Journal of Power Sources 283 (2015) 74–83

Contents lists available at ScienceDirect

Journal of Power Sources

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

Silver/iron oxide/graphitic carbon composites as bacteriostatic catalysts for enhancing oxygen reduction in microbial fuel cells

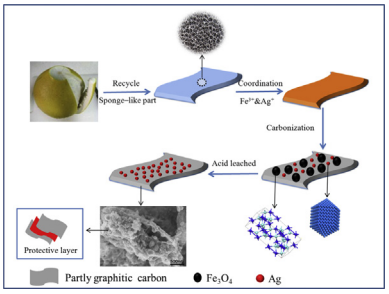
Ming Ma [a, b], Shijie You [c], Xiaobo Gong [c], Ying Dai [a], Jinlong Zou [a, b, *], Honggang Fu [a, **]

[a] Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education of the People's Republic of China, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China
[b] Key Laboratory of Chemical Engineering Process and Technology for High-Efficiency Conversion, College of Heilongjiang Province, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China
[c] State Key Laboratory of Urban Water Resource and Environment (SKLUWRE), Harbin Institute of Technology (HIT), Harbin 150090, China

HIGHLIGHTS

- Biofilm is inevitably formed over cathodic catalytic-sites in microbial fuel cells.
- AgNPs/Fe_3O_4/GC as antibacterial ORR catalysts is prepared from waste pomelo skin.
- The embedded AgNPs in GC skeleton can avoid the easy oxidation.
- Close conjunctions between AgNPs and Fe_3O_4 provide the efficient pathway for ORR.
- Antibacterial and ORR activity jointly contribute to the excellent power output.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 February 2015
Accepted 17 February 2015
Available online 20 February 2015

Keywords:
Bacteria inhibition
Biofouling
Durability
Microbial fuel cells
Nano silver/iron oxide/graphitic carbon composites
Oxygen reduction reaction

ABSTRACT

Biofilms from anode heterotrophic bacteria are inevitably formed over cathodic catalytic sites, limiting the performances of single-chamber microbial fuel cells (MFCs). Graphitic carbon (GC) – based nano silver/iron oxide (AgNPs/Fe_3O_4/GC) composites are prepared from waste pomelo skin and used as antibacterial oxygen reduction catalysts for MFCs. AgNPs and Fe_3O_4 are introduced in situ into the composites by one-step carbothermal reduction, enhancing their conductivity and catalytic activity. To investigate the effects of Fe species on the antibacterial and catalytic properties, AgNPs/Fe_3O_4/GC is washed with sulfuric acid (1 mol L^{-1}) for 0.5 h, 1 h, and 5 h and marked as AgNPs/Fe_3O_4/GC-x (x = 0.5 h, 1 h and 5 h, respectively). A maximum power density of 1712 ± 35 mW m^{-2} is obtained by AgNPs/Fe_3O_4/GC-1 h, which declines by 4.12% after 17 cycles. Under catalysis of all AgNP-containing catalysts, oxygen reduction reaction (ORR) proceeds via the $4e^-$ pathway, and no toxic effects to anode microorganisms result from inhibiting the cathodic biofilm overgrowth. With the exception of AgNPs/Fe_3O_4/GC-5 h, the AgNPs-containing composites exhibit remarkable power output and coulombic efficiency through lowering proton transfer resistance and air-cathode biofouling. This study provides a perspective for the practical application of MFCs using these efficient antibacterial ORR catalysts.

* Corresponding author. Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education of the People's Republic of China, School of Chemistry and Materials Science, Heilongjiang University, Xuefu Road 74#, Nangang District, Harbin 150080, China.
** Corresponding author. Xuefu Road 74#, Nangang District, Harbin 150080, China.
E-mail addresses: zoujinlong@aliyun.com (J. Zou), fuhg@vip.sina.com (H. Fu).

http://dx.doi.org/10.1016/j.jpowsour.2015.02.100
0378-7753/

1. Introduction

With the intensification of energy consumption and environmental pollution, energy and environmental issues have become a very serious challenge. Microbial fuel cells (MFCs) have attracted a great deal of attention as a novel technology for multiple energy production and wastewater treatment [1–4]. Single-chamber air-driven MFCs have been designed to increase power generation and lower the cost due to their lack of membranes [5]. Microorganisms on the anode serve as renewable biocatalysts to continuously convert biodegradable organics in wastewater into electricity, while the oxygen reduction reaction (ORR) generates H_2O on the air cathode [6]. However, due to the absence of a membrane and direct contact with nutrients in the anode electrolyte, biofilms will inevitably be formed on the cathode surface. These cathode heterotrophic aerobic bacteria originating from anode microorganisms are firmly believed to increase the proton transfer resistance for electricity generation [7–9]. In addition, the power output can also be reduced by the adverse effect of oxygen leaking into the reactor [10]. A variety of separators have been explored in MFCs to overcome the oxygen crossover and recede the overgrowth of cathode bacteria [11,12]. However, in most cases, a decrease in power generation and an increase in internal resistance occur due to the separator's ionic impedance [13]. Therefore, it is necessary to develop a cathodic catalyst with high ORR activity and inhibition capacity for bacterial overgrowth.

Many studies have been conducted to optimize the three-phase (O_2, H_2O or H_2O_2, and cathode) interface reaction to improve the ORR activity. For example, carbon-based materials such as graphene, carbon nanotubes, activated carbon, carbon black, and graphitic carbon (GC) have been considered as alternatives to Pt/C catalysts because of their particular structure, redox activity, relative low-cost, and superior electron transmission ability [14,15]. In particular, GC has been tested as a promising catalyst for MFCs due to its exceptional conductivity, high chemical stability, and low cost [16]. However, GC materials face the problem of low immanent electrocatalytic activity for ORR via the two-electron ($2e^-$) pathway, leading to a poor electrical output of MFCs [17]. Therefore, many attempts have been made to load some low-cost, high-efficiency transition metals with superior catalytic activity on GC. A series of carbon catalysts doped with Fe or Co species have shown excellent electron donor capacity as MFC cathodes by weakening O–O bonds and facilitating the disproportionation of H_2O_2 for biological electricity generation [18,19]. Combining nano-carbon materials with active metal species can improve the electrocatalytic activity and electron transport ability. These composites provide fast electron transport networks and sufficient active sites for ORR. Therefore, the above-mentioned results are of particular interest for the creation of active transition metal/GC-based catalysts for the four-electron ($4e^-$) ORR mechanism and the inhibition of cathode bacteria for MFCs.

It should be noted that silver nanoparticles (AgNPs) loaded on graphite plates or activated carbon (AC) have already been utilized as ORR electrocatalysts with bacteria-inhibiting ability [20,21]. However, the exposed AgNPs may not be sufficiently stable, leading to easy oxidation and depressed ORR activity [22]. Here, we intend to create a stable and highly efficient ORR catalyst by using the synergistic effect between AgNPs, transition metals, and GC that can improve the evolution of active sites and ORR efficiency and lower the biofouling and internal resistance of MFCs. Furthermore, by using this catalyst, the power output is expected to be improved via the acceleration of OH^- transportation [7], which can efficiently prevent overpotential loss in ORR and avoid using expensive and unstable (biodegradability) separators (Nafion). Therefore, the critical mechanism in determining power production should be further clarified to better understand the relationship between antibacterial reaction and ORR.

In this study, GC-based (containing amorphous carbon) AgNPs/iron oxide composites (marked as AgNPs/Fe_3O_4/GC) are synthesized by a facile in situ reduction method using waste pomelo skins as the carbon source. The sponge-like pomelo skins consist of a porous network with tunable functional organic groups that allow certain ionic guests (Fe^{3+} and Ag^+) to be simultaneously introduced into the carbon framework through a facile ion-exchange procedure. The introduction of Fe species can promote both the graphitization and desorption of H_2O_2, which may facilitate the desirable $4e^-$ ORR process. Furthermore, GC and Fe species can form protective layers or joints to prevent the oxidation of AgNPs in wastewater, leading to better antibacterial and catalytic activities. Based on the above considerations, the performance of MFCs with AgNPs/Fe_3O_4/GC cathodes will be improved by the strengthening of proton and OH^- transfer abilities. The relationship between the electrocatalytic activity, antibacterial ability, and structure of AgNPs/Fe_3O_4/GC is also discussed.

2. Experimental section

2.1. Synthesis of AgNPs/Fe_3O_4/GC composites

A simple in situ synthetic method was used to prepare the AgNPs/Fe_3O_4/GC composites. Wasted pomelo skins were used as the carbon source, as we reported previously [23]. Briefly, the sponge-like parts of the pomelo skins were immersed in a mixture of Fe^{3+} and Ag^+ to form a carbon–Fe^{3+}–Ag^+ coordinated complex with a mass ratio of 1: 0.8: 0.4. The resulting samples were dried at 60 °C and then carbonized at 1000 °C for 1.5 h with a heating rate of 5 °C min^{-1} under highly pure N_2 flow (50–60 mL min^{-1}). Parts of the carbonous precursors were converted into GC; meanwhile, the Ag^+ precursor was reduced in situ to nanoscale Ag particles, which were embedded in the skeleton of the composite body (Scheme 1, Supporting Information (SI)). A protective contact between the active components (AgNPs and Fe_3O_4) and GC was formed, which enhanced the catalytic activity and stability of the AgNPs/Fe_3O_4/GC catalyst [24]. To further study the effect of Fe species on the antibacterial and catalytic properties of the composite, AgNPs/Fe_3O_4/GC was washed with dilute sulfuric acid (H_2SO_4, 1 mol L^{-1}) for 0.5 h, 1 h, or 5 h to remove the Fe species; the resulting samples were marked as AgNPs/Fe_3O_4/GC-x (x = 0.5 h, 1 h and 5 h). In addition, the Fe_3O_4/GC and AgNPs/AC composites were synthesized for comparison according to the above method.

2.2. Electrode preparation for MFCs

Membrane-less single-chamber MFCs (air-driven) were built using carbon fiber brush as the anode; the anodes were pretreated with acetone and heating in the air as previously described [25]. The gas diffusion layer (GDL) of the air cathode was prepared by rolling carbon black and PTFE (60 wt.%) with a mass ratio of 7: 3 onto a stainless steel mesh (SSM) and then sintered at 340 °C for 25 min to form a hydrophobic fibrosis layer. The catalyst mixed with PTFE (mass ratio of 6:1) was uniformly rolled onto the opposite side of the GDL and dried at 80 °C according to the previously reported method [26]. Six cathodes were prepared (Fe_3O_4/GC, AgNPs/Fe_3O_4/GC, AgNPs/Fe_3O_4/GC-x (x = 0.5 h, 1 h, and 5 h) and