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Electrochemically exfoliated graphene anodes with enhanced biocurrent production in single-chamber air-breathing microbial fuel cells

Amin Taheri Najafabadi, Norvin Ng, Elődd Gyenge*

Department of Chemical and Biological Engineering, Clean Energy Research Centre, The University of British Columbia, 2360 East Mall, Vancouver, BC, Canada V6T 1Z3

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ABSTRACT

Microbial fuel cells (MFCs) present promising options for environmentally sustainable power generation especially in conjunction with waste water treatment. However, major challenges remain including low power density, difficult scale-up, and durability of the cell components. This study reports enhanced biocurrent production in a membrane-free MFC, using graphene microsheets (GNs) as anode and MnO_x catalyzed air cathode. The GNs are produced by ionic liquid assisted simultaneous anodic and cathodic electrochemical exfoliation of iso-molded graphite electrodes. The GNs produced by anodic exfoliation increase the MFC peak power density by over 300% compared to plain carbon cloth (i.e., 2.85 W m^{-2} vs 0.66 W m^{-2}, respectively), and by 90% compared to conventional carbon black (i.e., Vulcan XC-72) anode. These results exceed previously reported power densities for graphene-containing MFC anodes. The fuel cell polarization results are corroborated by electrochemical impedance spectroscopy indicating three times lower charge transfer resistance for the GN anode. Material characterizations suggest that the best performing GN samples were of relatively smaller size ($\sim$500 nm), with higher levels of ionic liquid induced surface functionalization during the electrochemical exfoliation process.

1. Introduction

Microbial fuel cells (MFCs) are devices capable of electricity generation by employing bacteria to decompose organic compounds through a series of electrochemical reactions (Logan et al., 2006). Perhaps, the most relevant and immediate implication of MFCs lies in the wastewater treatment for simultaneous power generation and degradation of organic matter (Zhuang et al., 2012). Studies have shown that wastewater in a modern treatment plant may contain as much as nine times the energy used for its treatment (Shizas and Bagley, 2004). Such significant amount of stored energy could potentially be harnessed by MFCs. Although their power output has not yet reached levels required for self-sustaining a wastewater treatment plant, they could theoretically be used to offset energy consumption throughout the treatment process (Wang and Ren, 2013); especially considering the energy-intense nature of the conventional wastewater treatment operations such as aeration (Rabaey and Verstraete, 2005).

Under anaerobic conditions, a typical MFC process involves bacterial decomposition of organic matter, from organic-rich sources such as wastewater, which produces electrons that are passed on to the anode, and transferred through an external circuit towards an electron acceptor at the cathode, usually air or oxygen, where reduction occurs (Liu et al., 2004). There are several technical challenges that need to be addressed for practical uses of MFCs in large-scale renewable energy production. One aspect is the slow degradation kinetics of organic compounds, and consequently the much low power output of MFCs compared to hydrogen fuel cells (Bullen et al., 2006; Khera and Chandra, 2012).

Enhancing the MFCs' performance requires further fundamental research on their design, and substrate composition along with exploring novel electrode materials (Chen et al., 2015), and better understanding the underlying mechanism of the anode-bacteria interactions (Yates et al., 2012). The majority of research has been devoted to studying the anode at the expense of the cathode and other components. This is mainly due to the fact that the organic matter oxidation on the anode is typically the main bottleneck, and any improvement on the anodic interactions translates into further increase in the overall efficiency (Schroder, 2012; Zhao et al., 2005).

* Corresponding author.
E-mail address: egyenge@chbe.ubc.ca (E. Gyenge).

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Among the materials used as the anode for MFCs, carbon-based electrodes are the most promising due to their chemical inertness, high surface area, and low cost (Minteer et al., 2012). Synthesis of unique carbon nanomaterials such as porous carbons, fullerenes, carbon nanotubes (CNTs) and graphene has had a great impact on the research and development of high-performance energy storage devices (Candelaria et al., 2012). Particularly graphene is employed in many areas of energy and environmental research owing to its numerous unique properties (Kemp et al., 2013; Zhao et al., 2012). This includes large surface area, high charge mobility, strong mechanical properties, and excellent thermal conductivity, while showing remarkable biocompatibility with potential applications in biomedical engineering and biotechnology (Gurunathan et al., 2013; Song et al., 2016). More importantly, chemical treatment of graphene, which tailors its electronic and surface properties, significantly broadens its applications in cross-disciplinary areas with structural doping and surface functionalization (Chen et al., 2013; Machado and Serp, 2012). Thus, graphene can be a promising alternative to the traditional MFC anodes such as graphite rod, activated carbon and carbon cloth (Wang et al., 2013).

Despite the extensive research on MFC electrode materials, the development of graphene-based anodes is still in the early stages, and the reports on related studies are relatively sparse in literature. Liu et al. (2012) examined the electrochemical performance of a graphene-modified carbon cloth anode, and reported a 2.7-fold improvement in power density compared to a plain carbon cloth anode. Xiao et al. (2012) observed that graphene-modified anodes can produce twice as much power as activated carbon anodes. Zhang et al. (2011) attributed the increase in power generation to the high surface area of the graphene-based anode, and subsequent promotion of microbial loading on the anode compared to an unmodified stainless steel mesh. Hou et al. synthesized graphene composites with polyaniline (PANI) reporting a maximum power density of 1.4 W m^{-2}, with ~40% improvement over reduced graphene oxide performance (Hou et al., 2013). Zhao et al. (2013) also modified graphene's surface using ionic liquids, and reported beneficial effects with power densities exceeding 0.6 W m^{-2}. Finally, Tang and coworkers obtained 1.7-fold higher power density with graphene sheets produced via graphite exfoliation in ammonium sulfate solutions (Tang et al., 2015).

We have recently introduced high-throughput graphite electrochemical exfoliation techniques for GN production using aprotic ionic liquids with prospects for in-situ functionalization of GNs (Taheri Najafabadi and Gyenge, 2014) along with simultaneous exfoliation of both anode and cathode (Taheri Najafabadi and Gyenge, 2015). Our approach offers a number of potential advantages including ease of operation, control over the entire synthesis process by optimizing the electrochemical cell voltage, elimination of harsh chemical oxidizers/reducers and fast exfoliation rates at ambient pressure and temperature. This created an opportunity to examine our GN products produced by simultaneous anodic and cathodic graphite exfoliation, as anode materials in MFCs.

Fig. 1a depicts the schematic diagram of the single-chamber MFC configuration used in the present work with biofilm growth on the graphene-based anode, and oxygen reduction on the air-cathode catalyzed by MnO_x along with images of the units constructed and tested (Fig. 1b and c). Removing the ion exchange membrane (Fig. 1) brings about substantial benefits by lowering the cost and improving the power density due to the overall lower ohmic voltage loss in the cell. Furthermore, the possibility of membrane fouling is also eliminated (Rismani-Yazdi et al., 2008). Employing non-precious metal catalysts, namely manganese oxide, for the oxygen reduction reaction (ORR), further contributes to cost reductions and improving the practical feasibility (Zhang et al., 2009).

2. Materials and methods

2.1. Graphene synthesis and characterization

GNs were synthesized using the simultaneous anodic and cathodic graphite electrochemical exfoliation procedure developed by us previously (Taheri Najafabadi and Gyenge, 2014, 2015). The exfoliation experiments were conducted in a divided H-cell separated by a semi-permeable ceramic frit (Pine Research Instrumentation – RRPG060). High-purity iso-molded graphite rods with 6.35 mm diameter and 4 cm effective length exposed to the electrolyte (Graphite Store – 99.99% purity) were used as both anode and cathode. The electrodes were placed 5 cm apart, and immersed in the 0.1 M butyltrimethyl ammonium tetrafluoroborate (N1114-BF4) ionic liquid (IL) solution in acetonitrile (ACN). A constant potential of 15 V was applied for 2 h at 293 K (B&K Precision – 9110 DC power supply), generating a current of about 80 mA, with slight decrease in the course of experiments. Fig. 2 shows the ionic liquid structure (obtained from Iolitec – 99.9% purity), the electrochemical stability window of the ionic liquid on a platinum electrode at 293 K and the time evolution of the graphite electrodes (anode and cathode) during exfoliation, respectively.

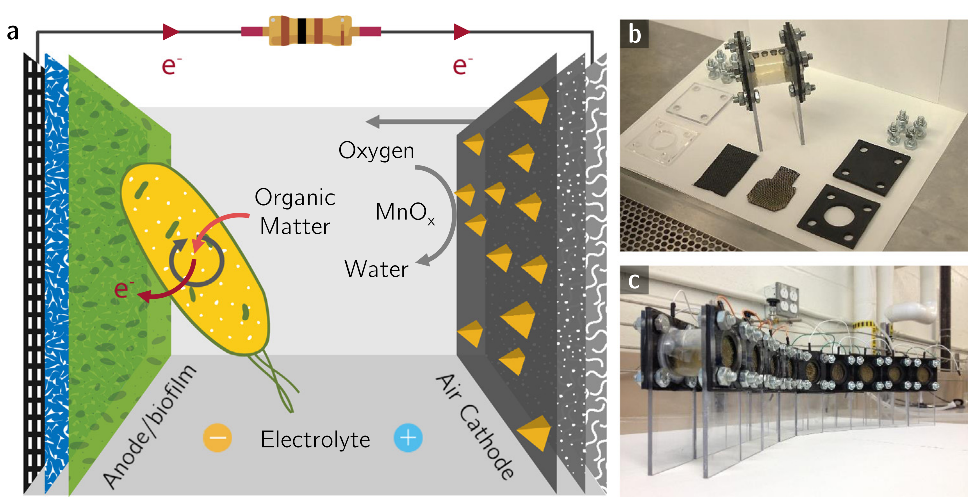

Fig. 1. (a) Graphical representation of the single-chamber MFC showing biofilm growth on the graphene-based anode, and oxygen reduction on the air-cathode catalyzed by MnO_x. The red arrows indicate the flow of electrons from the anode to the cathode through an external load. (b and c) Images of the MFC units used in the present work.