



Low-cost stainless-steel wool anodes modified with polyaniline and polypyrrole for high-performance microbial fuel cells

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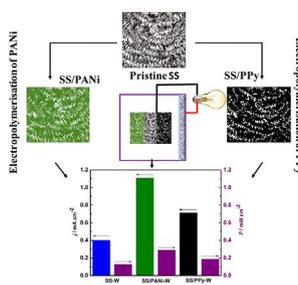
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HIGHLIGHTS

- First demonstration of stainless steel wool as a cheap and efficient MFC anode.
- Substantial improvement of SS-W anode performance with PANi and PPy coatings.
- SS/PANi-W anode exhibits 2.5 times higher kinetic activity than SS/PPy-W anode.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Microbial fuel cells
Anode
Stainless steel wool
Polyaniline
Polypyrrole
Power density

ABSTRACT

A conducting polymer coated stainless-steel wool (SS-W) is proposed for use as a low-cost anode for microbial fuel cells (MFCs). When coated with polyaniline (PANi) and polypyrrole (PPy), the pristine SS-W, SS/PANi-W and SS/PPy-W anodes produced maximum current densities of 0.30 ± 0.04 , 0.67 ± 0.05 , $0.56 \pm 0.07 \text{ mA cm}^{-2}$, respectively, in air-cathode MFCs. Also, based on achieved power density, both SS/PANi-W and SS/PPy-W achieved $0.288 \pm 0.036 \text{ mW cm}^{-2}$ and $0.187 \pm 0.017 \text{ mW cm}^{-2}$, respectively, which were superior to $0.127 \pm 0.011 \text{ mW cm}^{-2}$ obtained with pristine SS-W. Further, in comparison with SS-P based anodes, all SS-W based anodes gave improved power densities under similar experimental conditions by at least 70%. Moreover, the charge transfer resistance of the SS-W was much lower ($240 \pm 25 \Omega \text{cm}^{-2}$) than for the SS-P ($3192 \pm 239 \Omega \text{cm}^{-2}$). The $j_{o(\text{apparent})}$ values obtained for SS/PANi-W ($0.098 \pm 0.007 \text{ mA cm}^{-2}$) and SS/PPy-W ($0.036 \pm 0.004 \text{ mA cm}^{-2}$) anodes were also much higher than that of the pristine SS-W ($0.020 \pm 0.005 \text{ mA cm}^{-2}$), as well as than those of all SS-P based anodes. The observed enhancement of the bioelectrocatalytic performances were well supported by physicochemical and electrochemical characterisation.

1. Introduction

Despite the considerable scientific and technological advancements that have been made in microbial fuel cell (MFC) research over the years, several issues such as high material costs and low power outputs

have limited their wider adoption and applications [1]. The performance of MFC is affected by many intrinsic (such as microorganisms and chosen construction materials) and operational factors [2–7]. The microorganisms-anode interaction is amongst the most important factors that determine the bioelectrocatalytic performance of these

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Nomenclature

Cdl	Double layer capacitor
F	Faraday's constant [96,485 C mol ⁻¹]
i_0	Exchange current [mA]
j_0	Exchange current density [mA cm ⁻²]
Q	Constant phase element
R	Ideal gas constant [8.31 J mol ⁻¹ K ⁻¹]
R	Resistor [Ω]
R_{ct}	Charge transfer resistance [Ω]
R_s	Solution resistance [Ω]
T	Absolute temperature [K]
W	Warburg diffusion element [Ω]
η	Overpotential [mV]

Abbreviations

CPHs/CNTs	Conductive polypyrrole hydrogels/carbon nanotubes
EET	Extracellular electron transfer
MWCNTs	Multiwall carbon nanotubes
NT-MPMs	Multi-walled MnO ₂ /polypyrrole/MnO ₂ nanotubes
PANi	Polyaniline
PANi/GF	Polyaniline graphite felt

PANI/CC	Polyaniline carbon cloth
PANI/CNT/CP	Polyaniline carbon nanotubes
PANI/CP	Polyaniline carbon paper
PANI _{che} /SSFF	Polyaniline synthesised by chemical polymerisation
PANI _{ele} /SSFF	Polyaniline synthesised by electrochemical polymerisation
PPy	Polypyrrole
PPy/AQDS	Polypyrrole/antraquinone-2,6-disulphonic disodium salt
PPy/MnO ₂	Polypyrrole Manganese dioxide composite
PPy/RVC	Polypyrrole-Coated Reticulated Vitreous Carbon
PPy-CNTs	Polypyrrole carbon nanotubes
SS	Stainless steel
SS/PANi-P	Stainless steel plate modified with polyaniline
SS/PANi-W	Stainless steel wool modified with polyaniline
SS/PPy-P	Stainless steel plate modified with polypyrrole
SS/PPy-W	Stainless steel wool modified with polypyrrole
SSFF	Stainless steel fibre felt
SS-FO	Flame oxidised stainless steel
SS-P	Stainless steel plate
SS-W	Stainless steel wool

systems [8,9]. Exploration of different materials and approaches to find the most suitable anode material has thus been a major area of challenge in MFC research [1].

The required qualities for an ideal anode material include possession of properties such as biocompatibility, high electrical conductivity [10], large surface area for wide coverage by exoelectrogenic bacteria [11], corrosion resistance [12], suitable mechanical strength and toughness [13,14]. In addition, the chosen material must be relatively cheap to achieve low-cost scalability for practical applications [15]. A number of two and three-dimensional (2D and 3D) materials have been investigated for use as anodes for MFCs. The most widely used 2D carbon-based anode materials, such as graphite plates and rods, carbon cloth [16] have considerable limitations in relation to their low accessible surface area for microbial biofilm colonisation, high charge transfer resistance, high activation, and mass transfer overpotential [17]. To overcome some of the aforementioned limitations, surface modification of materials and the use of 3D carbon-based materials as anodes have gained widespread consideration. Different 3D materials, such as electrospun carbon fibre mats [18], carbon fibre veil [19], graphite fibre brush [20] and rotating spiral carbon brush have recently been used as anodes [21]. In order to reduce the precursor costs, attempts have been made successfully to construct 3D anodes from natural materials, such as king mushroom, wild mushroom and corn stem [22]. Composite anodes, such as carbon scaffold from polyacrylonitrile [23], carbon nanofibers modified graphite [24], activated carbon nanofibers nonwoven [25], nitrogen-doped graphene aerogels [26], and carbon-metal composites, such as carbon yarn with stainless steel [27], have also been investigated. These research efforts, in particular on 3D materials, have resulted in remarkable improvement in the current or power densities achieved in MFCs. The enhanced performance with 3D and composite electrodes is attributed primarily to their high surface area for efficient colonisation of bacterial communities, enhanced biocompatibility and electrical conductivity [27–31]. By increasing the surface area and controlling the pore size of these materials, the substrate access for electrogenic bacteria can be enhanced, which, in turn, results in relatively low mass transfer limitations [32,33]. However, the major limitations of 3D carbon materials include their brittle structure which has less strength and low conductivity leading to high Ohmic resistance. Metal-based electrodes are able to address these issues, as recently demonstrated by Baudler et al. [34].

Pocaznoi et al. [35] reported that stainless steel (SS) is the most commonly used metal-based anode material for MFCs due to its excellent mechanical strength, good conductivity, high rigidity and stability [1,36]. However, the major issues associated with the use of low-grade SS anodes include their relatively poor biocompatibility due to the hydrophobic nature and proneness of SS to corrosion. The biocompatibility issue can be addressed by heat treatment or flame oxidation, as proposed by Guo et al. [37].

Recently, various methods have been reported for the modification of SS-based anode materials, such as flame-oxidation, flame deposition, binder and binder-free nanocarbon coating [37–42]. The flame oxidation of SS results in node like sites, which mainly consisted of hematite (Fe₂O₃) on the surface of SS. The resulting anode produced a maximum power density of 0.106 mW cm⁻² [38]. In the other study, flame oxidation of SS generated iron oxide nanoparticles on the surface and produced a current density of 1.92 mA cm⁻² [37]. In another approach, carbon nanostructures were formed on SS using flame synthesis and a maximum power density of 0.0187 mW cm⁻² was achieved [39]. Carbon nanofibers were also coated onto SS by chemical vapour deposition, and the modified anode generated a maximum current density of 1.28 mA cm⁻² [40]. All of the above studies were investigated under controlled potentiostatic testing conditions. A carbon black/SS mesh composite anode was prepared by using a binder-free dipping method, and when employed in a continuous magnetic stirring batch-mode MFC, it gave a maximum power density of 0.321 mW cm⁻² [41]. Graphene with polytetrafluoroethylene (binder) coating on a SS mesh was also used, and it gave a maximum power density of 0.2668 mW cm⁻² [42].

In comparison with routinely used SS plate (SS-P) and mesh materials, SS wool (SS-W) offers compelling advantages, such as very high surface area, low cost and malleability, which allows it to be moulded into any shape according to the system architecture. To the best of our knowledge, SS-W has never been employed as an anode material in MFCs and also never previously coated with conducting polymers, but its high surface area and relatively low-cost warrant consideration as an alternative cheap anode. Furthermore, conducting polymer coatings, such as polyaniline (PANi) and polypyrrole (PPy), have been shown to be effective for corrosion reduction for carbon and composite based MFC anodes [43]. These polymers possess high electron mobility, stability, biocompatibility, anticorrosion nature, excellent electrokinetics

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