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Interfacial electron transfer and bioelectrocatalysis of carbonized plant material as effective anode of microbial fuel cell

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ABSTRACT

Effective use of natural materials to fabricate porous carbonaceous structures for anodes of microbial fuel cells (MFCs) has a high potential for substantial cost reduction in MFC. In this study, three kinds of plant materials, i.e. king mushroom, wild mushroom and corn stem, were investigated for fabrication of conductive electrode materials by simple carbonization procedures. Structure–reactivity relationships of these electrodes were systematically studied with electrochemical redox probe ($[Fe(CN)_6]^{3-/4-}$) and biofilm electroactivity. The electrochemical and bioelectrochemical accessibilities of the carbonized electrodes were evaluated by impedance, cyclic voltammetry and chronoamperometry techniques in order to study the electron transfer rate (K_{app}), charge transfer resistances, oxidative current density and bioelectroactive moieties. The results showed that the electron transfer resistance (R_{ct}) was 94 Ω for carbonized corn stem electrode with an electron transfer rate (K_{app}) of 3.44×10^{-2} cm s^{-1} for Fe^{2+}/Fe^{3+} redox probe. Higher bioelectroactivity (9.29×10^{-8} mol cm^{-2}) was found from biofilm on carbonized corn stem ($R_{biofilm}$, 45 Ω) with an electron transfer rate (bacteria-anode) of 63×10^{-5} cm s^{-1}. The maximum bioelectrocatalytic current (i_{max}) of 3.12 mA cm^{-2} was obtained on carbon electrode derived from corn stem. That is 8 times higher than plain graphite electrode. The porous architecture, high electron transfer rate and high electroactive biofilm growth are attributes that qualify natural-material carbon anodes as low-cost alternative for MFC.

1. Introduction

Over the past decade, interests in microbial electrochemistry have increased tremendously. Newly developed microbial electrochemical technologies arising include microbial fuel cells (MFC) for electricity production, microbial electrolysis cells (MEC) for hydrogen and biogas production, bielectrosynthesis cells for biochemical production, and microbial desalination cells for desalination and electricity production. The electron transfer at the bioanode plays a critical role in all of the above microbial electrotechnologies. Therefore, production of efficient microbial bioanodes is of fundamental importance [1]. Particularly for MFC which operates under anaerobic condition, the biofilm at the bioanode oxidizes the substrates and passes electrons through their respirative proteins at the outer membrane to the anode substrate [2,3]. Electrons accumulated at the anode will travel through an external circuit and reach the aerated cathode to complete the circuit. Hence, the production of electricity is strongly influenced by the bacteria-anode interface. In order to maximize the efficiency of power generation, the anode should facilitate the growth of biofilms to achieve high electrochemical performance.

In recent years, there has been great attention dedicated to finding new materials for MFC anodes to increase the cell performance and reduce costs [4,5]. The anode in a MFC should possess the following properties: biocompatibility, chemical stability, low resistance, high surface area, high mechanical strength and low cost. The anode material used in MFC can be classified into traditional carbon anode materials (e.g. graphite rods [6], graphite fiber brushes [7], carbon cloth [8], carbon paper [9], carbon felt [10], reticulated vitreous carbon(RVC) [11], carbon powder and conductive polymer [12], graphene [13], polyaniline [14], polypyrrole [15] and non-carbon anode materials(e.g. titanium [16], nickel [17] and stainless steel [18]. In general, carbon-based materials are more favorable to MFC applications due to better quality in biocompatibility, stability and

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feasibility. However, large-scale carbon-electrode MFC applications tend to have problems with high cost of the electrode materials and electrode fouling [7,19,20]. The cost of most refined carbon electrode materials, ranging from \$50 m^{-2} to over \$1000 m^{-2}, is too high for practical commercialization [4]. Hence, the present research aims to develop new carbon electrodes that are low-cost for large scale applications and have macroporous structures favorable to bacterial colonization for high cell performance.

Previously, it was reported that recycled tire crumb rubber coated with graphite paint produced higher columbic efficiency (25.1%) as an MFC anode, when compared with fine carbon materials [21]. The lightweight tire particles could effectively reduce the clogging effect but the conductivity is low. In order to investigate the effect of the diameter of fiber electrodes used in MFC, a series of fiber electrodes with diameter ranging from 0.1 to 10 μm were tested for the MFC anode [22]. The highest current density of 3.08 mA cm^{-2} was achieved with a fiber diameter of 0.87 μm (99% porosity). It could be explained that the high porosity and accessible three-dimensional surface of the electrode increased the MFC performance. In an economical way, a natural plant kenaf (*Hibiscus cannabinus*; a crop plant) has been carbonized to form macroporous carbon for high-performance MFC anodes [19]. The carbonized kenaf achieved the maximum current density of 3.2 mA cm^{-2}, despite the current density being restricted to the length of the electrode due to mass transport limitation and blocking of the micro-channels on the electrode surface. In comparison with commercial RVC anodes, natural RVC fabricated by direct carbonization of sponge-like natural product (e.g. Pomelo peel) can generate about five times higher current density (4.0 mA cm^{-2}) due to the advantageous macroporous structure [20]. The above findings imply the beneficial effect of the natural pores on the growth of biofilm. Moreover, the natural plant material resource is renewable, low-cost and derived from waste products; and the estimated mass production cost of carbonized material (Supporting information) is below \$20 m^{-2} [19,20,22–35].

Presently, the structure–performance relationship of carbon electrodes derived from natural resources is not yet well understood, such as the effects of specific surface properties on the electron transfer rate between carbon electrode and bacteria, i.e., bio-interface. The heterogeneity of carbon surface could retard or accelerate the electron transfer (ET) process of biofilm.

The present experimental study aimed to evaluate the variation of ET behaviors with redox probes and biofilm activity of natural carbon electrode surfaces. Different natural macroporous carbon MFC electrodes were fabricated from king mushroom, wild mushroom and corn stem. Electrochemical and bioelectrocatalytic studies were conducted systematically.

2. Materials and methods

2.1. Material selection and electrode fabrication

In this study, we chose three different types of vegetable for producing various macroporous structures of natural carbon materials. They are:

a) soft and fleshy king mushroom (*Pleurotuseryngii*) growing in water-rich soil;
b) hard, wild mushroom growing on trees as fascinating fungus; and
c) water and nutrient supplying stems of corn having lingocellulosic fibrous morphology.

These three natural plants had different physical structures (macropores/canal) for transporting nutrients during their life cycle. After carbonization, the naturally arranged porous structures had high potential to offer a favorable environment for MFC bacterial growth.

In the material fabrication of this study, corn stem, king mushroom and wild mushroom samples were first dried at 60 °C in an air oven for 48 hours. The dried samples were subjected to simple carbonization [22] in a N_2-atmosphere tube furnace (Carbolite®, UK) with a heating rate of 5 °C min^{-1} to reach 1000 °C. Annealing followed at 1000 °C (unless specified otherwise) in N_2 atmosphere for 1 hour. After the tube furnace cooled to room temperature, the samples were taken out and sonicated in a solvent mixture (1:1:1) of acetone (Sigma–Aldrich), trichloromethane(Sigma–Aldrich) and milli-Q water to remove loosely held carbon and impurities. The electrical resistivity was then measured by two probe methods. Finally, the working electrodes were prepared by cutting the samples into small pieces (area: 0.5 cm^2, thickness: 0.2 mm) and electrically connecting them with a titanium wire with conductive glue [22]. Four types of working electrodes were used for bio-electrochemical studies and surface characterizations, including (i) Graphite Electrode (GE) for comparison of planar structure, (ii) Carbon Electrode derived from King Mushroom (CEKM), (iii) Carbon Electrode derived from Wild Mushroom (CEWM) and (iv) Carbon Electrode derived from Corn Stem (CECS).

2.2. Material characterizations

The surface morphologies of carbon electrodes, such as samples CEKM, CEWM and CECS, were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S4800) and transmission electron microscopy (TEM, FEI Tecnai G^2 20 Scanning). The graphitic nature of the carbon electrodes was studied using an X-ray diffractometer (XRD, Bruker) equipped with Cu $K\alpha_{12}$ X-ray radiation and a LynxEye detector. The Raman spectra were obtained by using a Raman microscope (Renishaw'sinVia UK) equipped with a He-Ne laser (633 nm, 17 mW).

2.3. Electrochemical analysis

Electrochemical characterizations of as-prepared carbon electrodes were performed by an electrochemical work station (Modulab-Solartron Analytical, USA) with a conventional three-electrode setup. The as-prepared carbon electrode, a Pt-foil and an Ag/AgCl 1 M KCl were used as working, counter and reference electrodes, respectively. Phosphate buffer (pH7) was used as supporting electrolyte in all electrochemical studies unless otherwise specified. Cyclic voltammetry (CV) was performed with a simple redox probe ($[Fe(CN)_6]^{3-/4-}$) containing equimolar (10 mM) amounts of potassium ferrocyanide($K_4[FeCN]_6$, Sigma-Aldrich) and potassium ferricyanide($K_3[FeCN]_6$, Sigma-Aldrich) in phosphate buffer (pH7) to understand the electrochemical kinetic parameters and the electrode activity. Electrochemical impedance spectra (EIS) of carbon electrodes for $[Fe(CN)_6]^{3-/4-}$ redox reaction were obtained in the frequency range from1 to 10 MHz with an AC signal amplitude of 10 mV. The data obtained from EIS were fitted by ZSimpwin 3.10 software (Echem,US) based on the predetermined equivalent circuits. The scan range of the CV tests was between +1.0 V to −1.0 V vs Ag/AgCl and the scan rates were between 5 and 100 mV s^{-1} under diffusion-limited conditions. For Tafel polarization tests, the working electrode was polarized between ±0.25 V with respect to the open circuit voltage at a slow scan rate of 0.5 mV s^{-1}.

2.4. Biofilm enrichment and bioelectrochemical analysis

The carbon electrodes were subjected to formation of an electrochemically-active biofilm. The bioelectroactivity for current generation was also investigated by inserting each carbon