

A HIGHLY EFFICIENT BUCKYPAPER-BASED GLUCOSE FUEL CELL FOR MICRO-ENERGY HARVESTING

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Abstract: We present a novel direct glucose fuel cell (DGFC) based on metal nanoparticles-decorated buckypaper (BP) electrodes. The preparation of electrocatalysts, based on functionalized multi-walled carbon nanotubes (f-CNTs) and Pt and Au-Pt nanoparticles (NPs), are reported. Pt-NPs favors a higher ORR electrocatalytic activity compared to AuPt alloyed NPs and exhibits additionally a higher glucose-tolerance in a phosphate buffer solution (pH 7.4) containing glucose at 25 °C.

Furthermore, the potentiodynamic polarization curves of DGFC based on the decorated-BP electrodes are clearly demonstrated the significant improvement and performance enhancement under O₂-saturated condition. This abiotic approach is able to reach the highest power density so far.

Keywords: Carbon nanotubes, buckypaper, glucose biofuel cell, electrode support, cathode, nanocatalyst, oxygen reduction reaction.

INTRODUCTION

For implantable medical devices, the DGFC is considered to be an attractive micro-power source [1]. This mixed-reactant approach could greatly simplify the fuel cell design for such devices, but the electrocatalysts still need to be tolerant to the presence of the other reactant (e.g. oxygen or glucose) because with non-tolerant catalysts, glucose would directly transfer its electrons to the available oxygen and no power could be generated. This fuel cell also 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 [2].

As a biofuel, glucose as abundant and small organic molecule found to be very promising for low-temperature, one-compartment, DGFCs, and it has been the subject of many studies [1]. Normally large cathodic overpotential losses or depolarization (i.e. due to mixed potentials resulting from mixed reactants) and slow ORR kinetics occur at neutral medium (pH 7.4). One possibility for overcoming these difficulties is to conceive new efficient and selective electrocatalysts for the oxygen reduction, but inactivity towards glucose oxidation. Nowadays, several ORR electrocatalysts based on Pt, oxophilic metals (such as Pd, Co, Ni, Fe,

Cu) and Ag as well, even they are much lower oxophilic than Pt, have been investigated [1] for this purpose.

The overall electrocatalytic processes at the electrode are rather complex and involve a number of adsorbed intermediates and by-products. Up to now, most electrocatalysts are based on Pt or its alloys, which make the devices expensive and unsuitable for large scale applications. Replacing or reducing the amount of Pt, while maintaining the catalytic activity is an important issue for developing novel catalysts [3] and new supporting substrates [2,4]. In order to reduce Ohmic drops, as well as mass transport and manufacturing problems deriving from the use of thick electrodes, catalysts for glucose fuel cells are usually based on non-supported active noble metals [1]. It is also well known that the occurrence of catalyst agglomeration limits their effectiveness and utilization in fuel cell systems [2]. Recently carbon nanotubes (CNTs) have been explored as promising support material for fuel cell catalysts due to their high stability and unique mechanical properties [2,4]. Moreover the mesoporous network of nanotubes can assist the developing a laminar flow and combined with their excellent electronic conductivity allows a quick charge transport and easy accessibility of the reagent molecules to the catalytic active sites enabling better catalytic performance of CNT supported nanocatalysts compared to carbon black supported one [2,4].

Therefore, it is expected that CNT-based electrodes

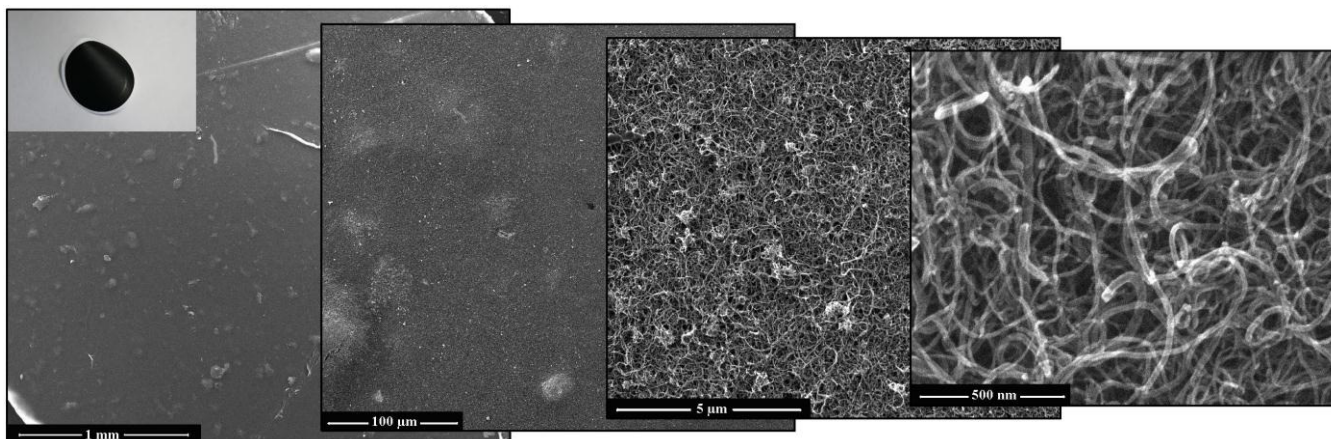


Fig. 1: SEM images of CNT-BP from low to high magnifications for the porous surface. A photograph of a BP deposited on a nylon membrane filter is displayed in the upper right corner.

would have a better long-term stability compared to carbon black supported electrocatalysts. The buckypaper (BP) fabricated from commercially available Multi-Walled Carbon Nanotubes (MWCNTs) is used before as electrode support material [2,4]. BP is highly mesoporous, mechanically stable and electrically conductive material.

In this work, we investigate the preparation and the electrochemical activity of f-CNT supported Pt and bimetallic Au-Pt nanoparticles as potential electrocatalysts for the cathodic oxygen reduction reaction and anodic glucose oxidation respectively. A comparison between them is made with respect to the ORR catalytic activity and the glucose-tolerance. Additionally, CNT BP was utilized as electrode support material, after decoration with the above electrocatalysts. Finally a complete biofuel cell test has been performed based on the NPs-decorated buckypaper-based electrode in a phosphate buffer solution containing glucose.

EXPERIMENTAL

MWNTs (Baytubes C 150-HP, Bayer Material Science AG, Germany) have been used to fabricate the BPs with a thickness of 20 μm as reported in previous work [4]. F-CNTs used as support for the 40 wt. % nanoparticles generated using a water in oil (W/O) microemulsion method [3].

All electrochemical measurements were conducted with a computer controlled Autolab potentiostat/galvanostat at room temperature and ambient pressure. BP electrode (2 cm^2) was electrically contacted with Pt wire using conductive carbon cement (Leit-C). A KCl saturated calomel electrode (SCE) and a glassy carbon plate (1 cm^2) were used as reference and counter electrodes respectively.

The surface areas of the electrocatalysts were determined using the electrochemical stripping of

an adsorbed CO monolayer, which is a commonly used method to characterize carbon supported Pt and Pt-based alloy electrocatalysts. Thus, normalizing the ORR catalytic activity with respect to the real surface areas of investigated nanocatalysts can be achieved. The Linear-sweep voltammetry was conducted at a rotation rate of 2500 rpm using a glassy carbon rotating disc electrode (3 mm diameter) in O_2 -saturated 0.2 M phosphate buffer solution (pH 7.4), in the absence and presence of glucose. The cyclic voltammetry were performed in a nitrogen-purged electrolyte, to clean and activate the electrode surface.

RESULTS AND DISCUSSION

The electrical conductivity of BP found to be approx. 25 S cm^{-1} , which is higher than the reported value for carbon black of 5 S cm^{-1} . The surface structure has been investigated using the HR-SEM and typical images are displayed in Fig. 1. The mesoporous structure of the BP surface is clearly visible with a wide pore size distribution (+/- 20 nm) with average pore sizes of 34 nm. Fig. 2 shows the TEM images of high density metal nanoparticles-decorated f-CNTs generated using a water in oil (W/O) microemulsion with less than 10 nm sizes.

The evaluation of the electrochemical activity:

I) Cyclic-voltammetry: The voltammograms in N_2 -purged phosphate buffer solution for the Pt/f-CNT and $\text{Au}_{70}\text{Pt}_{30}$ /f-CNT electrocatalysts are shown in Fig. 3a. They were generated after the 20th potential cycle at a sweep rate of 20 mV s^{-1} . $\text{Au}_{70}\text{Pt}_{30}$ /f-CNT catalyst was used for comparison because it is already known as an effective catalyst for glucose oxidation [3]. Characteristic peaks for hydrogen adsorption and desorption in this figure emerge between 0.1 and 0.35 V vs. RHE.

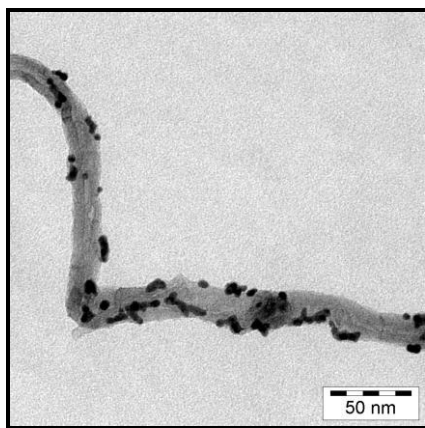


Fig. 2: TEM images of 40wt. % AuPt-NPs/MWNTs synthesized by a W/O microemulsion method.

These waves are strongly attenuated on the Pt-Au alloy because these peaks are not developed in Au metal atoms at the surface [3]. Moreover, the double layer region is not well defined as observed previously in NaOH [3, 4]. In these curves, the reduction peak of platinum oxides species centered at approx. 0.7 V vs. RHE for Pt-NPs/f-CNT, but there is a negative shift to approx. 0.6 V vs. RHE on AuPt/f-CNT.

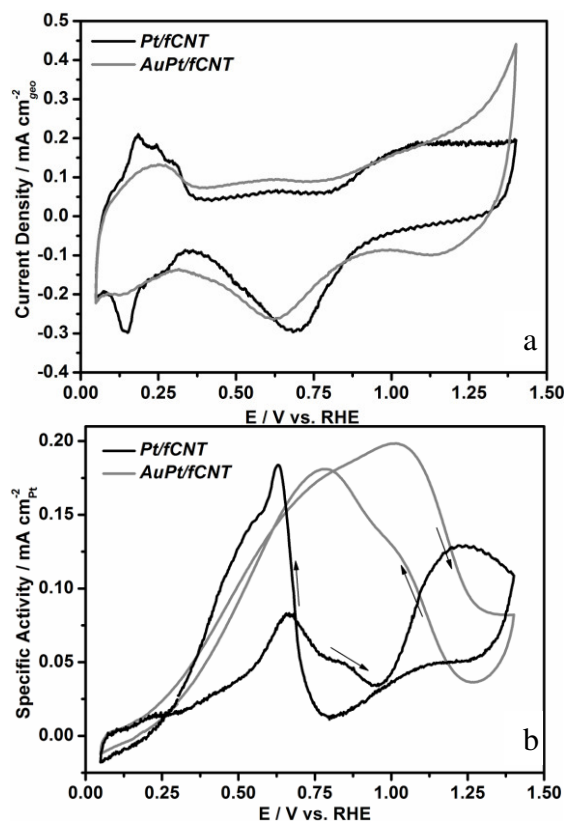


Fig. 3: Cyclic-voltammograms for the electrocatalysts, in a N_2 -purged phosphate buffer solution in the absence of glucose using sweep rate of 50 mV s^{-1} (3a) and in the presence of 0.2 M glucose are in 3b using sweep rate of 20 mV s^{-1} (3b), at 25°C .

This can be ascribed to the Au content in the catalyst which might facilitate the strong binding of oxygen on alloyed nanocatalyst.

It can be clearly observed in Fig. 3b (curves generated after 5 potential cycles using a scan rate of 20 mVs^{-1} at 25°C) that the addition of 0.2 M glucose induces a Faradic oxidation current for glucose on all catalysts. On the Pt supported catalyst the oxidation wave on the positive-going potential is limited in the double-layer region between the onset potential value (approx. 0.25V vs. RHE) and 1.0 V vs. RHE, due to the formation of platinum oxide species. This process is recovered again after the negative scan has been performed. In contrast to this, glucose oxidation occurred earlier at 0.15 V, indicating Au sites nucleate oxygenated species at low potentials and producing a reduced overpotential for glucose electro-oxidation potential, as expected. The oxidation potential sustained up to 1.25 V vs. RHE on the Pt-Au alloy was due to the fact that glucose oxidation is still carried out on Au-OH species which is in synergy with Pt-OH species.

In summary, cathode nanocatalyst (Pt/f-CNT) is less active towards glucose electro-oxidation compared to AuPt/f-CNTs anode catalyst.

II) Linear sweep voltammetry: In order to evaluate the degree of selectivity (tolerance) towards ORR, carbon supported Pt and Pt-Au nanocatalysts were measured under well-defined hydrodynamic conditions. Fig. 4 shows these results on Pt/f-CNT and $Au_{70}Pt_{30}$ /f-CNT catalysts in O_2 -saturated 0.2 M phosphate buffer solution (pH 7.4) in the absence (dashed curves) and the presence (solid curves) of 0.2 M glucose at 25°C . In the absence of glucose, Pt/f-CNT catalyst has a higher ORR activity compared with $Au_{70}Pt_{30}$ /f-CNT. It is clear that the former catalysts are more active than the alloy supported catalyst, first because for the later the diffusion-limiting current (0.35 to 0.1 V vs. RHE) is lower by factor 2. This might be due to the hydrogen peroxide channel pathways which are more favorable on the alloy nanocatalyst. In other hand, the presence of 0.2 M glucose, Pt/f-CNT catalyst showed a higher resistance towards glucose, since a depolarization of approx. -70 mV is observed, with concomitant decrease of the limiting current density. However, as expected, on $Au_{70}Pt_{30}$ /f-CNT the depolarization is more visible (approx. -395 mV) since the glucose has ability to depolarize the ORR catalysts, causing a decrease in the onset potential.

In summary, these results clearly demonstrate that the Pt/f-CNT electrocatalyst has a strongest electrocatalytic activity for the ORR compared to the AuPt/f-CNT. This can be ascribed to the lower activity towards the other parallel reactions (e.g. glucose electro-oxidation) on Pt-NPs.

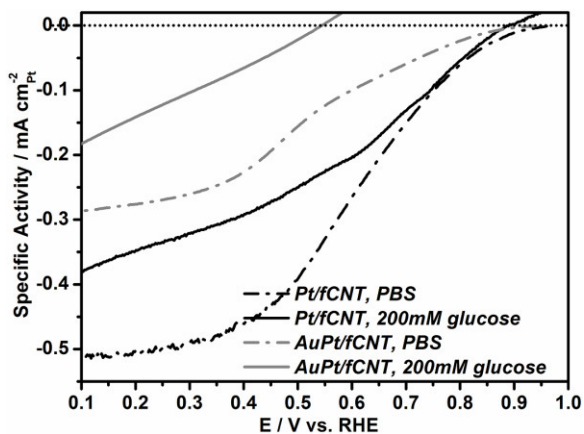


Fig. 4: Linear-sweep voltammograms for the ORR activity of the electrocatalysts recorded at 2500 rpm in the presence and absence of 0.2 M glucose at a sweep rate of 5mV s^{-1} at $25\text{ }^{\circ}\text{C}$.

III) Potentiodynamic polarization of DGFC: After depositing one layer of the above electrocatalysts onto the BP with a very low amount of noble metal loading (about $130\text{ }\mu\text{g cm}^{-2}$), the Pt-NPs decorated BP cathode and AuPt-NPs decorated BP anode are assembled with nylon membrane as electric insulating polymer using a home-made single-cell test fixture, and then subjected to complete biofuel cell test.

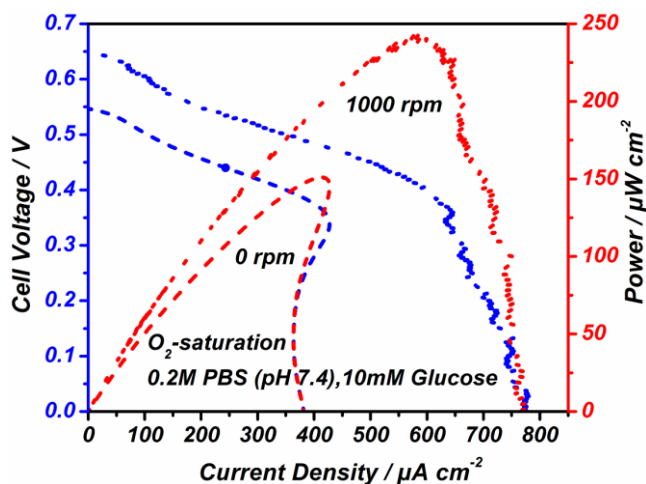


Fig. 5: Potentiodynamic polarization curves of BP-based DGFC, with and without electromagnetic stirring. Scan rate 5mV s^{-1} at $25\text{ }^{\circ}\text{C}$.

Our preliminary result in Fig. 5 shows a significant increasing of the power density in O_2 -saturated phosphate buffer solution (0.2 M, pH 7.4), containing 10 mM glucose. It was able to approach the highest power density so far, approx. $250\text{ }\mu\text{W cm}^{-2}$ and $150\text{ }\mu\text{W cm}^{-2}$, with applying electromagnetic stirring and in quiescent condition respectively.

This can be attributed to the superior activity of both nanocatalysts and to the high utilization of the nanoparticles. The other factor could be the effect of electrode substrate due to the mesoporous structure of BP along with a high electronic conductivity, compared to other carbon support material, can facilitate both the mass transport and the charge-transfer at the interface between the electrode and the supporting electrolyte.

CONCLUSION

In this contribution, we are successful in making a complete biofuel cell based on metal NPs-decorated BP electrodes. The Pt-NPs and AuPt-NPs decorated BPs can act as cathode and anode respectively.

The potentiodynamic tests of the above electrocatalytic system demonstrated that the Pt/f-CNT nanocatalyst possesses higher ORR electrocatalytic activity than AuPt/f-CNT in phosphate buffer solution, in absence and presence of glucose with high resistance to glucose. Nevertheless, in comparison with Pt-NPs, the AuPt-NPs showed also an effective promotion towards glucose electro-oxidation. This can be rationalized based on synergistic effect of Au-NPs for glucose electro-oxidation with Pt-NPs

Moreover the highest power density approx. $250\text{ }\mu\text{W cm}^{-2}$ and $150\text{ }\mu\text{W cm}^{-2}$, with applying electromagnetic stirring and in quiescent condition respectively can be achieved. This can be set as a new benchmark for future efforts in developing abiotic biofuel cell.

Further investigation of the device performance with respect to biocompatibility of BP-based electrodes for various fuel cells and sensor applications are currently in progress.

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