AN ABIOTICALLY CATALYZED GLUCOSE FUEL CELL BASED ON DECORATED BUCKYPAPER

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ABSTRACT

Highly efficient supported catalyst layers based on metallic/bimetallic (Pt, Au-Pt) nanoparticles decorated-single walled carbon nanotubes (SWNT) on Buckypaper (BP) for direct glucose fuel cell are presented here. The electrodes have been tested in mixed-reactant biofuel cell. High glucose-tolerance, stability and catalytic activity are observed for the oxygen reduction reaction (ORR) that resulted in a high limiting current density for Pt-NPs/BP-based electrode in a phosphate buffer solution (0.2 M PBS, pH 7.4) containing 10 mM glucose, in comparison to AuPt/BP-based electrode which is used as anode. The ability to realize the potential of BP-based biofuel cell has been demonstrated for this kind of electrodes. This novel abiotic catalytic system approaches a power density of 80 μA cm^{-2}, indicating that BP as a promising support material for biofuel cell electrodes to power small electronic medical devices.

KEYWORDS: carbon nanotubes, buckypaper, surfactant, glucose biofuel cell, supported electrocatalyst, SWNTs, nanocatalyst, oxygen reduction reaction

INTRODUCTION

Generally, there are two kinds of biofuel cell designs: one is called biotic design, and the other is called abiotic. The first relies on biocatalysts (e.g. enzymes and microorganisms). The other utilizes abiotic catalyst (e.g. inorganic or precious metal-based catalysts). The limited progress on the abiotic fuel cells is due to the poisoning effect, which results in a significant decrease in catalytic activity. Therefore most of the focus has been on utilizing biotic systems. Long-term performance, low power density and insufficient electrode design however, have been hindering the progress for many of biotic systems. Recently, there have been distinguished achievements made regarding the abiotic design, but these were done in an alkaline medium. It is based on an abiotic anode that was fabricated from inexpensive chemical dyes while a commercial air-breathing electrode was used as the cathode. The fuel cell was able to obtain more than 2.5 $mWcm^{-2}$ at 0.3 V [1].

The abiotic mixed-reactant approach could greatly simplify the fuel cell design for implantable device, but the electrocatalysts still need to be tolerant to the presence of the other reactant (e.g. oxygen or glucose). Since the fuel cells might be implanted they must run under physiological conditions as well [2,3]. With non-tolerant catalysts, glucose would directly transfer its electrons to the available oxygen and no power could be provided to an external circuit.

BP is a self-supported mat of entangled assemblies (ropes and bundles) of carbon nanotubes (CNTs) forming a well-defined membrane-like black film. It was originally developed to handle CNTs in a simpler and more efficient manner [2]. BP has several advantages over carbon nanotube films prepared by other methods. BP is highly porous, flexible, self-supporting, electrically conductive and can be formed to almost any arbitrary shape and size. Some of the properties of BP have been investigated for quite some time, but their potential use as fuel cell electrodes started relatively recently[2,3].

In this paper, we report on the fabrication of novel nanoparticles decorated BP-based electrodes as efficient abiotic cathodes and anodes. These BP-based electrodes have been tested by various electrochemical methods to check their suitability as electrode support materials for biofuel cell application.

EXPERIMENTAL

Multi-walled carbon nanotubes (MWNTs) from Bayer AG (Baytubes) and nylon membrane filters with pore sizes of 0.45 μm (Whatman, UK) were used during BP fabrication [3]. Functionalized single-walled carbon nanotubes (f-SWNTs) (3% COOH, Nanoarray) have been used as nanocatalyst support. Non-ionic surfactant Triton X-100, Brij 30, and chloroplatinic acid hydrate were purchased from Sigma Aldrich. Hydrogen tetrachloroaurate (III) hydrate was obtained from Chempur (Karlsruhe, Germany). Nanoparticles decorated-f-SWNTs was prepared using a water in oil (W/O) microemulsion method as described by Habrioux et al. [4] and then dispersed in Dimethylformamide (DMF). Finally the catalyst ink is filtered on BP to make hydrophilic catalyst layer with a very low amount of total noble metal content (about 0.125 mg cm^{-2}).

All electrochemical measurements were performed with a computer controlled potentiostat/galvanostat (Autolab). A stirring of the solution was applied to the cell during BP-electrode testing. We also conducted experiments with cells without mechanical stirring, All experiments were conducted at room temperature and ambient pressure. Pt wire was used for electrode contact to minimize corrosion interference. Saturated calomel electrode (SCE, 0.66 vs. RHE) and platinum plate were used as reference electrode and counter electrode respectively.

RESULTS AND DISCUSSION

Typical MWNTs -film with thicknesses 20 μm were prepared. The BP has a nanoporous surface structure with a BET specific surface area of 290 m^2 g^{-1} and a wide pore size distribution (SD ca. 20 nm) with an average pore sizes of 34 nm. The BP film is highly electrically conductive with conductivities in the order of 25 S cm^{-1}. The surface structure has been

investigated using the SEM and typical images are displayed in Fig. 1. The mesoporous structure of the BP-film is clearly visible. TEM images of nanoparticles decorated- SWNTs are shown in Fig. 2, generated using a (W/O) microemulsion method.

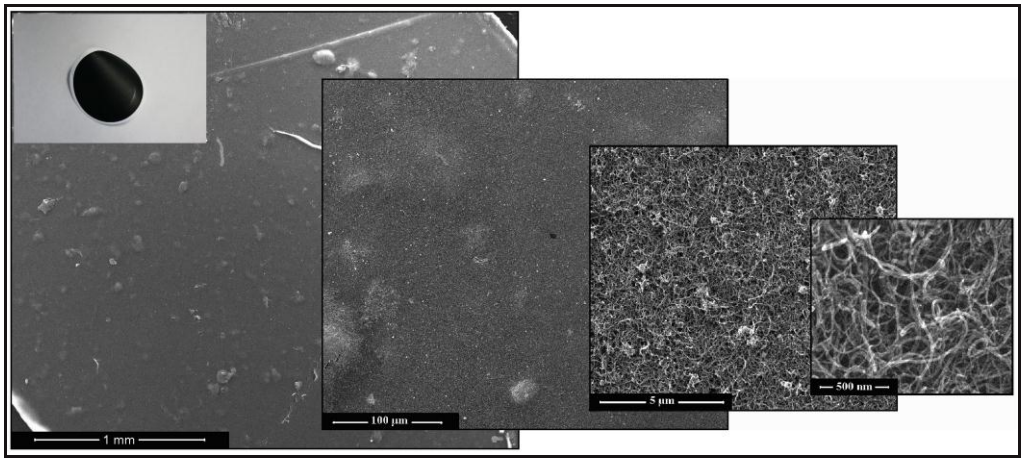

Figure 1: SEM images of BP supported on a nylon membrane with different magnifications of the porous surface. A photograph of a MWNTs-BP deposited on a nylon membrane filter is displayed in the upper left corner.

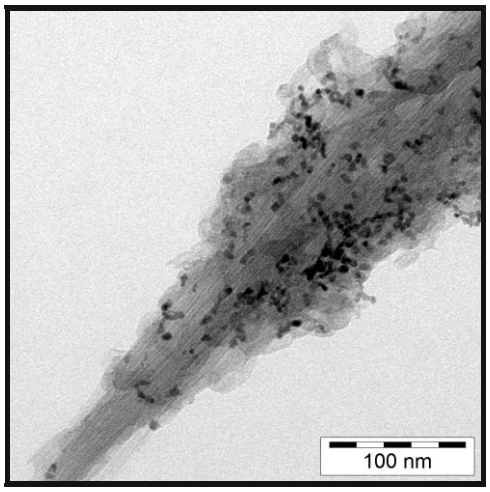

Figure 2: TEM images of 40wt. % Pt-NPs/f-SWNTs synthesized by a W/O microemulsion method.

The electrochemical characterization (Fig. 3) for biotic BP-based cathodes were performed to examine the ORR catalytic activity of electrocatalysts in phosphate buffer solution (0.2 M, pH 7.4) and to verify their glucose-tolerance as well in the presence of 10 mM glucose.

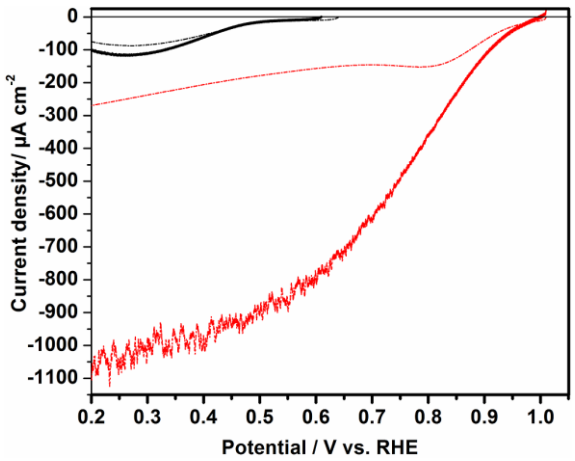

Figure 3: Potentiodynamic measurements for the ORR activity of Pt-NPs/BP (red) and AuPt-NPs/BP (black) based electrodes in O_2- saturated phosphate buffer solution (0.2 M, pH 7.4), in presence of 10 mM glucose, using a scan rate of 1.0 mV s^{-1}, with mechanical stirring (1000 rpm, solid line) and without mechanical stirring (dashed line), at 25°C.

Fig. 3 shows the ORR catalytic behaviors using potentiodynamic measurements for Pt/PB-based electrode and AuPt/BP-based electrodes and they can be directly compared as are follows:

- A fast kinetic reaction on the Pt/BP-based electrode with high onset potential can be observed, when compared to AuPt/BP-based electrode.
- The ORR is more favorable on Pt/BP-based electrode than on AuPt/BP-based electrode at 0.5 V vs. RHE.
- The magnitude of the ORR diffusion limiting current obtained with the Pt/PB-based electrode at 0.35 V vs. RHE is higher by a factor of about 10 than for AuPt/BP-based electrode.
- Lower overpotentials occur for the Pt/BP-based electrode which might be attributed to a lower poisoning effect.

In summary, potentiodynamic measurements were clearly able to demonstrate that the Pt/BP-based electrode has a better catalytic activity for the ORR and a higher stability during repetitive potential scans (data not shown) compared to AuPt/BP-based electrode.

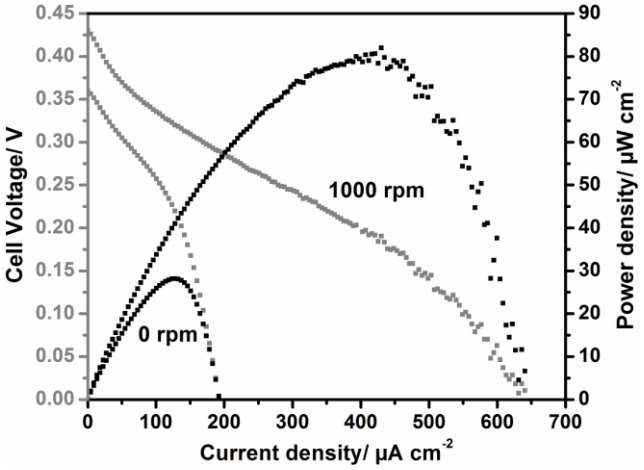

Figure 4: Galvanodynamic polarization curves for BP-based biofuel cell in phosphate buffer solution (0.2 M, pH 7.4) saturated with oxygen, in presence of 10 mM glucose, using a scan rate of 1µA/s, without mechanical stirring and with mechanical stirring (1000 rpm) at 25°C.

In Fig. 4 the polarization curves for BP-based biofuel cell in phosphate buffer solution saturated with oxygen, containing 10 mM glucose, using a scan rate of 1µA s^{-1}, and with or without mechanical stirring. This result exhibits stability and high power density in the range of 80 µA cm^{-2} which is very promising result so far for abiotic biofuel cell.
In summary this superior performance can be attributed to the structural properties, electrical properties, low impurities of BPs and their high mesopore (2-50 nm) area approx. 340 m^2g^{-1} that enhanced the laminar flow.

CONCLUSION

Here the first abiotic fuel cell system based on decorated BP are presented. The high performance of this BP-based biofuel cell is believed to be due to high mesopores area generated from and consistent with MWNTs in BP provided a laminar flow and sufficient O_2 diffusion . Since the BP has a high electrical conductivity with a very low contact resistance, this might assist electron transfer pathway. As a result, almost the entire surface of the Buckypaper was accessible electrochemically and can be used for active site. Furthermore, its microstructure, e.g. alignment, porosity, pore size and thickness can be tailored to achieve the required conditions for the optimized catalyst layer for the fuel cell applications.The high potential of f-SWNTs as catalyst supports for electrodes in fuel cells is demonstrated by make a hydrophilic catalyst layer with a very low amount of total noble metal content (about 0.125 mg cm^{-2}). Further investigations of device performance with respect to long-term-stability and biocompatibility of BP based electrodes for various biofuel cell and biosensor applications are currently in progress.

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