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Modified stainless steel for high performance and stable anode in microbial fuel cells

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ABSTRACT

The surface modification of the stainless steel mesh (SSM) was conducted by acid etching, binder-free carbon black (CB) coating and the low-temperature heat treatment below 400 °C to improve the microbial bioelectrocatalytic activity for use as high-performance anode in microbial fuel cells. The modified SSM, such as SSM/CB-400, could generate a high current density of up to 1.91 mA cm^{-2}, which was nearly three orders of magnitude higher than the untreated SSM electrode (0.0025 mA cm^{-2}). Moreover, it was stable and recovered the equal current density after removal of the formed biofilms. Surface characterization results demonstrate that the performance improvement was attributed to the CB/Fe_3O_4 composite layer formed onto the surface of the SSM, which protected the biofilms from being poisoned by the Cr component in the SSM and ensured a rapid electron transfer from biofilms to the SSM surface. The CB/Fe_3O_4 composite layer showed excellent corrosion-resistant under the oxidizing potential of + 0.2 V (vs. Ag/AgCl). Rising the heating temperature to 500 °C, the SSM-500 and SSM/CB-500 electrodes suffered from corrosion due to the formation of α-Fe_2O_3 crystals.

1. Introduction

Microbial fuel cell (MFC) is a device that use bacteria to oxide organic matters and transfer the chemical energy to electrical power [1]. MFC is able to use waste organic matters as fuels to generate electricity, thus is a promising technology for simultaneous wastewater treatment and energy recovery. Though, a tremendous progresses in the development of MFC and its related technologies has been made in the past few years [2–4], the increase of the performance of MFC is still a major challenge. As one of dominant factors that affect the performance of MFC, the anode has been attracting special attention. The function of anode is to provide the space for bacteria propagation and collect the electrons released by the electroactive bacteria. The microbial bioelectrocatalytic activity of the anode is mainly determined by the numbers of bacteria grown in the anode and the rate of electron transfer between the bacteria and the anode.

Carbon or graphite is one of popularly used anode materials for MFC due to its good conductivity and biocompatibility, excellent microbial adhesion performance and chemical stability. [2,5,6] Various types of carbon materials have been used as anodes in MFCs [5,7], such as bulk or particulate porous carbon, fibrous carbon and powdery carbon materials. However, the bulk carbon material shows comparatively low specific conductivity of $0.77 \sim 1.25 \times 10^5$ S m^{-1}, which is one order of magnitude lower than metal materials, e.g. stainless steel (1×10^6 S m^{-1}). Moreover, bulk carbon or graphite is in low mechanical property and mechanically rigid and is difficult to get into specific shapes.

Stainless steel (SS) materials show a sufficiently high electric conductivity and good corrosion resistance, as well as are comparatively inexpensive and easy to process and connect, thus are well suitable for up-scaling. The direct use of SS as anode material in microbial bioelectrochemical system is so far relatively rare [8], most likely because the Cr component in the SS would inhibit the microbial activity [9,10] and lead to a low microbial bioelectrocatalytic activity. Surface modification of SS electrodes, including flame-oxidization[11], flame-deposition[12], binder and binder-free nanocarbon coating [13–16] were recently taken to produce a more biocompatible electrode surface with enhanced microbial bioelectrocatalytic activity. However, the oxidation and deposition modification of SSs at the high temperature was stable under the negative potential of −0.2 V (vs Ag/AgCl), but they would face the risk of corrosion under the MFC environmental (under positive potential, e.g. +0.2 V vs Ag/AgCl) [17]; the coating of nanocarbon using polymer binder usually resulted in a high internal resistance and would hinder the electron transfer from the

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bacteria to the SS surface[16]; the coating of nanocarbon without polymer binder onto SS would have a low interaction and resulted in unstable current generation[15].

In this paper, the microbial bioelectrocatalysis of stainless steel mesh (SSM) was greatly enhanced by a surface modification process including steps of acid etching, binder-free carbon black (CB) coating and low-temperature heat treatment. The modified SSM electrode could generate a high current density of up to 1.91 mA cm^{-2}, is nearly three orders of magnitude higher than the untreated SSM electrode (0.0025 mA cm^{-2}). Moreover, the modification layer was firm and corrosion-resistant, it still could deliver the equal current density after removing the formed biofilms.

2. Experimental

2.1. Materials

304 stainless steel mesh (SSM) (Hongye Stainless Steel Wire Cloth Co.,Ltd, Hengshui, Hebei, containing about 19% Cr and 9% Ni) with mesh size of 50 and wire diameter of 0.20 mm, and carbon black (CB, VULCAN® XC72) were used as received.

2.2. Electrode preparation

The electrode preparation steps was illustrated in Scheme 1. SSM was washed by acetone to remove the impurity on the surface, then was immerged in 1 M H_2SO_4 solution and etched for different times under room temperature. The resulted SSM electrodes was named as SSM-*x h*. The *x* represent the time for the acid-treatment. Samples of SSM-*0.5h*, SSM-*1h*, SSM-*2h*, SSM-*4h* were prepared, which had different etching ratio (weight loss/weight of SSM before etching).

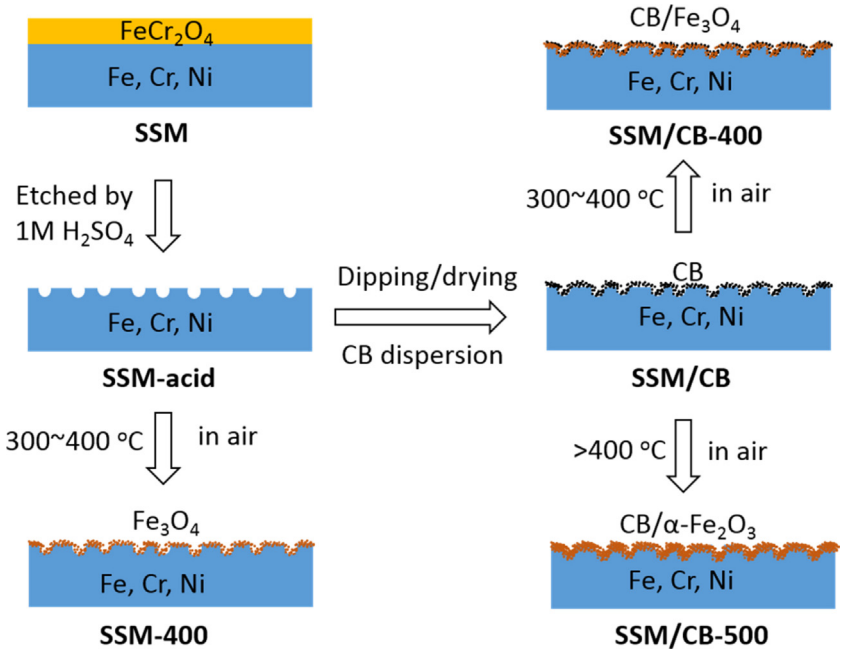
CB was dispersed in ethanol under the assistance of ultrasonic vibration to form a stable dispersion without addition of any other additives. The concentration of the CB dispersion was controlled as 5 g L^{-1}. SSM/CB electrodes were prepared using the acid-etched sample, SSM-*4h*, through a dipping/drying process. SSM-*4h* was dipped into 5 g L^{-1} CB dispersion in ethanol, then taking out and drying at room temperature; after dipping/drying process for three cycles, the SSM/CB composite electrode was obtained. The heat-treatment of the SSM-*4h* and SSM/CB electrodes were conducted by directly heating the electrodes in a furnace under air atmosphere and annealing for about 20 min at the final temperature. Samples of SSM/CB-200, SSM/CB-300, SSM/CB-400 and SSM/CB-500 were prepared by heat-treatment of the SSM/CB at temperature of 200, 300, 400 and 500 °C, respectively. For comparison, the SSM-400 and SSM-500 were also prepared by heat-treatment of the SSM-*4h* at temperature of 400 and 500 °C, respectively.

2.3. Characterization

The morphologies of the SSMs were observed using scanning electron microscope (SEM). The Raman spectra were recorded on a LabRAM Aramis (Horiba Jobin Yvon S.A.S) with a 633 nm wavelength laser. The element analyses were conducted using X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM™).

2.4. Bioelectrochemical tests

The bioelectrochemical experiments were conducted under anoxic conditions and potentiostatic control. Preselected bacterial cultures based on primary electroactive biofilms were used [18]. The bacterial source for the primary biofilm formation was primary wastewater from the local wastewater treatment plants QingShan (Nanchang, China). The electroactive microbial biofilms were grown and studied in half-cell, semi-batch experiments at a potential of +0.2 V vs. Ag/AgCl (sat. KCl, +0.195 V vs. standard hydrogen electrode, Tianjin Aida Electronic Co., Ltd, China) and at temperature of 35 °C. To assure comparability and reproducibility across the biofilm electrodes, usually working electrodes were prepared and tested simultaneously in one 500 mL electrochemical cell. Beside the working electrodes, the electrochemical cell contained one Ag/AgCl reference electrode and graphite plate (GP) counter electrode. Potentiostat CHI1040B (Shanghai Chenhua Instrument Co., Ltd, China) equipped with six working electrode channels allowing to address individual working electrodes was employed for the electrochemical measurement. To evaluate the



Scheme 1. Schematic diagram illustrates the surface modification of the stainless steel mesh and surface components.