



Ni-Coated Carbon Fiber as an Alternative Cathode Electrode Material to Improve Cost Efficiency of Microbial Fuel Cells



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ABSTRACT

Electrode material is a key component in microbial fuel cells (MFCs), and exploring cost-effective electrode materials will greatly help with MFC development, especially the scaling up. In this study, a commercially available material – nickel-coated carbon fiber (Ni-CF) has been investigated as an alternative cathode electrode material to carbon cloth (CC). Both three-electrode cell and MFC tests are carried to examine electrochemical performance and actual electricity generation of the prepared cathode electrodes. It is found that Ni-CF exhibited higher current generation in linear sweep voltammetry (LSV) and lower resistance in electrochemical impedance spectroscopy (EIS) tests than those of CC and CF. When being coated with AC, Ni-CF has the highest actual loading amount among the tested materials. As a result, AC/Ni-CF leads to lower charge transfer resistance (95.1Ω) and higher current density (8.07 mA m^{-2}) than AC/CC (115.3Ω and 3.40 mA m^{-2}). In the MFC test, the cathode using AC/Ni-CF results in the maximum power density of 6.50 W m^{-3} , higher than AC/CC at 4.29 W m^{-3} . This high power output gives cost efficiency of AC/Ni-CF at $299.0 \text{ mW \$}^{-1}$, nearly twice that of AC/CC ($151.7 \text{ mW \$}^{-1}$). The initial AC coating amount of 4 g is found to be the optimal amount to achieve optimally actual AC loading amount on the cathode electrode with balanced catalytic ability and (possible) oxygen transfer. Those results encourage further investigation of Ni-CF for MFC applications towards improved performance and cost efficiency.

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1. Introduction

Microbial fuel cells (MFCs) have attracted a great attention as an emerging technology for sustainable waste treatment and bioenergy recovery. In an MFC, electrochemically-active organisms oxidize organic compounds and release electrons to an anode electrode, which transfers the electrons to a cathode electrode for reducing terminal electron acceptors. When treating wastewater, MFCs can generate electrical energy directly, require low energy input, and produce a small amount of biosolids that need further disposal [1,2]. In the past two decades, MFCs have been greatly advanced in terms of understanding microbial-electrode interaction, new catalyst/electrode materials, reactor design and operation, and electrochemistry [3,4]. One of the major challenges for MFC development is system scaling up. There have been efforts to enlarge MFCs to a scale of several hundred liters for treating actual

wastewater [5]. Despite a preliminary analysis in a recent study that the capital cost of MFC systems could be lower than some small-scale wastewater treatment facilities [6], it is generally acknowledged that MFCs systems are expensive [7,8]; thus it is of great interest to explore cost-effective materials for MFC development.

Cost efficiency of an MFC can be improved by using low-cost materials that do not significantly sacrifice the performance. As an electrochemical system, electrode materials play an important role in MFC performance and cost. An anode electrode material can affect the power generation of MFCs through influencing microbial growth and electron transfer from microorganisms. Thus, the appropriate anode electrode material should have a large surface area for microbial attachment, good biocompatibility, and low resistance. Popular materials used as anode electrodes include carbon brush, carbon cloth, and granular carbon/graphite [9,10]. A cathode electrode can also greatly affect power generation, due to high reduction overpotential caused by slow rate of oxygen reduction potential (ORR) on the carbon surface [11,12]. For example, the main limiting factor for current generation occurs in

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Table 1

Unit cost of cathode electrode materials.

Cathode material	Unit cost	Additional material used
CC	\$ 45 m ⁻²	/
CF	\$ 0.027 m ⁻¹	/
Ni-CF	\$ 0.141 m ⁻¹	/
AC (4 g)/Ni-CF	\$ 1.445 m ⁻¹	100 mL ethanol, 2.5 mL 60 wt % PTFE
W-AC (4 g)/Ni-CF	\$ 7.722 m ⁻¹	100 mL ethanol, 2.5 mL 60 wt % PTFE, 50 mL concentrated H ₂ SO ₄ solution, 50 mL 3 M KOH solution, and 4 g KMnO ₄ solid

the cathode, because the kinetics of ORR in the cathode is lower than the organic oxidation in the anode, causing larger overpotential of the cathode than the anode [13,14]. The slow kinetics to limit MFC performance in ORR is possible because of the requirement of high activation energy (498 kJ mol⁻¹) to cleave the O=O bond of oxygen molecule [13].

The research of MFC cathode electrodes heavily focuses on catalysts, because of abovementioned ORR kinetics [15]. The function of a catalyst is to reduce the activation loss for stronger ORR, and the conventional catalyst such as platinum (Pt) can dramatically improve ORR [11]. However, the Pt-based cathode accounts for almost 50% total cost of lab-scale MFC systems [16]. Alternative catalysts are of great interest, and among them, activated carbon (AC) has been demonstrated effective in ORR catalysis with a much lower cost [17,18]. On the other hand, the cathode electrode, which is also the supporting material for catalysts, has not been studied in detail like that of catalysts. Carbonaceous materials (e.g., carbon paper, graphite granules) are the most widely utilized cathode electrode materials in MFCs, owing to their strong mechanical strength and high porosity to scaffold a large amount of catalysts for better ORR performance [19]. Among those materials, carbon cloth (CC) is commonly used as cathode electrodes [20], and the CC coated or pressed with AC (AC/CC) has been proved to have long-term stability and outstanding electrochemical performance to treat the real wastewater [1,6,9]. However, alternative cathode electrode materials that can produce similar performance to CC but be cheaper will still be worth exploration.

In this study, a commercially available and low-cost carbon fiber (CF) coated with nickel (Ni) was investigated as an alternative cathode electrode material to support AC catalysts. Cost efficiency, which is rarely reported in the previous studies of electrode materials, has been analyzed for the tested electrode materials. Ni has been studied as an effective electrode material [17], and Ni foam could act as a current collector for AC catalysts to achieve comparable performance to the MFC using Pt-based cathode [20]. The objectives of this study were to demonstrate that this nickel-

coated carbon fiber (Ni-CF) could outcompete CC as a cathode electrode for MFCs in terms of performance and cost, and to examine the effects of AC loading on the cost efficiency. For comparison, CC and Ni-CF coated with AC catalysts (AC/CC and AC/Ni-CF), CF without Ni (CF), and Ni-CF coated with acidic/alkaline washed AC (W-AC/Ni-CF) have also been studied for power generation and cost efficiency. Cost efficiency was quantified using numerical standard (mW \$⁻¹) [15].

2. Experimental

2.1. Cathode material preparation

The commercially available CF and Ni-CF (Toho Tenax, Rockwood, TN, US), and CC (PANEX 30PW03, Zoltek Corporation, St. Louis, MO, US) were used as the cathode materials (Fig. S1). It should be noted that CC (flat sheet) and CF (thread type) are very different in terms of dimensions, and the criterion to determine the amount of CC or CF is based on full coverage of the cation exchange membrane by one layer of the cathode material. All electrode materials were pretreated by acetone [21], and then coated with AC powder if needed. To coat AC on the electrode, Ni-CF or CC was submerged in a solution containing 100 mL ethanol, 4 g AC (specific electrode coating amount of 23.53 mg cm⁻²) and 2.5 mL 60 wt% PTFE (actual PTFE amount of 2.08 g) in an air-tight container (150 mL) to make the AC/PTFE mass ratio as 1.92, following the same procedure of a previous work [22]. Afterwards, the AC-coated Ni-CF (AC/Ni-CF) and CC (AC/CC) were dried and heated at 370 °C for 30 min, and were ready for tests. The method to make acid/alkaline washed AC/Ni-CF followed a previous study [23], and the temperature of heat treatment for AC/Ni-CF after alkaline washing rose up to 500 °C in a muffle oven [24]. The unit cost of each cathode material is listed in Table 1. Cost efficiency was calculated by using maximum power derived from polarization tests and normalized to the total cost of the cathode material only (cost efficiency = $\frac{\text{maximum power}}{\text{total cost of cathode material}}$) [15]. Both electrochemical test and MFC test were conducted to compare the

Table 2

Experimental design for tubular MFC operation in this study.

Experimental Group # and Experimental Target	Electrode Material	Initial amount of AC (g) (60 wt % PTFE in mL, and actual PTFE amount in g)
#1 intrinsic base material	AC/CC	4 (2.5, 2.08)
	AC/Ni-CF	4 (2.5, 2.08)
	W-AC/Ni-CF	4 (2.5, 2.08)
#2 different coating amount of AC/Ni-CF	AC/Ni-CF	0 (0, 0)
	AC/Ni-CF	2 (1.25, 1.04)
	AC/Ni-CF	4 (2.5, 2.08)
	AC/Ni-CF	6 (3.75, 3.12)
	AC/Ni-CF	10 (6.25, 5.20)

Note: the mass ratio of AC/PTFE is constant as 1.92 for all experiments; AC/CC represents activated carbon coated on carbon cloth; AC/Ni-CF represents activated carbon coated on Ni-coated carbon fiber; W-AC/Ni-CF represents acid/alkaline washed activated carbon coated on Ni-coated carbon fiber.

electrochemical performance among various electrode materials and test the effect of AC loading on a cathode electrode. In the comparison of electrochemical performance of basic electrode material, electrode materials coated without and with AC catalyst were tested. In the test of impact of different initial AC coating amount on the electrode performance, different AC amount was coated on Ni-CF with selected initial coating amount of AC powder (0, 2, 4, 6, 10 g) and corresponding volume of 60 wt% PTFE binder (actual PTFE amount of 0, 1.04, 2.08, 3.12, 5.20 g), to make the AC/PTFE mass ratio constant as 1.92 (Table 2). Thus, the expected AC coating densities on the electrode were 0, 11.76, 23.53, 35.29 and 58.82 mg cm⁻², respectively, and the actual AC loading densities (mg cm⁻²) in different experimental groups were indicated in the following results and discussion, calculated by multiplying 0.66 on total weight difference before and after AC coating process to exclude PTFE loading (derived from mass ratio between AC and total weight).

2.2. MFC setup and operation

Multiple tubular MFCs were constructed and placed horizontally in sequence from top to down with all the anodes electrode connected together while the cathode electrodes separated, and an external resistor of 10 Ω was connected in each anode-cathode circuit (Fig. 1). In each MFC, the total anode volume was 280 mL (working volume: 200 mL; diameter: 4.7 cm; length: 15 cm). The anode electrode material was the pretreated carbon brush, and the cathode material was described as section 2.1 mentioned (Table 1). The anode and cathode were separated by cation exchange membrane (CEM) that had a surface area of 170 cm². The pictures of individual tubular MFCs are shown in Fig. S2. The anolyte was synthetic wastewater, containing (per L of DI water): sodium acetate, 0.2 g; NH₄Cl, 0.15 g; NaCl, 0.5 g; MgSO₄, 0.015 g; CaCl₂, 0.02 g; NaHCO₃, 0.1 g; KH₂PO₄, 0.53 g; K₂HPO₄, 1.07 g; and trace element, 1 mL [25]. The catholyte was 20 mM phosphate buffered saline (PBS, with the initial pH of ~7.1). The anodes were inoculated with anaerobic sludge from a local wastewater treatment plant (Radford, VA, USA), and cultivated for about one month until all individual MFCs achieved steady performance

under the fixed resistance of 10 Ω . Both the anolyte circulation and catholyte dipping rate were controlled at 30 mL min⁻¹ by peristaltic pumps without any refreshment during one operation cycle (BT600-2J, Langer Instruments Corp., NJ, USA). The MFCs were operated in a batch mode, and all the anolytes and the catholyte were completely refreshed every 24 hours at the end of each operation cycle. The reason to connect all MFC anodes together (Fig. 1) was to keep the anode potential same for all individual MFCs to eliminate or minimize the anodic impact on MFC performance. The cathode material was also exchanged between different individual MFCs to examine any interfering impact of CEM difference on MFC performance, as mentioned in section 3.2. The experimental design for the tubular MFC test is listed in Table 2.

2.3. Measurements and analyses

The cathode electrodes were characterized in both three-electrode systems and MFCs. To evaluate the electrochemical properties of the materials using linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS), a three-electrode electrochemical cell was set up containing a working electrode (the cathode material), a reference electrode (Ag/AgCl, 0.201 V vs standard hydrogen electrode, SHE), and a counter electrode (Pt wire). LSV was performed in 50 mM PBS with a potential range from 0.4 to -0.8 V (vs reference Ag/AgCl electrode; scan rate: 5 mV s⁻¹), and EIS was conducted at scanning frequency of 1×10^5 to 2×10^{-3} Hz by using a potentiostat (Reference 600, Gamry Instruments, Warminster, PA, USA).

In the MFC test, the weight of each cathode material (e.g., AC/Ni-CF, AC/CC) before and after AC coating was measured by a digital balance, and the weight difference (triplicate results) was the actual AC loading amount on the electrode material. The voltage was continuously recorded every 5 min by a digital multimeter (2700, Keithley Instruments Inc., Cleveland, OH, USA). The polarization test (scan rate: 0.5 mV s⁻¹) was performed by using a potentiostat (Reference 600, Gamry Instruments). The concentration of chemical oxygen demand (COD) was measured using a DR/890 colorimeter (HACH Co., Ltd., USA). Total Coulombs (TC),

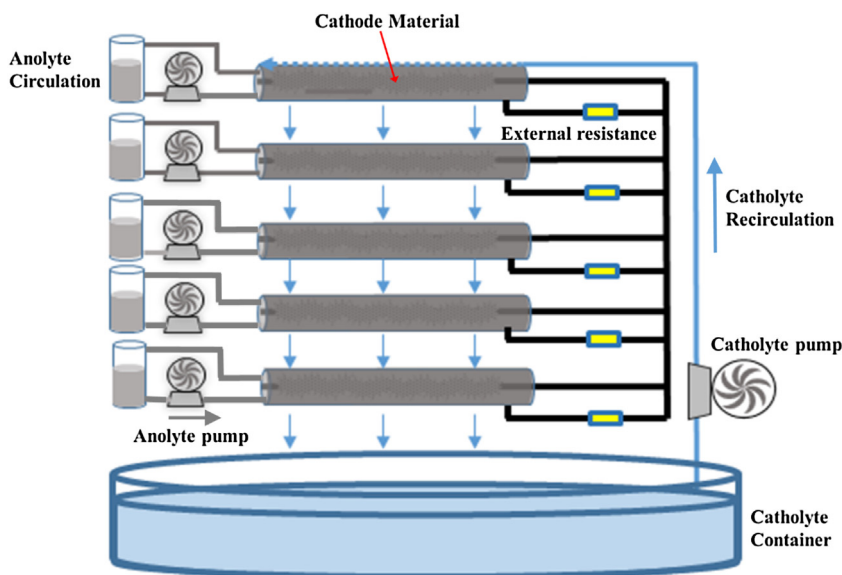


Fig. 1. Setup schematic of the tubular MFCs with the anode electrodes connected together, but the cathode electrodes separated from each other to form individual electrical circuits.

Coulombic efficiency (CE) and COD removal efficiency (COD_R) were calculated according to the previous work [1,26].

3. Results and discussion

3.1. Bare cathode electrode without AC catalysts

The cathode electrode materials were firstly examined without AC catalysts to evaluate base material in the three-electrode cell, including CC, CF and Ni-CF. The LSV results show that the onset potentials for these electrode materials were similar, but the peak absolute current density of Ni-CF (3.87 mA cm^{-2}) was much higher than that of CC (0.39 mA cm^{-2}) or CF (0.63 mA cm^{-2}) (Fig. 2A), indicating the greater electron conductivity of Ni-CF than other two materials. The Nyquist plots derived by EIS was used to obtain the charge transfer resistance for different cathode materials (Fig. 2B), based on the equivalent circuit (EC) model shown in Fig. S3. The charge transfer resistance of Ni-CF was 2413.5Ω , much lower than that of CC (3954.2Ω) or CF (3214.9Ω) (Fig. 2C), indicating the stronger ability of Ni-CF to transfer electrons through the electrode material. It was expected that Ni-CF would have a lower ohmic resistance, because of the conductivity enhancement due to the metallic coating, semi-conductive carbon fibers, and the electrical contacts generated from the fiber networks [27]. Therefore, Ni-CF could be an effective base material for MFC cathode electrode to replace CC.

3.2. Cathode electrode coated with AC catalysts

Next, the cathode electrodes coated with AC catalysts were examined, including AC/CC, AC/Ni-CF, and pre-treated AC on Ni-CF (W-AC/Ni-CF). The pre-treatment of AC powder by the acidic/basic wash aimed to increase the catalytic performance introduction of oxygen-rich group by acid washing and activation of AC by basic washing [21]. With the same initial AC coating amount (4 g), the actual loading density of AC on Ni-CF was $8.08 \pm 0.23 \text{ mg cm}^{-2}$ (excluding PTFE assuming the AC/PTFE weight ratio fixed as 1.92), much greater than that of CC with a loading density of $3.61 \pm 0.11 \text{ mg cm}^{-2}$ (Fig. 3A); this suggests that that Ni-CF could be a better electrode material base with stronger affinity with AC than CC, and such a difference in AC loading would result in different electrochemical performance.

The coated electrodes were examined by using LSV in the three-electrode cell. With potential change until -0.8 V (vs. Ag/AgCl), the current density of AC/Ni-CF was 8.07 mA m^{-2} , much greater than 3.40 mA m^{-2} of AC/CC and 6.00 mA m^{-2} of W-AC/Ni-CF (Fig. 3B), likely benefiting from its lower charge transfer resistance of 95.1Ω obtained from EIS tests (Fig. 3C and 3D). For comparison, the charge transfer resistance of AC/CC and W-AC/Ni-CF was 115.3Ω and 187.4Ω , respectively. It was unexpected that W-AC/Ni-CF had the poorer electrochemical performance than AC/Ni-CF. The possible reason for decreased performance of W-AC/Ni-CF was that the acid and alkaline pretreatment on AC under high temperature exposed to the air might have introduced acidic surface oxides on AC itself [21,28], to make affinity barrier of AC onto Ni-CF, resulting in a much lower AC loading density of $1.89 \pm 0.59 \text{ mg cm}^{-2}$ on the W-AC/Ni-CF (Fig. 3A). In addition, the increasing oxygen content on carbon surface could increase the electrical resistivity to lower the electrochemical performance [29]. However, the exact reason for lower performance of W-AC/Ni-CF warrants further investigation. The LSV and EIS results have demonstrated that AC/Ni-CF had a stronger ORR catalytic ability than AC/CC.

To further investigate the electrode performance with bioelectricity generation, the AC coated materials were examined in the tubular MFCs. The batch profiles of current generation with three

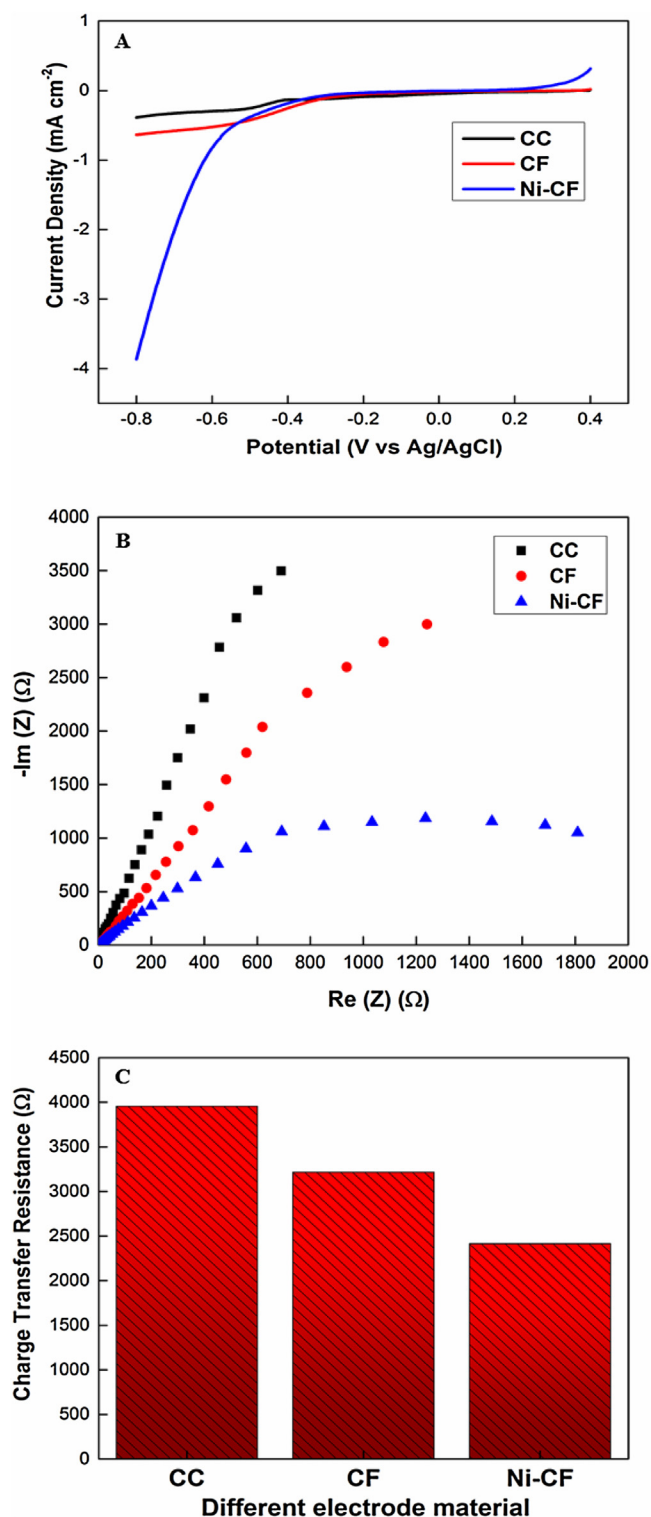


Fig. 2. Electrochemical analysis of bare electrode materials in the three-electrode cell system, including CC, CF and Ni-CF: A) LSV result; B) EIS Nyquist plot; and C) charge transfer resistance derived from EIS result. Note: CC represents carbon cloth; CF represents carbon fiber; and Ni-CF represents Ni-coated carbon fiber.

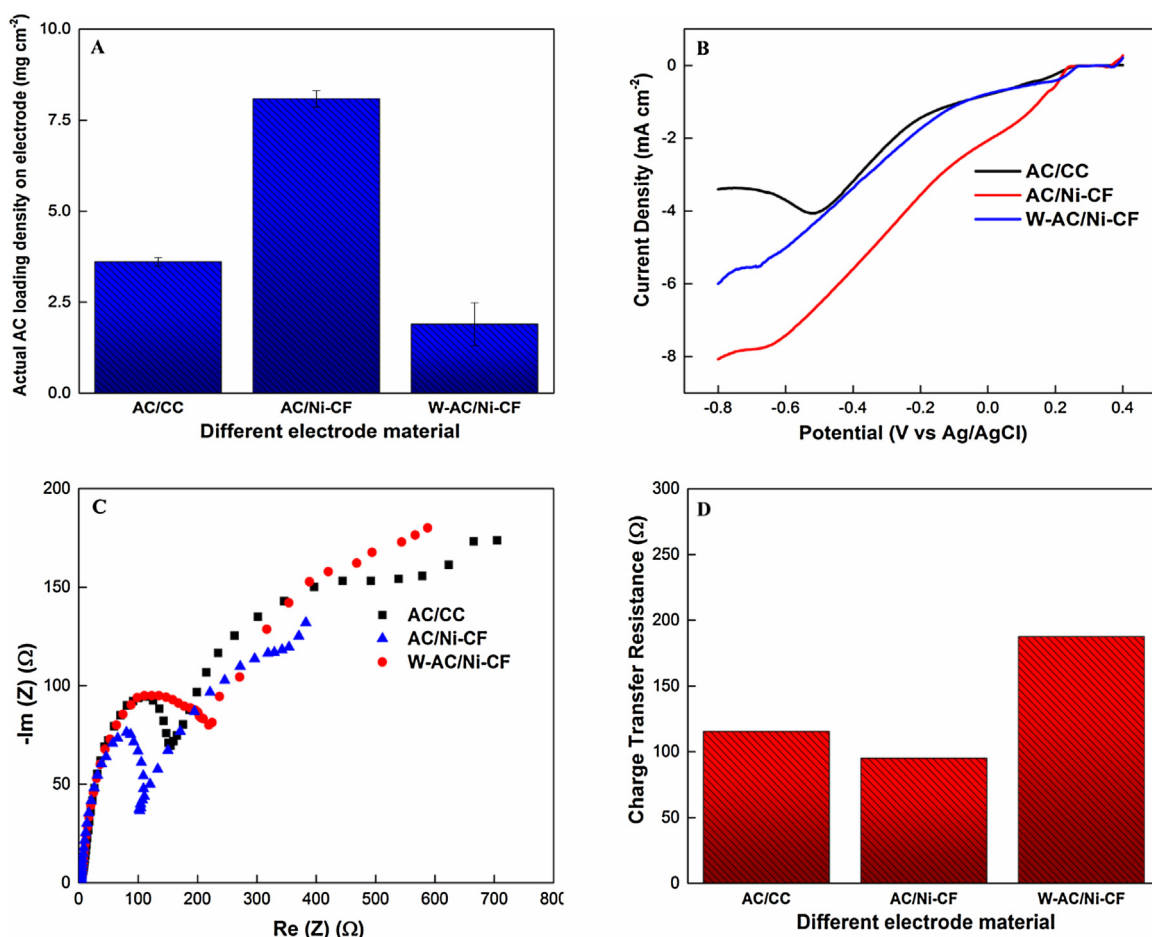


Fig. 3. Examination of AC coated electrodes in the three-electrode cell system, including AC/CC, AC/Ni-CF and W-AC/Ni-CF: A) actual AC loading density (mg cm^{-2}) on different electrode material applied in the MFC test (surface area: 170 cm^2); B) LSV result; C) EIS Nyquist plot; D) charge transfer resistance derived from EIS result. Note: AC/CC represents activated carbon coated on carbon cloth; AC/Ni-CF represents activated carbon coated on Ni-coated carbon fiber; W-AC/Ni-CF represents acid/alkaline washed activated carbon coated on Ni-coated carbon fiber.

cathode electrodes are shown in Fig. 4A. The highest maximum current of 1.7 mA was obtained with AC/Ni-CF, while the other materials generated 1.3 mA (AC/CC) and 1.0 mA (W-AC/Ni-CF), respectively. As a result, the total Coulomb production in a batch was $118.3 \pm 9.8 \text{ C}$ with AC/Ni-CF, much higher than $82.1 \pm 11.0 \text{ C}$ with AC/CC or $86.8 \pm 6.3 \text{ C}$ with W-AC/Ni-CF (Fig. 4B). To ensure that those differences were not due to different reactor preparation, the cathode materials of AC/Ni-CF and AC/CC were exchanged between the MFCs, and the similar current output was obtained, thereby confirming the superior electrochemical performance of AC/Ni-CF (data not shown). COD removal is a key parameter to evaluate MFC performance, especially for its application in wastewater treatment. The cathode electrode materials clearly affected COD removal (Fig. 4B): the highest COD_R of $74.0 \pm 1.6\%$ was obtained with AC/Ni-CF, followed by $65.6 \pm 5.1\%$ with AC/CC and $61.1 \pm 1.0\%$ with W-AC/Ni-CF. Consequently, Coulombic efficiency (CE) was estimated as $46.6 \pm 4.7\%$ (AC/Ni-CF), $36.4 \pm 3.3\%$ (AC/CC), and $41.4 \pm 4.0\%$ (W-AC/Ni-CF), respectively. Those results suggest that the better electrochemical performance of AC/Ni-CF can also result in better treatment performance. The cost efficiency of the cathode materials was estimated based on the maximum power output. The power density curves show that the maximum power density was 6.50 W m^{-3} with AC/Ni-CF, 4.29 W m^{-3} with AC/CC, and 1.85 W m^{-3} with W-AC/Ni-CF, respectively (Fig. 5A),

confirming the superior electrochemical performance of Ni-CF. The cost efficiency of AC/Ni-CF was $299.0 \text{ mW \$}^{-1}$, much higher than that of AC/CC ($151.7 \text{ mW \$}^{-1}$) or of W-AC/Ni-CF ($15.9 \text{ mW \$}^{-1}$) (Fig. 5B). Furthermore, the cost efficiency of AC/Ni-CF in this study is also much higher than conventional Pt-catalyzed cathode, which was reported as $5.8 \sim 10.2 \text{ mW \$}^{-1}$ [30–32]. Therefore, Ni-CF was proved to be an effective cathode electrode material alternative to CC with higher electricity generation and cost efficiency.

3.3. Effects of AC catalyst loading

The AC/Ni-CF was further investigated with different AC coating amounts for electrochemical performance and cost efficiency. The actual AC loading density on the electrode increased from 0 to $21.15 \pm 0.21 \text{ mg cm}^{-2}$ with increasing initial coating amount from 0 g to 10 g (Fig. 6A). The following presentation of the data will be based on “initial AC coating amount”, while the “actual loading amount” is the actual amount of AC loaded on the electrode. LSV tests show that the current density increased with increasing the initial AC coating amount from 0 to 4 g and reached the maximum current density of 9.30 mA cm^{-2} (potential at -0.8 V vs Ag/AgCl) with 4 g. A higher initial AC coating amount than 4 g actually decreased the current density, and the highest initial AC coating amount of 10 g had a very low current density of 2.32 mA cm^{-2}

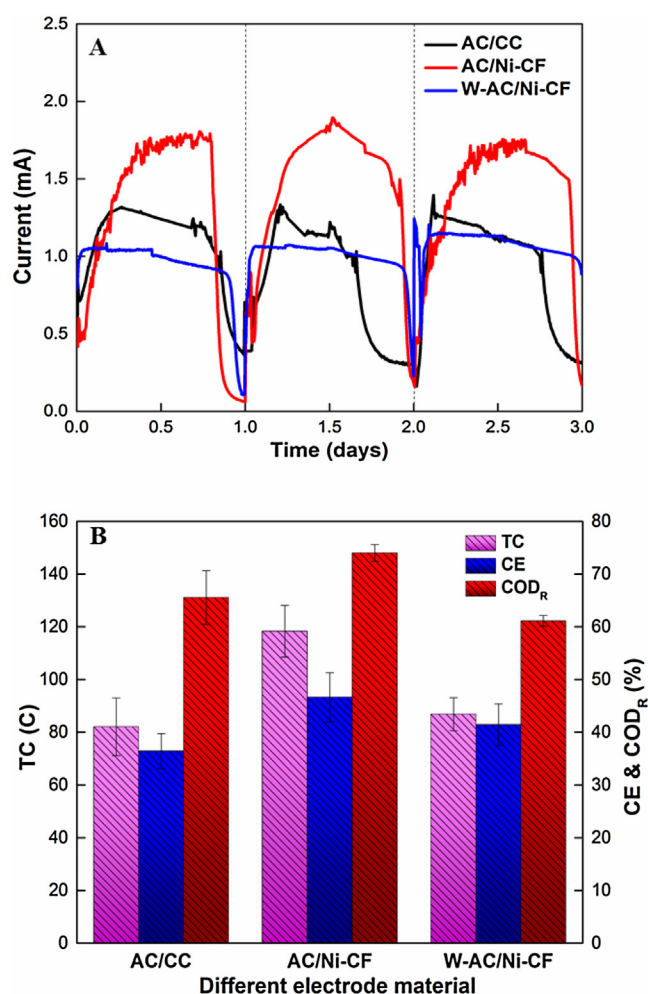


Fig. 4. The MFC tests of the AC coated cathode electrodes, including AC/CC, AC/Ni-CF and W-AC/Ni-CF: A) batch current profile; and B) average TC, CE and COD_r. AC/CC represents activated carbon coated on carbon cloth; AC/Ni-CF represents activated carbon coated on Ni-coated carbon fiber; W-AC/Ni-CF represents acid/alkaline washed activated carbon coated on Ni-coated carbon fiber.

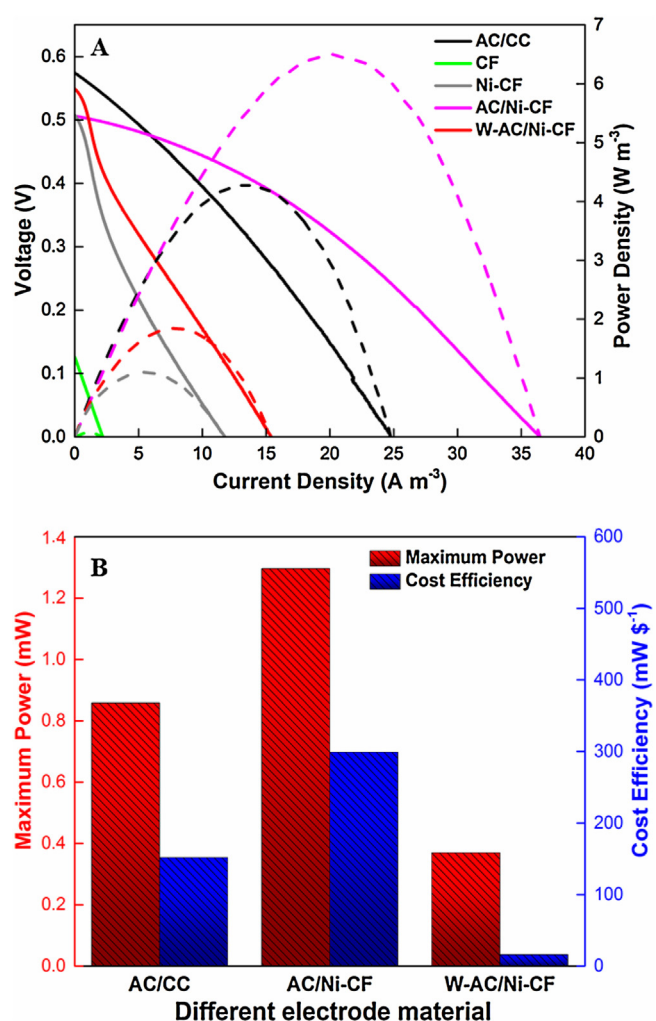


Fig. 5. Polarization curve of the MFC (A) and cost efficiency analysis (B) of AC coated cathode electrodes, including AC/CC, AC/Ni-CF and W-AC/Ni-CF. AC/CC represents activated carbon coated on carbon cloth; AC/Ni-CF represents activated carbon coated on Ni-coated carbon fiber; W-AC/Ni-CF represents acid/alkaline washed activated carbon coated on Ni-coated carbon fiber.

(Fig. 6B). Such a relationship between current density and initial AC coating amount could be due to insufficient AC catalytic ability or supply of terminal electron acceptors, affected by AC coating. In the first half range of initial AC coating amount within 0–4 g, increasing initial AC coating amount can increase actual loading amount to enhance ORR catalytic ability because of more catalysts. Further increasing initial AC coating amount might have caused the overload of AC and PTFE mixture, which resulted in excessive filling material inside the interconnecting network and created a barrier for oxygen transfer to the active sites, thereby impeding the electrochemical reduction of oxygen [33]. In addition, a higher amount of PTFE on Ni-CF could also increase the hydrophobicity of the cathode electrode, which would impede the proton supply to the cathode electrode and thus limit current generation [34,35]. The excessive amounts of PTFE binder will increase the electrode resistance [28], and this was proved by EIS tests. The Nyquist plot for Ni-CF with different initial AC coating amounts is shown in Fig. 6C. The charge transfer resistance exhibited an opposite trend to that of current density: the lowest resistance of 181.4 Ω was obtained with initial AC coating amount at 4 g, while both lower and higher coating amount gave higher resistance, for example 326.3 Ω with initial AC coating amount of 0 g and 294.3 Ω with

initial AC coating amount of 10 g (Fig. 6D). The results of both LSV and EIS tests demonstrate that there is an optimal initial coating amount (e.g., initial coating amount of AC at 4 g in this study) to guarantee optimal actual loading amount on the electrode, and higher or lower AC loading will decrease current generation via decreasing ORR catalytic ability or (possibly) supply of electron acceptors.

The MFC test of the coated electrodes confirmed the finding of electrochemical tests that the highest current output was obtained with the initial AC coating amount at 4 g, while the current output decreased to a lower level with higher initial AC coating amount at 10 g (Fig. 7A). Accordingly, the highest total Coulomb production of 84.8 ± 2.8 C was also obtained with the initial AC coating amount at 4 g, which achieved $74.2 \pm 2.6\%$ of COD removal and $33.7 \pm 4.2\%$ of CE, higher than those with other initial AC coating amount (Fig. 7B). Based on the maximum power density of 8.70 W m^{-3} (Fig. 8A), the cost efficiency with the initial AC coating amount at 4 g was estimated to be $399.4 \text{ mW \$}^{-1}$, significantly higher than $79.4 \text{ mW \$}^{-1}$ with initial 0 g or $95.5 \text{ mW \$}^{-1}$ with initial 10 g (Fig. 8B). It should be noted that the difference in cost efficiency with initial AC coating amount at 4 g between this section and the

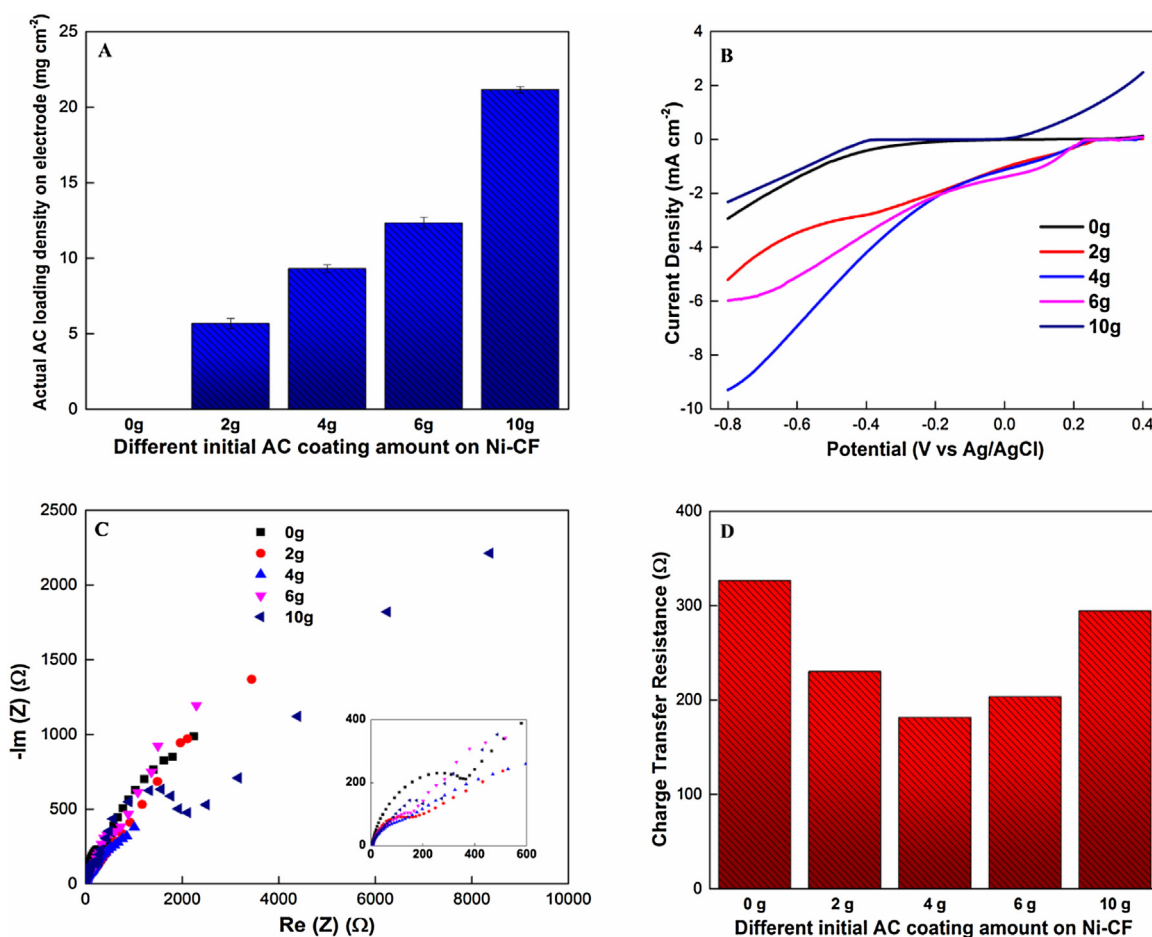


Fig. 6. Examination of different initial AC coating amount on Ni-CF in the three-electrode cell system: A) actual AC loading density (mg cm^{-2}) on Ni-CF applied in the MFC test (surface area: 170 cm^2); B) LSV result; C) EIS Nyquist plot; and D) charge transfer resistance derived from EIS result. Note: “0, 2, 4, 6, 10 g” represent the initial coating amount of AC added to the solution for coating Ni-CF.

section 3.2 was due to different power output affected by MFC operation, and the conclusion of comparison is valid in both cases. Those results have collectively demonstrated that the initial AC coating amount at 4 g appeared to achieve optimal actual loading amount on Ni-CF in this study.

3.4. Perspectives

The outstanding performance of Ni-CF in terms of electricity generation and cost efficiency suggests that it is a feasible approach to explore “new cathode electrode materials” from commercially available products. Many conductive materials have been developed for various purposes, but not specifically for electrode applications, for example Ni-CF is originally designed for electromagnetic shielding and light strike protection for aircraft. Examining those products and selecting optimal ones for MFC applications will avoid the need for scaling up manufacturing processes, which is always a key challenge for newly synthesized materials.

Further applications of Ni-CF for MFC cathodes will need to address several fundamental and practical questions. First, the mechanism of the improved AC loading with Ni-coated carbon fiber surface is not fully understood and the relevant surface chemistry should be investigated further. This is very important to achieve optimal loading, because our results have demonstrated that AC loading played a key role in electricity generation and thus

cost efficiency. Second, because of the importance of AC loading, it will be of strong interest to explore whether the actual AC loading can be further increased without sacrificing MFC performance. A key factor here is the function of binding agent. PTFE, though at a relatively low cost, can cause problems of oxygen transfer when being applied in an excessive amount. Alternative binding agents that can be electrically conductive and create porous conditions to facilitate oxygen transfer will be of great interest. The popular binding agent – Nafion may not be suitable for MFC applications because of its high cost. Third, pretreatment of Ni-CF to enhance AC affinity can be further explored. Understanding of surface chemistry during AC coating process onto Ni-CF will help with formulating an effective pretreatment method. Fourth, the role of Ni in ORR catalysis should be further studied. Our data demonstrate that Ni-CF had a lower charge transfer resistance than CF, indicating potential ORR catalysis with Ni. However, the charge transfer resistance of Ni-CF was an order of magnitude higher than that of AC/Ni-CF, suggesting that the major ORR catalysis was carried out by AC, instead of Ni. Thus, investigation of Ni for its ORR catalysis may further improve the benefits of using Ni-CF as MFC cathode electrode materials. Fifth, other earth abundant metals (e.g., Mn, Fe) are also proved to be promising alternative cathode catalysts, and addition of these metals on the cathode material using certain techniques (e.g., hot-pressing, electrodeposition) deserves further consideration to enhance the catalytic performance of AC/Ni-CF [15,36,37]. Last but not the least, the application

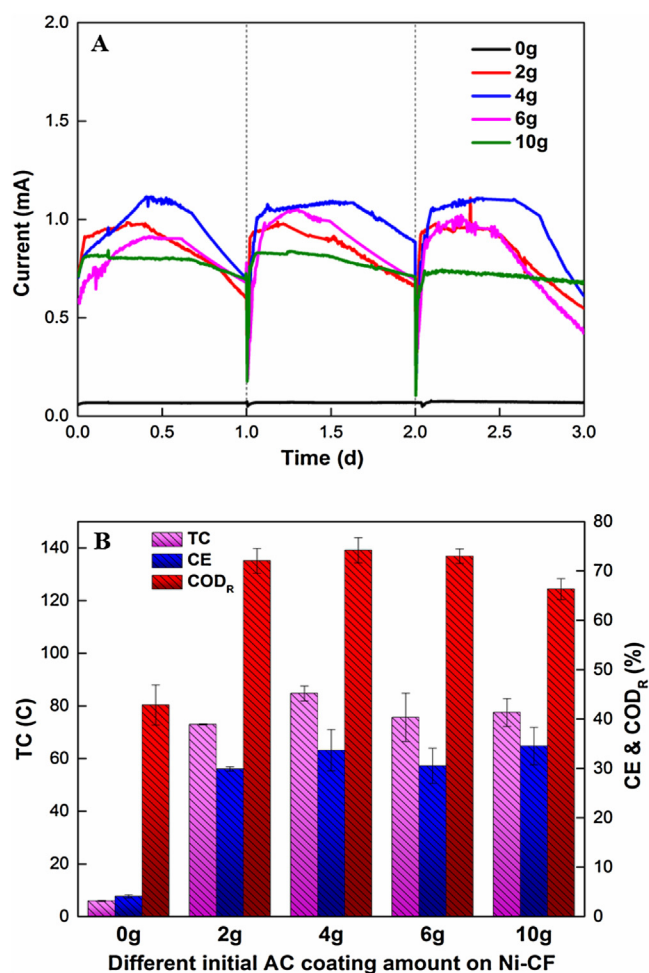


Fig. 7. The MFC tests of the Ni-CF electrode initially coated with different amounts of AC catalysts: A) batch current profile; B) TC, CE and COD_r. Note: “0, 2, 4, 6, 10 g” represent the initial coating amount of AC added to the solution for coating Ni-CF.

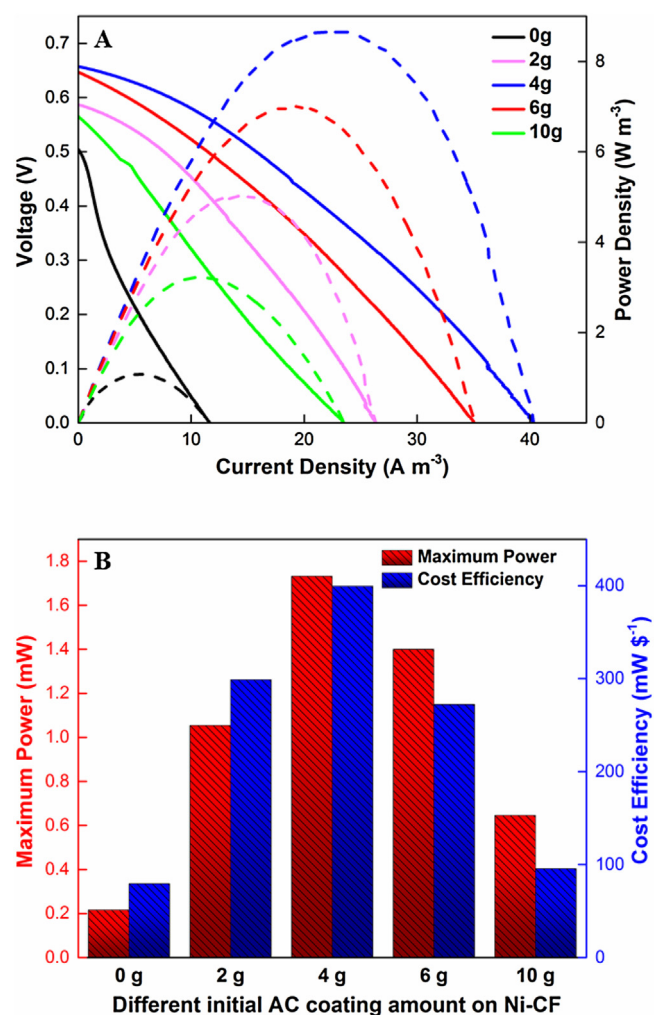


Fig. 8. Polarization curve of the MFC (A) and cost efficiency analysis (B) of Ni-CF initially coated with different amounts of AC catalysts. Note: “0, 2, 4, 6, 10 g” represent the initial coating amount of AC added to the solution for coating Ni-CF.

of Ni-CF in MFCs must be examined with a long-term operation for its stability under actual condition such as real wastewater treatment.

4. Conclusions

In this study, Ni-CF has been demonstrated as an effective cathode electrode material alternative to carbon cloth with superior performance in both electricity generation and cost efficiency. The improved performance benefited from both Ni coated surface and a higher loading of AC catalyst on Ni-CF, though the exact mechanism for enhanced AC affinity on Ni-CF warrants further investigation. The acid/alkaline pretreated AC powder exhibited a lower affinity to Ni-CF, resulting in worse performance than AC/Ni-CF. It was found that the initial AC coating amount of 4 g would be helpful to achieve an optimal loading amount on Ni-CF; a lower initial coating amount could result in insufficiently actual loading amount of AC catalyst and thus a lower ORR catalytic ability, while a higher loading might have blocked the supply of terminal electron acceptors – oxygen. The success of employing Ni-CF as a cathode electrode material in MFCs suggests that exploring suitable electrode materials from commercially available products that are not designed for electrodes could avoid scaling

up manufacturing processes, although several fundamental and practical problems need to be further investigated.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2016.10.178>.

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