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Iron chelates as low-cost and effective electrocatalyst for oxygen reduction reaction in microbial fuel cells

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ARTICLE INFO

Article history:

Received 10 August 2013

Received in revised form

10 February 2014

Accepted 12 February 2014

Available online 14 March 2014

Keywords:

Iron-based catalyst

Iron chelates

Oxygen reduction reaction (ORR)

Microbial fuel cell (MFC)

ABSTRACT

Iron-chelated electrocatalysts for the oxygen reduction reaction (ORR) in a microbial fuel cell (MFC) were prepared from sodium ferric ethylenediamine-N,N'-bis(2-hydroxyphenylacetic acid) (FeE), sodium ferric diethylene triamine pentaacetic acid (FeD) supported on carbon Vulcan XC-72R carbon black and multi-walled carbon nanotubes (CNTs). Catalyst morphology was investigated by TEM; and the total surfaces areas as well as the pore volumes of catalysts were examined by nitrogen physisorption characterization. The catalytic activity of the iron based catalysts towards ORR was studied by cyclic voltammetry, showing the higher electrochemical activity of FeE in comparison with FeD and the superior performance of catalysts supported on CNT rather than on Vulcan XC-72R carbon black. FeE/CNT was used as cathodic catalyst in a microbial fuel cell (MFC) using domestic wastewater as fuel. The maximum current density and power density recorded are $110 \text{ (mA m}^{-2}\text{)}$ and $127 \pm 0.9 \text{ (mW m}^{-2}\text{)}$, respectively. These values are comparable with those obtained using platinum on carbon Vulcan (0.13 mA m^{-2} and $226 \pm 0.2 \text{ mW m}^{-2}$), demonstrating that these catalysts can be used as substitutes for commercial Pt/C.

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1. Introduction

Among the numerous systems under investigation to develop sustainable energy production devices, microbial fuel cells (MFCs) have the added value to contribute to wastewater treatment while producing energy. These bio-electrochemical

systems in fact, convert the chemical energy stored in the biodegradable organic matter present in wastewater into electrical energy through the catalytic action of microorganisms [1–3]. Several limiting factors regulate MFC performance, most important being reactor configuration, internal resistance, and electrode reactions. The power density of MFC is greatly affected by the cathode side [4], where oxygen is the

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most popular cathodic electron acceptor due to its charge-free nature and high redox potential characteristic. The use of platinum as catalyst for the oxygen reduction reaction (ORR) significantly contributes to device cost, thus representing one obstacle to the commercial development of MFCs. The cathodic materials account for 47% of the MFC total cost [5,6] which would be largely reduced by decreasing the platinum loading or replacing platinum with less expensive species.

The platinum loading has been successfully reduced from 0.5 to 0.1 mg cm⁻² with a slight decrease of air-cathode MFC power density [7]. Other studies have reported on the use of platinum alloys containing less expensive metals such as iron [8], nickel [9], cobalt [10]. These catalysts however, are still Pt-containing and suffer from catalyst poisoning when the cell is operated in single-chamber configuration. Thus, several non-platinum materials, i.e. cobalt [7,11], manganese [12], titanium [13], lead [14], copper [15], have been investigated. Among these metals, iron is particularly appealing because of its low cost and high abundance.

At iron chelated cathodes of MFCs, the ORR can proceed through either a 4 electron pathway producing water, or through a 2 electron pathway producing hydrogen peroxide as an intermediate [16]. The peroxide pathway and the consequent possible production of other intermediate reactive oxygen species does not necessarily impair the final MFC performance by reducing microbial catalytic activity. In fact, the production of hydroxyl radicals could be considered beneficial based on their ability to degrade wastewater industrial pollutants, such as 4-nitrophenol [17], or to treat the residual COD in the effluent stream. Different iron-based catalysts such as iron phthalocyanine [18], iron acetate, Cl–Fe^{III} tetramethoxyphenylporphyrin [19], iron ethylenediaminetetraacetic acid [20–22] have been explored as cathodic catalysts for MFC applications demonstrating that Fe-containing species are promising candidates as ORR cathodic catalysts.

The design of a catalyst implies depositing the metal species on a carbon support. Carbon nanotubes (CNTs) are characterized by high electronic conductivity, uniform pore size distribution, meso- and macro-pore structure, inert surface properties, and resistance to acidic and basic environment [23]. Some examples on the use of CNTs as support material for the cathodic catalyst in MFCs have been reported [24–26].

In this study, catalysts containing iron chelates of ethylenediamine-N,N'-bis(2-hydroxyphenylacetic acid) and diethylene triamine pentaacetic acid supported on multiwalled carbon nanotubes (CNTs) or Vulcan XC-72R carbon black were prepared and characterized. The structure and catalytic activity of the prepared catalysts were investigated by TEM, BET, and cyclic voltammetry. Their performance as cathodic

catalyst of an MFC fed with domestic wastewaters was tested and compared with that of reference Platinum.

2. Experimental

2.1. Catalyst preparation

Multi-walled carbon nanotubes (CNTs, >95% carbon content, diameter × length 6–9 nm × 1 μm) were purchased from Aldrich and purified by heat-treatment at 300 °C for 3 h to eliminate the amorphous carbon, and refluxing in HNO₃ 65 wt.% at 90 °C for 16 h to remove metal impurities [27]. Purified CNTs were separated by filtration and washed with pure water until neutral pH, obtaining a carbon paste which was dried at 70 °C overnight.

Sodium ferric ethylenediamine-N,N'-bis(2-hydroxyphenylacetic acid) (Fe EDDHA) and diethylene triamine pentaacetic acid pentasodium salt solution (DTPA) were purchased from Aldrich and used as received.

Catalysts were prepared as follows: solutions of iron containing precursors were prepared either dissolving sodium Fe EDDHA (0.392 g) or a mixture of sodium DTPA (1.132 g) and FeCl₃·6H₂O (0.243 g) in water (100 mL). Vulcan XC-72R or purified CNTs (0.5 g) was added to the solution. The mixture was stirred for 0.5 h, filtered and the resulting wet solid dried at 70 °C overnight. The powder was ground, placed in a ceramic vessel and heated for 1.5 h at 800 °C under argon to obtain the catalysts which were labeled as indicated in Table 1.

Commercial platinum 10 wt.% on Vulcan XC-72R carbon black (Pt/C) was obtained by Quintech and used as reference.

2.2. Catalyst characterization

The morphology of the iron based catalysts was investigated by TEM images acquired with a Philips CM 12 instrument operating at 120 kV. Elemental analysis was carried out by energy dispersive X-ray (EDX) analysis using an Oxford INCA ver. 4.04 year 2003 system.

To measure the total surface area and the pore volume of the catalysts, nitrogen sorption isotherms were measured at –196 °C down to relative pressure P/P₀ 5 × 10⁻⁷ with a Quantachrome Instrument Autosorb-1. Before sorption measurements, each sample was heated to 120 °C for 2 h under vacuum. Sorption data were analyzed using Autosorb Software from Quantachrome Instrument.

Cyclic voltammetry (CV) experiments were carried out using a Ring-Disk Electrode Model 636A (Princeton Applied Research, Ametek) and a Potentiostat VMP3 (Bio Logic Science Instruments). The system was integrated with a personal

Table 1 – Catalysts labeling, total surface area, total pore volume, potential (E_p), and current (I) peak.

Sample	Label	Total surface area (m ² g ⁻¹)	Total pore volume (cc g ⁻¹)	E_p (V versus SCE)	I_p (mA cm ⁻²)
Purified MWCNTs	CNT	275	1.59	–0.244	–0.388
Carbon Vulcan	C	212	1.09	–0.329	–0.775
NaFe/EDDHA/CNTs	FeE/CNT	171	1.03	–0.017	–0.702
NaFe/EDDHA/C	FeE/C	116	0.58	–0.114	–0.587
NaFe/DTPA/CNTs	FeD/CNT	164	0.87	–0.22	–0.396
NaFe/DTPA/C	FeD/C	117	0.57	–0.288	–0.396

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