



Crumpled graphene particles for microbial fuel cell electrodes

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ABSTRACT

Graphene has a promising role in electrode fabrication/modification for microbial fuel cell (MFC) applications but there is a lack of research on graphene in MFCs. This study has systematically investigated two types of graphene materials with very different morphologies, namely regular graphene (like flat sheets of paper) and crumpled particles (like crumpled paper balls), respectively, to modify anode and cathode electrodes in MFCs. The higher electricity generation with the crumpled graphene particles is attributed to their higher electrical conductivity in the thickness direction, their larger surface area, catalytic activities of oxygen reduction, and the open structure they pack into that facilitates mass transfer of the fuels and ions. The crumpled graphene-modified anode electrode produces the highest maximum power density (3.6 W m^{-3}), twice that of the activated carbon-modified anode electrode (1.7 W m^{-3}). The maximum power densities with the crumpled graphene- and flat graphene-modified cathode electrodes are 3.3 W m^{-3} and 2.5 W m^{-3} , significantly higher than 0.3 W m^{-3} with the unmodified carbon cloth, although still lower than a platinum cathode electrode. These results have demonstrated that graphene-based materials, especially the crumpled graphene particles, can be effective electrode modifying materials for improving electricity generation in MFCs.

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1. Introduction

Wastewater contains a high content of organic matter that can be used as a source of energy to offset energy consumption by treatment processes [1]. The use of microbial fuel cells (MFCs) offers one of the most promising approaches for extracting useful energy from wastewater. Through bioelectrochemical reactions, MFCs can convert the energy stored in the chemical bonds of organic compounds to electrical energy [2]; however, the low power output of MFCs currently restricts their practical applications. Research towards improving MFC power production focuses on understanding microbial activities, optimizing MFC configuration and operation, reducing electrochemical limitation, and exploring new materials for electrodes and membranes. Among these, electrode materials (including electrodes and their modifying materials) are of special interest because of rapid developments in material sciences [3–5].

The key criteria for electrode materials in MFCs include high surface area, high conductivity, good stability (resistant to chemical and microbes), and low cost [2]. Electrodes can also be modified by coating additional materials to achieve those properties [6]. The

most commonly used materials for anode electrodes are carbon-based, such as carbon paper, carbon cloth, and graphite felt [4], because they are inexpensive, easy to use, and have a defined surface area. Carbon materials can be modified with nanoparticles to improve the power density [7–9]. Cathode electrodes, on the other hand, require catalytic ability to reduce terminal electron acceptors, in addition to those properties described with anode electrodes. Cathode electrodes can also be modified with nanomaterials to improve catalyst activities and/or facilitate catalyst support [10,11]. The most popular catalyst for cathode electrodes is platinum (Pt), an expensive noble metal. Several other catalysts have been studied, such as manganese oxides, metal tetramethoxy phenylephrine (CoTMPP and FeCoTMPP), and metal phthalocyanine (FePc, CoPc and FeCuPc) [12]. These alternatives can achieve a comparable performance to Pt, but their long-term stability requires further examination, especially for the presence of metals like iron and manganese, which could be involved in a microbial metabolism. Therefore, it is necessary to explore more options for simple and stable materials used for preparing electrodes in MFCs.

Since the isolation of graphene in 2004, researchers have found a variety of unique and desirable properties for electrochemical applications – high electrical conductivity, large surface area, applicable electrocatalytic activities, and low production costs [13–16]. As a result, graphene is studied as an

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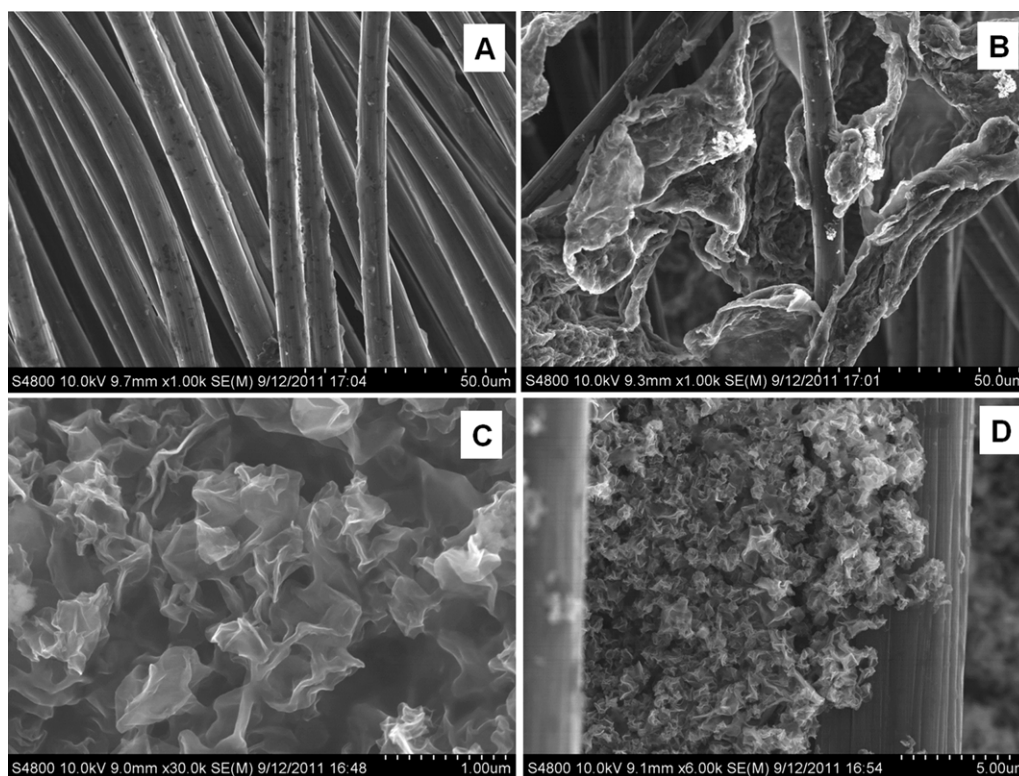


Fig. 1. Morphologies of electrodes: (A) carbon fibers in unmodified carbon cloth; (B) regular r-GO sheets deposited on carbon cloth; (C) crumpled r-GO particles before being applied; and (D) crumpled r-GO particles stacked on carbon cloth, still maintaining a high surface area, 3D open structure.

electrode material in many electrochemical applications, such as solar cells, lithium-based rechargeable batteries, and ultracapacitors [17–19]. Recently, Zhang and his co-workers reported the improved electrochemical performance of a dual-chamber MFC operated with a graphene-modified anode electrode [20], and Huang and his co-workers found that graphene oxide nanoribbons could enhance extracellular electron transfer in bio-electrochemical systems [21]. These studies revealed the great potential of using graphene to improve electrode performance in MFCs.

The graphene material is made by thermal annealing of graphene oxide (GO), which is prepared by a modified Hummers' synthesis [22,23]. Such prepared graphene materials are usually called chemically modified graphene, or reduced GO (r-GO), as they are more defective than pristine graphene [24,25]. Regular r-GO is made by thermal exfoliation of GO at 200 °C and the resulting material is typically flat sheet with wrinkles (Fig. 1B). We have developed a new type of r-GO particles by crumpling the sheets into crumpled paper ball-like structure by an aerosol-assisted capillary compression process [26]. In the synthesis, the soft GO sheets were subject to near isotropic compression during rapid evaporation of the aerosol droplets and subsequently reduced by *in situ* heating. The particles' morphology resembles crumpled paper balls (Fig. 1C). While regular sheet-like graphene materials are prone to aggregation, making their surface area and processability sensitive to the materials' processing history, the crumpled particles are remarkably aggregation-resistant in both solution and solid state and have a much more stable, consistently higher surface area and excellent solution processability that are much less sensitive to processing history. Like crumpled paper balls, crumpled graphene (*i.e.*, r-GO) particles can also tightly pack into a three-dimensional (3D), porous structure without significantly losing surface area. Therefore, it is expected that electrodes modified with the crumpled graphene particles should have a much higher surface area than

those modified with regular graphene sheets, resulting in a much better MFC performance.

In this study, we systematically examined electricity generation with the graphene-modified (anode or cathode) electrodes and employed electrochemical techniques such as cyclic voltammetry and electrochemical impedance spectroscopy to characterize the electrochemical properties of the electrodes. For comparison, we tested an activated carbon (AC)-modified anode electrode and platinum-modified and unmodified cathode electrodes (carbon cloth – CC) in parallel with the graphene-modified electrodes.

2. Materials and methods

2.1. Electrode modification

The details of preparation and characterization of r-GO particles can be found in our previous publication [26]. The base material, carbon cloth (PANEX®30PW03, Zoltek Corporation, St. Louis, MO, USA) was used for modification. For anode tests, carbon cloth modified with regular r-GO sheets, crumpled r-GO particles and AC were tested. For cathode tests, carbon cloth modified with regular r-GO sheets, crumpled r-GO particles, and Pt/C (10% Pt in black carbon powder) were measured. An unmodified carbon cloth (CC) electrode was also used in the cathode test as a control. The project surface area for each electrode was 4.5 cm² each side. For modification, 45 mg r-GO particles were mixed with 0.5 mL deionized water in a 5-mL centrifuge tube and the mixture was sonicated for 30 min. Then 0.3 mL Nafion solution was added into the mixture, which was sonicated again for 5 min. This mixture was applied to both sides of the carbon cloth and dried in air for 24 h. The final loading rate of the modifying material was ~5 mg cm⁻². Other modified electrodes were prepared by the same method with the same loading rate.

2.2. MFC construction and operation

Two-chamber microbial fuel cells were built with glass bottles jointed by a cation exchange membrane (CEM) (Ultex CMI 7000, Membranes International, Inc., Glen Rock, NJ, USA). Each chamber had a liquid volume of 120 mL. Three electrodes were installed in the same chamber to minimize the effect of the (different) counter electrode on MFC performance (Fig. S1). For example, the anode-MFC for the anode electrode test contained the r-GO particles-, the r-GO sheets- and the AC-modified electrodes in its anode chamber and one single cathode electrode (carbon brush, Gordon Brush Mfg. Co., Inc., Commerce, CA, USA) in the cathode chamber. In contrast, the cathode-MFC for the cathode electrode test had the r-GO particles-, the r-GO sheets- and the Pt- (or CC) modified electrodes in the cathode chamber and one single anode electrode (carbon brush) in the anode chamber. Before use, carbon brush electrodes were pre-treated by immersing in acetone overnight and heating at 450 °C for 30 min. We did not find obvious effects of the location of electrode placement on electricity generation, although there was a slight difference in the distance between different electrodes and the membrane. The multiple electrodes in the same chamber were connected individually with copper wires to their common counter electrode. One resistance decade box was connected in each electrical circuit to adjust the external resistance between each electrode couple. Both the anode and the cathode chambers were continuously stirred with magnetic bars. A reference electrode (Ag/AgCl) was installed in the testing chamber for *in situ* electrochemical analysis.

The MFCs were operated in batch mode at room temperature (about 20 °C). The anodes were inoculated with the anaerobic sludge from a local municipal wastewater treatment plant (South Shore, Milwaukee, WI, USA). The nutrient solution in the anode chamber contained (per 1 L of tap water): sodium acetate, 0.5 g; NH₄Cl, 0.3 g; NaCl, 1 g; MgSO₄, 0.03 g; CaCl₂, 0.04 g; NaHCO₃, 0.2 g; KH₂PO₄, 5.3 g; K₂HPO₄, 10.7 g and 1 mL trace elements [27]. The anode solution was replaced (~80%) when the voltages of all three electrode couples dropped below 4 mV. The cathode of the anode-MFC was filled with 1 M potassium ferricyanide, while the cathode of the cathode-MFC was filled with 100 mM phosphate buffer solution (5.3 g L⁻¹ KH₂PO₄ and 10.7 g L⁻¹ K₂HPO₄) and aerated with air flow.

2.3. Measurement and analysis

The cell voltage was recorded every 5 min by a digital multimeter (2700, Keithley Instruments, Inc., Cleveland, OH, USA). A potentiostat (Reference 600, Gamry Instruments, Warminster, PA, USA) performed the polarization curve at a scan rate of 0.8 mV s⁻¹ for anode electrode tests and 0.2 mV s⁻¹ for cathode electrodes tests. The power density and current density were calculated based on the anode liquid volume. The total charge produced in one batch cycle was calculated by integrating current with time (the period of a cycle). The cyclic voltammogram (CV) was also performed using the Gamry reference 600 potentiostat at a scan rate of 5 mV s⁻¹ in two ways: the *in situ* test was conducted in the (anode) MFC that used the anode electrode as a working electrode, the cathode electrode as a counter electrode and an Ag/AgCl reference electrode (200 mV vs. SHE), and *vice versa* for the cathode MFC; the *ex situ* test was conducted in an electrochemical cell that contained a glassy carbon electrode modified with r-GO particles or Pt powder as a working electrode, a Pt wire as a counter electrode and an Ag/AgCl reference electrode. The gas phase of the electrochemical cell was flushed with either oxygen or nitrogen gas. The r-GO particles, carbon cloth and graphene-modified electrodes were imaged using a scanning electron microscope (SEM) (Hitachi S4800, Japan).

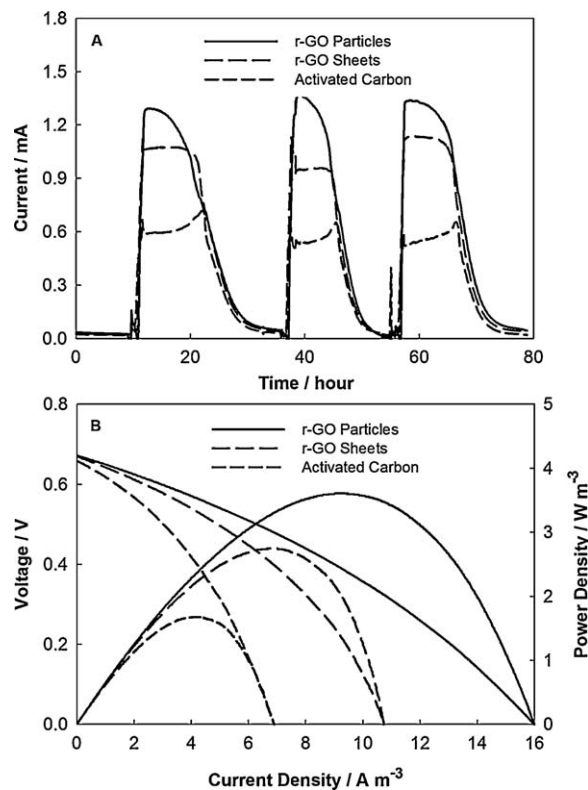


Fig. 2. Electricity generation with graphene-modified anode electrodes: (A) current generation at 100 Ω; and (B) polarization curves.

2.4. Electrochemical impedance spectroscopy (EIS)

The impedance spectra were collected at the open-circuit potential (OCP) of the anode and the cathode using a Gamry reference 600 potentiostat. An ac voltage signal of 10 mV was applied in a frequency range from 100 kHz to 5 mHz. EIS measurements were conducted in a three-electrode mode by recording the impedance spectrum of the anode, with the cathode acting as a counter electrode (CE) in the anode-MFC, and *vice versa* for the cathode-MFC. The reference electrode was Ag/AgCl. The EIS data was analyzed using ANALEIS with an equivalent circuit containing two time constants. R_s represents solution resistance, R_{p1} is related to pore resistance of coating layer, and R_{p2} is the reaction (polarization) resistance at the coating/substrate interface.

3. Results

3.1. Graphene-modified anode electrodes

3.1.1. Electricity generation

Electricity generation was observed from all three anode electrodes in the anode-MFC and the graphene modification exhibited a beneficial effect on the MFC performance. Batch operation resulted in a profile of current production, with a rapid increase upon the replacement of the fresh anode solution and a gradual decrease due to the depletion of the substrate. At an external resistance of 100 Ω, all three current profiles exhibited a similar trend of increase and decrease, although at different levels (Fig. 2A). The current generations were clearly affected by the substrate consumption because three anode electrodes were in the same anode chamber. Each cycle of current production lasted for about 20 h. The currents reached peak values of 1.30 ± 0.04 mA, 1.05 ± 0.09 mA and 0.57 ± 0.03 mA for the r-GO particles-, the r-GO sheets- and the AC-modified electrodes, respectively. The total charges produced in

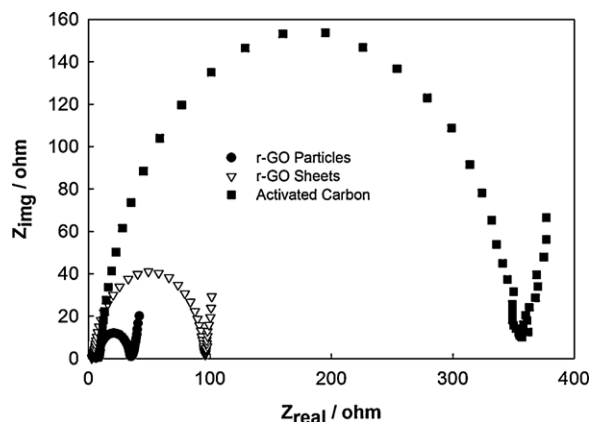


Fig. 3. EIS (Nyquist plots) of the modified anode electrodes.

one cycle amounted to 50.5 ± 7.3 C for the r-GO particles-modified electrode, 44.5 ± 9.0 C for the r-GO sheets-modified electrode, and 27.8 ± 5.9 C for the AC-modified electrode. The anode-MFC was operated for more than three months and electricity generation with all three anode electrodes was stable, suggesting good stability and reproducibility of the tested electrode materials.

Polarization tests confirmed the difference in electricity generation from three modified anode electrodes. As shown in Fig. 2B, the open cell voltages (OCV) of three electrodes were almost the same (~ 0.66 V), comparable with OCVs in other MFC studies. However, the maximum power densities were apparently different. The AC-modified anode electrode produced 1.7 W m^{-3} , which was 61% of the r-GO sheets-modified anode electrode (2.7 W m^{-3}) and 46% of the r-GO particles-modified anode electrode (3.6 W m^{-3}). Accordingly, the AC-modified anode electrode generated the lowest short-circuit current of 6.9 A m^{-3} ; while the r-GO particles- and the r-GO sheets-modified anode electrodes produced 16.0 and 10.8 A m^{-3} , respectively.

3.1.2. Electrochemical analysis

The electrochemical behavior of the modified anode electrodes in the anode-MFC was analyzed by using CV and EIS. The *in situ* voltammograms of the r-GO particles-modified and the r-GO sheets-modified anode electrodes showed larger currents than that of the AC-modified anode electrode, indicating either an enhanced surface area or an optimized structure (Fig. S2). By fitting the data of the Nyquist plots (Fig. 3), we obtained the values of each parameter (Table S1). The solution (ohmic) resistances, R_s resulting from the ionic resistance of electrolyte, the intrinsic resistance of active materials, and the contact resistance, were generally lower than 10Ω for all three modified anode electrodes. The pore resistance of the coating layer (R_{p1}) behaved very differently, with the highest value of 182Ω from AC-modified anode electrode and the lowest value of 16Ω from r-GO particles-modified anode electrode. Similarly, the highest polarization resistance (R_{p2}) of 304Ω also occurred from the AC-modified anode electrode; while the r-GO particles-modified anode electrode had 33Ω , almost one tenth of that of the AC-modified anode electrode. Both resistances with the r-GO sheets-modified anode electrode were higher than those of the r-GO particles-modified anode electrode but much lower than those of the AC-modified anode electrode.

3.2. Graphene-modified cathode electrodes

3.2.1. Electricity generation

To examine the graphene modification for cathode reactions, two groups of cathode electrodes were studied in the cathode-MFC: first, r-GO particles-, r-GO sheets- and Pt/C-modified cathode

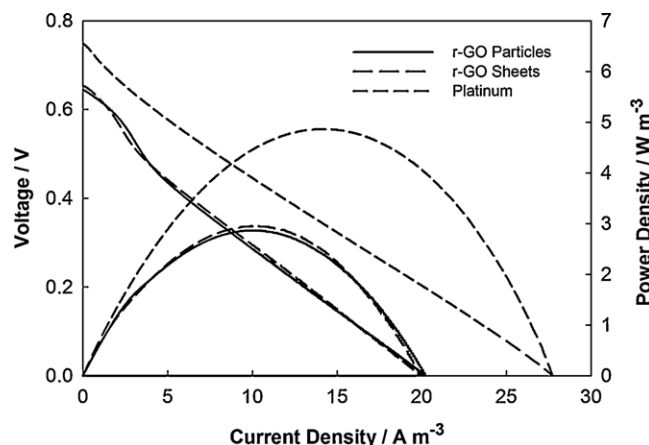


Fig. 4. Polarization curves with the modified cathode electrodes in the cathode-MFC. Pt cathode was used as a control.

electrodes; and second, r-GO particles-, r-GO sheets- and unmodified CC cathode electrodes. Polarization tests were employed to determine the overall performance of graphene materials compared with either Pt/C or CC. In the first group, the Pt/C-modified cathode electrode exhibited the best performance, while the r-GO particles- and the r-GO sheets-modified cathode electrodes behaved almost identically (Fig. 4). The OCV of the r-GO particles- and the r-GO sheets-modified cathode electrode were about 0.65 V, lower than 0.75 V of the Pt/C-modified cathode electrode. Likewise, the maximum power density of either the r-GO particles- or the r-GO sheets-modified cathode electrode (2.9 W m^{-3}) was 60% of the Pt/C-modified cathode electrode (4.8 W m^{-3}). Compared with the unmodified electrode (CC), the use of r-GO particles or r-GO sheets had clearly improved the MFC's performance (Fig. 5B). The maximum power densities of the r-GO particles- and the r-GO sheets-modified cathode electrodes were 3.3 W m^{-3} and

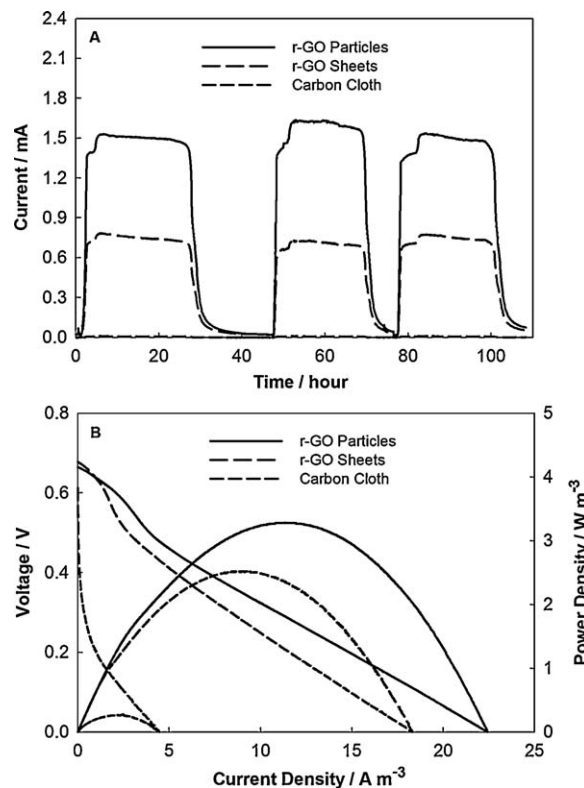


Fig. 5. Electricity generation with graphene-modified cathode electrodes: (A) current generation under 33Ω ; and (B) polarization curves.

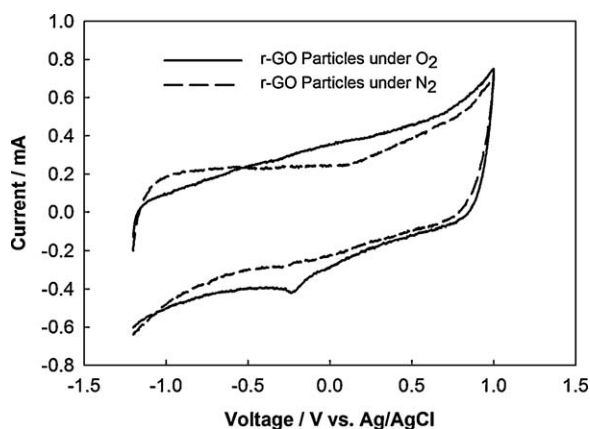


Fig. 6. Cyclic voltammetry of r-GO particles with oxygen or nitrogen.

2.5 W m^{-3} , respectively, significantly higher than 0.3 W m^{-3} with the unmodified cathode electrode.

To further confirm the findings from the polarization test, the cathode-MFC was operated under the 33Ω external resistance with the second group of cathode electrodes (Fig. 5A). Both the r-GO particles- and the r-GO sheets-modified cathode electrodes showed a batch profile of current generation over substrate consumption. The total charges of the r-GO particles-modified cathode electrode were $133.3 \pm 8.7 \text{ C}$, twice as much as the r-GO sheets-modified cathode electrode ($65.0 \pm 7.3 \text{ C}$). No obvious electricity production was observed from the unmodified cathode electrode. In parallel with the anode-MFC, the cathode-MFC was operated for a period of 3 months and stable performance was achieved.

3.2.2. Electrochemical analysis

The cathode-MFC was also characterized by CV and EIS. No distinct redox peak was observed from all three cathode electrodes during the *in situ* CV test, but the currents of the r-GO particles- and the r-GO sheets-modified cathode electrodes were much higher than the current of the unmodified electrode (Fig. S3). It should be noted that the *in situ* CV test was conducted on carbon cloth that did not have a uniform surface like glass carbon electrodes used in the *ex situ* CV test; therefore, the results of the *in situ* CV test were more complex and no redox peaks did not necessarily mean no catalytic activities. The *ex situ* CV test of the r-GO particles clearly exhibited a reduction peak at -0.2 V (vs. Ag/AgCl) with oxygen gas but not with nitrogen gas (Fig. 6). The CV of the Pt powder also showed a reduction peak close to -0.2 V (vs. Ag/AgCl) (Fig. S4). EIS tests were carried out to determine the internal resistance of three electrodes (Fig. 7) and the fitting parameters are shown in Table S1. The solution resistances of the r-GO particles-modified cathode electrode (7Ω) and the r-GO sheets-modified cathode electrode (9Ω) were slightly lower than carbon cloth (11Ω). Like the modified anode electrodes, the crumpled r-GO balls-modified cathode electrode had the lowest pore resistance (21Ω). A significant difference between the modified and unmodified cathode electrodes occurred with the polarization resistance. The unmodified carbon cloth had a polarization resistance of $16,680 \Omega$, several hundred times higher than those of the modified cathode electrodes.

4. Discussion

The results have collectively demonstrated that graphene modification is generally beneficial to the electrode performance, with some difference between the anode and the cathode applications.

Graphene-modified anode electrodes could improve electricity generation compared with activated carbon modification, most likely because of graphene's superior properties, such as its large

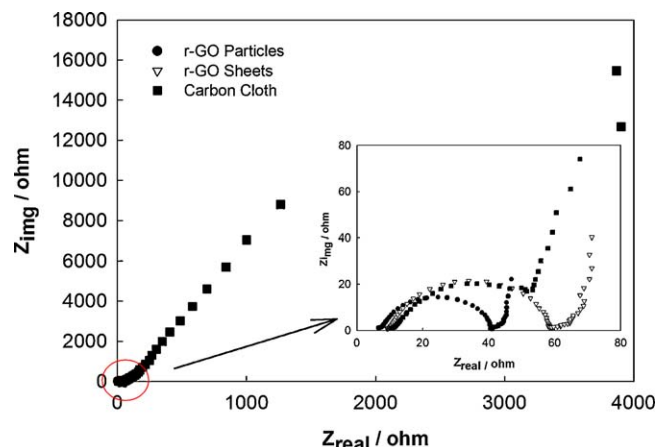


Fig. 7. EIS (Nyquist plots) of the modified cathode electrodes. The inset shows the details at high frequency.

surface area and open structure. The results also confirmed the finding in a recent study that achieved a higher maximum power density with the graphene-modified stainless steel mesh (SSM) than plain SSM and polytetrafluoroethylene (PTFE) modified SSM [20]. The authors attributed the better performance to the fact that the graphene-modified electrode possessed a high surface area, facilitated bacterial adhesion, and exhibited an excellent efficiency of electron transfer. The electrodes modified by a porous layer of crumpled graphene particles used in our study have an even higher surface area than regular graphene because of its unique three-dimensional open structure [26], and thus is potentially more advantageous, as demonstrated by a higher electricity production with the r-GO particles-anode electrode than the r-GO sheets- and AC-anode electrodes.

The electrochemical analysis supported the finding with the best electrochemical activity and lowest impedance from the r-GO particles-anode electrode. Although no distinct redox peaks were observed from all three modified anode electrodes, the currents of the r-GO particles- and the r-GO sheets-modified anode electrodes were much higher than those of the AC-modified anode electrode, indicating that the graphene-modified electrode had a higher faradic charge capacity, which could be proportional to the electrode surface area [28]. With the same projected areas, the r-GO particles-modified anode electrode had the highest actual surface area [26], which also helped with biofilm formation. Its unique pore structure could facilitate bacterial adhesion and substrate supply. As a result, in the anode-MFC, most of the charges were transferred through the r-GO particles-modified anode electrode during the oxidation of substrates. The low resistances of the r-GO particles- and the r-GO sheets-modified anode electrodes suggested a better mass transfer of fuel and ions, compared with activated carbon.

Graphene-modified cathode electrodes have exhibited catalytic activities of oxygen, which is supported by the *ex situ* CV test of r-GO particles that showed a reduction peak in oxygen but not in nitrogen gas. This reduction peak was similar to the one with the Pt CV test. Our results are also supported by a previous finding that graphene sheets had high catalytic activity for the reduction of oxygen [29]. The authors studied the electrochemical reduction of oxygen with graphene sheets by cyclic, rotating disk electrode, and rotating ring-disk electrode voltammetry. They found that graphene sheets could effectively catalyze the disproportionation of H_2O_2 and that such catalytic activity enables a 4-electron reduction of O_2 at a relatively low overpotential in neutral media. In the present study, the maximum power densities of the r-GO particles- and the r-GO sheets-modified cathode electrodes were about 60% of the Pt/C-modified cathode electrode, but much higher than the

unmodified electrode, demonstrating that r-GO particles and r-GO sheets can improve the oxygen reduction reaction at the cathode of an MFC, although not as well as the Pt/C.

It is worth noting that the maximum power densities of r-GO particles- and r-GO sheets-modified cathode electrodes in Fig. 5B (the cathode-MFC with CC as the control) were different from those in Fig. 4 (the cathode-MFC with Pt/C as the control). Because the Pt/C-modified cathode electrode dominated oxygen reduction in the cathode chamber, the difference between r-GO particles-modified and r-GO sheets-modified cathode electrodes was much smaller than that when they were compared with a Pt/C-modified cathode electrode. After changing Pt/C to bared carbon cloth (unmodified electrode), the main reaction in the cathode chamber was with r-GO particles-modified and r-GO sheets-modified cathode electrodes, as they were competing with each other and the difference between these two became apparent. The r-GO particles-modified cathode electrode performed the fastest electrode reaction rate and charge transfer rate compared with r-GO sheets- and unmodified cathode electrodes, suggested by the largest current from the *in situ* CV tests and the lowest resistance from EIS tests.

The EIS analysis also indicated different roles of graphene materials between anode and cathode modification. For anode modification, graphene helped to optimize the surface structure of the electrode, suggested by the lower pore resistances (R_{p1}). As a result, biofilm formation could be improved, leading to a reduced polarization resistance (R_{p2}) compared with the AC modification. For cathode modification, the effect of the electrode surface improvement was limited, indicated by the closeness of the three R_{p1} values, although graphene still improved the electrode surface. The key function of the graphene modification was to directly improve the cathode reaction through its catalytic function, which resulted in a great reduction of R_{p2} and significant higher electricity generation compared with the unmodified carbon cloth.

The r-GO particles are a novel type of graphene-based material with superior properties and processability. The MFC tests have shown that r-GO particles can significantly enhance bioreaction/electrochemical kinetics and mass transfer because of a high surface area, open structure and high electrical conductivity; however, these characteristics highly depend on graphene processing history. In order to produce a high surface area, graphene oxide (the precursor of graphene) needs to be heated rapidly to trigger a violent gas evolution for efficient exfoliation; otherwise, the surface area of graphene reduces by more than 84% of its original surface area [26]. In contrast, r-GO particles always yielded a high surface area regardless of the heating rate [26]; therefore, r-GO particles are easier to prepare compared with regular graphene. In addition, due to their crumpled three-dimensional structure, r-GO particles possess a high surface area to facilitate the electron conductance and possibly biofilm formation in the anode and higher catalytic activity for reducing oxygen in the cathode. Although r-GO particles did not outperform the Pt/C for cathode reaction under the same loading rate in this study, the performance could be compensated for or improved by increasing the loading rate applied to the cathode electrode. The lower cost of graphene compared with Pt would make it a more viable option to increase graphene concentration for enhancing the electrode performance.

5. Conclusions

We demonstrated that r-GO particles and r-GO sheets could increase the power production in MFCs *via* modifying the anode or the cathode electrodes. Both graphene materials exhibited better electrochemical performance and lower impedance compared with activated carbon or unmodified electrode; in particular, r-GO particles, a novel structure of graphene, performed even

better than regular r-GO sheets. With further understanding of graphene's role in electron transfer and biofilm formation in MFCs, and reducing the cost of graphene preparation, graphene materials could be promising in the future design of large-scale MFC or MFC-related applications, such as microbial electrolysis cells and microbial desalination cells.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2012.02.036.

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