

NOVEL NANOTUBE BUCKYPAPER AS ELECTRODE MATERIAL FOR FUEL CELL APPLICATIONS

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Abstract: We present novel supported electro-catalytic systems based on metallic/bimetallic (Pt, Au-Pt) nanoparticles decorated carbon nanotubes Buckypaper (BP), and Bilirubin Oxidase (BOD) decorated Buckypaper-based biocathodes in neutral medium for direct glucose fuel cell. The electrodes have been tested for their suitability in mixed-reactant biofuel cell applications in a phosphate buffer solution (0.2 M PBS, pH 7.4) containing 10 mM glucose by applying a Potentiodynamic polarization method. High efficiency, stability and catalytic activity are observed for the Oxygen Reduction Reaction (ORR) that resulted in a high limiting current density for this biocathode. The ability to catalyze electrode reaction via a mediatorless (direct) electron transfer has been demonstrated. The electron is transferred directly from the BP-based electrode to the substrate molecule (O_2) via the active site of the enzyme (BOD). Furthermore, enhanced glucose-tolerance and catalytic properties are demonstrated in regards to ORR for abiotic (Pt nanoparticles) BP-based cathode in comparison to AuPt/BP-based electrode. Our decorated-BP exhibits superior properties making it a promising support material for biofuel cell electrodes to power small devices and biosensors.

Keywords: Carbon nanotubes, buckypaper, surfactant, glucose biofuel cell, supported electrocatalyst, biocathode, nanocatalyst, Oxygen Reduction Reaction.

INTRODUCTION

In contrast to conventional direct fuel cells, the challenge of an implantable direct glucose fuel cell is that it must run under physiological conditions while the fluid contains both reactants (glucose and oxygen) in one compartment. These so-called mixed-reactant fuel cells are considered as an attractive power source and are in high demand for small medical devices (e.g. cardiac pacemaker) and biosensors. For these types of abiotic fuel cells, still need further improvement before implementation, but improvement has been shown regarding the cell design demonstrating electricity obtained from a high energy glucose molecule [1].

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. 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 impressive 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 [2].

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 would be implanted they must run under physiological conditions as well. Furthermore the catalytic systems have to be highly selective for the formation of the desired product, especially for the cathodic reaction (ORR) to suppress the formation of hydrogen peroxide which normally enhances the corrosion of the electrode material and polymer membrane [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 CNTs forming a well defined membrane-like black film. It was originally developed to handle CNTs in a simpler and more efficient manner [4]. 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 MWNT BP have been investigated for quite some time, but their potential use as fuel cell electrodes [3] and sensor devices started relatively recently.

In this paper, we report on the fabrication of a novel enzyme decorated BP-based biocathode and nanoparticles decorated-BP as efficient abiotic cathodes and anodes. These BP-based electrodes have been tested by various electrochemical methods and found superior in comparison to well-known electrodes based on carbon black as electrode support material.

EXPERIMENTAL

Multi-walled carbon nanotubes (MWNTs) (Baytubes C 150-HP, Bayer Material Science AG, Germany) have been functionalized (f-MWNTs) according to the procedure reported in previous work [4]. Nylon membrane filters with pore sizes of 0.45 μm (Whatman, UK) were used during BP fabrication [4]. Bilirubin oxidase (BOD, Amano, [EC 1.3.3.5] from *M. verrucaria*) was obtained from Amano Pharmaceutical Co., Japan and was used without further purification. Mediator (2,2'-azino-bis(3-ethylbenzothiazoline)-6-sulfonic acid) (ABTS), non-ionic surfactant Triton X-100, and chloroplatinic acid hydrate were purchased from Sigma Aldrich. Hydrogen tetrachloroaurate (III) hydrate was purchased from Chempur, Germany. All electrochemical measurements were performed with a computer controlled a Bio-Logic 6-channel VMP2-potentiostat/galvanostat. No stirring or agitation of the solution was applied to the cell during BP-electrode testing. We also conducted experiments with cells under mechanical stirring, and the performance of the cells was greatly improved. All experiments were conducted at room temperature and ambient pressure. Pt wire was used for electrode contact to minimize corrosion interference.

RESULTS AND DISCUSSION

Typical BP-film is 41 mm in diameter with thicknesses ranging between 1 μm and 200 μm were prepared. The BP has a highly porous surface structure with a BET specific surface area of 290 $\text{cm}^2 \text{g}^{-1}$ and has high wide pore size distribution (± 20 nm) with an average pore sizes of 34 nm. The BP film is highly electrically conductive with conductivities in the order of 2000-4000 S m^{-1} . The surface structure has been investigated using the HRSEM and typical images are displayed in Fig. 1. The mesoporous

structure of the BP-film is clearly visible. TEM images of nanoparticles decorated f-MWNTs generated using a water in oil (W/O) microemulsion method (Fig. 2) as described by Habrioux et al. [5].

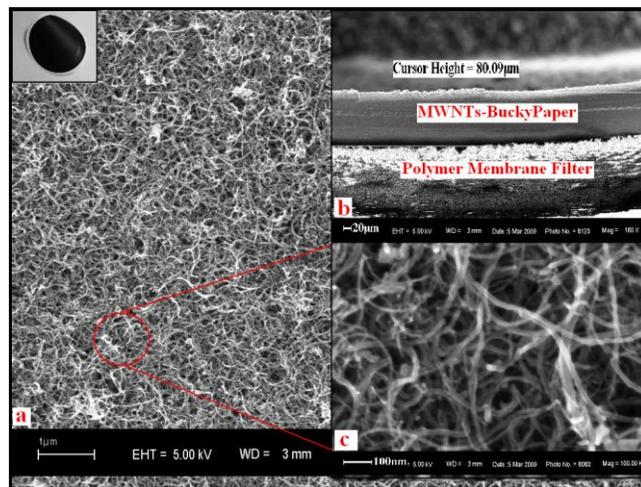


Fig. 1: SEM images of CNT-BP supported on a nylon membrane (a), a cross section view (b) and high magnification images of the porous surface (c). A photograph of a MWNTs-BP deposited on a nylon membrane filter is displayed in the upper left corner.

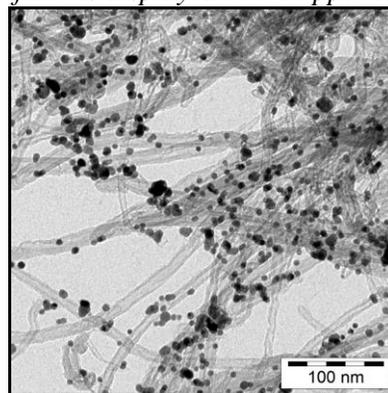


Fig. 2: TEM images of 40wt. % Pt-NPs/MWNTs synthesized by a W/O microemulsion method.

A) Abiotic anode electrocatalyst: Bimetallic AuPt nanoparticles supported on MWNTs with a 40 wt. % metallic loading were prepared by a W/O microemulsion technique. These nanoparticles exhibit a high catalytic activity for the glucose oxidation reaction [5]. Since no severe thermal treatment was necessary, particle agglomeration was avoided. A key factor of this preparation technique is that the nucleation of both metals, Pt and Au occurs concomitantly. The electrochemical responses of 40 wt. % Pt or ($\text{Au}_{70}\text{Pt}_{30}$) nanocatalysts supported on MWNTs respectively are shown in Fig. 3. The cyclic voltammetric measurements were performed in 0.1 M NaOH to electrochemically define the surface

composition from reduction current region of formed metal oxides. Electrochemical measurements were taken using a mercury/mercuric oxide reference electrode (570 mV vs. reversible hydrogen electrode) and a standard glassy carbon working electrode. The scans were repeated several times to ensure reproducibility. The results reveal:

- The oxide reduction peaks for Au at +200 mV and Pt at -300 mV vs. Hg/HgO are characteristic for Au-Pt bimetallic alloyed nanoparticles and reflect well-defined surface alloyed composition.
- The relatively small H-adsorption/H-desorption waves of platinum in AuPt/f-MWNTs confirm additionally the well defined chemical mixing of Au and Pt (bimetallic alloy).
- A high electrochemical double layer capacitance was found for both MWNT-based electrocatalysts.

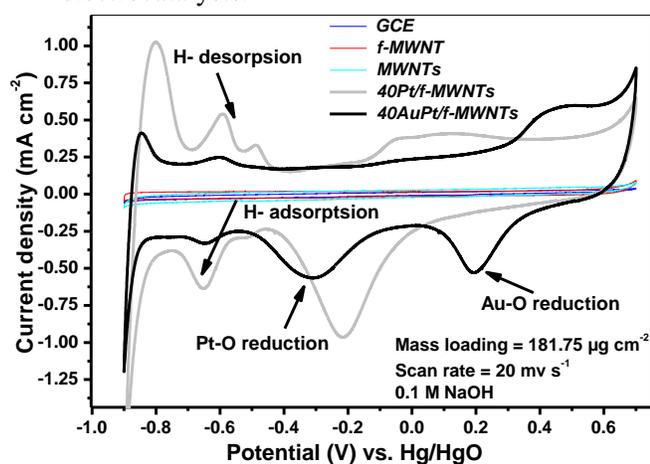


Fig. 3: Cyclic voltammograms of metallic Pt and bimetallic Au-Pt electrocatalysts on f-MWNT. The scans were performed in 0.1 M NaOH at a scan rate of 20 mV/s. Total mass loading 181.76 $\mu\text{g cm}^{-2}$.

B) Abiotic BP-based cathode: To overcome the sluggish kinetic response in ORR electrocatalysts at neutral medium we tested the ORR electrocatalytic activities of abiotic BP-based electrodes (Fig. 4) and respective electrocatalysts to verify their glucose-tolerance in phosphate buffer solution (0.2 M, pH 7.4) in the presence of 10 mM glucose. Fig. 4 shows the ORR behavior using Potentiodynamic measurements for Pt/PB-based electrode and AuPt/BP-based electrodes and their electrochemical responses. They can be directly compared as are follows:

- A fast kinetic reaction on the Pt/BP-based electrode can be observed when compared to a plateau-like diffusion process for AuPt/BP-based electrode.
- The ORR is more favorable on Pt/BP-based

electrode than on AuPt/BP-based electrode at 300 mV vs. Hg/HgO.

- The magnitude of the ORR diffusion limiting current obtained with the Pt/PB-based electrode at -300 mV vs. Hg/HgO is higher by a factor of about 1.23 than for AuPt/BP-based electrode.
- The half wave potential obtained with the AuPt/BP-based electrode is 166.3 mV vs. Hg/HgO, lower than Pt/BP-based electrode with negative potential shift of about 50 mV vs. Hg/HgO, which means that the first electrode is mass transport limited.
- Lower overpotentials occur for the Pt/BP-based electrode which might be attributed to a lower poisoning effect of phosphate ions and glucose on Pt nanoparticles than on AuPt nanoparticles.

Here, Potentiodynamic measurements clearly 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.

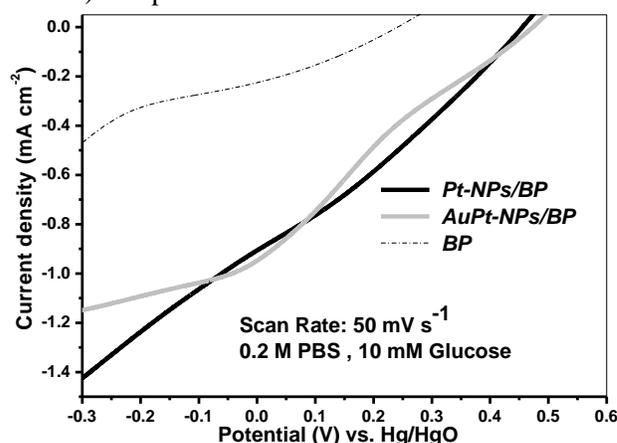


Fig. 4: Potentiodynamic measurements for the ORR activity of Pt/PB and AuPt/BP-based electrodes in phosphate buffer solution (0.2 M, pH 7.4) saturated with oxygen, in presence of 10 mM glucose, using a scan rate of 50 mV/s, without mechanical stirring.

C) BP based-biocathodes: To probe the effectiveness of BP as an electrode support material, two BOD BP-based biocathodes (geometric area 2.25 cm^2) were prepared. Both of them were 15 μm thick and were prepared using BOD as a biocatalyst immobilized on MWNTs in phosphate buffer solution (0.2 M, pH=7.4). The first was prepared without a mediator (ABTS) and the second was prepared in the presence of ABTS, which are noted as BP-based biocathodes normally after adsorption onto BP. The following can be deduced from Fig. 5:

- A fast kinetic reaction occurs for both BP-based electrodes with a well-defined diffusion-limiting

plateau. The peak at 465 mV vs. Hg/HgO is assigned to the reduction of ABTS [5].

- The BP-based biocathode in the presence of ABTS exhibits a slightly positive ORR onset potential shift (about 50 mV) in comparison to the ORR onset in the absence of ABTS.
- The ORR activity is similar on both BP-based biocathodes. There was a slight potential shift (20 mV) at 175 mA cm⁻² vs. Hg/HgO. Fig. 5 demonstrates the reduction of oxygen follows a 4-electron mechanism for both electrodes (confirmed by Tafel plot).

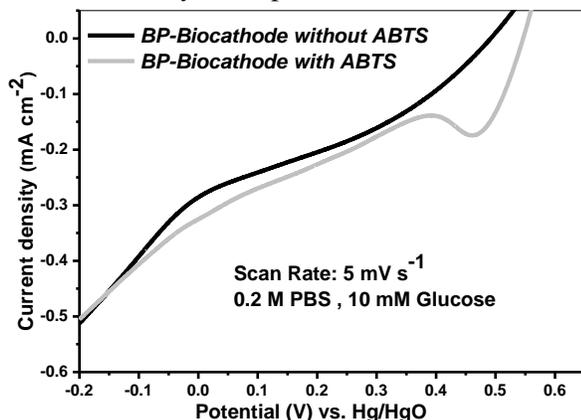


Fig. 5: Potentiodynamic measurements for the ORR activity on different biocathodes: BOD-BP without ABTS (black line) and with ABTS (grey line) in phosphate buffer solution (0.2 M, pH 7.4) saturated with oxygen, in the presence of 10 mM glucose, using a scan rate of 5 mV/s, without mechanical stirring.

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 m²g⁻¹. Therefore a high current density and high enzyme utilization can be achieved. Moreover, the activity enhancement of BP-based biocathode, especially in the absence of mediator (i.e. direct electron transfer) could be explained on the basis of specificity and accessibility for adsorbed BOD on BP to oxygen molecules resulting in increasing the ORR kinetics.

CONCLUSION

The high catalytic efficiency of BP-based biocathode is believed to be due to (1) the tailor-made microstructure generated from and consistent with MWNTs provided sufficient O₂ diffusion and electron transport path and relatively large surface area and accessibility for supporting enzymes; and (2) since BP has a high electrical conductivity the enzyme might be adsorbed on the most efficient contact zones for the

electronic and electrolytic pathways of the Buckypaper materials (i.e. contacting the electrolyte membrane directly) and might assist direct electron transfer. 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.

Finally, we conclude that decorated MWNT-BPs exhibit an improved resistance against corrosion as well as better mass transport properties compared to the currently commonly used carbon black support material and are promising electrocatalysts.

Our results demonstrate the high potential of MWNTs as catalyst supports for electrodes in fuel cells. The shape and size of the electrodes can be adjusted to specific needs and integrated into devices. Further investigations of device performance with respect to biocompatibility of BP based electrodes for various fuel cell and sensor applications are currently in progress.

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