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Stainless steel mesh coated with MnO_2/carbon nanotube and polymethylphenyl siloxane as low-cost and high-performance microbial fuel cell cathode materials

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ABSTRACT

The use of inexpensive and high-performance cathode materials is important for constructing large-scale microbial fuel cells (MFCs) for wastewater treatment and bioelectricity production. We show that the air-breathing MFC with a MnO_2 (68%)/CNT and polymethylphenyl siloxane (PMPS) coated-stainless steel mesh cathode delivers a maximum power density of 2676 mW m^{-2} (normalized to the cathode surface area) or 86 W m^{-3} (normalized to the anode chamber volume). The cathode performance is found to be highly replied on the percentage of MnO_2 in the as-prepared MnO_2/CNT nanocomposites, in which the birnessite-type MnO_2 is uniformly formed on the exterior CNT surfaces, as revealed by the scanning electron microscopy (SEM) and X-ray diffraction (XRD) results. Furthermore, it is found that PMPS coated onto the mesh electrode offers the advantages of low cost, easy handling and low water loss and exhibits improved cathode performance as compared to polydimethyl siloxane (PDMS). These findings suggest that the cathode materials, MnO_2/CNT and PMPS in MFCs can function well as the electrocatalysts and the water-repellent gas-diffusion layer, respectively.

1. Introduction

A microbial fuel cell (MFC) is a biological reactor for bioelectricity generation, in which bacteria help to oxidize organic matter and transfer electrons to the anode, and electrons pass through an external circuit and arrive at the cathode to react with electron-acceptors (i.e., oxygen). Air-breathing microbial fuel cells (MFCs), typically characterized by using natural convection air-flow to their cathodes, are attractive for wastewater treatment applications due to their simple single-chamber construction and their unique ability to remove organic matter and generate bioelectricity. The high cost of cathode materials represents one of the significant challenges for their large-scale applications, because it is estimated to account for 47% (this value can be further raised to 75% if the membrane is removed from the cells) of MFC capital costs [1]. Such high cost is caused by the use of expensive Pt electrocatalysts, carbon cloth/paper electrode, catalyst binders like Nafion and polytetrafluoroethylene (PTFE). This prompts a growing body of research [2–10] to seek cost-effective cathode materials that are essential for manufacturing MFC on a large scale. These inexpensive materials, however once integrated into cathodes, are expected to offer even better, or at least comparable performance compared to the traditionally used expensive counterparts.

Several research groups [9–14] have previously shown that non-precious MnO_2 electrocatalysts as alternatives to Pt used in MFCs were highly efficient for catalyzing oxygen reduction reaction (ORR) and at the same time lowering overall costs. For example, Li et al. [11,12] experimentally compared the performance of a MnO_2 MFC and a Pt MFC in terms of their energy output and ability to remove organic contaminant, concluding that MnO_2 with a cryptomelane-type octahedral molecular sieve structure and doped with Co performed better than commercial Pt due to the enhanced reaction rate of ORR. Recent studies [2–4] have also paid their attention towards development of air-breathing MFCs equipped with stainless steel mesh to replace carbon cloth as the cathode catalyst support, because this material is more conductive and adjustable in addition to its low cost. Zhang et al. [2] showed that a maximum power density of 1610 mW m^{-2} was achieved for the air-breathing MFC with its cathode constructed onto stainless steel mesh and coated with polydimethyl siloxane (PDMS, which functions as the water-repellent gas diffusion layer), comparable to 1635 mW m^{-2} obtained with a carbon cloth MFC. Similar results were reported in the work [3] also using stainless steel mesh as gas diffusion electrode but coated with PTFE.

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These previous results accelerated development of MFCs for large-scale fabrication and pave the way for further cost reduction by using inexpensive cathode materials. In this contribution, we investigated the role of low-cost carbon nanotube (CNT) supported MnO_2 (MnO_2/CNT) electrocatalysts in enhancing the cathode performance and therefore the bioelectricity generation. Considerable reports [15–18] have demonstrated that low-cost carbon supported MnO_x nanoparticles exhibited remarkable catalytic activity for ORR occurring at the air-cathode of alkaline metal-air batteries and alkaline fuel cells. Here, CNT was selected as the cathode material thanks to their advantages of large surface area, good conductivity and superior electrochemical activity [19]. Furthermore, we examined the use of polymethylphenyl siloxane (PMPS) coated onto the stainless steel mesh to serve as the water-repellent gas diffusion layer. In comparison with PDMS, PMPS not only possesses the water-proof property induced by the presence of methyl groups, but also offers better stability and adhesion due to the introduction of phenyl groups that provides steric hindrance towards chain motion [20].

In order to experimentally verify the feasibility and efficacy of using MnO_2/CNT and PMPS as low-cost and high-performance MFC cathode materials, we constructed a series of air-breathing cathodes onto stainless steel mesh combined with coatings of these materials and compared their cell performance with that obtained from benchmark MFCs. The MnO_2/CNT electrocatalysts were prepared by a direct redox reaction of CNT with $KMnO_4$ at a controlled pH and characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. Because the catalytic activity of carbon supported MnO_x nanoparticles for ORR was highly sensitive to the percentage of MnO_x in the carbon material and its crystal structure [18], we also examined the effect of catalyst composition on MFC performance.

2. Materials and methods

2.1. Synthesis and characterizations of MnO_2/CNT composites

CNTs with a diameter of 10–20 nm and a length of 5–15 μm (Shenzhen NanoHarbo Co., China) were used as the catalyst supports. The preparation of CNT supported MnO_2 nanocomposites were conducted by a direct redox reaction between the CNTs and $KMnO_4$, according to the procedures described in the literature [21,22]. First, a $KMnO_4$ solution having a total volume of 200 mL was preheated to 70 °C. Then, 1.0 g of the CNTs were added to the hot $KMnO_4$ solution and left to react with stirring and at a controlled temperature of 70 °C. The pH of the reaction solution was controlled at 1.0 by adding 2 M HCl solution. Different MnO_2/CNT samples varying in the percentage of MnO_2 in the composite were obtained using different concentrations of $KMnO_4$ solution in the range from 0.01 to 0.1 M. After 6-h reaction, the complete disappearance of the violet color of MnO_4^- was observed in all samples. The resulting colorless suspension was then filtered, washed several times with distilled water until the pH approached 7.0, and dried at 100 °C for 12 h in a vacuum oven. Assuming that MnO_4^- was completely reduced to MnO_2 in all cases, we can obtain the desired MnO_2/CNT composites containing 15%, 30%, 45%, 60% and 68% of MnO_2, in relation to the initial $KMnO_4$ solution of 0.01, 0.025, 0.045, 0.075 and 0.10 M, respectively. It should be noted that when the concentration of $KMnO_4$ solution exceeded 0.10 M, incomplete reaction between the CNTs and $KMnO_4$ occurred, as evidenced from the observation of violet solution even when the reaction time lasted for 12 h.

The surface morphologies of the unmodified CNTs and the as-prepared MnO_2/CNT composites varying in the percentage of MnO_2 were examined by a LEO 1530 VP scanning electron microscope. The powder X-ray diffraction (XRD) patterns of these materials were recorded on a Bruker D8 Advance X-ray diffractometer with Cu Ka radiation (1.54178 Å).

2.2. Electrochemical characterization using a rotating disk electrode (RDE)

A glassy carbon (GC) disk electrode with a diameter of 3 mm was used as the RDE on which a thin catalyst layer was coated to form the catalyst-modified electrode. Prior to use, the bare GC electrode was first polished with emery paper and then with Al_2O_3 powders (particle sizes of 1 and 0.06 μm). The polished electrode was successively cleaned with ethanol and distilled water in an ultrasonic bath for 10 min, respectively. The catalyst-modified RDE was prepared as follows. A catalyst ink containing 5 mg of catalyst was prepared in a dilute Nafion solution (0.5 wt%, 250 μL, diluted by 2-propanol) ultrasonically for 20 min. Aliquots (2 μL) of the ink was then pipetted onto the electrode surface using a micro-syringe to form a thin catalyst layer. After air-drying for 30 min to evaporate the solvent, the RDE was transferred into the three-electrode electrochemical cell for measurements. The linear scanning voltammetry (LSV) tests were performed at room temperature in 0.1 M Na_2SO_4 solution using the prepared RDE as the working electrode, a platinum spiral as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. If not mentioned otherwise, all the reported voltages were referred to SCE. Before each test, the solution was bubbled with O_2 (99.999%) for 20 min to obtain the O_2-saturated environment. Voltammograms were recorded from 0.3 to −0.6 V with a scan rate of 10 mV s^{-1}.

2.3. Cathode preparation

A series of cathodes were prepared based on a conductive current collector, stainless steel mesh, onto which PMPS and MnO_2/CNT composites were added to function as water-repellent gas diffusion layer and catalyst layer, respectively. The stainless steel mesh (opening size of 104 μm; wire diameter of 66 μm; open area ratio of 37%; thickness of 135 μm) was purchased from Anping County Resen Screen Co., Ltd. (China). Prior to use, it was ultrasonically cleaned and degreased in acetone and ethanol successively each for 10 min, followed by rinsing with distilled water. PMPS (10 mg cm^{-2}) purchased from Guangzhou XSJ Co., Ltd. (China) was mixed with carbon black (2.4 mg cm^{-2}) to form a slurry. The slurry was then painted on one side of the stainless steel mesh that faced the air. The PDMS layer was allowed to be dried at room temperature for 30 min. Subsequently, the MnO_2/CNT electrocatalysts having different content of MnO_2 were coated on the other side of the stainless steel mesh that faced the anode solution. Before coating, the catalyst slurry was prepared by mixing 8.0 mg cm^{-2} MnO_2/CNT composites with 24.2 μL cm^{-2} 5 wt% Nafion (catalyst binder and proton conductor). In benchmarking performance of these cathodes, a control cathode was also prepared using PMPS and 5% Pt/C catalyst (5 mg cm^{-2}, Johnson Matthey). For all the cathodes, the projected cathode surface area was 2.4 cm × 3.3 cm.

2.4. MFC construction, operation and tests

Air-breathing membraneless MFCs consisting of a cathode described above and an anode were constructed with a rectangular anode chamber (made of polycarbonate) having an effective volume of 25 mL. The anode used for these MFC reactors was a piece of PPy/AQDS (anthraquinone-2,6-disulphonic disodium salt)-modified carbon felt (2.2 cm × 2.3 cm × 0.5 cm) prepared according to the procedures described previously [23,24]. All MFCs were inoculated with Shewanella decolorationis S12 bacteria which were