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Pyrolytic carbon-coated stainless steel felt as a high-performance anode for bioelectrochemical systems

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HIGHLIGHTS

- Pyrolytic carbon coating generates a thin carbon layer on SS felt surface.
- The carbon layer dramatically enhances anodic biofilm formation on SS felt surface.
- High current density (3.65 mA/cm^2) was achieved on carbon-coated SS felt anodes.
- Carbon-SS felt outcompetes carbon-based materials as scalable anode material.

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ABSTRACT

Scale up of bioelectrochemical systems (BESs) requires highly conductive, biocompatible and stable electrodes. Here we present pyrolytic carbon-coated stainless steel felt (C-SS felt) as a high-performance and scalable anode. The electrode is created by generating a carbon layer on stainless steel felt (SS felt) via a multi-step deposition process involving α-D-glucose impregnation, caramelization, and pyrolysis. Physicochemical characterizations of the surface elucidate that a thin (20 ± 5 μm) and homogenous layer of polycrystalline graphitic carbon was obtained on SS felt surface after modification. The carbon coating significantly increases the biocompatibility, enabling robust electroactive biofilm formation. The C-SS felt electrodes reach current densities (j_{max}) of 3.65 ± 0.14 mA/cm^2 within 7 days of operation, which is 11 times higher than plain SS felt electrodes (0.30 ± 0.04 mA/cm^2). The excellent biocompatibility, high specific surface area, high conductivity, good mechanical strength, and low cost make C-SS felt a promising electrode for BESs.

1. Introduction

Microbial bioelectrochemical systems (BESs) are bioreactors that use electrochemically active microorganisms to catalyze oxidation and/or reduction reactions at electrodes (Rabaey, 2010). The potential applications of this technology include wastewater treatment, power production, hydrogen production, desalination, biosensors, and production of valuable chemicals (Logan and Rabaey, 2012; Rabaey and Rozendal, 2010). Thus far, the relatively low current density and high capital cost are the main bottlenecks for its practical application (Rozendal et al., 2008). Electrode materials have a strong impact on performance and cost of BESs, therefore finding cheap but still scalable and effective electrode materials is of key importance (Guo et al., 2015a; Zhou et al., 2011).

Carbon-based materials have been extensively utilized as electrodes in BESs due to their good biocompatibility and chemical stability. Their relative low conductivity, high cost, and weak mechanical strength restrain their usage at large scales (Guo et al., 2015a). Metallic electrodes such as gold, platinum, titanium, silver, stainless steel (SS), nickel, copper, cobalt have also been tested in BESs (Baudler et al., 2015; Wei et al., 2011). Among them, SS appeared to be the most promising material because of its low cost, good corrosion resistance, excellent electrical conductivity, and great scale-up potential. However, the passive layer on SS surface makes it less biocompatible and also hinders the electron transfer between electrode and bacteria. Consequently, the current density achieved on bare SS electrodes are normally lower than carbonaceous electrodes (Ferrari and Robertson, 2000; Zheng et al., 2015) unless the system is operated under marine conditions (Pocaznoi et al., 2012).

To improve the current density of SS electrodes, several surface modifications have been carried out and excellent results were

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achieved. Oxidization of SS felt anode by flame or high temperature dramatically enhanced the biofilm formation on SS felt and thereby a high current density (1.5 mA/cm^2) was achieved (Guo et al., 2014a, 2015b). However, oxidised SS has the risk of corrosion if the electrode potential is not well-controlled. Coating SS electrode surface with carbon materials is another efficient strategy to improve its performance in BESs. The addition of carbon nanostructures to a SS mesh anode via flame deposition resulted in a 60-fold increase in the power density (Lamp et al., 2011). Binding SS felt anode with activated carbon, carbon nanotubes (CNTs), and graphene using nafion increased the current density from 0.004 to 0.147, 0.376, and 0.61 mA/cm^2, respectively (Hou et al., 2014). Recently, a carbon black/SS mesh composite electrode prepared by absorbing a thin carbon black layer onto SS mesh via a binder-free dipping/drying procedure delivered a similar current density (1.53 mA/cm^2) (Zheng et al., 2015). However, all of these carbon coating methods are hardly applicable to large scale SS electrodes for BESs. Coating/binding carbon directly on the SS surface without removing the passive layer will leave a high interfacial contact resistance between the carbon layer and bulk SS substrate. Carbon nanoparticles such as CNTs and graphene are still too expensive to be used for BES electrode surface modification. In situ synthesis of carbon nanoparticle by flame seems to be attractive, but it is only applicable for small scale electrodes. Carbon black coated on SS surface via the binder-free dipping/drying procedure have the chance to be washed out from the surface. Therefore, a more cost-effective carbon coating method is still required for SS electrode surface modification.

Pyrolytic carbon coating is an efficient, cheap, and scalable method to introduce a thin carbon layer on the substrate surface (Hidalgo et al., 2015, 2014). As pyrolysis of hydrocarbon precursors requires high temperature, this high temperature treatment can break down the passive layer of SS (Fukutsuka et al., 2007; Guo et al., 2014a) delivering a well-connected, low contact resistance, and biocompatible coating. The aim of this study was thus to modify SS felt electrode with pyrolytic carbon coating and investigate its performance as an anode in BESs.

2. Materials and methods

2.1. Electrode preparation and modification

316L SS felt with a thickness of 1 mm and a filter rating of 20 μm was purchased from Lier Filter Ltd (China). The felt was cut into 1 cm × 1 cm (projected surface area 1 cm^2, volume 0.1 cm^3) pieces as electrodes. α-D-glucose was used to prepare a conductive carbon layer on SS felt. The carbon layer was deposited on the SS felt surface following a procedure described before (Hidalgo et al., 2015, 2014) and flowchart of the procedure can be seen in Fig. S1. Briefly, the SS felts were firstly cleaned in an ultrasonic bath for 10 min at 60 Hz using ethanol to remove pollutants from the surface and then dried in air at room temperature. Subsequently, the felts were immersed in glucose solution (500 g/L) in water under gently orbital shaking conditions for 24 h. Then, the felts were separated by filtration from the glucose solution, and caramelized at 185 °C under vacuum for 24 h. After that, the caramelized material was pyrolyzed at 800 °C under nitrogen flux (500 mL/min) in a horizontal tube furnace for 2 h (heating rate of 5 °C/min), and finally let them to cool down overnight.

2.2. Electrode surface characterization

The morphology of the SS felt before and after carbon layer deposition were investigated by means of a Field Emission Scanning Electron Microscope (FESEM, ZEISS Dual Beam Auriga) equipped with Energy Dispersive Spectroscopy (EDS, Inca XSight; Oxford Instrument). Raman spectra of both SS felt and C-SS felt electrodes were acquired using a standard Renishaw InVia Raman microscope with laser excitation wavelength at 785 nm and laser spot size of 20 μm. The resistivity (Ω·cm) of both felts was measured by Femto Amperometer (Agilent B2912A) in four-point probe configuration. The mechanical characterization under uniaxial forces was carried out for both SS felt and C-SS felt electrodes using a standard mechanical testing machine (MTS Qtest 10) equipped with a load cell (500 N full scale) as reported in details (Canavese et al., 2012). The tensile strength was steadily increasing and applied to the sample until the material ruptured.

2.3. BES setup and operation

Both the SS felt and C-SS felt electrodes (1 cm^2) were tested as microbial anode materials in a multi-electrode BES which has been previously described (Guo et al., 2014a) (Fig. S2). This two-compartment reactor setup allowed us to simultaneously test several working electrodes (WE, SS felt anodes) with one counter electrode (CE, SS mesh cathode) and one reference electrode (RE, Ag/AgCl 3 M KCl, +0.20 V vs. SHE at 28 °C). In this study, two SS felt electrodes (as controls) and two C-SS felt electrodes were tested in the same reactor. A CHI 1000C Multi-Potentiostat (CH Instruments, Austin, TX, USA) was connected to all electrodes to conduct all electrochemical experiments.

The anodic and cathodic chambers were filled with 650 mL and 100 mL of modified M9 medium (Guo et al., 2013), respectively. This medium contains 2 g/L (24 mM) sodium acetate which was used as the electron donor. The anolyte was sparged with nitrogen gas for 30 min before inoculation of 50 mL of fresh anodic effluent from an existing acetate-fed BES. The anolyte was continuously mixed by a magnetic stirrer at a speed of 350 rpm. Each of the felt electrodes were poised at −0.2 V vs. Ag/AgCl and the current data was recorded by the potentiostat. The reactor was run in fed-batch mode and all the experiments were carried out in a 28 °C temperature-controlled room.

2.4. Biofilm characterization

At the end of current production experiments, the electrodes were taken out of the reactor and initially observed directly by a stereomicroscope (Leica S8APO, Belgium). Subsequently, viability staining was performed (Guo et al., 2015b) and the stained biofilms were visualized by a confocal laser scanning microscope (CLSM, Nikon C1, The Netherlands). Fiji software was used to process the CLSM images.

3. Results and discussion

3.1. Electrode surface modification and characterization

Stereomicroscope images show the 3D, fibrous, and porous structure of the SS felt and C-SS felt (Fig. S3). Pristine SS felt consisted of fibers with a random organization and smooth surface, characterized by the presence of spots. After pyrolysis, the new composite material (C-SS felt) leads to a more smooth surface due to the deposition of the conductive carbon layer on the SS felt surface. The thickness of the carbon layer in the C-SS felt measured by FESEM was about 20 ± 5 μm and showed a high homogeneity in coating the SS fibers. Moreover, after pyrolysis some holes of the SS felt were blocked with pyrolytic carbon. Thus, pyrolytic carbon coating reduces the porosity of SS felt. EDS results indicated that SS felt was mainly composed of (at.%): Fe (60.9), Cr (18.8), Ni