Performance improvement of air-cathode single-chamber microbial fuel cell using a mesoporous carbon modified anode

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ABSTRACT

A novel mesoporous carbon (MC) modified carbon paper has been constructed using layer-by-layer self-assembly method and is used as anode in an air-cathode single-chamber microbial fuel cell (MFC) for performance improvement. Using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), we have demonstrated that the MC modified electrode exhibits a more favorable and stable electrochemical behavior, such as increased active surface area and enhanced electron-transfer rate, than that of the bare carbon paper. The MFC equipped with MC modified carbon paper anode achieves considerably better performance than the one equipped with bare carbon paper anode: the maximum power density is 81% higher and the startup time is 68% shorter. CV and EIS analysis confirm that the MC layer coated on the carbon paper promotes the electrochemical activity of the anodic biofilm and decreases the charge transfer resistance from 300 to 99 Ω. In addition, the anode and cathode polarization curves reveal negligible difference in cathode potentials but significant difference in anode potentials, indicating that the MC modified anode other than the cathode was responsible for the performance improvement of MFC. In this paper, we have demonstrated the utilization of MC modified carbon paper to enhance the performance of MFC.

1. Introduction

Microbial fuel cells (MFCs) have attracted substantial attention as a promising biotechnology for decomposition of organic matter in water and simultaneously harvesting electricity [1,2]. Among many kinds of bioreactor configurations, the air-cathode single-chamber MFC using oxygen in the air as the cathodic electron acceptor, substantially reduces both internal resistance and energy consumption, and thus improves the overall performance [3,4]. However, the power density of MFCs remains too low for their applications, mainly due to the low rate of electron transfer from the microbial cells (acting as the biocatalyst) to the solid electrode [5]. In particular, the anode material and its surface structure directly affect bacteria attachment, electron transfer efficiency, and substrate oxidation [6]. To date, a variety of carbon-based materials including carbon paper, carbon cloth, graphite brush or plate, activated carbon fiber, and carbon mesh, have been evaluated as anodes for MFCs due to their good compatibility with the biocatalyst, high conductivity, and high specific surface area [7,8]. Unfortunately, they have little electrocatalytic activity for the anode microbial reactions. Further modification of the carbon anode material is required to increase the electron transfer between the anode and the biocatalyst.

Over the years, considerable efforts were made to improve the power density by modifying the surface of carbon anodes. For example, immobilization of electron redox mediators such as neutral red, anthraquinone-1,6-disulfonic acid (AQDS), methylene blue, or 1,4-naphthoquinone (NQ), all resulted in increased current generation [9–13]. Use of metals and metal oxides in carbon anodes also were successful in improving power performance [14–18]. In addition, due to the unique properties of nanostructured materials (such as higher active surface area, excellent conductivity, tailored nanostructure to adsorb bacteria), they have been employed to modify the MFC anode to improve anodic performance. Carbon nanotubes (CNTs), as a new class of carbon nanomaterials, have been evaluated as possible anode materials in MFCs. Sharma et al. [19] reported that the maximum power density achieved by using CNT-Pt modified graphite as an anode could be six times higher than that achieved with bare graphite. Use of natural polymers

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such as chitosan [20] and conducting polymers such as polypyrrole (PPy)–CNTs [21] and polyaniline (PANI)–CNTs mixtures [22], also improved the power density of MFCs. In recent studies, the multi-wall carbon nanotube (MWNT) base electrode prepared by drop-coating technique [23] or by layer-by-layer self-assembly technique [24] have been used as anodes to improve the MFCs performance. Specially, nanoporous materials are excellent candidates for anode materials in MFCs. Qiao et al. [25] demonstrated that the power density of the *E. coli* MFC was increased to 1495 mW m^{-2} by using PANI/mesoporous TiO_2 composite as an anode material, which was two fold than the highest value 760 mW m^{-2} of *E. coli*-catalyzed MFC reported by Zhang et al. [26]. Discovery of appropriate nanomaterials to modify anodes for MFCs is still at its infancy, thus additional investigation into other nanomaterial is warranted.

It is widely recognized that mesoporous carbon (MC) is one kind of novel nanomaterial owing to its exceptional properties, such as tailored pore structure, high specific surface areas, and large pore volume. Thus, it is expected to bring about better three-phase contacts and therefore better performance for electrodes [27,28]. MC modified electrode has been reported to show a faster electron transfer rate and high electrocatalytic activities toward the oxidation of dopamine [29], and its application to polymer electrolyte membrane fuel cells catalysts support has been proved successful in enhancing cell performance [28,30]. Furthermore, it is important to note that high surface area and mesopore-volume of MC are recommended for bacterial adsorption [31], facilitating electron transfer from exocelectrogens to the electrode. Despite such advantages of MC, one review article reported that the maximum power density of 1600 mW m^{-2} was achieved when ordered mesoporous carbon modified anode was used [2]. To our best knowledge there has been no detailed report yet to use MC to modify anodes in MFCs.

In the present work, we report a novel MC modified carbon paper constructed with a layer-by-layer self-assembly method. The electrochemical catalytic activity of the MC modified carbon paper was examined by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in $K_3[Fe(CN)_6]$ solution. The results suggest that the MC modified carbon paper exhibits improved electron transfer capability and remarkable electrocatalytic activity. Then, the performance (such as startup time, power density, and the anode and cathode polarization) of air-cathode single-chamber MFC equipped with MC modified carbon paper anode is compared to that with bare carbon paper anode. The electrochemical capability of anodic biofilms and the electrochemical impedance behavior of the MC modified carbon paper and bare paper anodes were also characterized by CV and EIS, respectively. This study aims to demonstrate the feasibility of enhancing power density by using MC modified carbon paper as anode, and hopefully provide a new nanomaterial to modify anodes for improving the performance of MFCs.

2. Materials and methods

2.1. Electrode preparation

Mesoporous carbons (MC, 10 ± 1 nm average pore diameter, 0.5 cm^3 g^{-1} pore volume, 150–250 m^2 g^{-1} specific surface area, purchased from Aldrich) were ultrasonically dispersed in a mixture of H_2SO_4–HNO_3 (volume ratio: 3:1) for 5 h then filtered through a polytetrafluoroethylene filter membrane (pore diameter 0.4 μm) and washed with de-ionized water until slurry with pH 6–7 was obtained. The carboxylated MC were prepared and were well-dispersed in de-ionized water by ultrasonication for another 1 h to obtain a homogeneous solution (0.2 mg ml^{-1}). Polyethyleneimine (PEI) (M.W. 60,000, 50 wt% aq, ACROS) was diluted with de-ionized

water to 1% in weight. Carbon papers (without waterproofing) were first cleaned by soaking them in pure acetone for 3 h and were leached and washed under vacuum to remove oil-soluble substances. Then, the carbon paper were boiled in de-ionized water for 4 h and dried at 120 °C overnight and soaked in the mixture of H_2SO_4–HNO_3 (volume ratio: 3:1) for 1 h to introduce carboxyl groups on the surface of the carbon paper. After thoroughly washed and dried, the surfaces of the carbon paper became hydrophilic and negatively charged in aqueous solutions [32].

MC modified carbon paper was produced using layer-by-layer (LBL) self-assembly procedure as follows. The negatively charged carbon paper were first dipped into the positively charged PEI solution for 10 min, and rinsed with de-ionized water. Then the carbon paper was dipped into the MC suspension for 10 min and rinsed again. At the end of each cycle, the carbon paper was dried with hot air to enhance the toughness of the multilayer films [33]. By repeating procedure above, desirable cycle number was obtained, and then the electrode was used for morphological and electrocatalytic analysis, and used as a bio-anode in MFC.

2.2. Inoculants and medium

Anaerobic sludge collected from the Liede municipal wastewater treatment plant (Guangzhou, China) was used as the anodic inoculums of MFCs. Before inoculation, the sludge was washed several times using de-ionized water to remove soluble carbon sources and then filtered through a 0.22-mm pore size sieve to remove impurities The sludge was added into the MFC anode chamber with a final concentration of 2 g of volatile suspended solids per liter (VSS l^{-1}). The medium added to MFC anode chamber contained 1 g l^{-1} glucose and 50 mM PBS-based nutrient solution consisting of (per liter of de-ionized water): 2.98 g $NaH_2PO_4 \cdot 2H_2O$, 9.28 g $NaHPO_4 \cdot 12H_2O$, 0.31 g NH_4Cl, 0.13 g KCl, 12.5 ml mineral solution, and 12.5 ml vitamin solution [34].

2.3. MFC construction and operation

Air-cathode single-chamber MFCs were constructed as reported previously [35] the only exception being the cell volume. Total volume of the MFC was reduced to 216 ml (6 cm × 6 cm × 6 cm in height with an operating volume of approximately 180 ml plus a 36 ml headspace). Bare carbon paper, MC modified carbon paper electrodes with a projected surface area of 3 cm × 3 cm, was respectively used as anode, whereas the air cathode was similar to the anode in size and consisted of a catalyst layer (containing 0.5 mg cm^{-2} Pt) as previously described by Cheng et al. [4]. Ultra-filtration membrane with a molecular cutoff weight of 1 K Dalton was applied directly onto the water-facing side of the cathode. All MFCs were operated in fed-batch mode conditions and were mixed using a small magnetic stirrer to enhance mass transfer. Copper wire was used to connect the circuit (500 Ω external resistor except stated otherwise). The anode solution was replaced when the voltage decreased below 20 mV and the suspended biomasses were reserved just in the first fed-batch cycle (for more efficient inoculation), forming a fed-batch cycle. Before each batch cycle, N_2 gas was flushed continuously for 15 min to maintain anaerobic conditions and prevent aerobic oxidation of the organic substrates. All experiments were conducted in a temperature-controlled room at 30 ± 1 °C in duplicate, and the average value was reported.

2.4. Data acquisition and electrochemical measurements

The voltage output across the 500 Ω resistor was recorded every 11 min with a multimeter and data acquisition system (Model 2700, Keithly Instruments, USA). Polarization curves were obtained by

varying the external resistor (R_{ex}) over a range from 50 to 1000 Ω when the voltage output approached a steady and repeatable state. Current density (A m^{-2}) was calculated as $I = U/(R_{ex}S)$, and power density (mW m^{-2}) was calculated according to $P = 1000UI/A$, where I (A) is the current, U (V) is the voltage, and A (m^2) is the projected surface area of the anode electrode.

Electrochemical analysis of the bare carbon paper, MC modified carbon paper electrodes, and electrochemical performance of their applications as anodes in MFCs were investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), which were performed using an electrochemical workstation (Model 2273, Princeton Applied Research) with a three-electrode consisting of a working electrode (bare carbon paper or MC modified carbon paper), a Ag/AgCl (saturated KCl) reference electrode, and a platinum foil counter electrode. All the working electrodes were cut to 3 cm × 3 cm to assure exactly the same size as that used for anodes in MFCs during electrochemical measurement. EIS tests were conducted under open circuit voltage (OCV) conditions over a frequency range of 10 kHz–5 mHz with sinusoidal perturbation of 10 mV amplitude and the obtained data were fitted and simulated to predetermined equivalent electrical circuit and were then analyzed using ZSimpWin 3.10 software (Echem, US). The surface morphologies of MC modified carbon paper, bare carbon paper were observed by an environmental scanning electron microscope (SEM) (XL-30, Philips Holland).

3. Results and discussion

3.1. Characterization of MC modified carbon paper electrode

The electrochemical properties of bare carbon paper and LBL self-assembled MC/PEI modified carbon paper (with 5, 15, and 25 cycle layers) electrodes were evaluated by CV and EIS in 0.1 M KCl containing 10 mM K$_3$[Fe(CN)$_6$]. The electrodes modified by MC exhibited excellent catalytic activity. As shown in Fig. 1A, on the CV of the bare carbon paper electrodes, no obvious redox peak was observed. However, there was a series of well defined redox peaks on the CVs of MC modified carbon paper, and the increase of current response was directly proportional to the growth of cycle layers. This tendency indicates that MC/PEI layers grow steadily in accordance with the LBL self-assembled method. Moreover, the redox peaks of the MC modified carbon paper were much higher than that of the bare carbon paper, indicating that the MC modified carbon paper had a higher faradic charge capacity, which is known to be proportional to the electroactive surface area [25]. Thus, with the same projected areas, the reaction surface area of the MC modified carbon paper (modified with 25 cycles) is much higher than that of the bare carbon paper. Since the potential separation (ΔE_p) between the anodic and cathodic peaks ($E_{pa} - E_{pc}$) is inversely proportional to the rate of electron transfer, a decrease in ΔE_p represents an increase in electron transfer rate [36]. Along with the growth of MC/PEI multifilms, the value of ΔE_p for MC modified electrodes reduced gradually, which not only indicates that the MC could enhance the electron-transfer rate, but also suggests that MC/PEI could be coated on carbon paper layer by layer successfully. CV experiments of MC carbon paper electrode (modified with 25 cycles) in 0.1 M KCl containing 10 mM K$_3$[Fe(CN)$_6$] solution have also been performed at various scan rates (Fig. 1B). The anodic peak current was linearly ($R = 0.9996$) proportional to the square root of the scan rates ranging from 10 to 100 mV s^{-1} (Fig. 1B insert). This result reveals that the redox reaction was a diffusion controlled process, which confirms that the MC coated on the carbon paper electrode was rather stable even at a high scan rate.

The complex impedance (Z) versus frequency, known as Nyquist plot was measured on the electrodes with different cycle layers (Fig. 2). The insert in Fig. 2 illustrates the high-frequency part of
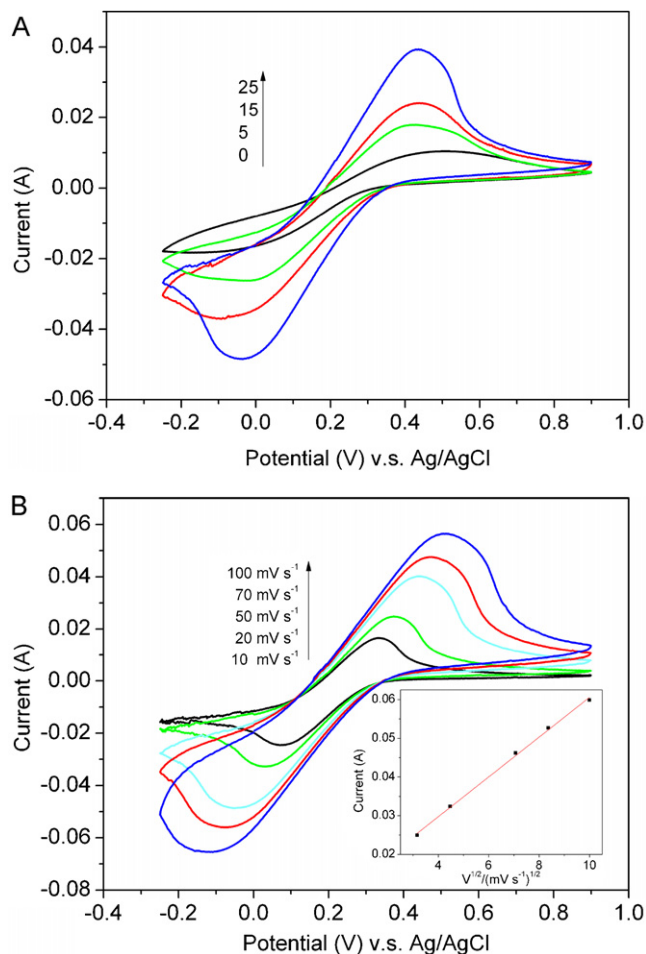

Fig. 1. Cyclic voltammograms of (A) {MC/PEI}$_n$ ($n = 0, 5, 15, 25$ cycles; from inner to outer) multilayer films assembled on carbon paper electrode at scan rate of 50 mV s^{-1}, and (B) {MC/PEI}$_5$ multilayer films assembled on carbon paper electrode at the scan rate (from inner to outer) 10, 20, 50, 70, 100 mV s^{-1} in 0.1 M KCl containing 10 mM K$_3$[Fe(CN)$_6$]. $n = 0$ referred to bare carbon paper electrode.

the EIS. The Nyquist plot of the bare carbon paper electrode represented a well-defined frequency-dependent semicircle impedance curve over high frequency followed by straight line, but the MC modified carbon paper electrodes had no defined semicircle. A Randle equivalent circuit [36] was usually chosen to model the
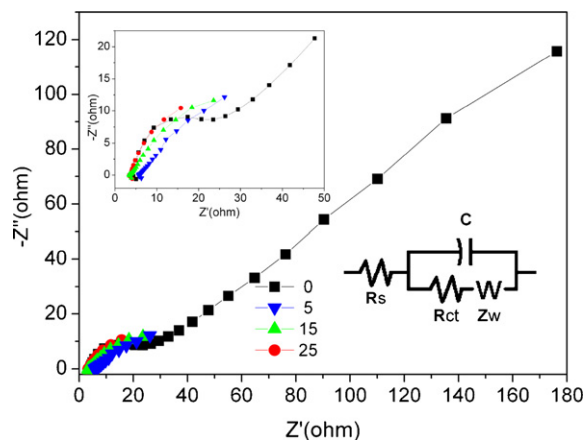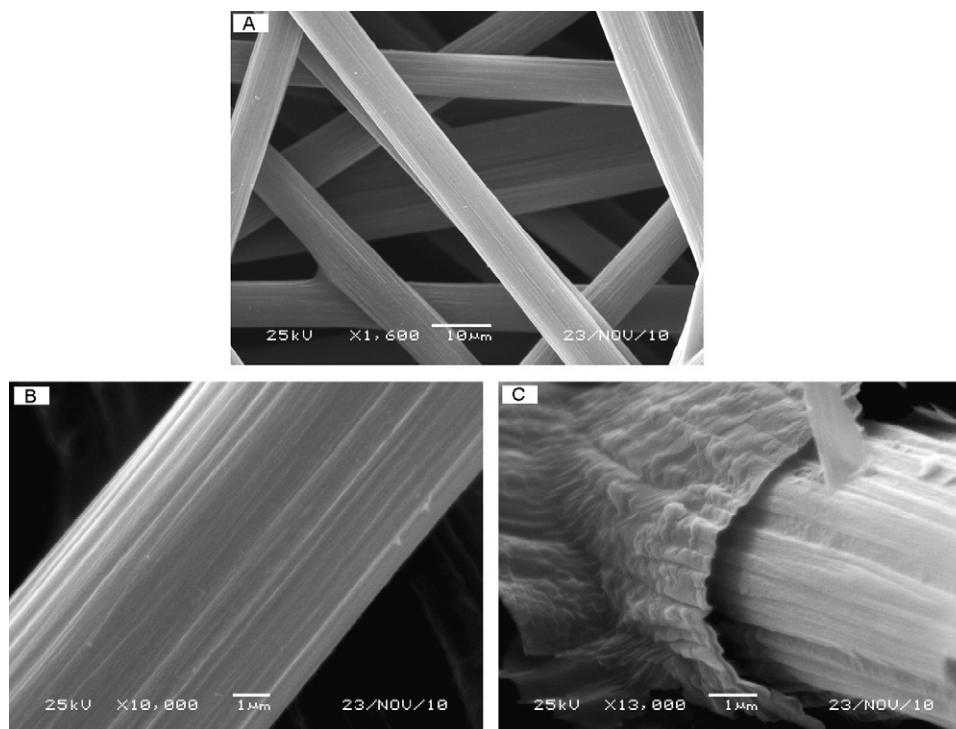

Fig. 2. Nyquist plots and equivalent circuit of {MC/PEI}$_n$ ($n = 0, 5, 15, 25$) multilayer films assembled on carbon paper electrode in 0.1 M KCl containing 10 mM K$_3$[Fe(CN)$_6$]. The insert illustrates the high-frequency part of the result.

Fig. 3. SEM images of (A) and (B) as-received carbon paper with different magnifications, and (C) MC modified carbon paper.

complex impedance in an electrochemical cell, in which the charge-transfer resistance (R_{ct}) at the electrode/electrolyte interface is equal to the diameter of the semicircle. Small R_{ct} indicates a faster electron-transfer rate between electrode and electrolyte. The value of R_{ct} for the bare carbon paper electrode was calculated to be 19.5 Ω. After being coated by MC, the R_{ct} decreased dramatically, nearly to zero (0.26 Ω, 0.25 Ω and 0.21 Ω for 5, 15, and 25 cycle layers, respectively), indicating that MC significantly reduced the electron-transfer resistance and revealed a faster reaction between the electrode and electrolyte. At the same time, the straight line region over low frequency of MC modified carbon paper electrode after the high frequency-dependent semicircle was significantly smaller than that of bare carbon paper electrode. The straight line region is usually characteristic of a diffusion-limiting step in an electrochemical process [36]. This indicates that MC modified carbon paper electrodes had a good micro/nanostructure for reactants to access the reaction centers [22], and obviously improved the diffusion of electrolyte toward the electrode surface. Both CVs and EIS results demonstrate that the MC modified carbon paper electrode exhibited a favorable and stable electrochemical behavior, such as increased active surface area and enhanced electron-transfer rate. The reasons for this unusual electrochemical response may attribute to high specific surface area (150–250 $m^2\,g^{-1}$), pore volume (0.5 $cm^3\,g^{-1}$) of MC, and the existence of edge plane defect sites in the MC nanomaterials [29,37].

SEM images further confirmed the successful binding of the MC with the carbon paper. As shown in Fig. 3A, the bare carbon paper consists of a number of carbon fibers with diameter of about 10 μm. The unmodified carbon features a relatively smooth surface (Fig. 3B). In contrast, the surface of the LBL self-assembled MC/PEI multifilms coated-carbon paper is much rougher (Fig. 3C), and hence its surface area is significantly larger. This implies that the incorporation of MC on carbon paper would supply edge plane defect sites in the MC nanomaterials [37] and increased surface area, thus resulting in an enhancement in the performance of the electrode. Based on all the analysis mentioned above, the MC modified carbon paper electrode is highly suitable for application in MFCs as anode.

3.2. Performances of MFC

3.2.1. Electricity generation

As the improvement of electrochemical behavior for the MC modified carbon paper electrode, the air-cathode single-chamber MFC equipped with MC modified carbon paper anode (MFC-A) achieved much better performance than that prepared with bare carbon paper anode (MFC-B). Fig. 4 shows the cell voltage curves, anode and cathode polarization curves, and power density curves of the two individual MFC reactors. After inoculation, stable maximum voltages of 0.34–0.38 V (500 Ω external resistance) were obtained for both MFC-A and MFC-B (Fig. 4A). Within a lag time of about 40 h during their first feeding cycles, the MFC-A reached a steady cell voltage of 0.35 V which was 2.0 times higher than that of MFC-B (0.15 V). Moreover, the start-time for the initial maximum stable voltage was 140 h for the MFC-A compared to 440 h for MFC-B and the MFC-A delivered a maximum stable voltages of 0.38 V which was slightly higher than that of MFC-B (0.34 V). The time to achieve maximum repeatable voltages of the MFC-A was shortened by 68% as compared to that of MFC-B. The MC significantly improved surface area of the carbon paper, and the electron transfers from the electrolyte to the electrode and inside the electrode were thus enhanced, as supported by the CV, EIS and SEM analysis above. Such improved surface area and more readily electron-transfer were favorable for bacterial to attach to the electrode and donate electrons. Therefore, bacterial adhesion, the most important step in biofilm formation and growth [38], could be enhanced and accelerated by MC on the electrode. This contributed to the shortening of startup time. In addition, nine reproducible cycles of voltage generation (corresponding to an operation of 50 days) were obtained for the MFC-A and the average value of voltages were substantially higher than that produced from MFC-B, suggesting the improved stability of the MC modified anode.
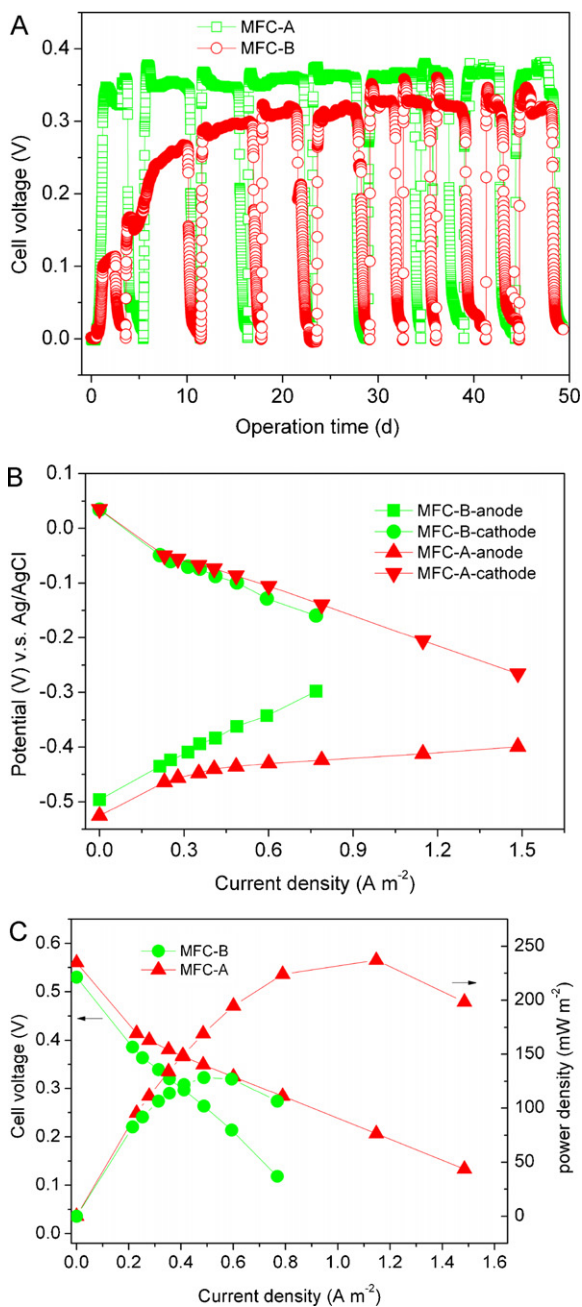
Fig. 4. Performance of MFCs equipped with a MC modified carbon paper anode (MFC-A) and a bare carbon paper anode (MFC-B): (A) voltage production as a function of time, (B) anode and cathode polarization curves, and (C) power density and cell polarization curves.

Fig. 4B shows anode and cathode polarization curves of the two MFCs. Since both MFCs were configured in the same way except for the anode, we can see that the two MFCs exhibit small difference in their cathode potentials. However, the open circuit potential (OCP) and polarization curves varied between the MC modified carbon paper and bare carbon paper. This reveals that the differences in performance of the two MFCs were due to the performance of the anode and not the cathode. It was observed that the anode OPC moved toward more negative value from −0.49 V (MFC-B) to −0.53 V (MFC-A). Also, a sharp decrease in the slope of the anode polarization curve was found in MFCs using the MC modified anode versus those using the unmodified anode. In addition, in the MFC-B, with the increase of current density from 0 to 0.77 A m^{-2}, the anode working potential decreased by 39% from −0.49 (OCP) to −0.30 V;
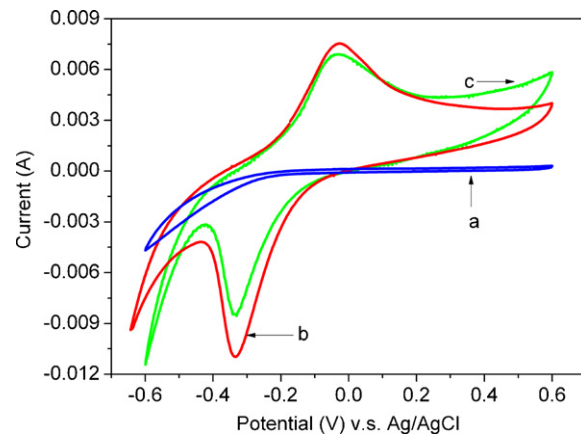
Fig. 5. Cyclic voltammograms of MC modified carbon paper in the MFC containing (a) 50 mM PBS + 0.5 mg l^{-1} glucose, (b) a + bacteria in absence of suspended biomass; (c) bare carbon paper in the MFC containing (b). Scan rate: 10 mV s^{-1}.

whereas, the anode working potential of MFC-A decreased only by 20% from −0.53 to −0.42 V. These results indicate that using the MC modified anode could markedly reduce the loss in potential of bacterial metabolism and thus enhanced bioelectroactivity of the anode in MFCs.

As shown in Fig. 4C, the maximum power density achieved by the MFC-A was 237 mW m^{-2} at the current density of 1.15 A m^{-2}, which is 1.9 times larger than that (128 mW m^{-2}) produced form the MFC-B. On the whole, the MC modified anode (MFC-A) significantly improved the performance of MFCs, as evidenced from the shortening of startup time, the increased OCP, the decreased slop of cell polarization curves, and the increase of the maximum power density as compared to the bare carbon paper anode (MFC-B). These results are the consequence of an enhanced anode performance by the increased anode surface area and biocompatibility of the substrate, and the accelerated bacterial adhesion [12,21,25,39]. Moreover, CV and EIS tests were carried out to determine the electrocatalytic behavior of different anode materials in MFCs in the following part.

3.2.2. CV and EIS studies

Cyclic voltammetry is increasingly exploited to examine the redox properties of species in MFCs, and to confirm the capability of anodic biofilms to electrocatalyze substrate oxidation. Fig. 5 presents the CVs of MC modified carbon paper and bare carbon paper in MFCs. Although different in their overall performance, the thermodynamics and the mechanisms of the anodic electron transfer in the MFC-A and the MFC-B appear to be one and the same. Thus, except for the different Faradaic current, their voltammetric features are virtually identical, as illustrated in Fig. 5. Specifically, both MFCs with an enriched-anode biofilm and glucose as the substrate showed distinguishable two current peaks: the first peak in the forward scan at −43 mV (vs. Ag/AgCl), which might be ascribed to the bio-electrocatalytic oxidation of glucose; and the second peak in the reverse scan at −340 mV, might be belong to the reduction of the glucose-oxidized products (curve b and c of Fig. 5). In contrast, there was no peak response from the MFC with a virgin anode (curve a of Fig. 5). This demonstrates the contribution of the attached anode biofilm to the generation of electricity in MFCs, as consistent with the explanation of other investigators. That is, electrochemically active bacteria attached to the anode plays a critical role in MFCs in transfering electrons from the substrate to the anode [40]. In addition, the Faradaic currents of 11 and 8 mA at the redox peaks of MC modified electrode was higher than that of the bare electrode, indicating that the redox species was of a high level [41]. Thus, it
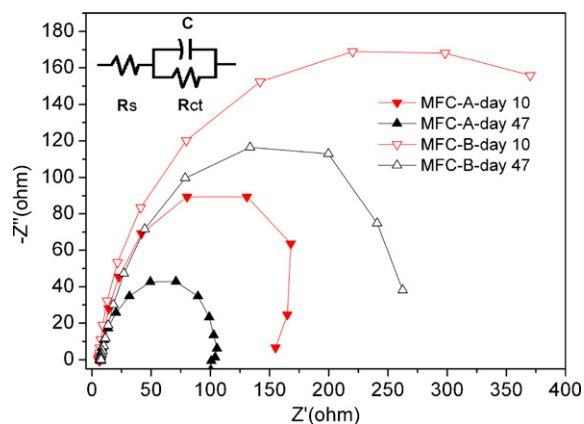
Fig. 6. Nyquist plots and equivalent circuit of anode in MFC-A and MFC-B on the operation day 10 and 47 at open circuit potential.

could be concluded that the electrochemical activity of the biofilm was promoted by MC.

Fig. 6 presents the Nyquist plots for the MC modified carbon paper and the bare carbon paper anode in two identical MFCs at different stages of the microbial growth. Each of the Nyquist plots in Fig. 6 is a semicircle without a straight line following it, which is characteristic of an electrode reaction controlled by the charge transfer step. This phenomenon was also reported by Ramasamy et al. [42] and Borole et al. [43]. We also confirmed that the Nyquist plots fit well with the equivalent circuit (R_s, C_{dl} and R_{ct} representing solution resistance, double layer capacitance, and charge transfer resistance, respectively) inserted in Fig. 6. The R_{ct} for the MC modified carbon paper anode on day 10 (MFC reactor operated for 10 days) was 184 Ω and this value decreased to 99 Ω on day 47. The R_{ct} for the bare carbon paper anode also decreased from 428 (day 10) to 300 Ω (day 47). These impedances can be compared since they both were measured at open circuit. Ramasamy et al. [42] demonstrated the positive effect of initial anodic microbial enrichment on anode impedance over time. Thus, the decrease in anode impedance can be attributed to establishment and development of the anodic biofilm on the electrode surface. Moreover, the R_{ct} for the MC modified carbon paper anode was substantially lower than that of the bare carbon paper anode on day 10 and 47. These results indicate that the formation of composite biofilms by using MC was beneficial to stabilize the anodic resistance, thus contributing to stable long-term power generation of MFC-A. In addition, it is known that the electrochemical reaction rate is inversely proportional to the electron transfer resistance (R_{ct}) [42]. Therefore, this significant improvement in R_{ct} strongly suggests that the superior performance of the MC modified carbon paper anode relative to that of the bare carbon paper anode is due in large part to the much higher rate of the anodic bio-electrochemical reaction. The higher electron transfer efficiency of the anodic bio-electrochemical reaction likely results from the increased rate of electron transfer from microbe to electrode and enhanced mature microbial biofilms on the anode that are necessary to improve MFC performance. These results indicate that the electrochemical activity of the anodic biofilm was promoted by MC, which is consistent with the result of the CV test. However, future studies are still needed to further understand the mechanisms of the improvement.

3.3. Implications of MC for better application in MFCs

The MC modified carbon paper offers a high degree of versatility for electrode fabrication in MFCs. MC is an ideal supporting nanomaterial in electrode fabrication, and can be chemically modified by metals [28,44], conducting polymer [45,46], and enzymes

[47]. Because of its high specific surface area, high pore volume, and well-developed interconnected mesoporosity, MC can be easily assembled with various functional groups. Potentially, we could combine MC with electrochemical (conducting polymers or metal oxides) or bioelectrochemical substance (enzymes) to construct nanostructured composites, thus taking advantage of the merits of both components to further enhance the performance of MFCs. As a result, larger scale application of MFCs may be realized earlier.

4. Conclusions

The results of this study demonstrate that the MC modified carbon paper electrode is well-suited as the anode in MFCs due to its excellent electron transfer capability and remarkable electrocatalytic activity. The MFC equipped with MC-carbon paper anode achieves considerably better performance than the one equipped with bare carbon paper anode: the maximum power density is 81% higher and the startup time is 68% shorter. The MC layer coated on the carbon paper promotes the electrochemical activity of the anodic biofilm and decreases charge transfer resistance of the MC modified carbon paper anode, thus resulting in the significantly enhanced performance of MFCs and the promoted stabilization of long-term electricity generation performance for two months. The nanomaterial MC therefore offers a good prospect for application in MFCs, and more studies are necessary to combine the MC with other conducting polymers or metal oxides to construct nanostructured composites to further enhance the performance of MFCs.

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