–3]. In less than a decade, researchers have increased power densities by several orders of magnitude, from mW m^{-3} to kW m^{-3} [3,4]. These increases have come primarily from addressing the physical and chemical constraints on MFC performance by exploring new materials and optimizing reactor architectures. A remaining challenge for MFCs as they become more technically feasible for full-scale applications such as simultaneous wastewater treatment and bioenergy recovery is the high cost of electrode material currently used in lab scale studies. Many anode materials have been tested to improve biofilm attachment and conductivity. The popular materials include graphite granules [5], carbon paper [6], carbon cloth [7], carbon mesh [1], and activated carbon [8]. The recent development of graphite brush anodes with high specific surface area and an open structure to prevent fouling problems provides a solution for scaling up [9]. However, the cost of most electrode materials, from ~$50 m^{-2} to over $1000 m^{-2}, is prohibitive to use in large scale [1,4].

We investigated the performance of a recycled material-crumb rubber (granular particles produced by grinding waste tires) – as a potential inexpensive and abundant alternative material for MFCs. The Rubber Manufactures Association (RMA) estimated that 303.2 million scrapped tires were produced in the U.S. in 2007; approximately one discarded tire per person per year [10]. In addition, more than 300 million tires are currently stockpiled throughout the country due to the lack of end-use markets. These stockpiles pose great environmental, safety, and health concerns. The materials are fire hazards, non-biodegradable, and occupy significant landfill space. Current disposal solutions include incineration for tire derived fuels, reuse of crumb rubber as surfaces for playgrounds and sports fields, and reuse of tire rubber in asphaltic concrete mixtures [11]. Recently Tang et al. developed a new crumb rubber filtration system to treat wastewater and ship ballast water [12,13]. They found that crumb rubber filters significantly reduced clogging compared to sand filters without compromising pollutant removal. Tire derived rubber particles also showed better organic adsorption capacity than sand particles, as well as exhibited good performance as high surface area, non-toxic media for biofilm attachment in bioreactors [14].

In this study, we tested for the first time the feasibility of using crumb rubber with a conductive graphite coating as the anode material for electricity production in MFCs, and compared its performance with graphite granule anodes. Statistical and electrochemical analyses were conducted to evaluate the performance of the coated material in terms of conductivity, resistances, and

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specific surface area. The potential benefits of using crumb rubber as MFC electrode was also discussed.

2. Materials and methods

2.1. MFC construction and operation

Single-chamber MFCs were constructed from Wheaton graduated media bottles (250 mL, Wheaton, NJ) by adding one glass extension tube on the side [9,15]. Rubber top caps were used to provide an air-tight condition. Air cathodes (projected area of 4.5 cm^2, one side) were made by applying Pt/C (0.5 mg cm^{-2}) and four PTFE diffusion layers on 30% wet-proofed carbon cloth (Fuel Cell Earth, MA, USA) as previously described [16]. Recycled tire crumb rubber was donated by AcuGreen Inc. (CO, USA). The crumb rubber was pre-shredded from recycled tires and sieved to collect particles with 4–8 mm diameter. The rubber particles were washed with deionized water and air dried before the application of the conductive coating (E-34, Superior Graphite Co., OH, USA) to the particle surface [17]. To determine the optimal coating condition, additional coatings were applied to some of the particles after the previous coating was completely dried in air. Coated crumb rubber was packed into the MFC anode chamber to a volume of 140 mL (71.5 g). A twisted titanium wire was inserted into the anode pack as a current collector and connected to the external circuit. The same volume (140 mL, 133.6 g) of graphite granules (D = 2–6 mm, Graphite Sales Inc., OH) was used as the control anode material in a separate MFC.

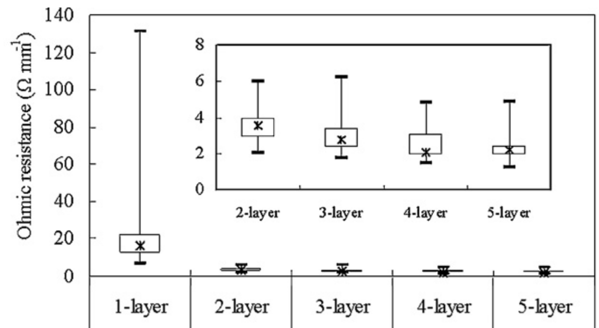
MFCs were inoculated with anaerobic sludge obtained from the Englewood-Littleton Wastewater Treatment Plant (Englewood, CO). The reactors were fed with 190 mL medium containing: 1.25 g L^{-1} of sodium acetate, 0.31 g L^{-1} of NH_4Cl, 0.13 g L^{-1} of KCl, 3.321 g L^{-1} of $NaH_2PO_4 \cdot 2H_2O$, 10.317 g L^{-1} of $Na_2HPO_4 \cdot 12H_2O$, 12.5 mL L^{-1} of mineral solution and 5 mL L^{-1} of vitamin solution [15]. All MFCs were operated in fed-batch mode at room temperature. Growth media was replaced with fresh media when the voltage dropped below 50 mV (1000 Ω resistance).

2.2. Statistical and electrochemical analyses

The optimal number of coatings on the crumb rubber was determined by resistance measurement and statistical analysis. After each coat was finished and completely dried in air, 35 coated rubber samples were randomly selected and the ohmic resistance across a 4 mm distance was measured repeatedly by a programmable multimeter. The t distribution was used to calculate confidence intervals (CIs) for the mean changes between the resistances on two adjacent coatings. The 95% CIs were calculated by $\bar{X} \pm 2.032S/\sqrt{n}$, where $\bar{X} = \sum_{i=1}^{n} X_i/n$ was sample mean, $S = \sqrt{(\sum_{i=1}^{n}(X_i - \bar{X})^2)/(n-1)}$ was sample standard variation, and n was the sample size.

MFC cell voltage was continuously monitored using a data acquisition system (Keithley Instruments, OH). The circuits were operated under a fixed load of 1000 Ω. During the stable power production stage of each batch experiment polarization measurements were made using a variable resistor box (50–50 kΩ). Current ($I = V/R$), power ($P = IV$), and coulombic efficiency (CE, based on COD) were calculated as previously described [18]. Electrochemical impedance spectroscopy (EIS) tests were conducted using a Potentiostat (PC 4/300, Gamry Instruments, NJ, USA) to measure the internal resistances with the anode as the working electrode, and the cathode as the counter electrode and reference electrode. The scan range was from 10^5 Hz to 0.005 Hz with a small sinusoidal perturbation of ±10 mV.

Specific surface area and pore size distribution of the particles were estimated by Brunauer–Emmett–Teller (BET) method using a five-point N_2 gas adsorption technique (ASAP 2020; Micromeritics, Norcross, GA) [19]. The average pore size and pore size distribution were determined from desorption of N_2 according to the method developed by Barrett, Joyner, and Halenda (BJH) [20].



	1-layer	2-layer	3-layer	4-layer	5-layer
Maximum (Ω mm⁻¹)	131	6	6.2	4.8	4.9
Minimum (Ω mm⁻¹)	6.5	2.0	1.7	1.4	1.3
Median (Ω mm⁻¹)	16	3.5	2.8	2.1	2.2
95%CI* (Ω mm⁻¹)	22.0±8.1	3.5±0.3	3.0±0.4	2.5±0.3	2.3±0.2

*n=35, $t_{0.025,34}$=2.032

Fig. 1. Box plot of resistance measurement and statistics on tire crumb particle surface with different coating layers.

3. Results and discussion

3.1. Resistance characterization of coated crumb rubber electrode

To convert the almost non-conductive crumb rubber into electrically conductive electrode, multiple layers of graphite paint were applied to the rubber particle surface. Such approach has been successfully applied on ultrafiltration membrane MFC cathodes, as described previously [17]. Fig. 1 is the box plot showing the statistics of ohmic resistance variations of the 35 randomly selected particles coated with different layers of graphite paint. It appears that additional coatings reduced the particle surface ohmic resistance and heterogeneity. After the first coating, a particle has an average ohmic resistance of 22.0 Ω mm^{-1}, but the numbers across the 35 samples varied significantly, from 6.5 to 131 Ω mm^{-1}, resulting in a huge standard deviation. The second layer of coating reduced the ohmic resistance by a factor of 6, to an average of 3.5 Ω mm^{-1}. The variation was also considerably reduced. Additional coatings showed only minor improvements: the difference between 4 coatings and 5 coatings was not statistically significant at the 5% level (Fig. 1). In order to conserve coating material and reduce cost, the rubber particles with 4 layers of coating was used in further MFC and electrochemical characterizations. The average ohmic resistance of the particles was 2.5 Ω mm^{-1}, ~10 times greater than graphite granules. EIS shows a similar trend in reactor ohmic resistance in coated crumb rubber or graphite granules MFC reactors (Fig. 2). The system resistance decreased along with additional coatings. The average system resistance of the MFC with 4-layer coated rubber was 574 Ω, and the resistance using same volume of graphite granule was 210 Ω.

3.2. Surface characterization of coated crumb rubber electrode

High specific surface area is a crucial parameter of the MFC anode. It allows higher biofilm density and thus making higher current output possible. Surface characterization shows that the crumb rubber particle with 4-layer coating has an average BET surface area of 4.5 $m^2 g^{-1}$ (32,143 $m^2 m^{-3}$), more than one order of magnitude greater than the graphite granule (0.3 $m^2 g^{-1}$, or 2143 $m^2 m^{-3}$).

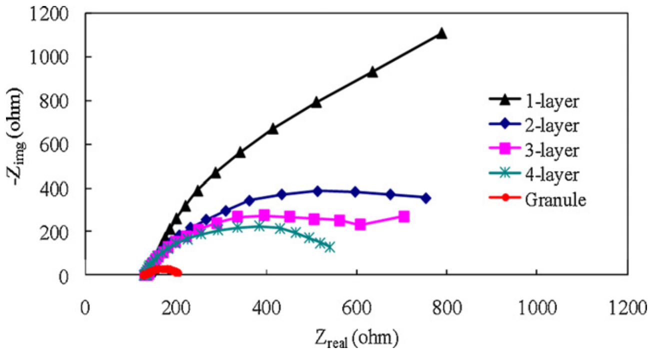


Fig. 2. System resistance of single chamber bottle reactor filled with graphite granules and tire particles with different coating layers.

The BJH desorption cumulative pore volume of the coated rubber particle was 0.013 $cm^3\,g^{-1}$ and BJH desorption average pore diameter was 88 Å, also significantly higher than the graphite granule in terms of the same parameters. The granule has a BJH desorption cumulative pore volume of 0.0006 $cm^3\,g^{-1}$ and BJH desorption average pore diameter of 54 Å. Fig. 3 compares the pore size distribution of the 4-layer coated tire particle and graphite granule. The incremental pore area and cumulative pore area of the tire particle are each one order of magnitude greater than those of the graphite granule. Specifically, the desorption cumulative pore area of tire particle and graphite granule was 5.78 $cm^2\,g^{-1}$ and 0.45 $cm^2\,g^{-1}$, respectively.

3.3. Power production from tire rubber MFCs and graphite granule MFCs

Repeatable cycles of power production were obtained from both tire rubber and graphite granule MFCs after 3–4 feeding cycles with fresh media. The stable voltages over a 1000 Ω external resistor in tire and graphite MFCs were around 390 mV and 430 mV, respectively. The tire reactor generally showed longer batch durations than the graphite MFC. A regular batch cycle for graphite MFCs took around 20 days before the media change, while a batch cycle for tire MFCs took about 30 days. Polarization and power density curves obtained by varying the external circuit resistances from 50 to 50,000 Ω showed that the crumb rubber MFC produced less power than graphite granule MFC. Fig. 4 shows that the maximum power density of the 4-layer coating tire MFC was 421 mW m^{-2} (cathode projected area), ∼20% less than the power density of the graphite MFC (528 mW m^{-2}). The COD removal of the tire reactor (85.0%) within a batch was less than that from the graphite MFC (92.8%), but the columbic efficiency obtained from the tire reactor (25.1%) was nearly one and half times higher than that calculated from the graphite granule MFC (15.6%).

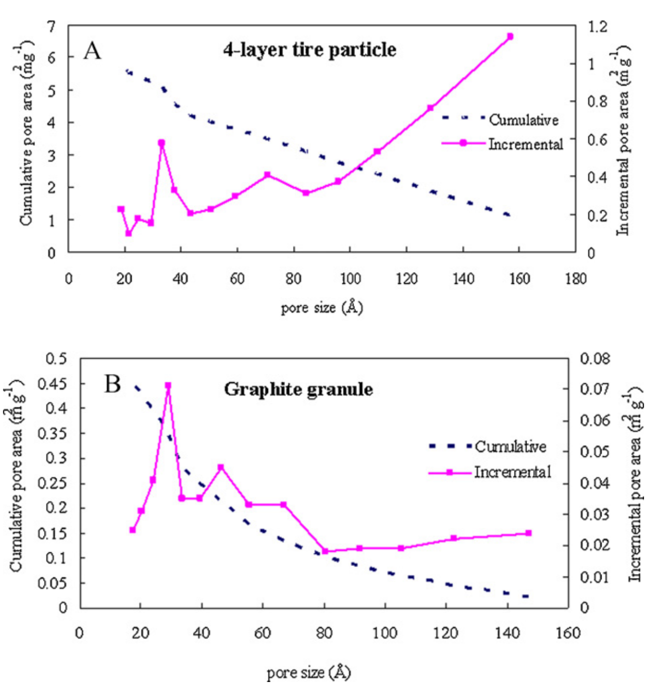


Fig. 3. Pore size distribution of (A) rubber particle with 4-layer coating and (B) graphite granule as the MFC anode.

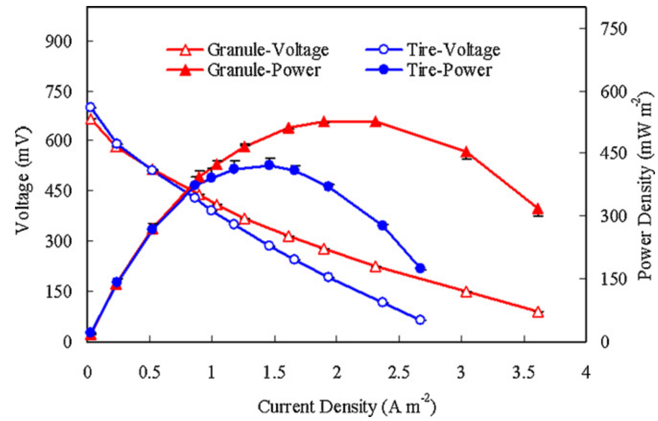


Fig. 4. Voltage and power density as a function of current density for coated tire anode MFCs and graphite granule anode MFCs.

The difference in power production from the two types of reactors is a result of several factors. It was noted that the specific area of the coated rubber particle was much higher than the graphite granule, which could result in higher attachment and current output, but the high ohmic resistance of the coated tire particle outweighed the benefit of surface area and caused lower power generation. The conductive coating only allows the electrons transfer across the surface of the tire particle rather than through the diameter of the granule, which increased the length of the transfer route. Additionally, the density of the crumb rubber is about 1.1 g cm^{-3}, only a little greater than water but much less than the density of the graphite (2.2 g cm^{-3}). The low density of crumb rubber media has the benefits with reduced maintenance cost and clogging potential [12], but it results in a loose packing that hinders conductive connection. The integration of metal current collectors into the anode pack could alleviate the problem in larger scale systems by compacting tire particles and generating a highly conductive network for more efficient electron transfers [21].

3.4. Cost-benefit outlook

The use of recycled tire crumb rubber instead of expensive carbon products as MFC electrode material is believed to carry economical and environmental benefits. Compared to the high cost of refined carbon electrode ($50 to over $1000 m^{-2}), the crumb rubber is free except for the minimal cost of the coating material. Our preliminary cost calculation shows the cost of coated tire electrode is $0.71 m^{-2} and $1.42 m^{-2} for 2-layer coating and 4-layer coating, respectively, which is comparable to graphite granules ($1.29 m^{-2}). Moreover, many countries currently have tire disposal tax ($1–3 per tire) and reuse subsidy programs ($0.1–0.5 per tire) to encourage tire recycle and reuse. These policies make the use of crumb rubber more economically competitive and can reduce the cost of rubber electrode by another $0.12–0.38 m^{-2} [22]. In addition, government regulations and higher public expectation on waste recycle and renewable energy production make the technology more attractive to industries, as the use of recycled tire rubber in MFCs will reduce the cost of tire disposal and bring more environmental benefits by increasing tire reuse, treating wastewater, and generate alternative energy.

4. Conclusions

Recycled tire crumb rubber was tested for the first time as an alternative electrode material in microbial fuel cells. The tire particles showed good conductivity after 2–4 layers of graphite coating. The specific surface area of the coated tire particle was more than 10 times greater than similarly sized graphite granules, which provides improved attachment surface for microbes. The single chamber air-cathode tire MFC produced the same level of power, COD removal, and coulombic efficiency as the graphite granule MFCs did. The concept of using recycled material as MFC electrodes opens up a whole new approach toward MFC design and application that carries significant economic and environmental benefits.

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