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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 (95.1 Ω) and higher current density (8.07 mA m^{-2}) than AC/CC (115.3 Ω 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 mW $\$^{-1}$, nearly twice that of AC/CC (151.7 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.

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_2SO_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($\text{cost efficiency} = \frac{\text{maximum power}}{\text{total cost of cathode material}}$) [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	AC/CC	4 (2.5, 2.08)
intrinsic base material	AC/Ni-CF	4 (2.5, 2.08)
	W-AC/Ni-CF	4 (2.5, 2.08)
#2	AC/Ni-CF	0 (0, 0)
different coating amount of AC/Ni-CF	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.