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Heat-treated stainless steel felt as scalable anode material for bioelectrochemical systems

Kun Guo [a], Alexander H. Soeriyadi [b], Huajun Feng [a,c], Antonin Prévoteau [a], Sunil A. Patil [a], J. Justin Gooding [b], Korneel Rabaey [a,*]

[a] Laboratory of Microbial Ecology and Technology, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium
[b] School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia
[c] School of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310012, China

HIGHLIGHTS

- Heat treatment generates an iron oxide layer on stainless steel (SS) felt surface.
- The iron oxide layer enhances the anodic biofilm formation on SS felt surface.
- High current density (1.5 mA/cm^2) were achieved on heat-treated SS felt electrodes.
- Heat-treated SS felt outcompetes carbon-based materials as scalable anode material.

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ABSTRACT

This work reports a simple and scalable method to convert stainless steel (SS) felt into an effective anode for bioelectrochemical systems (BESs) by means of heat treatment. X-ray photoelectron spectroscopy and cyclic voltammetry elucidated that the heat treatment generated an iron oxide rich layer on the SS felt surface. The iron oxide layer dramatically enhanced the electroactive biofilm formation on SS felt surface in BESs. Consequently, the sustained current densities achieved on the treated electrodes (1 cm^2) were around 1.5 ± 0.13 mA/cm^2, which was seven times higher than the untreated electrodes (0.22 ± 0.04 mA/cm^2). To test the scalability of this material, the heat-treated SS felt was scaled up to 150 cm^2 and similar current density (1.5 mA/cm^2) was achieved on the larger electrode. The low cost, straightforwardness of the treatment, high conductivity and high bioelectrocatalytic performance make heat-treated SS felt a scalable anodic material for BESs.

1. Introduction

Bioelectrochemical systems (BESs) use microbes as catalysts to drive oxidation and/or reduction reactions at electrode (Rabaey et al., 2007). The potential applications of BESs have been extended from wastewater treatment and electricity generation to the synthesis of valuable chemicals (Logan and Rabaey, 2012; Rabaey and Rozendal, 2010). However, the real-world or practical applications of the technology are still held back by high capital costs and low current densities achieved, especially once the BESs are scaled up (Logan, 2010; Rozendal et al., 2008). In a BES, electrodes determine the price and the performance to a large extent. Therefore, finding and designing cheap, stable and highly performing electrode materials for BESs draws increasing interest and attention (Guo et al., 2015).

Carbon-based materials such as carbon felt, carbon mesh, and carbon cloth have been extensively used as electrodes in BESs, but unfortunately scale-up of these electrodes is normally limited by their low conductivity and high capital cost (Guo et al., 2015; Wei et al., 2011). Due to its high conductivity, relatively lower cost, high specific surface area, and great scale-up potential, SS mesh/felts have been proposed as alternative electrode material for BESs. However, their poor biocompatibility and relative low current density restricts their direct use as anode in BESs (Guo et al., 2015). It is reported that coating the SS surface with carbon materials (e.g. activated carbon, carbon nanotubes, graphene, carbon nanoparticles, and carbon black) could greatly enhance the biocompatibility and therefore the current production of this material as anode (Hou et al., 2014, 2015; Lamp et al., 2011; Zheng et al., 2015). It has also been reported that flame treatment

* Corresponding author. Tel.: +32 (0) 9 264 59 76; fax: +32 (0) 9 264 62 48.
E-mail address: korneel.rabaey@ugent.be (K. Rabaey).

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using a natural gas flame can generate iron oxides on SS felt surface leading to a dramatic improvement in its performance as bioanode (Guo et al., 2014a; Ledezma et al., 2015). However, these material treatment methods are hardly applicable to large scale SS felts as they are either too expensive or too complex e.g. to uniformly modify the whole electrode surface.

It has been demonstrated that an iron oxide layer could instead be generated on SS surface via oxidation of SS at high temperature in a furnace (Li et al., 2005; Vesel et al., 2008). Compared to flame treatment, heat treatment using a muffle furnace is more controllable in terms of temperature and it is compatible with large size SS felt electrode with no time variation for different sized electrodes. Therefore, the aim of this study was to investigate whether heat-treated SS felt is a scalable anodic material for BESs.

2. 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 LierFilter Ltd. (China). The felt was cut into 1 cm × 1 cm (projected surface area 1 cm^2) and 7.5 cm × 20 cm (projected surface area 150 cm^2) pieces as electrodes. The SS felt electrodes were treated by the following procedure: (1) preheating the muffle furnace to 600 °C; (2) placing SS felts in preheated furnace for 5 min; and (3) taking SS felts out and cooling them down to ambient temperature under air.

2.2. Electrode surface characterization

The surface topography was characterized by stereo microscopy (Leica S8APO, Belgium) and scanning electron microscopy (RAITH150 Two, USA). The surface chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS) performed as described in Guo et al. (2013a). The abiotic electrocatalytic response of these electrodes was studied by cyclic voltammetry (CV) in the anaerobic and pH 7 anolyte of the BES reactor mentioned below.

2.3. BES setup and operation

Both the untreated and treated small (1 cm^2) SS felt electrodes were tested as microbial anode in a high-throughput BES reactor as previously described (Guo et al., 2014a). This two-compartment reactor enabled to simultaneously test several working electrodes (SS felt anodes) with one counter electrode (SS mesh cathode) and one reference electrode (Ag/AgCl 3 M KCl, +0.20 V vs. SHE at 28 °C). In this study, two treated and two untreated SS felts (as controls) were tested in the same reactor. All electrodes were connected to a CHI 1000C Multi-Potentiostat (CH Instruments, Austin, TX, USA) to conduct all electrochemical experiments.

The anodic chamber was filled with 650 mL of modified M9 medium (Guo et al., 2013b) at pH 7.0, with 2 g/L (24 mM) sodium acetate as the electron donor. The cathodic chamber was filled up with 100 mL of modified M9 medium. The anolyte was sparged with nitrogen gas for 30 min to remove dissolved oxygen. CVs were recorded on the electrodes prior to inoculation with 50 mL of fresh anodic effluent from an existing acetate-fed BES. Chronoamperometry (CA) was recorded for each electrode at −0.2 V vs. Ag/AgCl. A magnetic stirrer was used to mix the anolyte continuously at a speed of 350 rpm. Experiments were conducted at 28 °C in a temperature-controlled room. The reactor was run in a fed-batch mode; at the end of each batch 600 mL of the total 700 mL anolyte was replaced with fresh modified M9 medium with 2 g/L sodium acetate.

The large (150 cm^2) SS felt electrode was tested in the same reactor and experimental conditions but with a VSP Potentiostat (Biologic, France). The reactor was firstly operated in a batch mode to allow electroactive biofilm formation on the SS felt anode and then switched to a continuous feed mode with a hydraulic retention time (HRT) of 1.03 d and sodium acetate loading rate of 2.88 g/d (i.e. 0.72 L of modified M9 medium with 4 g/L sodium acetate per day). The level of modified M9 medium was adjusted in the cathodic chamber occasionally to compensate water electrolysis.

2.4. Biofilm characterization

At the end of CA experiment, CVs were recorded at 1 mV/s to investigate the electrochemical activity of the electroactive biofilms under acetate turnover conditions. After completion of electrochemical experiments, half of the electrodes were observed directly by a stereomicroscope (Leica S8APO, Belgium), and the other half sections were subjected to Live/Dead staining (Guo et al., 2014a). The stained biofilms were visualized and *z*-stacks were captured using a confocal laser scanning microscope (CLSM, Nikon C1, The Netherlands). CLSM image data were processed by Fiji software.

3. Results and discussion

3.1. Electrode surface modification and characterization

Stereomicroscope images provided a macro-scale view of the materials, which clearly show the 3D, fibrous and porous structure of the SS felts (Fig. S1a and b in Supplementary Information). Heat treatment did not impact the 3D structure of the electrodes, but changed the surface color. The untreated SS felt surfaces appeared silver colored and were shiny, while treated SS felts became blue and lost their metallic luster. The SS surface contains a chromium-rich oxide film (~5 nm thick) that prevents it from corrosion (Sudesh et al., 2006). Heat treatment changes the chemical composition and thickness of the passive film, and the blue color of the treated surface is due to the interference of light at the new passive film (Somervuori et al., 2004; Tomislav et al., 2013). The SEM images of single SS fibers reveal a change in surface topography after the heat treatment (Fig. S1c and d in Supplementary Information). The untreated SS felt surface was mostly smooth, while the treated SS electrodes were homogeneously covered with nanoparticles of diameters ranging from 100 to 200 nm. These observations suggest that high temperature treatment modified the original passive layer on SS felt surface and generated new metal oxide nanoparticles on the SS felt surface.

XPS was conducted to characterize the surface chemical composition (Fig. 1a and b). The heat treatment increased the surface iron and oxygen content from 9.03% and 48.56% to 14.54% and 67.11%, respectively, while the carbon and chromium content decreased from 38.74% and 1.72% to 15.90% and 0.25%, respectively. Further high-resolution narrow scans of the iron and oxygen, and peak fitting (Fig. S2 in Supplementary Information) indicate that: (1) 4.54% of the iron in the untreated surface could be assigned to Fe(0), while Fe(0) only accounted for 1.12% of the total iron in the treated samples; (2) more oxygen in the oxidized samples were attributed to the metal oxides (62.34% compared to 54.32%). The decrease of the carbon content can be attributed to the burn off the adventitious organic matter adsorbed on the SS felt surface, and the considerable increase in the iron and oxygen contents is due to the generation of iron oxide on the SS surface. These results demonstrated that the new passive layer generated by heat treatment