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Research article

Effective strategies for anode surface modification for power harvesting and industrial wastewater treatment using microbial fuel cells

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ABSTRACT

This study investigates three different strategies for anode surface treatment by doping superficial nitrogen groups on the anode surfaces of carbon cloth (CC) and carbon paper (CP). The chosen anodes were hydrothermally treated in the presence of an ammonia solution (AST), a mixture of nitric acid and sulfuric acid (AHT), and solid urea (UT) at 180 °C for 3 h. The utilized characterization techniques confirmed doping of nitrogen on the anode surfaces and a decrease in the oxygen-bonded carbon content. Furthermore, the results showed that the power and current densities were significantly affected by the surface modification techniques. Interestingly, the AST strategy achieved the highest power density of 159.3 mW^{-2} and 91.6 mWm^{-2}, which revealed an increase in power of 115% and 56.8% for CC-AST and CP-AST, respectively. Additionally, the maximum coulombic efficiencies were 63.9% and 27.5% for the CC-AST and CP-AST anodes, respectively. Overall, these results highlight the significance of anode surface modification for enhancing MFC performance to generate electricity and treat actual wastewater.

1. Introduction

Recently, attention has been devoted to developing renewable energy sources and water treatment methods to overcome the shortage of energy and water resources. Therefore, microbial fuel cell (MFC) technology has attracted considerable interest because it provides the dual benefits of providing energy and wastewater treatment simultaneously in which the organic matter is metabolized by anodic microbes to produce electrons and protons. The produced electrons are transferred from the anode to the cathode via an external circuit. Instantaneously, the protons reach the cathode through a proton exchange membrane (PEM) where the proton and electron are accepted by an electron acceptor to generate electricity (Hernández-Flores et al., 2015; Huang et al., 2016; Logan, 2008; Lovley, 2006).

In addition to wastewater treatment (Choi and Ahn, 2013; Jayashree et al., 2016), MFC can be used in many applications, such as sensors for biochemical oxygen demand (BOD) (Chang et al., 2004; Rodrigo et al., 2007), production of electrofuels (Chandrasekhar et al., 2015), removal and recovery of toxic metal from wastewater (Wang et al., 2011), denitrification (Hussain et al., 2016), and as bioreactors for hydrogen generation (Chandrasekhar and Mohan, 2014; Sharma and Li, 2010). The unique properties of MFC compared with conventional fuel cells is that the microbes act as biocatalysts and control the electrode reactions, (Asghary et al., 2016), whereas in other types of fuel cells, a chemical catalyst, such as platinum or nickel, determines the kinetics of the electrode

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reactions. This technology has several advantages over the anaerobic process, such as an improved conversion efficiency, low operating temperature, and being environmentally benign (Logan et al., 2006). Unfortunately, for significant practical implementation, MFCs usually have more limitations, such as low power generation and a high cost (Ge et al., 2015). However, several factors affect the MFC performance, such as the solution properties, electrodes type, microbial culture, electron transfer process, cell configurations (Singh et al., 2016), internal and external resistances, and membrane type (Mohamed et al., 2016a; Qiao et al., 2007; Rabaey et al., 2004). In practical terms, the anode material is the major key to increasing the power performance due to its direct contact with the microorganism and its strong influence on the electron efficiency transfer. The general characteristics of a suitable anode can be summarized as a high surface area, high electrical conductivity, excellent chemical and microbial stability, biocompatibility, and low cost (Logan et al., 2006).

Most of these properties exist in carbon materials; thus, the most widely used anode materials in MFCs are carbon-based, such as carbon plates, fibers, cloth, activated carbon, foam, paper, and graphite felt (Mohamed et al., 2017; Xiao et al., 2012). However, to date, these materials have not shown satisfactory performance. Therefore, several strategies for anode surface modification to enhance the anode properties and increase cell attachment have been introduced. Superficial nitrogen groups for anode surface modification have been widely used, and studies have primarily focused on enhancing microbe attachment and generating energy (Guo et al., 2013; Santoro et al., 2014). Accordingly, doping of the nitrogen groups on the anode surface can be achieved by various methodologies, including ammonia gas treatment (Feng et al., 2010), sulfuric acid treatment (Jin et al., 2012) and nitric acid treatment (Zhu et al., 2011). Additionally, heat treatment of the anode surface has been demonstrated (Karra et al., 2013). The addition of nitrogen groups on the anode surface attracts electroactive microorganisms and decreases the carbon-bonded oxygen content, which interferes with the charge transfer from the bacteria to the anode (Feng et al., 2010; Karra et al., 2013; Li et al., 2014; Wei et al., 2011).

This study introduces different novel and simple procedures for nitrogen doping on surfaces of widely used anode materials: carbon cloth (CC) and carbon paper (CP). Three typical methods have been investigated: (1) hydrothermal treatment using ammonia solution, (2) hydrothermal treatment using a mixture of nitric and sulfuric acids, and (3) thermal treatment using solid urea. The modified anodes have been used in MFCs to treat industrial wastewater and for power generation. Although the proposed methods are notably simple compared to the reported ones, the results showed improved MFC performance for the modified anodes.

2. Materials and methods

2.1. Electrodes and materials

Untreated carbon cloth (CC, 2.5 × 2.5 cm EC-AC- cloth, Electro Chem. Inc., USA) and untreated carbon paper (CP, 2.5 × 2.5 cm EC-TP1-120, Electro Chem. Inc., USA) were used as the anodes with dimensions of 2.5 × 2.5 cm. The cathode was a Pt-loaded carbon paper (0.5 mg/cm^2, EC-20-5, Electro Chem, Inc., USA). Nitric acid (70%, HNO_3; Sigma-Aldrich), Sulfuric acid (98%, H_2SO_4; Samchun chemical), Ammonia solution (30% NH_4OH; Sigma-Aldrich) and Urea (98%; Alfa Aesar) were used for the modification process. In addition, acetone and distilled water were used to clean the anodes.

2.2. Anode modification methods

2.2.1. Ammonia solution treatment (AST)

First, the CC and CP electrodes were cleaned by soaking in pure acetone overnight and were later immersed in 30 ml of the 30% ammonia solution. Later, the mixture of electrodes/ammonia solution was transferred to a Teflon crucible and placed in an autoclave hydrothermal reactor. The reactor was heated to 180 °C for 3 h in a muffle furnace. The autoclave was left to cool inside the furnace; next, the treated electrodes were washed carefully with distilled water before use in the MFC. The treated anodes were named as CC-AST and CP-AST for the CC and CP electrodes, respectively.

2.2.2. Acid heat treatment (AHT)

In this process, the acetone-cleaned anodes were soaked in an aqueous solution of nitric acid/sulfuric acid (weight ratio of 1:1 and solution concentration of 100 mL/L). Moreover, the anodes were treated hydrothermally using the autoclave hydrothermal reactor. The furnace temperature was ramped to 180 °C and held for 3 h; next, the treated anodes were washed to remove any attached chemicals before being used in the MFCs. The treated anodes were named CC-AHT and CP-AHT for the CC and CP electrodes, respectively.

2.2.3. Urea treatment (UT)

This treatment method is based on using urea in the solid state. Typically, the cleaned electrodes were immersed in 20 g of solid urea powder placed in a Teflon crucible and were treated thermally at 180 °C for 3 h. Finally, the electrodes were washed carefully with distilled water before use. The treated anodes were named as CC-UT and CP-UT for the CC and CP electrodes, respectively.

2.3. Microorganism media and industrial wastewater

In this study, industrial wastewater collected from a local food factory in Jeonju, South Korea was utilized as the electrolyte for the MFC. Moreover, no external microorganisms or mediators were applied. Instead, the microorganisms in the wastewater were used to form the bio-anode. The wastewater was first characterized at the Water Environment Research Center in Jeonju, South Korea, and the results are presented in Table S1 (in the supporting information). Additionally, the mixed culture of microorganisms was investigated via an agar cultivation test, and agar dishes were examined under a microscope (U-25ND25 (BXSL) Olympust2, Japan) using 10× magnification (MPLOON10*0.25) as shown in Fig. S1A (in the supporting information) with the number of bacteria counted as shown in Fig. S1B. Fig. S1 confirmed that the utilized food wastewater was rich with a mixed culture of microorganisms, where the microorganisms grew on the agar dish and formed 1.2 × 10^5 colony/ml (Fig. S1B).

2.4. MFC constructions

A single air-cathode MFC with a total volume of 84 cm^3 in which the cathode contacts directly with air was constructed as shown in Fig. S2. The anode was fixed on the stainless steel current collector with an electrode spacing of 4 cm. The pretreated cation exchange membrane was used as a proton exchange membrane (PEM) as previously described (Mohamed et al., 2016b). Moreover, the cathode was sandwiched between the cation exchange membrane and cathode current collector. The current density was calculated based on an anode surface area of 6.25 cm^2.