Energy 99 (2016) 193–201

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Surface modification of commercial carbon felt used as anode for Microbial Fuel Cells

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ARTICLE INFO

Article history:
Received 28 February 2015
Received in revised form
16 December 2015
Accepted 16 January 2016
Available online 12 February 2016

Keywords:
Nitric acid activation
Polyaniline deposition
Biological fuel cell
Activation loss evaluation

ABSTRACT

Commercial carbon felt is frequently used as anodic material in MFCs (Microbial Fuel Cells). In this work, it is modified through nitric acid activation and polyaniline deposition with the aim of improving power density. The modified anodic materials are characterized from both morphological and chemical point of views by FESEM (Field Emission Scanning Electron Microscope), EDS (Energy Dispersive Spectroscopy), FT-IR (Fourier Transform Infrared Spectroscopy), resistivity measurements and impedance spectroscopy. In addition, their performances are evaluated by comparing them with commercial carbon felt as anode material in a two-compartment laboratory MFC prototype using *Saccaromyces cerevisiae* as active microorganism in the anodic chamber. The electrochemical measurements are performed by means of LSV (Linear Sweep Voltammetry) and CI (Current Interrupt) techniques. The power density of the HNO_3-treated and the polyaniline-covered carbon felts results 2.5 and 2.9 fold higher than commercial carbon felt, respectively. The increase of the power density obtained by both surface treatments seems to be related with a strong reduction of resistivity of the anodic material.

1. Introduction

MFCs (Microbial Fuel Cells) are bio-electrochemical systems that directly convert chemical energy of organic compounds into electricity via microbial metabolism. In the anode chamber of MFCs, active microorganisms adhere on the surface of electrode, generate electrons by substrate oxidation, and transfer them to anode material. Electron transfer phenomena involve two main different mechanisms: direct electron transfer, via a physical contact of the bacterial cell membrane with the material and mediated electron transfer, via exogenous mediators such as methylene blue (artificial) or natural redox mediator produced by the microorganism itself [1]. The ability to generate electricity using bacteria in MFC inoculated with domestic wastewater, river and marine sediments [2,3], agro-food wastewaters [4–7] and fed with a variety of substrates including glucose, acetate, lactate, and proteins, make MFCs a promising technology for wastewater treatment and energy generation [4,8–13]. Even with the remarkable improvements in power density obtained up-to date, the large-scale applications of MFCs have yet to be implemented due to low energy generation and high costs [14,15]. In order to make MFCs a suitable energy production process, the power density should be significantly increased; in this respect, the electron transfer from bacteria to the anode seems to be one of the limiting steps in the energy generation in MFCs [16,17]. An ideal anode material should promote bacterial attachment and facilitate electron transfer. For this reason, in order to promote a high bio-catalytic activity, some specific features of electrode materials are required such as high surface roughness and good biocompatibility in order to have an efficient electron transfer between bacteria and electrode surface [14]. Conventional carbon materials such as carbon brush, carbon felt, graphite granules, carbon mesh, reticulated vitrified carbon and carbon paper, were widely used as anode materials thanks to their good conductivity, stability, biocompatibility and low cost [18]. Among them, carbon felt was frequently used as electrode in MFCs because it offers a suitable support for bacteria growth, high mechanical strength and a flat-plate surface, which allows the reduction of the distance between the two electrodes, thus

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http://dx.doi.org/10.1016/j.energy.2016.01.039
0360-5442/

improving the performance of the MFCs [9], however, the limited surface area of this material seems to restrict biofilm formation and power generation [19,20]. In order to improve bacterial adhesion and electron transfer, electrode surface modification and/or activation have become a new topic of interest in the research field of MFCs. To address these issues, several strategies were developed on carbon-based materials to improve the performances of MFC anode, such as metal and non-metal materials modification [21], conductive polymers deposition [22], carbon nanotubes coating [23], ammonium treatment [24] and self-made metal-graphite composite [5].

Recently, incorporation of nitrogen groups in carbon-based materials was studied as anode-modification for MFC, which was reported to be beneficial in facilitating the electron transfer from the microorganisms to the electrode. The results reported in literature evidence that high temperature treatments in presence of air or ammonia gas on carbon mesh, can produce an increase on power density of 14% and 25%, respectively than untreated commercial carbon mesh, likely due to an increase in the ratio between nitrogen and carbon (N/C) at the surface of the material [25]. Heating carbon cloth surfaces at high temperatures with ammonia gas (700 °C for 1 h) showed an increase in power density of 20% compared to untreated carbon cloth and a reduction of the start-up time of the MFCs, likely due to an increase of the amine groups on the surface of the carbon cloth [24]. Power density of 28.4 mW m^{-2} was obtained using graphite felt after HNO_3 treatment, in a single chamber MFC configuration with brewery wastewater diluted with sewage feeding [26]. Carbon cloth anodes treated by concentrated nitric acid and high temperature resulted in improved power generation around 1.4 and 2 folds higher, respectively than the untreated carbon cloth [27].

Conductive polymer materials such as polyaniline (PANI), polypyrrole (PPy) and composite materials based on them, in combination with other carbon-based materials, were studied with the purpose of improving MFC performances [22,28–30]. PANI can be produced by simple processes, it has good electrical conductivity, high biochemical compatibility and it is stable in the MFC working conditions, and thus it has great potential application in the field. In previous works reported in literature, PANI was obtained by direct polymerization of the aniline in aqueous solution and then used as surface modifier of the electrode materials in the MFCs [22,29]. Results obtained in a two-chamber MFC using a microbial community of *Clostridiaceae* and two conductive polymers, PANI and polyaniline-co-o-aminophenol (PAOA) to modify carbon felt anode, reached a maximum power density of 27.4 mW m^{-2} and 23.8 mW m^{-2}, respectively. The comparison with unmodified carbon felt, shows an increase of 35% and 18%, respectively [22]. In addition, power density of 26.5 mW m^{-2} was achieved by PANI deposition on graphite felt as support in an MFC operated in batch mode, with brewery wastewater diluted with sewage [26]. Besides the interesting potentialities of PANI, there are some drawbacks related to its preparation methods. In fact, these methods included the precipitation of already formed PANI on the carbon materials without any specific linking procedure and with the use of a mutagen substance such as aniline. In addition the selected doping agent was hydrochloridic acid and thus the PANI at the operational conditions inside the MFC was in the basic electrically insulating form [31].

In this paper, differently than existing literature, a novel strategy is proposed to modify the surface of carbon felt either by nitrogen groups incorporation on the surface or by polymer deposition, in order to increase the electrochemical performances of C-FELT (commercial carbon felt) as anode in MFCs. The new strategies include: HNO_3 activation at low temperature (C–HNO_3) and in situ deposition of PANI (C-PANI) on commercial carbon felt. A new chemically safe synthesis procedure able to reach an in-situ deposition of PANI as surface modifier has been used. It consider the use of aniline dimer, which is a non toxic/mutagenic compound and the polystyrensulfonate (PSS) polymer as emulsioning/doping agent which provides the necessary conditions for the use of PANI.

The surface properties of the C-FELT, C–HNO_3 and C-PANI were analysed and characterized by several methods: FESEM (Field Emission Scanning Electron Microscope), EDS (Energy Dispersive Spectroscopy), FT-IR (Fourier Transformed Infrared Spectra), resistivity measurements and impedance spectroscopy. The electrochemical performances of the anode materials were evaluated in a dual-chamber MFC using *Saccaromyces cerevisiae* as active microorganism.

2. Materials and methods

2.1. Materials

Commercial carbon felt (C-FELT) (Soft felt SIGRATHERM GFA5, SGL Carbon, Germany) and carbon paper (Carolina, USA) were used as electrode materials for anode and cathode chambers, respectively. Nitric acid (HNO_3, 70%), N-phenyl-1,4-phenylendiamine (DANI, 98%), poly (sodium 4-styrenesulfonate) (PSS), ammonium persulfate (APS, 98%), chloridric acid (HCl, 37%) and methanol (CH_4O, 99.9%) were used to perform nitric acid activation and polyaniline deposition on C-FELT. Baker's dried yeast, i.e. commercial *Saccharomyces cerevisiae* was used as active microorganism. α-D-glucose (96%), methylene blue, potassium ferricyanide (≥99%), sodium phosphate dibasic dihydrate (≥98%) and sodium phosphate monobasic monohydrate (≥98%) were used to conduct electrochemical experiments in the MFC. All reagents used were purchased from Sigma Aldrich.

2.2. Anode material preparation

2.2.1. Activation of commercial carbon felt by nitric acid

Carbon felt was cleaned in acetone for 10 min to remove organic residues on the surface and then dried in air at room temperature. Subsequently, it was dipped in 500 mL of HNO_3 (5% v/v) and maintained under agitation for 10 h at 80 °C. After the draining of the acid solution, the treated C-FELT was washed with distilled water until a neutral pH was detected in the water; and finally it was dried in an oven at 110 °C for 12 h.

2.2.2. Synthesis and deposition of PANI on C-FELT

The deposition of PANI on C-FELT was made by using a layer by layer technique deposition, where the PANI doped by PSS was grown in successive steps by alternating immersion in positively charged monomer solution and negatively charged PSS solution. The oxidizing agent was also included, thus providing a successive polymerization-deposition as described below.

PANI deposition was performed in situ on C-FELT adapting a synthesis methodology developed for the realization of a conductive ink [32–34] using the aniline dimer according to the following procedure: (1) the C-FELT was treated with a solution of 0.01 M of PSS in a solution 0.1 M of HCl for 15 min, (2) rinsed in distilled water and thus immersed in a solution 0.01 M of DANI in methanol for 15 min, and (3) rinsed again in distilled water and immersed in a solution of 0.01 M in APS, 0.01 M of PSS and 0.1 M of HCl for 15 min. The material was slightly pressed on absorbent paper to remove the excess of solution between stages. Steps (2) and (3) were repeated 8 times each, and at the end of the deposition the modified carbon material was washed in distilled water. Finally, the material was dried in air at room temperature for at least 12 h before being used in the MFCs.