GRAPHENE ELECTRODES ENHANCE PERFORMANCE FOR MICRO-LITER SCALE MICROBIAL FUEL CELLS

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ABSTRACT
Recently, microliter-scale microbial fuel cells (µMFCs) have garnered significant interest as effective energy harvesters for low power biological and electronic systems. Although researchers have attained high current densities and columbic efficiencies from such fuel cells, low power outputs and working potentials caused by the use of Au/Cr electrodes have limited the implementation of µMFCs in practical applications. To overcome these limitations, here we present a graphene-based µMFC (G-MFC) that utilizes laser synthesized graphene electrodes to generate open circuit potentials (OCPs) of 0.8 ± 0.05 V and power densities of 1820 ± 10 W/m³. Furthermore, the G-MFC produces a maximum power output of 364 µW. The stackable and low cost design of our G-MFC allows for a wide range of applications and also serves as a platform for repeatable electrode and substrate based testing. These results suggest that our G-MFC methodology could offer an effective route to achieve viable energy harvesters for low power systems.

INTRODUCTION
Microbial fuel cells (MFCs) enable electricity harvesting directly from organic or inorganic matter through bacterial catalysis [1-11]. Benefits including relatively non-toxic components, flexibility of usable substrates, ambient operating temperatures, and mediator-less electron transfer from exoelectrogenic bacteria to solid electrode surfaces have all contributed to increased scientific interest in MFCs as a renewable source of sustainable energy [2, 11, 12]. At present, the majority of MFCs are milliliter-scale devices, which allows for the easy use of carbon-based electrodes, air cathodes and simple operating techniques [4]; however, reducing MFCs to microliter-scales enables: (i) higher surface area to volume ratios, (ii) increased control over electrode and chamber environments, (iii) superior reaction kinetics, and (iv) greater mass transfer flux [13]. Additionally due to their smaller chamber volumes and low start-up times, µMFCs are ideal testing platforms for electrode, microbe, and substrate-based experiments [13]. As a result, µMFCs could potentially be used for a variety of electronic and biological applications, such as powering low power devices in remote areas and powering on-chip systems [14, 15]. Using microfabrication techniques, researchers have managed to obtain increased columbic efficiencies and current densities from µMFCs [13]. Unfortunately, current µMFCs produce orders of magnitude lower power outputs and much lower potentials than their milliliter-scale counterparts. This is caused predominantly by high internal resistances and inefficient biological systems in the anode. Gold has been the primary electrode material in most µMFC works thus far as it is easy to fabricate and control with microscale precision using existing microfabrication techniques; however, researchers have found that gold electrodes result in increased contact resistance at the bacteria-electrode interface [14, 15]. This increased contact resistance has been the primary cause

Figure 1: Conceptual Illustrations of the graphene-based microliter-scale microbial fuel cells (G-MFC). (a) Graphite oxide is converted into graphene using a programmable laser. Graphene sheets were attached to graphite leads to make electrodes. (b) Exploded schematic of the G-MFC. (c) Bacteria catalyze the decomposition of carbohydrates in the cow dung, releasing electrons and protons. The electrons are transferred to the graphene anode via nanowires/endogenous mediators/direct contact. The electrons reduce the catholyte (ferricyanide) while the protons traverse the proton exchange membrane (PEM) and re-oxidize it.
of low power outputs in \( \mu \)MFCs, restricting their use to laboratory testing [4, 13]. To overcome these issues, here we present a G-MFC that exploits the advantages offered by \( \mu \)MFCs while utilizing graphene electrodes to reduce the internal resistance and increase power output.

CONCEPT AND MATERIALS

The basic concepts behind the G-MFC are included in figure 1. Figure 1a shows a conceptual illustration of the LightScribe method of converting graphite oxide into graphene under high intensity light [16]. Laser synthesized graphene offers a simple and controllable fabrication process combined with favorable electrical properties and high surface area, which make it an ideal electrode material for MFCs. Figure 1b shows an exploded schematic of the fuel cell. The end plates were made of acrylic and both the neoprene chambers had volumes of 200 \( \mu \)L. Neoprene was chosen as the chamber material to ensure that both chambers remained anaerobic during operation. In our previous work we demonstrated that cow dung was an ideal anodic substrate for microbial fuel cells as it: (i) contains a rich consortium of anaerobically respiring bacteria, (ii) has a diverse range of carbohydrates, (iii) is readily available in remote rural areas, (iv) is low cost, and (v) doesn’t require complex inoculum preparation techniques [10]. Figure 1c shows the operating concept of G-MFC. A 1:1:1 (wt%) mixture of water, dried and anaerobically digested cow dung was used at the anode and a 100 mM potassium ferricyanide solution in water was used at the cathode. Anaerobically digested cow dung was obtained by placing fresh cow dung in air tight container for 48 hours as described previously [15]. The G-MFC utilized 1 \( \text{cm}^2 \) graphene electrodes and Ultrex CMI-7000 as the proton exchange membrane (PEM).

FABRICATION

Figure 2 shows the graphene electrode fabrication process and results. A standard LightScribe (LS) CD was cleaned and covered with a PET sheet (416-T PET sheet, MG Chemicals). A 3 mg/ml graphite oxide (GO) solution in water was then drop cast onto the PET substrate and left to dry overnight, resulting in a thin, golden brown film of GO. An ultrasonic bath was used to ensure the complete dispersion of the GO in the solution. The desired pattern was then programmed into the LS software and the assembly was exposed to the laser. The CD was exposed six times to obtain black graphene as shown in figure 3a. Finally, the PET substrate containing the graphene was cut out and the graphene was joined with graphite leads using insulating tape to make electrodes. Stainless steel screws and washers were then used to connect wires to the graphite leads to allow for ease of operation and testing. Figure 3c shows an image of a fully assembled G-MFC prototype.

METHODS

Although several studies have shown that allowing time for biofilm formation results in better performance in MFCs [4, 5], here we conducted experiments immediately after fuel cell assembly and loading to examine the minimum outputs of the G-MFCs. OCPs were measured using a digital multimeter (Actron) and polarization curves were drawn with the help of a potentiostat (Ivium Technologies Inc). The potentiostat was operated in a two electrode setup, wherein both the reference and counter electrodes were connected to the anode while the working electrode was connected to the cathode. A scan rate of 1 mV/s was chosen as indicated in prior works [4, 5, 15]. Power density curves were subsequently plotted using the data. All current and power densities reported here were
calculated with respect to the volume of the G-MFC’s chambers (200 µL). Each experiment was repeated five times to establish consistency of the results. SEM images were obtained using an FEI Nova NanoSEM scanning electron microscope. All experimental results are reported as mean ± s.e.m.

RESULTS AND DISCUSSION

Figure 4 shows the experimental results for the G-MFC. Figure 4a shows the OCPs of a single G-MFC and two G-MFCs in series plotted versus time. The G-MFC produced a maximum OCP of 0.8 ± 0.05 V and two cells in series produced a maximum OCP of 1.6 ± 0.05 V. The OCPs remained stable for approximately 2.5 hours before declining sharply. The G-MFC lasted approximately 108% longer than our previous work in which gold electrodes were used [15]. The drop in potential in the G-MFC was most likely caused by the inefficiency of the PEM as a relatively high quantity of ferrocyanide was found in the cathode chamber. When the ferrocyanide was replaced, similar results were obtained. Where new gold cathodes were needed with every replacement of ferrocyanide in our prior work, the graphene was surprisingly resistant to wear and flaking [15]. A buffer was not required in the anode chamber to maintain the pH during operation. This suggests that the cow dung-water mixture contains naturally existing buffers; however, further investigation is required to identify the specific compounds responsible for this behavior [4, 5, 15]. Figure 4b shows the polarization and power density curves for a single G-MFC. The G-MFC produced a maximum power density of 1820 ± 10 W/m³. This power density translates into a maximum power output of approximately 364 µW, which, to the authors’ knowledge, represents the highest value reported for a µMFC in the literature at present. This performance can be attributed to the excellent electrical properties of graphene and to the high surface area of the synthesized electrode as evidenced by Figure 3b. Additionally, researchers have shown that the contact resistance associated with the bacteria-electrode interface is much lower in carbon-based electrodes than in gold-based electrodes [14]. The polarization curve’s shape indicates that the voltage losses are caused predominantly by Ohmic resistance [4]. From the polarization and power density curves the internal resistance of the G-MFC was found to be approximately 336.5 Ω. This represents a 98% reduction from our previous work [15].

Although our G-MFC has demonstrated power densities

Figure 4: Experimental results. (a) Average Open circuit potentials of a single G-MFC and two G-MFCs in series plotted versus time. (b) Power density and polarization curves of the G-MFC.
comparable to macroscale microbial fuel cells, significant improvement of overall power output is still needed to enable use in practical applications. Established techniques to improve the power outputs of macroscale fuel cells could be employed to μMFCs as well. For instance, using air cathodes, moving away from PEMs, allowing for biofilm formation, and quantitatively analyzing different sources of internal resistance are all potential approaches that could lead to enhanced power outputs [4, 5, 13, 15]. Introducing additional mediators, functionalizing the anode, engineering more efficient membrane electrode assemblies and increasing electrode surface area are also methodologies that could improve performance.

CONCLUSION

Despite their vast potential, low power outputs and potentials have limited μMFCs from implementation in practical applications. In this work, we presented a G-MFC, the first stackable μMFC that utilizes graphene electrodes. The G-MFC utilized these high surface area electrodes and a complex natural anodic environment to produce high power outputs and potentials. Specifically, the G-MFC produced OCPs of 0.8 ± 0.05 V and power densities of 1820 ± 10 W/m², which represent some of the highest values reported [13-15]. Conventionally, biofilm formation is allowed when maximum power outputs are reported as power generally increases significantly with film thickness; however, the G-MFC produced 364 μW of power – one of the highest values recorded – even without complete film formation. These high power outputs were attained due to the low internal resistance of the G-MFC, which was approximately 336 Ω. The G-MFC architecture also permits simple stacking, which allows for a wider range of applications and enables the G-MFC to potentially power devices with increased energy and power requirements. Established methods exist to further improve the scope of implementation of the G-MFC in terms of power outputs and longevity. Switching to air-cathodes or membrane-less architectures as well as employing techniques to reduce internal resistance could all substantially improve the applicability of the G-MFC. Consequently, the presented G-MFC represents an important step towards moving μMFCs out of the laboratory and into practical applications.

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REFERENCES


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