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Silver electrodeposition on the activated carbon air cathode for performance improvement in microbial fuel cells

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HIGHLIGHTS

- Silver was electrodeposited on AC air cathode using a potentiostatic method.
- The maximum power density of the treated sample was 69% higher than the untreated.
- The ORR at the cathode took place through four-electron pathway.
- The total resistance of the electrodes was largely reduced.
- Ag deposition was not harmful to anode culture and improved cathode performance.

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ABSTRACT

The present work was to study silver electrodeposition on the activated carbon (AC) air cathode for performance improvement in microbial fuel cells (MFCs). The treated cathodes were proved to be effective to enhance the performance of MFCs. The maximum power density of MFC with silver electrodeposition time of 50 s (Ag-50) cathode was 1080 ± 60 mW m^{-2}, 69% higher than the bare AC air cathode. X-ray photoelectron spectroscopy (XPS) results showed that zero-valent, monovalent and divalent silver were present to transform mutually, which illustrated that the oxygen reduction reaction (ORR) at the cathode took place through four-electron pathway. From electrochemical impedance spectroscopy (EIS) analysis, the electrodeposition method made the total resistance of the electrodes largely reduced. Meanwhile the deposited silver had no toxic effects on anode culture but inhibited the biofilm growth of the cathodes. This kind of antimicrobial efficient cathode, prepared with a simple, fast and economical method, was of good benefit to the performance improvement of MFCs.

1. Introduction

Facing today's energy resource depletion and environmental pollution, it is desirable to look for a kind of energy which can guarantee a sufficient supply for long-term and will not cause environmental problem. Nowadays, microbial fuel cells (MFCs) attract more and more attentions due to meeting the requirements. MFCs are devices which use electrochemical active microorganisms as the catalysts to oxidize organic and inorganic matter under ambient conditions and generate current [1]. Great progress has been made to improve the performance of MFCs in the last few years [2,3].

Compared to other oxidants, the most promising electron acceptor in the cathode for MFCs is oxygen due to the inexhaustible availability, high redox potential and the avoidance of energy intensive water aeration [4,5], so the air-cathode MFCs are becoming more popular. In such oxygen system, the cathode materials would largely affect the function of MFCs because of the poor kinetics of oxygen reduction in the medium [6]. Platinum is the most commonly used catalyst for oxygen reduction reaction (ORR), but its relatively high cost prohibits the practical application of large scale MFCs [7]. Therefore, it is very necessary to develop effective and low-cost catalysts to replace platinum. The electrochemical ORR on non-Pt catalysts are becoming highly sought for fuel cells applications [8]. Iron phthalocyanine [9], Co-naphthalocyanine (CoNPc) [10], carnation-like MnO_2 [11] and so on, had aroused extensive research interest. Recently, a low-cost and effective activated carbon (AC) has become a hot spot. The cathode made with AC and polytetrafluoroethylene (PTFE) showed

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a comparable performance with a Pt cathode [12]. In addition, AC was a material for oxygen reduction that could produce a power density of 750 mW m^{-2} after a year, which showed that it had long-term performance [13]. So the AC air-cathode was applied extensively.

The price of silver is cheaper than platinum and as available electrocatalyst, silver had been applied in many reactions, which was active for chemical reduction of peroxide [12] and ORR [14], particularly in alkaline condition. Moreover, Ag-base catalysts had shown comparable performance to Pt at similar loadings, and the above two materials were able to promote the ORR via direct four-electron pathway [15].

In previous research, silver particles with various morphologies and surface chemical states were used as catalysts for ORR [16,17]. In addition, graphene or carbon black supported silver nanoparticle catalyst could enhance electrocatalytic activity towards ORR in alkaline medium [18,19]. Gong et al. used hydrothermal method to synthesize the carbon-supported nanometer silver/tungsten carbide hybrid (Ag–WC/C) as the cathodic electrocatalyst, which produced a comparable magnitude of power density to commercial Pt/C catalyst in MFC [20]. Graphite felt coated with silver nanoparticles as a cathode in MFC for microbial growth inhibition, led to a high current generation [21]. Electrodeposition is a simple, fast and economical method. Nowadays, electrodeposition technology has gotten great progress. Lv et al. prepared RuO_2-decorated carbon felt anode in a way of cathodic electrodeposition, which resulted in the maximum power density increased by 17 times as compared to that obtained with the MFC with the bare anode [22].

However, there is little research about the performance and mechanism of treated ACs by electrodeposited silver in MFCs. In this study, silver was electrodeposited on AC cathode with different time (25 s, 50 s, 75 s) and the pretreated cathodes were evaluated in MFCs for their performance. Meanwhile, tests were used to investigate the catalytic mechanism of silver electrodeposited on AC.

2. Materials and methods

2.1. Electrode materials and chemicals

Air cathodes consisted of a stainless steel mesh with a gas diffusion layer (GDL) and a catalyst layer (CL). And all the air cathodes were made by rolling-press method [23]. The GDL was prepared by carbon black and PTFE with a mass ratio of 3:7 and then heated at 340 °C for 20 min, while CL was made of AC (2100 m^2 g^{-1}, Yihuan Carbon Co. Ltd., Fujian, China) and PTFE with a mass ratio of 6:1 [24]. The amount of AC used in each CL was about 0.3 g. The prepared cathodes were modified by electrodeposition with potentiostatic plating technique. The electrodeposition was carried out using a Corrtest CS120 model electrochemical workstation (Wuhan, China) in a conventional three-electrode cell with Ag/AgCl (0.195 V versus standard hydrogen electrode) as reference electrode and platinum sheet as counter electrode. Silver was electrodeposited on the surface of AC with a potentiostatic polarization voltage of −0.8 V [25]. The electrolyte was $AgNO_3$ (2.2 mM, pH = 11) solution. Silver was electrodeposited successively with different time. The deposition time was 25 s, 50 s and 75 s, namely Ag-25, Ag-50and Ag-75. For each deposition time, three cathodes were made to determine the reproducibility of data. Thus, 12 cathode samples were prepared. The remaining silver nitrate was recycled. The anode was carbon felt which was immersed in acetone for 12 h and then was washed with distilled water for 3 or 4 times before putting it into the MFC.

2.2. MFC construction and operation

The single-chamber MFCs were constructed with an inner cylindrical chamber 3 cm in diameter and an electrode spacing of 4 cm [26]. The inner volume was 28 mL. Both electrodes had a projected area of 7 cm^2. Titanium wire had highly anti-corrosion and good conductivity, so it was used to connect the anode and cathode with the whole circuit to transfer the electrons. The external resistance was 1000 Ω. Domestic waste water was used as the inoculum. In the first 3–4 cycles (one cycle 1–2 days) of cell culture, the nutrient solution consisted of waste water and 50 mM phosphoric acid buffer solution (PBS, pH = 7) with sodium acetate (1 g L^{-1}) as the substrate. The PBS contained NH_4Cl (0.31 g L^{-1}), KCl (0.13 g L^{-1}), $NaH_2PO_4 \cdot 2H_2O$ (3.321 g L^{-1}), Na_2HPO_4 (4.090 g L^{-1}), trace mineral (12.5 mL L^{-1}), and vitamin (5 mL L^{-1}) solution [27]. All the reactors were controlled at 30 °C and the voltages of MFCs were recorded every minute by data acquisition card (Morpheus Electronic Co. Ltd, Beijing, China).

2.3. Electrochemical and material analysis

Polarization curves and power density curves were obtained by varying the external resistance from 9000 Ω to 50 Ω. Each resistor was tested for fixed time (about 10 min) to ensure a stable voltage. Cathode and anode potentials during polarization were measured using Ag/AgCl as a reference electrode. Linear sweep voltammetry (LSV) of all the cathodes were tested by a potentiostat (Wuhan, China). LSV was conducted from OCP to −0.3 V with a scan rate of 0.1 mV s^{-1}. Ag/AgCl (saturated KCl) was used as reference electrode and platinum sheet (1 cm^2) was used as counter electrode. The voltages in the text were measured with Ag/AgCl as reference voltage. These two electrodes were both fixed with a 0.5 cm spacing from the working electrode. Before the tests, the cathodes should be immersed in 50 mM PBS for about 24 h.

Electrochemical impedance spectroscopy (EIS) of all the cathodes was performed over a frequency range of 100 kHz–10 mHz at open circuit potential [28] using a potentiostat (CHI600E, ChenHua Instruments Co., Ltd., Shanghai, China). Tests of treated or untreated AC cathodes were kept under the same conditions, such as using the same electrolyte and fixed reference electrode.

X-ray photoelectron spectroscopy (XPS) was employed to obtain information about the valence of deposited silver species on the surface of AC. The measurements were carried out using an XPS spectrometer (K-Aepna, Thermo Fisher Scientific Inc., USA). Survey scans of Ag3d, C1s, and O1s core-level spectra were taken for the most effective silver/carbon sample (Ag-50). The deconvolution of the main Ag3d peaks was performed by applying Casa XPS software and the positions were determined according to reports from the literature and empirically derived values. In addition, the peaks for silver element were calibrated with reference to C1s (284.6 eV).

Scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer was applied for analyzing the morphology of the modified and bare AC surface using S–3500N made by Hitachi. The structures magnified 40,000 times were respectively observed and compared.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was employed to detect whether silver element existed in the solution and the microorganisms of the anode and cathode using IRIS Intrepid II XSP made by Thermo Elemental company in the USA. The measurement was carried out using an ICP-OES spectrometer. Ag-75 cathode was used as the test sample because it had the highest silver content. Before testing, a certain amount of the solution taken from the cell was filtered through a 0.2 μm membrane filter. The filtered solution was used for test. A small amount of microorganisms was scraped from the surface of the electrodes