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Polypyrrole/sargassum activated carbon modified stainless-steel sponge as high-performance and low-cost bioanode for microbial fuel cells

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HIGHLIGHTS

- Stainless-steel sponge is used as a 3D macroporous MFC anode skeleton.
- Sargassum derived activated carbon is used as a low-cost electrode dopant.
- Ppy/SAC layer can greatly improve biocompatibility of the SS sponge electrode.
- MFC equipped with a Ppy/SAC/SS anode shows high electricity production performance.

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ABSTRACT

Anode materials, as the core component of microbial fuel cells (MFCs), have huge impacts on power generation performance and overall cost. Stainless-steel sponge (SS) can be a promising material for MFC anodes, due to its open continuous three-dimensional structure, high conductivity and low cost. However, poor biocompatibility limits its application. In this paper, a polypyrrole/sargassum activated carbon modified SS anode (Ppy/SAC/SS) is developed by electrochemical polymerization of pyrrole on the SS with the SAC as a dopant. The maximum power density achieved with the Ppy/SAC/SS anode is 45.2 W/m^3, which is increased by 2 orders of magnitude and 2.9 times compared with an unmodified SS anode and a solely Ppy modified SS anode (Ppy/SS), respectively. In addition, the Ppy/SAC layer effectively eliminates electrochemical corrosion of the SS substrate. Electrochemical impedance spectroscopy reveals that Ppy/SAC modification decreases electron transfer resistance between the bacteria and the electrode. Furthermore, *in vivo* fluorescence imaging indicates that a more uniform biofilm is formed on the Ppy/SAC/SS compared to the unmodified SS and Ppy/SS. Due to the low cost of the materials, easy fabrication process and relatively high performance, our developed Ppy/SAC/SS can be a cost efficient anode material for MFCs in practical applications.

1. Introduction

Microbial fuel cells (MFCs) are novel bioelectrochemical devices that can catalyze certain chemical reactions with electrochemically active bacteria (EAB) to achieve the conversion of the chemical energy into electrical energy [1]. MFCs are considered as a promising technology in wastewater treatment, remote power sources, biosensors and desalination [2–4]. As for big pilot practical applications of MFCs, anode material has huge impacts both on power generation performance and overall cost [5–7]. Therefore, many studies on electrode materials and structures have been reported [8–12]. Current articles have suggested that materials with the characteristics of high conductivity, good biocompatibility, high specific surface area, remarkable mechanical strength, low cost and chemical stability are ideal for MFC anodes [9,10,13,14].

Although carbon materials, which are biocompatible and chemically stable, are the most commonly used anode materials, low conductivity and poor mechanical strength are two main drawbacks [10,15–19]. Compared to carbon materials, stainless-steel, with high conductivity, good mechanical strength and low price, is considered as a more promising electrode material for large scale MFCs [8]. However, the lack of 3D structure and poor biocompatibility limit the performance of most stainless-steel electrodes [18–21]. In order to overcome these limitations, many researchers have developed stainless-steel brushes, stainless-steel fiber felts and even stainless-steel foam electrodes with open 3D structures to increase the specific surface area

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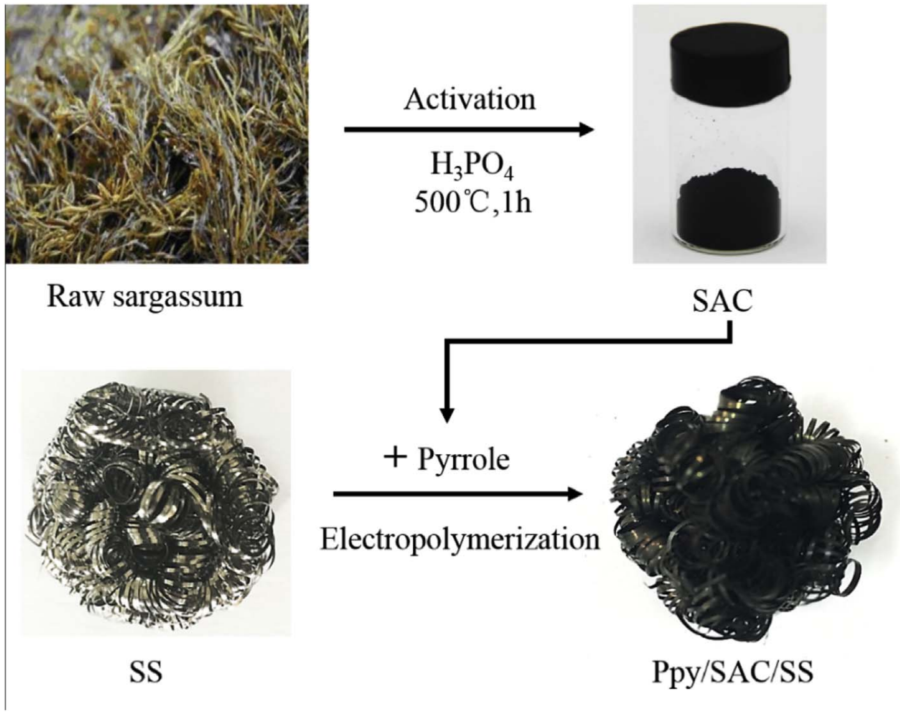

Fig. 1. Schematic of fabricating the Ppy/SAC/SS.

[9,10,22]. These types of electrodes can greatly improve the MFC current production performance. However, their preparation processes are usually complex and thus the cost is much higher than ordinary stainless-steel electrodes, even more expensive than some carbon materials. For example, the cost of a stainless-steel foam with a thickness of 6.35 mm is 2.5 times and 26 times higher than that of a carbon foam and a carbon felt with the same size, respectively [10]. Therefore, developing an easy fabricated and low-cost 3D stainless-steel electrode has a great significance. A stainless-steel sponge (SS) is a common kitchen cleaning appliance, made of continuous and intertwined stainless-steel filament, which is cheap, resistant to corrosion and with a continuous open 3D structure. Thus, the SS can be an ideal anode material for MFCs.

Besides the structure, good biocompatibility is another important consideration for MFC anodes. Studies have shown that the biofilm formation rate on the surface of the SS is much lower than that on carbon material [18]. Consequently, improving SS biocompatibility through surface modification is necessary. Considering the excellent biocompatibility of carbon materials, modifying the SS surfaces with carbon materials (such as activated carbon, carbon nanotubes and graphene, etc.) is an effective method [23–28]. Among a diversity of carbon materials, multi-walled carbon nanotubes (CNTs) have exhibited very promising properties as a catalyst in various areas due to their unique electrochemical and structural properties [29]. Compared to some traditional materials, e.g., carbon black, CNTs show better performance in many aspects and thus CNTs were widely used in electrode modification to increase MFC performance [30–32]. But using expensive carbon nanomaterials will increase the overall electrode cost significantly. As alternatives, in recent years, low cost biomass derived carbon materials (carbonized loofah, grapefruit, linen and cardboard) have been used as anode materials in MFCs [33–36]. Inspired by these studies, sargassum derived activated carbon (SAC) was used to modify SS in this work. Sargassum is a kind of marine algae, which is cheap, easy to breed and collect and does not take up land and fresh water resources. SAC has already been developed as a low-cost De-NOx catalyst [37]. More importantly, SAC has relatively higher nitrogen content (2.52%) compared with activated carbon derived from other marine algae [37]. Higher nitrogen content makes SAC possible to have good biocompatibility after carbonization [38]. Thereby, SAC is a suitable and low cost electrode dopant. Polypyrrole (Ppy) is a type of widely used conductive polymers due to its relatively easy processability, high electrical conductivity and environmental stability [39–41]. Furthermore, Ppy is inert in most solutions and has good biocompatibility [42]. Therefore, using the SAC and Ppy to modify SS electrodes will provide new ideas for preparing high performance and low-cost bioelectrodes.

This work developed a novel MFC anode by employing Ppy and the SAC to modify SS. The fabricated anode possesses not only excellent conductivity, mechanical strength and macro 3D structure, but also good biocompatibility and low price. In a two-chamber stack MFC, the fabricated Ppy/SAC/SS electrode exhibited great electricity production performance. Electrochemical impedance spectroscopy (EIS) together with polarization curves tests were conducted to reveal the improvement mechanism. This study will offer a new idea for developing high-performance and low cost MFC anodes.

2. Experiments

2.1. Materials

Pyrrole, hydrochloric acid, phosphoric acid and multi-walled CNTs (MWCNTs, 5–15 nm in inner diameter, 50 nm in outer diameter and 0.5–2 μm in length) used in this paper were purchased from Aladdin Biochemical Technology Co., Ltd. The SS was made of 304 stainless-steel (Scotch-Brite™, 3M Company). The pretreatment procedures of the sargassum (Qingdao Haijie Aquatic Technology Co., Ltd.) are: 1) the raw sargassum was washed with ultrapure water to remove impurities and salts, and then dried at 100 °C for 24 h to constant weight; 2) After drying, the sargassum samples were crushed and sieved to get a uniform mesh size of 40–60 [37].

2.2. Preparation of the SAC and modified electrodes

The activation procedures of the SAC preparation are: 1) the