

Graphene: A promising electrode for microbial fuel cells

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Abstract:

Microbial fuel cells (MFCs) are promising sustainable technology for electricity production from waste organic matter. The anode employed for this purpose plays a major role in the performance of the MFC system. The coating of graphene on stainless steel has been investigated in this study for improving the performance of an anode in a MFC system. The use of graphene coating on a stainless steel (SS-316) plate produced a maximum power density of 201 mWm⁻², while a bare stainless steel plate only gave a maximum power density of 100 mWm⁻². The use of graphene coating on copper foil gave even higher

maximum power density of 262 mW/m⁻². The maximum open circuit potentials observed were 0.95 V, 1.0 V and 1.12 V for SS anode, SS anode with graphene and copper foil with graphene, respectively. The system internal resistance of pristine stainless steel, graphene-stainless steel and copper-graphene anodes were 43±4 Ω, 42±1 Ω and 36±5 Ω, respectively.

Introduction:

Microbial fuel cells (MFCs) are environmentally friendly technology capable of converting chemical energy stored in waste-waters directly into electrical energy by using microorganisms as biocatalysts. However, the overall low power density of the MFC and the high cost of its components are two major barriers for its commercialization. Among all the factors, the electrodes (cathode and anode) materials play the significant role in affecting the performance of MFCs. Recently,

the performance of MFCs has been improved by using graphene-based electrodes that are more conductive and mechanically stable with larger surface area and higher electrocatalytic activity compared to the conventional carbon materials. This paper provides an overview of recent research progress in graphene-based materials as electrodes for MFCs, which will be the promising candidates for developing MFCs and other bioelectrochemical systems to achieve sustainable water/wastewater treatment and bioenergy production.

In the past decade, microbial fuel cells (MFCs) have been emerging as one of the promising alternative technologies for harvesting renewable energy through wastewater treatment [1–3]. The traditional two chamber-MFCs typically have an anode and a cathode separated by a proton ex-change membrane in a two chamber setup (Fig. 1). When organic compounds (e.g., organic wastes in wastewater) are infused into the anode chamber, electrochemically active bacteria oxidize the substrates with producing protons and electrons. The protons pass through the proton ex-change membrane to the cathode. Electrons are transferred through an external circuit from the anode to the cathode, driving an external load and reducing the electron acceptor (e.g., oxygen) at the cathode. As the electrodes are the sites for electron transfer, excellent electrical conductivity is the favorite properties for the potential electrode material. Besides this, a desirable anode material should be biocompatible so that bacteria introduced into the system will form a biofilm on the anode, while a favorable cathode material should have a highly electrocatalytic activity toward oxidants (e.g., oxygen) reduction reaction. However, high cost of cathode catalysts and low charge transfer

efficacy of electrodes restrict the development of MFC technology [4]. To address these issues, a variety of materials and their modifications, including carbon/graphite materials, carbon nanotubes (CNTs), nanostructured materials and non-precious metals, have been studied, as reviewed in detail elsewhere [1,5]. While some traditional materials have shown certain promise in MFCs, their applications are still limited by their intrinsic issues, such as low specific surface area, low conductivity, poor biocompatibility, and/or complicated synthesis procedures. For instance, the synthesis of multiwall CNTs (MWCNTs) is normally carried out at a higher temperature (>500°C) in the presence of metal catalyst using the chemical vapour deposition (CVD) technique [6]. The presence of metal catalyst in the MWCNTs-based cathode can also have negative effects on the performance of MFC. Graphene, as a newly developed material, can be synthesized at room temperature using simple solution chemistry at a much lower cost than that of MWCNTs, during which toxic metal catalysts are not used. In this prospect, graphene is a desired alternative to MWCNTs for application in the MFCs [7]. So far, graphene based materials have been extensively investigated and envisaged as potential electrode materials for lithium ion batteries, supercapacitors, biosensors, photovoltaic cells, and catalysis due to its attractive properties, including high surface area (theoretical value 2630 m² g⁻¹), high conductivity, and easy synthesis process [8,9]. Recent studies show the maximum power density of the MFCs has been significantly improved by using the graphene as the catalyst support due to the better dispersion of the metal

GRAPHENE-BASED CATHODE MATERIALS

Like conventional fuel cells, electrons produced on the anode side of MFCs pass through an external electric circuit and then are consumed on the cathode side (Fig. 1). Therefore, a proper electron acceptor, e.g., potassium ferri-cyanide (K₃[Fe(CN)₆]) or oxygen (O₂), should be present in the cathode

chamber to accept the electrons through a reduction reaction. Nowadays, O₂ is the most popular oxidant applied in MFCs due to its ubiquity and high oxidation potential. The oxygen reduction reaction (ORR) may take place by inserting the cathode into an aqueous solution and allowing O₂ to diffuse to the cathode (aqueous-cathode) or by placing the cathode in direct contact with the air (air-cathode) [8–10]. However, the development of the O₂ cathode-based MFCs still faces daunting challenges, such as the slow rate due to the sluggish kinetics of ORR and the high overpotential of oxygen reduction on the surface of the cathode at neutral pH, as well as poor contact between O₂ and the cathode electrode. A variety of approaches have been proposed to improve the performance of the cathode by lowering the reaction overpotential, including the use of mediators, electrode modification with catalysts, and optimizing operational conditions within the cathodic compartment. The ORR involves a series of electron transfer processes depending on the type of catalysts used at the cathode of the fuel cells. Generally, the electroreduction of O₂ may proceed either directly to water by a 4-electron reaction (Reaction 1) or by a two-step reaction via hydrogen peroxide (H₂O₂) as the intermediate. Certainly, a direct 4-electron transfer in ORR is the most favorable pathway for an MFC system. Whereas some catalysts are incapable of oxidizing H₂O₂ at sufficient rates, the reduction will terminate after the first two electron reduction steps. In this case, the 2-electron pathway produces H₂O₂ as an intermediate or the end product of the oxygen reduction, causing degradation of the cathode catalysts and leading to a high overpotential [13]. So far, the main problems with practical applications of the MFC are the low power output and the high cost of platinum (Pt), a conventional cathode catalyst. Therefore, it is highly desirable to explore alternative materials to Pt-based catalysts. Recently, breakthrough has been achieved in developing new materials as inexpensive alternative to the costly Pt. In the following section, we outline the highlights of the last decade of progress in the field of cathode catalysts for MFC