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Short communication

Treatment of carbon fiber brush anodes for improving power generation in air–cathode microbial fuel cells

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ABSTRACT

Carbon brush electrodes have been used to provide high surface areas for bacterial growth and high power densities in microbial fuel cells (MFCs). A high-temperature ammonia gas treatment has been used to enhance power generation, but less energy-intensive methods are needed for treating these electrodes in practice. Three different treatment methods are examined here for enhancing power generation of carbon fiber brushes: acid soaking (CF-A), heating (CF-H), and a combination of both processes (CF-AH). The combined heat and acid treatment improve power production to 1370 mW m^{-2}, which is 34% larger than the untreated control (CF-C, 1020 mW m^{-2}). This power density is 25% higher than using only acid treatment (1100 mW m^{-2}) and 7% higher than that using only heat treatment (1280 mW m^{-2}). XPS analysis of the treated and untreated anode materials indicates that power increases are related to higher N1s/C1s ratios and a lower C–O composition. These findings demonstrate efficient and simple methods for improving power generation using graphite fiber brushes, and provide insight into reasons for improving performance that may help to further increase power through other graphite fiber modifications.

1. Introduction

Microbial fuel cells (MFCs) are promising devices for generating electrical energy during wastewater treatment [1,2]. In MFCs, electrons are extracted from organic wastes by exoelectrogenic bacteria attached to the anode that are then transferred through an external circuit to the cathode. At the cathode, protons and electrons typically are catalyzed to react with oxygen, forming water. Recent advances in MFCs have increased power production by optimization of the activity of the exoelectrogenic biofilm [3,4], improvement in MFC architecture and configurations [5], and through changes in solution chemistry [6]. However, the performance of these systems still needs to be improved for practical applications, and the costs of the materials need to be reduced and their preparation methods simplified.

Modification of the anode using different materials has been a successful approach for improving power production. Several methods have been developed that are based on adding mediators to the anode. For example, by immobilizing neutral red onto the surface of a woven graphite electrode, the maximum power density increased from 0.02 to 9.1 mW m^{-2} in an MFC with a pure culture of *Shewanella putrefacians* [7]. Lowy et al. [8] demonstrated that the power output by sediment MFCs could be increased by 1.5–1.7 times if the graphite anode was modified using anthraquinone-1,6-disulfonic acid (AQDS) or 1,4-naphthoquinone (NQ). Other methods for increasing power include adding metals or modifying the carbon surface. In an MFC with anaerobic sludge as the inoculum, power was increased from 0.65 to 788 mW m^{-2} when the woven graphite electrode was modified with Mn^{4+} [9]. Cheng and Logan [10] showed that power production was improved by 20% when a carbon cloth was treated using a high-temperature (700 °C) ammonia gas process.

While these methods all resulted in increased power production, the development of MFCs for large-scale applications will require less expensive and simpler methods for creating anodes capable of high power generation. Using ammonia gas treatment, for example, is useful for laboratory experiments but it would be costly for large-scale production of anodes. Several different materials have been used as anodes, including graphite blocks, graphite fibers, carbon cloth, carbon paper, and carbon foams [11–16]. Graphite fiber brush anodes appear particularly promising for achieving high power densities, but so far the only successful method for treating these materials that has been reported is using a high-temperature ammonia gas process [10]. The reason for improved power generation using the ammonia gas process appears related to creating a positively charged surface [10]. Recent studies have shown that heat treatment is effective at improving power production using woven carbon cloth, and that improvement in power production was associated with an increase in the N:C ratio [17]. We therefore investigated here whether heat treat-

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ment or acid soaking the brush fibers, as well as a combination of acid soaking and heating approaches, might be used to improve power generation. In addition, we examined chemical changes that occurred on the surface of these fibers as a result of these treatment methods.

2. Materials and methods

2.1. MFC configuration and anode pretreatments

Air–cathode single chamber cubic MFCs (4 cm long, 3 cm diameter, 28 mL volume) were constructed as previously described [11]. Cathodes were carbon cloth (30% wet proofed) containing 0.35 mg m^{-2} Pt catalyst. Anodes were carbon fiber brush electrodes constructed as described by Logan et al. [18], that had a two-wire Ti core that served as a current collector, and brushes made of carbon fibers (Jilin Carbon Plant, China, with Young's Modulus 210–220 GPa). All brushes were first cleaned by soaking them in pure acetone overnight (CF-C). These brushes were then acid treated (CF-A) by soaking the brushes in a solution of ammonium peroxydisulfate (200 g L^{-1}) and concentrated sulfuric acid (100 mL L^{-1}) for 15 min. Brush electrodes were heat-treated (CF-H) in a muffle furnace at 450 °C for 30 min. Brushes treated by both methods were first acid treated and then heat treated (CF-AH). Following treatments, all brushes were washed three times with distilled water before being used in MFCs.

2.2. MFC operation

MFCs were inoculated with 20% domestic wastewater which was collected from a municipal pipe network (Harbin, China), and a medium containing sodium acetate (1 g L^{-1}) and a 50 mM phosphate buffer solution (PBS) [11] containing vitamins (5 mL L^{-1}) and minerals (12.5 mL L^{-1}) prepared as previously described [19]. The external resistance was fixed at 1000 Ω and all reactors were operated in duplicate in fed-batch mode conditions in a temperature-controlled room at 30 °C.

2.3. Analysis method

The external resistance voltages were collected using a data acquisition board (PISO-813, ICP DAS Co., Ltd.) with on-line monitoring and recording every 30 min. Electrochemical impedance spectroscopy (EIS) and polarization curves were measured using a potentiostat (model 263A, E&G, USA). For EIS measurements, the frequency range was 100 kHz to 10 mHz. Polarization data were obtained at a scan rate of 1 mV s^{-1}.

Carbon fiber surfaces were analyzed by X-ray photoelectron spectra (XPS; PHI 5700 ESCA System, Physical Electronics, USA) with Al Kα (h_υ = 1486.6 eV) as the X-ray source. Surface area was measured based on a Brunauer–Emmett–Teller (BET) adsorption isotherm (ASAP 2020 M, Micromeritics Instrument Corporation, USA).

3. Results and discussion

3.1. Power generation using different pretreatment anodes

Two hundred hours after inoculation, stable maximum voltages of 550–570 mV were obtained for all MFCs. The lag time for a voltage of 520 mV was 140 h for the MFC with acid-treated anodes (CF-A) compared to 240 h for the heat-treated anodes (CF-H; 240 h). The MFC control (CF-C) and the acid- and heat-treated MFCs (CF-AH) both required ~200 h to achieve maximum stable voltages (Fig. 1a).

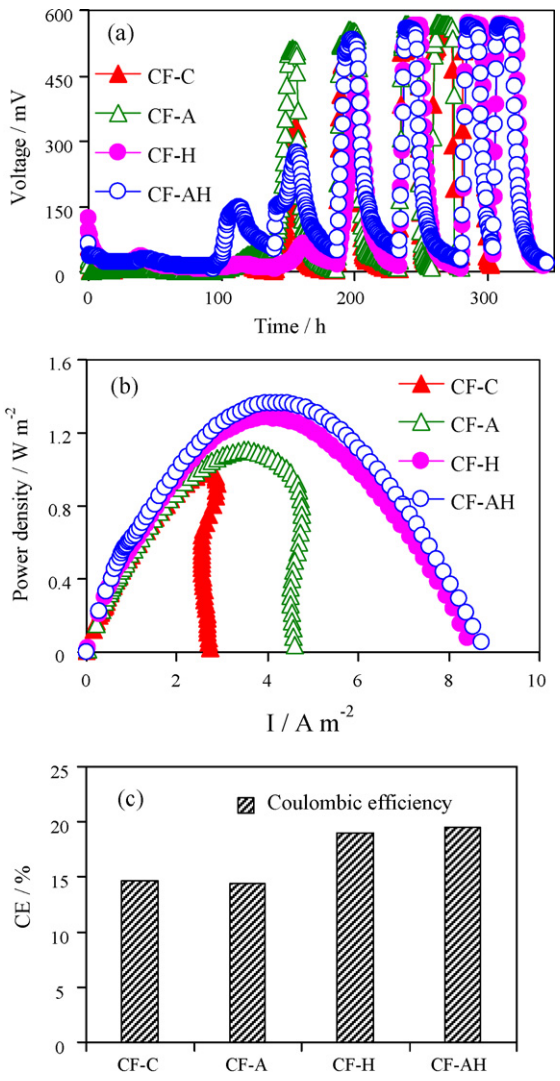

Fig. 1. Performance of MFCs with anodes acid (CF-A), heat (CF-H), and acid- and heat-treated (CF-AH) anodes, compared to the control (CF-C): (a) voltage production, (b) power density, and (c) coulombic efficiencies.

Based on polarization and power density curves, the maximum power densities produced by the different treatments were all larger than that of the control (CF-C; 1020 mW m^{-2}) (Fig. 1b). Acid treatment increased power by 8% to 1100 mW m^{-2}, and heat treatment increased power by 25% to 1280 mW m^{-2}. The combined acid and heat anode treatments produced the highest power density of 1370 mW m^{-2}, which was 34% larger than the control.

Coulombic efficiencies (CEs) ranged from 14.4–19.5% (Fig. 1c), and in all cases the CEs increased as a result of treatment. The highest CEs of ~19.5% were obtained for the acid-heat and heat-treated anodes (CF-AH and CF-H). Previous tests have shown that the CE increases with current density [6]. EIS analysis indicated that all treatment methods reduced the ohmic resistance from 23 Ω (control reactor) to 17–18 Ω (treated anodes). Thus, the higher CEs observed here likely resulted from higher current densities achieved through a reduction in ohmic resistance.

Carbon brush anodes achieve a good dispersion of the graphite filaments and contain an efficient current collector, making them useful as anodes for large-scale application of MFCs [18]. The high Young's modulus of the carbon fibers (210–220 GPa) is helpful for good dispersion of the fibers in the brush.

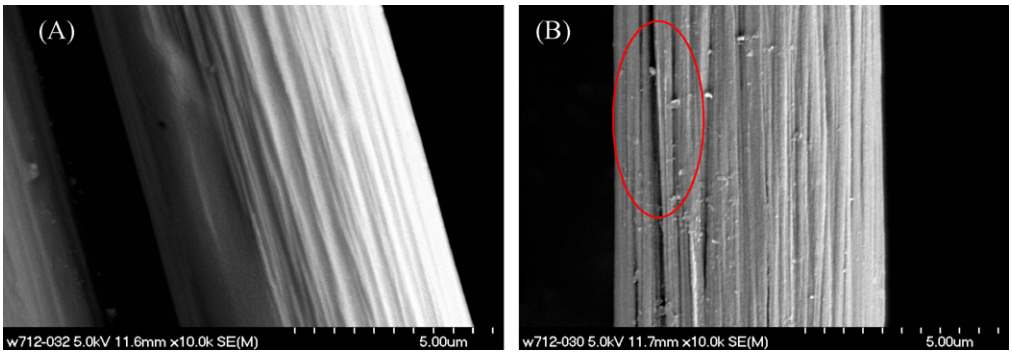

Fig. 2. Electron microscope photograph of carbon fiber before (A) and after heat treatment (B).

3.2. Surface characteristics of carbon fibers with different treatments

The different chemical treatments all resulted in modification of the graphite fiber surfaces. Based on BET adsorption isotherms, the measured surface area of the fibers on the anode before treatment (control) was 7.11 $m^2\ g^{-1}$. For comparison, the surface area based on the projected area of the individual fibers was 0.422 $m^2\ g^{-1}$. Heat treatment increased the actual surface area by 6.94 times to 49.3 $m^2\ g^{-1}$ compared to untreated fibers. Acid treatment alone increased the surface area by only 32.5% (9.42 $m^2\ g^{-1}$), while the area of the acid- and heat-treated anode had a surface area of 43.9 $m^2\ g^{-1}$. The increase of surface area was caused by the generation of cracks during the heat treatment process (Fig. 2). Increasing the surface area can increase the power density when the materials have the same characteristics [20]. However, it is not known to what extent changes in molecular-scale surface area of the anode will affect power production. It is more likely here that changes in the surface chemistry affected power production.

XPS analysis of the different carbon fibers indicated the presence of primarily C, N, and O on the surface, with relatively smaller amounts of S, Cl, Si, and others elements (Fig. 3a and Table 1). The different treatment methods produced changes in the N1s/C1s, and the magnitude of this ratio was correlated with power density increases, consistent with previous findings [17]. The N1s/C1s ratio increased from 0.0163 (control) to 0.0261 (acid and heat treatment), which is a 60% increase in the atomic ratio of N in the electrode surface compared to the control. The N1s spectra of the different samples (Fig. 3b) showed a maximum peak at BE ≈ 400 eV, with a shoulder around 401.9 eV; these signals are assigned to tertiary amines and protonated nitrogen, respectively [21]. The ratio of protonated N to the total N for the heat-treated anode (0.74) and the acid- and heat-treated anode (0.48) were also both much higher than those of control (0.21) or the acid-treated anode (0.20) (Fig. 3b and Table 1). Thus, it appears that the increase in protonated N is an important factor for increasing power generation using these different anodes.

In the acid pretreatment process, ammonium persulfate was used as an etching agent as it reacts with water to form H_2O_2. The applied concentration was chosen based on optimum conditions obtained in tests to improve carbon fiber hydrophilic characteristics in an electroless plating process [22]. H_2O_2 is a strong oxidant that is rapidly decomposed to O_2. We know little about the relationship between the nascent oxygen and the oxygen in the treated fiber surface, but XPS results showed that the oxygen content in

Table 1
Elemental content (%) of the carbon fibers and atomic ratios of N/C, O/C and C–O/O1s with different treatment methods based on the XPS analysis.

Element	CF-C	CF-A	CF-H	CF-AH
C1s	79.32	76.79	86.30	82.81
O1s	18.94	21.25	11.01	14.94
N1s	1.29	1.26	1.88	2.16
N1s/C1s	0.0163	0.0164	0.0218	0.0261
Tertiary amine	1.08	1.06	1.14	1.68
Protonated nitrogen	0.21	0.20	0.74	0.48
O1s/C1s	0.24	0.28	0.13	0.18
C=O	1.32	1.79	3.50	5.21
C–O	17.62	19.46	7.51	9.73
C–O/O1s	0.93	0.91	0.68	0.65

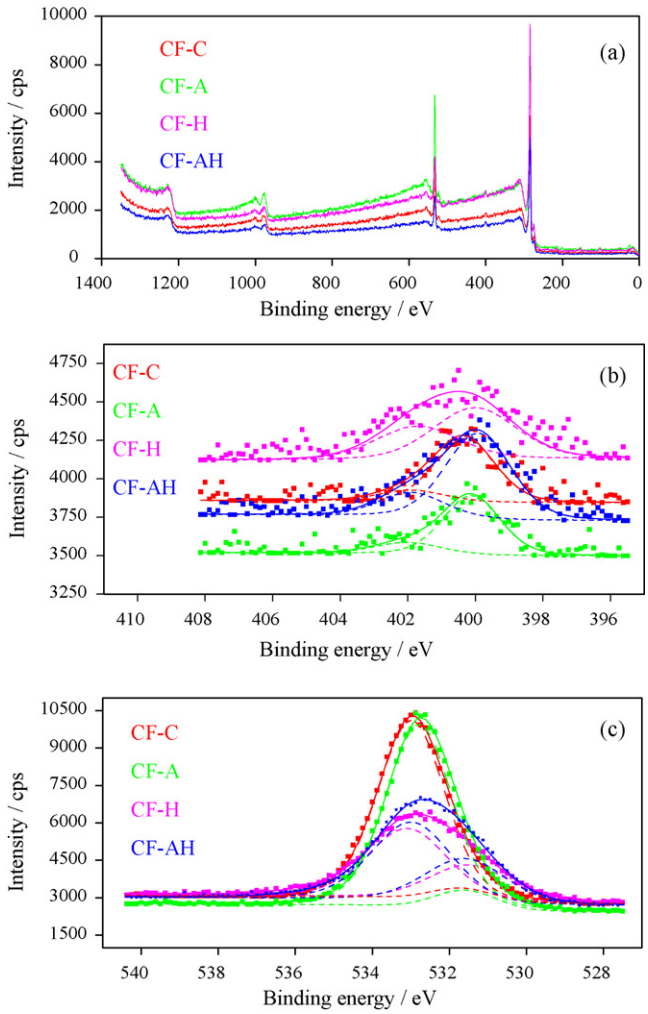

Fig. 3. XPS spectra of the acid (CF-A), heat (CF-H), and acid and heat (CF-AH) treated anodes compared to the control (CF-C): (a) whole spectra, (b) N1s and (c) O1s.

the spectra changed as a result of the different treatments (Fig. 3c and Table 1). The O1s/C1s atom ratio was 0.28 after acid treatment, and it decreased to 0.13 as a result of heat treatment. The XPS survey spectrum also showed two O1s peaks at 533 and 531.7 eV (Fig. 3c), presumably arising from C–O and C=O bonds, respectively. The ratio of C–O to O1s was calculated as 0.91 for the acid-treated anode, and it decreased into 0.65 after further heating, showing that the oxygen decline was mainly due to the decrease in the number of C–O bonds (Table 1). The decrease of the O-content has been shown to be connected with an increase in power by others [17]. This occurs due to a decrease in the oxygen content by first converting C–O to C=O, and then to CO_2. The oxidation (C–O to C=O) results in a decrease in the O-content, and therefore the decrease in the ratios of C–O/O (increase in C=O/O) was observed here to be associated with an increase in power.

4. Conclusions

Treatment of carbon fiber materials by a simple acid and heat treatment process increased power production by 34% from 1020 to 1370 mW m^{-2}. In addition, the average CE values increased from 14.6% to 19.5% due to increased current densities that resulted from reduced ohmic resistances. A 20% increase in power of carbon cloth anodes has previously been accomplished by an ammonia gas and heat treatment [10]. Heat treatment alone, however, increased power by 15% compared to the carbon mesh control [17]. Considering costs and complexity of treatment, high-temperature ammonia gas treatment methods are probably not warranted for future practical applications.

Increased performance of the treated graphite fibers was associated with a number of changes in the surfaces, including an increase in the N1s/C1s ratio from 0.0164 to 0.0261. These changes provide guidance for further improvements in the performance of graphite fibers in these systems. Additional chemical treatments for surface modifications, for example, should focus on increasing the N1s/C1s ratios, as well as increasing the concentration of protonated N species on the surface. Through these changes, it may be possible to increase performance of the MFCs through improved power generation and increased CEs.

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