Electrochimica Acta 128 (2014) 311–317

Contents lists available at ScienceDirect

Electrochimica Acta

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

Application of carbon black and iron phthalocyanine composites in bioelectricity production at a brewery wastewater fed microbial fuel cell

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ARTICLE INFO

Article history:
Received 7 July 2013
Received in revised form 5 November 2013
Accepted 5 November 2013
Available online 14 November 2013

Keywords:
Carbon black
Microbial fuel cells
Iron phthalocyanine
Beer brewery wastewater
Enterobacter cloacae

ABSTRACT

Aerobic cathode microbial fuel cells (MFCs) have been widely researched to provide bioremediation of wastewaters, coupled to sustainable energy production. In order to effectively accomplish this aim, suitable catalysts and catalyst supports for oxygen reduction reaction (ORR) are required. While iron phthaloycanine (FePc), supported on multi-walled carbon nanotubes has previously been studied for this function, cost of industrial production may hinder this. Importantly, this study examines the use of several available grades of carbon black for their relative suitability to perform as supports for FePc in MFC formats. Voltammetric studies showed that the different grades of carbon black provided varying lowering of the ORR overpotential, between ~160 and ~270 mV relative to unmodified GCEs, and an optimum grade (N326) was selected for further study. Carbon black/FePC composite electrodes exhibited comparable lowering of the ORR overpotential (606 mV) to potentials previously reported to nanotube/FePc composites (620 mV), as well as lowered charge-transfer resistance compared to electrodes solely modified with FePc. When applied as cathode modifiers in dual chambered MFCs utilising *Enterobacter cloacae*, the combined use of carbon black and FePc provided greater power densities than either alone; composite electrodes obtaining ~400% power density, compared to unmodified electrodes. Modification of the anode with carbon black further increased power density, generating power densities an order of magnitude larger than those obtained at unmodified electrodes. The ability of beer brewery waste water (BBWW) to generate power at these modified surfaces yielded permissible power densities (~40% that of reinforced clostridial media). Differences observed, in particular under agitation, are attributed to variations in nutrient content and nutrient complexity, between the two fuel substrates.

1. Introduction

The need for viable, cost-effective and energy-efficient solutions for wastewater treatment remains an enduring concern. Microbial fuel cells (MFCs) hold promise as alternative means for wastewater treatment with the added benefit of electrical energy generation. MFCs are devices that use exoelectrogenic microorganisms (mainly bacteria) as biocatalysts to catabolise complex organic matter in the presence of electrodes to gather electrons arising from this catabolism [1–3]. MFCs present distinct advantages when compared to either conventional treatments of wastewater or chemical fuel cells, primarily in their relative operational robustness, coupled with their numerous substrate sources [2,4,5].

Beer brewery wastewater (BBWW) has been investigated in recent years as a potential fuel substrate for MFCs [6,7]. BBWW is a collective term for the waste-water produced from the cleaning and cooling of fermentation units during the production of beer [6,7]. It presents a promising substrate for MFC exploitation due to its low costs and high production volumes [6–8]. In addition, its food-derived nature ensures that it maintains a high nutrient level and low concentrations of inhibitory substances e.g. ammonia when compared to other industrial wastewaters of similar abundance [6–8].

Research conducted on oxygen-fed MFC cathodes has identified electron transfer to dioxygen, the final MFC electron acceptor, as one of the rate-limiting steps [1,5]. To improve the rate of the oxygen reduction reaction (ORR), many electrode material alternatives, as well as the use of catalysts and catalyst supports have been investigated [9]. Although platinum metal has been found to be the most efficient catalyst for oxygen reduction, its high cost makes the upscale of MFCs impractical [4,5]. The use of iron phthalocyanine (FePc) as an oxygen electrocatalyst has been demonstrated

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http://dx.doi.org/10.1016/j.electacta.2013.11.016

to improve the power density obtained in aerobic cathode MFCs, due to the enhancement of the oxygen reduction reaction rate [5,10,11].

Oxygen reduction catalysis afforded through FePc modification of cathodes has also been shown to be further increased through the inclusion of catalyst supports such as multiwalled carbon nanotubes (MWCNTs) [5,10]. Carbon nanotubes have also found application as anode modifiers in MFCs [10,12]. However given the high cost of MWCNTs, a more cost effective and similarly efficient catalyst support is required if this configuration is to be researched for large-scale MFCs. Carbon black has been demonstrated to have the potential to fulfil these requirements [4,11,13] and shown to provide similar improvements in MFC cathode performance as a FePc support [4,11]. Carbon black is a form of carbon structurally similar to graphite, similarly formed by the incomplete combustion of aromatic hydrocarbons at high temperatures. Under these conditions, aromatic carbon radicals form layered structures composed of hexagonal rings which stack into 3-4 layers, giving carbon black a multilayered, polymeric, three-dimensional structure [13,14]. Industrially, carbon black is generally used to prolong the lifetime of rubber, as a colorant, and as an ultraviolet light stabilizer [14].

Commercially, carbon black is roughly graded according to average particle size, providing a potential range of surface modifiers with differing physico-chemical properties, notably porosity. Scope exists for the further interrogation of the application of different grades of carbon black as supports for FePc as cathode modifiers for MFCs as well as the influence of carbon black as an anode modifier, in dual-chambered MFC configurations.

The aims of this research were to investigate more fully carbon black as an alternative to MWCNT as electrode modifiers and FePc catalyst supports for application in MFCs. The study aimed to provide preliminary investigations into the various grades of carbon black for their suitability as catalyst supports for FePc-catalysed oxygen reduction, via voltammetric and impedimetric studies at glassy carbon electrodes. The study also examined the applicability of BBWW as a fuel substrate [compared to reinforced clostridial growth medium (RCM)] for use in MFCs comprising of carbon black/FePc composite electrodes, using *Enterobacter cloacae* as biocatalysts. Trends between electrode modifications examined at MFCs fuelled by either RCM or BBWW were contrasted with similar studies utilising MWCNTs.

2. Experimental

2.1. Voltammetric studies and instrumentation

All electrochemical data was collected using an Autolab PGSTAT 302 connected to a 663 VA stand (Metrohm). A three electrode cell, consisting of a silver/silver chloride (Ag/AgCl) reference electrode (BioAnalytical Systems), a glassy carbon electrode (GCE) working electrode (3 mm in diameter, BioAnalytical Systems) and a platinum wire counter electrode was used. The supporting electrolyte was 50 mM phosphate buffer, pH 7. To assess the reproducibility of electro-analytical responses, four separate GCEs were used throughout the study.

GCEs were polished thoroughly before each scan using aluminium oxide slurry (> 10 microns, 99.7% metals, from Sigma Aldrich) on a Buehler felt pad. Following polishing, GCEs were ultrasonicated successively in absolute ethanol, followed by double-distilled water, for 1 minute each to remove any physically-attached contaminants. Electrodes were dried at 70 °C in an oven for 10 min.

2.2. Modification of glassy carbon electrode surface for voltammetric studies

All electrode modifications were performed by drop-casting of suspensions onto GCE surfaces. This method was used to modify GCEs with FePc (Sigma Aldrich), carbon black and carbon black/FePc composites. The modifier (either FePc, carbon black or carbon black/FePc) was dispersed in absolute ethanol (to a final concentration of 2.5 mg/ml of each component) and then resuspended by ultrasonication for 30 min to reduce aggregation. Ten microliters of the suspended modifier was dropped onto the electrode surface and allowed to dry at 70 °C for 10 min.

The effect of FePc loading was investigated at 1, 2.5 and 5 mg/ml suspensions. Ten microliters of dispersed FePc was dropped onto a cleaned unmodified GCE surface and dried at 70 °C for 10 minutes.

Five grades of carbon black were obtained as a gift from Orion Engineered Carbons (South Africa): Corax N220, Corax N234, Corax N326, Corax N339 and Corax N375. The grades differ in several properties such as particle size (ranging from 20 nm to 30 nm), porosity (as measured by external nitrogen surface area) and method of manufacture. The greatest lowering in the overpotential for ORR of these grades was observed for Corax N326. Carbon black/FePc hereafter refers to a mixed composite comprising 2.5 mg/ml FePc and 2.5 mg/ml (Corax N326) carbon black.

2.3. Examination of the effect of electrode modification on the ORR overpotential

Cyclic voltammetry scans were conducted at a scan rate of 0.1 V/s, within a potential window of +0.2 to -1.0 V (vs. Ag/AgCl). The various electrode surfaces were analysed in both aerated and de-aerated electrolyte, to identify peaks associated with oxygen reduction reactions. The electrolyte was de-aerated for at least 5 min with nitrogen gas prior to use and maintained under a nitrogen blanket during analysis.

2.4. Electrochemical impedance studies

Potassium ferri/ferrocyanide (Sigma Aldrich) (equimolar, to a combined final concentration of 1 mM) was used to analyse charge transfer resistance of the electrode modifications relative to a bare GCE. A sinusoidal potential (5 mV rms), centred around the open circuit potential (0.265 V) was applied between the frequency range of 0.1 Hz to 10 kHz in phosphate buffer containing ferri/ferrocyanide redox probe. The open circuit potential was confirmed by cyclic voltammetry to be the average of peak potentials for the ferri/ferrocyanide redox probes in phosphate buffer.

2.5. Microbial fuel cell studies

2.5.1. Bacterial growth and inoculation

Enterobacter cloacae strain 16657 (Deutsche Sammlung von Mikroorganismen und Zellkulturen) was cultured in reinforced clostridium medium (RCM) (Fluka analytical) at 35 °C for 48 hours. Growth curves were measured at hourly intervals spectrophotometrically, at a detection wavelength of 600 nm (OD_{600}). Cultures in exponential growth phase were used for inoculation of the MFC.

2.5.2. MFC electrode modifications

Modified MFC electrodes were fabricated using 2 × 2 cm of Toray Carbon Paper (TGP-H-60). Electrode modifiers were applied by drop casting 200 μl of 2.5 mg/ml FePc, 2.5 mg/ml carbon black or a composite comprising of equivalent mass loadings (2.5 mg/ml each) of carbon black/FePc followed by drying at 70 °C for 10 min. For the cathode modification, a 2.5 mg/ml suspension of carbon