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Biofouling inhibition on nano-silver/ferrous sulfide/partly-graphitized carbon cathode with enhanced catalytic activity and durability for microbial fuel cells

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ABSTRACT

In single-chamber microbial fuel cells (SC-MFCs), microorganisms attached on air-cathode can suppress catalyst activity and electron/proton transport to lower oxygen reduction reaction (ORR) efficiency. To enhance power output of SC-MFCs, an efficient way is to improve durability of ORR catalyst by inhibiting bacterial overgrowth on cathode. Silver/ferrous sulfide/partly-graphitized carbon (Ag/FeS/PGC) catalysts are synthesized from waste pomelo skins as carbon source. Anti-biofouling mechanisms and ORR pathways of Ag/FeS/PGC cathodes are deeply clarified. Ag/FeS/PGC (Fe: Ag of 1: 0.6) exhibits the maximum power density (1361 mW m^{-2}) and the best durability with a decline of 19.9% after 90 d operation, which are better than those of Pt/C. Positively charged sites on Ag are favorable for O_2 adsorption, meanwhile the enhanced electron poverty in PGC can weaken O—O bonding in O_2, which contribute to both biofouling inhibition and ORR activity. Metallic state of FeS can be enhanced by embedding in PGC skeleton or integrating with Ag (Ag/FeS heterojunctions), which improves electrical conductivity and ORR activity of Ag/FeS/PGC. Synergistic effects among Ag, FeS and PGC contribute to the high antibacterial capacity, easy electron transport and promising ORR performance. This work provides a new idea for MFCs application using efficient antibacterial ORR catalysts.

1. Introduction

Microbial fuel cells (MFCs) as a classical and widely-studied energy recovery technology, which can fulfill the double task of wastewater treatment and electricity generation, are being explored [1,2]. In the anode of MFCs, electro-active bacteria are used to oxidize organic molecules for directly converting chemical energy into electrical energy [3,4]. Air cathode is widely used in single-chamber MFCs (SC-MFCs) to produce high power output from readily available oxygen (O_2) in air, without the need of additional aeration [5,6]. However, the electrocatalytic activity for oxygen reduction reaction (ORR) and high cost of the air cathode catalyst in SC-MFCs are the important factors that limit the practical applications [7]. The cathode is a problematic element in SC-MFCs design, because the high ORR overpotential, cathode surface biofouling and catalyst poisoning can greatly influence the SC-MFCs performance [8]. To improve the ORR performance of SC-MFCs cathodes and maximize the power density, the investigation of an efficient and stable catalyst with four-electron ($4e^-$) ORR process (dominant) is necessary [9]. To date, Pt-based materials are still recognized as the most widely used ORR catalysts, even though the further application is limited by their high cost, limited stability, poor tolerance and sluggish ORR kinetics [10].

Therefore, the Pt-free catalysts with high ORR performance and

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low cost have been investigated to find alternative ORR catalysts for Pt/C [11]. The carbon-based catalysts, including carbon black, activated carbon, graphitized carbon (GC), carbon nanofibers/nanotubes, graphene, metal oxides/carbon, metal-nitrogen-carbon (M-N-C) complexes, metal sulfides/carbon, etc, are continuously explored [12]. Recently, transition metal sulfides/carbon as a new class of catalysts has attracted lots of attention [13,14]. Wei et al. prepare the flexible carbon-coated ferrous sulfide (FeS) on carbon cloth films through the hydrothermal and carbonization methods, and the obtained FeS@C (500 °C) can be used as a promising electrode for Li-ion battery [15]. However, the studies about FeS/carbon or FeS/carbon-based catalysts for ORR are rare, which deserve further investigation [16]. As previously reported [17], an insulating layer can easily be formed on the surface of FeS, which greatly decreases the body electrical conductivity and even influences the further electrochemical reactions. Therefore, it is necessary to find ways to improve the physicochemical stability of metallic state FeS nanoparticles in carbon skeleton [15–17]. In this study, the work partly focuses on the investigation for improving both the stability and ORR activity of the carbon-supported FeS.

In SC-MFCs, one of the main factors that limit the long-term durability/stability of SC-MFCs is the overgrowth of microorganisms on the surface of cathodic ORR catalyst [6,18]. The attached microorganisms on cathode can suppress the electrical conductivity and electron transport to lower the ORR durability of the catalysts [6,18,19]. So far, many researchers have concentrated on controlling the overgrowth of microorganisms (heterotrophic aerobic bacteria) on the SC-MFCs cathodes [6,18,19]. Silver (Ag) nanoparticles loaded materials, which can exert toxic effects on the natural and environmental bacterial communities, are widely used as the antibacterial agents [19,20]. In previous studies, Ag/plain graphite [21], Ag/Fe_3O_4/C [18] and Ag/Fe/N/C [22] catalysts are successfully used as the antibacterial cathodes in SC-MFCs. The introduction of metallic Ag can effectively maintain the performance durability for a long-term operation (more than three months) by inhibiting the biofilm overgrowth on SC-MFCs cathodes [21–23]. Therefore, we intend to synthesize a new catalyst, which is more active, stable and cost-effective through the synergistic effects among Ag, FeS and partly-graphitized carbon (PGC). Furthermore, the critical mechanisms for the antibacterial reaction and ORR activity need to be investigated more deeply.

Herein, for the first time, the Ag/FeS/PGC composites are synthesized by using waste pomelo skins as the carbon source in this study. Waste pomelo skins consisted of cellulose, hemicelluloses, and pectin are considered as a promising carbon source [18], which can effectively absorb various metal ions in the sponge-like structure with abundant carbonaceous oxygen groups. The Ag/FeS/PGC composites are used as cathode catalysts in SC-MFCs, which are expected to achieve an excellent performance including high power generation and long-time durability. Ag/FeS/PGC catalysts are also expected to significantly inhibit the bacterial growth on the cathode surface and enhance the ORR activity. Ag and Fe species are firmly embedded in the skeleton of the PGC, which can greatly improve the electrical conductivity of the materials and reduce the internal resistance of SC-MFCs. The optimum proportion of Ag and Fe in Ag/FeS/PGC is investigated through structural characterizations and electrochemical measurements. The particles-embedded structure of Ag/FeS/PGC facilitates the well dispersion of Ag and FeS nanoparticles to provide abundant exposed active sites, which are energetic for enhancing the catalytic ORR activity. The close contacts among Ag, FeS and PGC can avoid the formation of inactive (oxide) layers on the FeS surface to improve the physicochemical stability of Ag/FeS/PGC. The critical mechanisms for antibacterial reaction and ORR activity are also analyzed. This study suggests a prospective strategy to explore bifunctional ORR electrocatalysts in SC-MFCs by exploiting the synergies among the individual components.

2. Experimental section

2.1. Synthesis of the Ag/FeS/PGC catalysts

The carbon precursor of the Ag/FeS/PGC catalysts was the waste pomelo skins, which were cut into small pieces (approximately 0.5 cm) and dried completely. The pomelo skins were serially impregnated with $FeCl_3$ solution (at a molar ratio of 2: 1) and CN_2H_4S solution (at a molar ratio of 1.5: 1). After ultrasonic treatment for 30 min, the paste mixture was soaked for 24 h. $AgNO_3$ solution was added into the paste mixture with Fe: Ag of 1: 0.1 (or molar ratios of 1: 0.2, 1: 0.4, 1: 0.6, and 1: 0.8) and stirred completely, and then the Ag^{+}-Fe^{3+}-S^{2-}-chelated complex was obtained after drying at 50 °C in an oven for 24 h. The obtained complex was carbonized at 900 °C for 2 h in a tubular furnace with a heating rate of 3 °C min^{-1} under highly pure N_2 flow (50–60 mL min^{-1}), and then cooled down to room temperature naturally under N_2 flow. The obtained products were ground into powder and washed with deionized water for three times. After drying, the final samples were marked as Ag/FeS/PGC-x (x = 0.1, 0.2, 0.4, 0.6, and 0.8).

2.2. Air-cathode fabrication for SC-MFCs

The cube-shaped SC-MFCs reactor with a volume of 28 mL was made of organic glass with a cylindrical chamber (diameter of 3 cm and length of 4 cm). The SC-MFCs anode was the carbon fiber brush, which was soaked with acetone overnight and washed with deionized water, and then heated at 450 °C in a muffle furnace before use [24]. The air-cathode of SC-MFCs consisted of the stainless steel mesh (SSM), gas diffusion layer (GDL) and catalyst layer (CL). The mixture of carbon black and 60 wt.% of PTFE with a mass ratio of 7: 3 was rolled onto one side of SSM, followed by heating at 340 °C for 30 min in a muffle furnace to obtain the GDL [25]. The mixture of as-synthesized Ag/FeS/PGC catalysts and 60 wt.% PTFE (with a mass ratio of 2:1) was then rolled onto the other side of the SSM as the CL and dried at room temperature overnight, and finally the air-cathode was obtained.

2.3. Setup and operation of SC-MFCs

The as-prepared Ag/FeS/PGC catalysts were loaded on the SC-MFCs cathodes with the electrode area of 7 cm^2 [18]. Commercial Pt/C (10 wt.%) was used as a reference sample under the same operation condition. Bacteria (*Escherichia coli*) originated from a stable running SC-MFCs of our research group were inoculated into the new reactors. Glucose (1 g L^{-1}) and phosphate buffer saline (PBS) consisted of NH_4Cl (0.31 g L^{-1}), $NaH_2PO_4 \cdot 2H_2O$ (3.321 g L^{-1}), $Na_2HPO_4 \cdot 12H_2O$ (10.3174 g L^{-1}), KCl (0.13 g L^{-1}), trace minerals (12.5 mL L^{-1}) and vitamins (5 mL L^{-1}) was used as neutral electrolyte (pH = 7.4) [26]. The SC-MFCs were normally operated at a constant temperature of 30 °C with a 1000 Ω external circuit resistance. The feeding solution was replaced once the voltage output down to 50 mV, which was considered as the ending of a cycle for power generation [27]. The as-prepared electrolyte with bacterial liquid and the pure electrolyte were used as the replaced feeding solution for the start-up (unstable) cycle and the stable cycle, respectively. In order to achieve the statistical soundness of experimental data, at least three reactors were parallel operated [18,27].