



Carbon Nanofiber-skinned Three Dimensional Ni/Carbon Micropillars: High Performance Electrodes of a Microbial Fuel Cell



Prateek Khare^a, Janakranjan Ramkumar^b, Nishith Verma^{a,c,*}

^a Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, 208016, India

^b Department of Mechanical Engineering, Indian Institute of Technology Kanpur, Kanpur, 208016, India

^c Center for Environmental Science and Engineering, Indian Institute of Technology Kanpur, Kanpur, 208016, India

ARTICLE INFO

Article history:

Received 5 June 2016

Received in revised form 23 September 2016

Accepted 27 September 2016

Available online 28 September 2016

Keywords:

microbial fuel cell
3D microstructured electrodes
carbon nanofibers
Ni nanoparticles
laser-ablation

ABSTRACT

Nickel (Ni) nanoparticle (NP)-doped carbon film (~1 mm thick) was prepared by the carbonization and activation of the phenol-melamine precursor-based polymeric film. The polymeric film was *in situ* dispersed with the Ni NPs during the polymerization step. Melamine served as the source of nitrogen (N) in the material. Three dimensional (3D) micropillars were fabricated on both sides of the carbon film, using laser-ablation technique. Decorated with carbon nanofibers (CNFs) using chemical vapor deposition technique, the N-enriched Ni/carbon micropillar-embedded carbon film was used as the electrode of a double chamber microbial fuel cell (MFC). The MFC generated a high open circuit potential (~0.75 V) and maximum power density (~2496 mW/m²). The maximum power density of such MFCs was approximately ten times greater than that generated using the pristine carbon film-based electrodes. The high performance of the electrodes prepared in this study is attributed to the synergetic effects of the graphitic CNFs, electrocatalytic N and Ni NPs, and 3D microstructure providing support to biofilm.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Microbial fuel cells (MFCs) are considered to be a potentially viable device for harvesting energy from wastewater. The MFCs use the electrochemical route for converting the chemical energy of the organic matter present in wastewater into electrical energy. Unfortunately, a low power generation is the major hurdle in commercializing MFCs from the bench scale prototypes [1]. In this context, most of recent studies are geared towards developing high performing electrodes for MFCs with a view to generating high power densities. A comprehensive review of such electrode materials is available [2,3]. In principle, an efficient electrode should have a good electrical conductivity with minimal charge transfer resistance (R_{ct}), biocompatibility, chemical stability, and large surface area [1–5]. Apart from these properties, electrode materials should be inexpensive and scalable.

Chemical modification of a carbon substrate with the precious noble metal catalysts is commonly used to prepare high performing MFC electrodes. Common examples of the metal catalysts are platinum (Pt) and its combination with the other noble metals such as titanium [6], ruthenium [7], and gold [8]. The noble

metal-dispersed carbon facilitates oxygen reduction reaction (ORR) at cathode. Different types of carbon substrate have been used to disperse the metal catalysts. Common examples are carbon cloth [9], carbon nanotubes (CNTs) [8,10] and carbon nanofibers (CNFs) [11]. Recently, chemical modification of the electrode materials has been performed using inexpensive transition metals such as nickel (Ni), tungsten, titanium, manganese, iron, and aluminum, and their oxides [12–17]. Such metal nanoparticles (NPs) show good catalytic and high electrical conductivity when used as electrodes in MFCs. The chemical modifications have been performed by either doping or coating the carbon substrate with metal catalysts.

A significant enhancement in the performance of MFCs has been achieved by nitrogen (N)-doping of the electrode materials [18–21]. The N hetero atoms in the electrode materials serve as electron donors, catalyzing the ORR at cathode. The hetro atoms also increase electrical conductivity at anode. Recently, the N-doped Ni-CNF has been used as an efficient electrode of MFCs, producing a high open circuit potential (OCP) (~0.89 V), current density (~7490 mA/m²) and power density (1850 mW/m²) [22].

* Corresponding author. Tel.: +91 512 2596352/7704; fax: +91 512 2590104.
E-mail addresses: vermanishith@gmail.com, nishith@iitk.ac.in (N. Verma).

Lately, expanding the geometrical surface of the electrodes from two dimensions (2D) to three dimensions (3D) has been shown to be a promising means for increasing the electrochemical performance, preferably for anode materials. Various 3D-structured materials used in MFCs, either as a substrate or an additive to the substrate, are graphene aerogels [23], CNTs [24], graphene foams [25], graphene-coated stainless steel (SS) fibers [26], CNT-coated sponge [27], carbon-coated berl saddles [28] and graphene-coated Ni foam [29]. Such materials are electro-conductive, and therefore, their use as a substrate or inclusion in the composite increases the electrical conductivity of the electrode material. The electro-conductive structures facilitate electron transfer to anode. Moreover, a 3D space (approximately few microns-dimensions) provides surface for biofilm formation at anode, thereby enhancing the interaction between microbes and anode. In contrast to 3D electrodes, the biofilm grown on the 2D flat surface of the electrode at anode has limited bacterial loading [24,25].

In the present study, laser-ablation was used to create the porous carbon micropillars of square cross-section on both sides of the Ni NP-dispersed carbon film (~1 mm thick). The laser-ablation not only exposed the *in-situ* dispersed electrocatalytic N and Ni NPs from within the carbon film, but also created a large 3D interfacial area for the growth of biofilm. To the best of our knowledge this is the first time that laser-ablation technique has been used to modify the two dimensional (2D) surface by creating the 3D microstructure on the carbon surface. Further, the fabricated micropillars were hierarchically decorated with the graphitic 3D CNFs, using chemical vapor deposition (CVD) technique. The carbon film was derived from the phenol-melamine polymeric precursor, in which the Ni NPs were *in situ* mixed. Thus, melamine served as the source of N in the synthesized electrode material, whereas the Ni NPs used as the CVD catalyst to grow the CNFs increased the electro-conductivity of the material. Thus fabricated carbon film embedded with the Ni-CNF-skinned 3D carbon micropillars was experimentally demonstrated to be the efficient electrodes of a high performing double chamber MFC.

2. Materials and methods

2.1. Materials

Phenol, nickel(II) nitrate hexahydrate ((Ni(NO₃)₂·6H₂O) (purity > 97%), potassium hexacyanoferrate (K₃Fe(CN)₆, purity > 99%), sodium acetate (CH₃COONa, purity > 98%), sucrose and other reagents, used for preparing phosphate buffer, such as sodium chloride (NaCl), potassium chloride KCl, sodium hydrogen phosphate (Na₂HPO₄) and potassium dihydrogen phosphate (KH₂PO₄) were purchased from Merck, Germany. Formaldehyde (HCHO), triethylamine (TEA), melamine (2,4,6-triamine), polyvinyl alcohol (PVA), benzene (C₆H₆) and hexamethylenetetramine (HMTA) were also purchased from Merck, Germany. Hydrogen (H₂) (purity > 99.999%) and N₂ (purity > 99.999%) gases were purchased from Sigma Gases, India. The *Escherichia coli* (*E. coli*) (K-12) culture was indigenously purchased. The reagents used to prepare the Luria Bertani (LB) medium, including tryptone and yeast extract, were purchased from Merck, India. All aqueous solutions used in this study were prepared in Milli-Q water. Proton exchange membrane (PEM, nafion 117) and the standard Pt-dispersed carbon electrode (Pt-loading = 0.5 mg/cm² and Brunauer-Emmett-Teller surface area (S_{BET}) = ~80 m²/g) were provided by Sinsil International, India.

2.2. Electrode preparation

Phenol as the monomer, melamine as the N-providing compound, and HCHO as the solvent were mixed at a fixed molar

ratio (6:2:27) in a 2-L round bottom flask at room temperature (27 ± 3 °C). The speed of the stirrer was maintained constant at 60 revolutions per min (rpm). After approximately 30 min of mixing, ~1.5-mL of TEA was mixed into the polymerization mixture and the temperature of the mixture was increased to 40 ± 2 °C. Approximately 200 mL-water, used as the polymerization reaction medium, was mixed into the solution and the mixture-temperature was increased to 70 °C. Approximately 2.5 g-HMTA as the cross-linking agent and 1.7 g-PVA as the curing agent were mixed into the solution. Approximately 9 g of Ni(NO₃)₃ salt was mixed into the solution at the early stage of gel formation before curing. After ~30 min, the heater was switched off and the reaction mixture was allowed to cool to room temperature. The produced thick solution of the cross-linked phenol-HCHO-melamine (PM) resin was then cast in a rectangular Teflon mould. The film was vacuum dried for 12 h at 80 °C to remove excess water. The dried PM film was carbonized in N₂ (inert) atmosphere at 850 °C for 2 h, converting the polymeric film into a carbon film. The produced carbon film was subjected to steam activation at 750 °C for 1 h, followed by the H₂-reduction at 650 °C for 1.5 h. The flowrate of H₂ was maintained constant at 200 standard cubic centimeters per min (sccm). The prepared Ni NP-containing carbon film samples were termed as Ni-PMC for the reference purposes in this study. Some polymeric samples were prepared without Ni for the comparison purposes. Some polymeric samples were prepared without melamine. Both types of the samples were also subjected to carbonization, activation and H₂-reduction. Such carbon film samples were termed as PMC and Ni-PFC, respectively, for the reference purposes.

The 3D structured micropillars were fabricated on the Ni-PMC carbon film by laser-ablation technique using the 30 W-power Epilog laser (Fiber Mark Fusion, USA) machine with the solid state pulsed Ytterbium source. Operating parameters of the laser machine were optimized at 1200 dots per inch, 80% of maximum power and 60% of the maximum speed, in the raster mode. A total numbers of 192 free-standing micropillars of approximately 100 μm height and 500 μm × 500 μm cross-section were fabricated over the 20 mm × 10 mm film-area. The distance between two adjacent structures was fixed at ~500 μm. The microstructures were also produced on the other side of the film. Some samples of Ni-PMC were not laser ablated for the comparison purposes.

The CNFs were grown on both types of the Ni-PMC samples, i.e., with and without micropillars, by CVD technique, for the comparison purposes. The CVD was performed at 800 °C for 2.5 h, using the benzene vapor-saturated N₂ gas at 240 sccm-flowrate. The CNF-grown Ni-PMC samples with and without laser ablation (or micropillars) were termed as Ni-PMC-L-CNF and Ni-PMC-CNF, respectively. Previous studies have also used NPs of various transition metals for growing the CNFs [16,22,30].

2.3. Surface characterization of prepared electrodes

The fabricated electrode samples were characterized using several analytical and spectroscopic techniques including the Brunauer, Emmett and Teller (BET) surface area (S_{BET}) and pore-size distribution (PSD) measurements, C-H-N elemental analysis, field emission scanning electron microscope (Fe-SEM) (MIRA 3 LM, TESCAN, Czech Republic), energy dispersive X-ray (EDX) spectroscopy, transition electron microscopy (TEM) (FEI Technai, 20 U Twin, United States), and X-ray photoelectron spectroscopy (XPS) (FEI Inc., PHI 5000 Versa Prob II, United States). The S_{BET}, PSD, and total pore volume (V_T) of the prepared electrodes were determined using the Autosorb-1C (Quantachrome, United States) instrument and N₂ as the probe molecule at 77 K. The S_{BET} was calculated using BET isotherms for P/P₀ < 0.1. Micropore volume (V_{micro}) was

Download English Version:

<https://daneshyari.com/en/article/6472865>

Download Persian Version:

<https://daneshyari.com/article/6472865>

[Daneshyari.com](https://daneshyari.com)