Buckypaper as Pt-free cathode electrode in photoactivated fuel cells

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The possibility to substitute a standard Pt/carbon-black/carbon-clot oxygen-reducing cathode by buckypaper has been studied in a photoactivated fuel cell. It was found that a buckypaper bearing NiO can very well compete with a standard cathode, thus offering a Pt-free alternative. The buckypaper was made through a process of epoxidation of multiwall carbon nanotubes while NiO was casted through a simple procedure employing surfactant templates.

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1. Introduction

Photoactivated fuel cells (Photo-Fuel-Cells, PFCs) are devices, which can produce electricity by photocatalytic oxidation of organic fuels [1,2]. These cells comprise a photoanode electrode bearing a photocatalyst, typically, nanocrystalline titania, a cathode electrode bearing an oxygen reducing electrocatalyst and an electrolyte. Most efficient cells are divided into two compartments separated by an ion transfer membrane [2–5]. The fuel is introduced in the anode compartment. PFCs resemble alkaline fuel cells. Their major difference from the latter is that, instead of an electrocatalyst on the anode electrode, they utilize a photocatalyst that is activated by absorption of light. Since photocatalysts are not specific towards photodegradable fuels, PFCs may run with aqueous organic wastes as fuel [1,2,6] thus providing the double environmental benefit of producing renewable energy with water cleaning.

We have been recently studying various aspects of PFCs focusing at the optimization of device functionality as well as the investigation of new materials that may reduce device cost [7–11]. The major cost in the construction of a PFC is due to Pt utilized as electrocatalyst on the cathode electrode. It is then beneficial to examine alternative cost-effective materials. The reductive capacity of the cathode electrode is an issue that concerns not only PFCs but it is equally important for other similar types of cells, namely, fuel cells, microbial fuel cells, etc. A typical cathode electrode, which may serve as gas diffusing electrode (GDE) in membrane–electrode assemblies (MEA) is a carbon cloth bearing a hydrophobic paste enriched with amorphous carbon (for example, carbon black) and Pt nanoparticles. In most cases, Pt loadings are rather high ranging from 0.1 to 1 mg cm⁻² [12] thus precluding massive application due to the scarcity of this precious metal. In addition, loss of activity due to Pt aggregation as well as Pt passivation in aggressive environments makes the search for alternative electrocatalysts a very important issue. In the present paper, we propose the employment of buckypaper, i.e. a nanostructured porous sheet based on entangled ropes and bundles of multiwall carbon nanotubes (MWCNTs) [13–15], plain or enriched with NiO, as possible substitutes of standard Pt on amorphous carbon electrodes.

The cells we have employed to test the applicability of alternative cathodes carry a photoanode bearing nanocrystalline titania (nc-TiO₂), photosensitized in the visible spectrum by ZnS–CdS quantum dots (QDs). Such combinations were previously shown to be effective in PFCs running with alkaline electrolyte and with ethanol as fuel [8]. Pure ethanol is, of course, not a waste but the PFC may well work with products of biomass, of which aqueous ethanol is a representative model appropriate for research purposes. The ZnS–CdS QDs comprised 75% Cd and 25% Zn, could absorb visible light up to about 500 nm and were more effective in PFC function than neat CdS. In the present work we used a PFC with the following configuration and geometry, also depicted in Fig. 1. The photoanode consisted of a transparent fluorine-doped tin oxide electrode (FTO)
on which nc-TiO$_2$ and QD sensitizers were deposited as thin film, as described in Section 2. The photoanode assembly was used as window, through which light reached the photocatalyst. Alkaline electrolyte and fuel were in contact with the active side of the photoanode. A glass frit was used as an ion-transfer membrane limiting the fuel only in the anode compartment. Anode and cathode were connected through an external electric circuit. Electrons are generated by absorption of photons and they are directed to the cathode electrode, where they participate in reductive interactions:

\[ \text{H}_2\text{O} + \text{O}_2 + 4e^- \rightarrow 4\text{OH}^- \]  

(1)

The efficiency of (1) depends on the electrocatalytic properties of the materials comprising the cathode electrode. The present work deals with the study of a few different types of cathode electrodes, which are expected to facilitate reaction (1).

2. Experimental

2.1. Materials

Unless otherwise indicated, reagents were obtained from Aldrich and were used as received. 3-Chloroperoxybenzoic acid (70–75%) was supplied by Acros Organics. The commercial nanocrystalline titania was Degussa P25 (specific surface area 50 m$^2$/g). Millipore water was used in all experiments. FTO transparent conductive electrodes (resistance 8 Ω/square) were purchased from Pilkington, plain carbon cloth from Fuel Cell Earth, Pt/carbon black electrocatalyst (30% on Vulcan XC72) from BASF Fuel Cell, Inc. and carbon black, Vulcan XC72R, was a gift from CABOT Corporation. Multi-walled carbon nanotubes were grown by a CVD method and were supplied by Nanocyl (Belgium).

2.2. Fabrication of the anode electrodes

2.2.1. Deposition process of nc-TiO$_2$ films on FTO electrodes

The following procedures were undertaken in order to construct the photoanode electrodes. First the nc-TiO$_2$ film was synthesized; it was deposited in two layers, a bottom compact layer and a top open structure. The bottom layer was synthesized by the sol–gel method while the top layer was deposited by using a paste made of commercial titania nanoparticles. A densely packed nanocrystalline titania layer was first deposited on a patterned FTO electrode, cleaned by sonication in acetone, isopropanol and ethanol, according to the following procedure: 3.5 g of the non-ionic surfactant Triton X-100 was mixed with 19 ml ethanol. Then 3.4ml glacial acetic acid (AcOH) and 1.8 ml of Titanium Tetraisopropoxide were added under vigorous stirring. After a few minutes stirring, the film was deposited by dipping and then left to dry in air for a few minutes. Finally, it was calcined at 550 °C. The temperature ramp rate was 20 °C/min up to 550 °C and the sample was left for about 10 min at that temperature. The procedure was repeated once more. Each layer gave a thin nanostructured film of about 170 nm thickness, as measured by its FE-SEM profile [16]. On the top of this compact nanostructured layer a porous titania film was deposited. For this purpose, a paste of titania was prepared by using commercial P25 powder according to Ref. [17]. The paste was applied by screen printing using a 90 mesh screen. It was finally calcined again at 550 °C. The thickness of the top layer was about 3.4 μm as measured by its FE-SEM profile [16]. The procedure was repeated once more so that the final nc-TiO$_2$ film was about 7.5 μm thick. The active area of the film was 1 cm$^2$ (1 cm x 1 cm).

2.2.2. Deposition of the CdS–ZnS quantum dots by the SILAR method

A CdS–ZnS composite catalyst corresponding to a proportion of 75% Cd and 25% Zn were deposited on the nc-TiO$_2$ film by Successive Ionic Layer Adsorption and Reaction (SILAR) method [16,18]. For this purpose, two aqueous solutions were used, one containing 75 mmol L$^{-1}$ Cd(NO$_3$)$_2$·4H$_2$O and 25 mmol L$^{-1}$ Zn(NO$_3$)$_2$·6H$_2$O and the second containing 100 mmol L$^{-1}$ Na$_2$S·9H$_2$O. The freshly prepared titania electrode was immersed for 5 min in the metal salt solution, then copiously washed with triple-distilled water. In the next step, it was immersed for 5 min in the Na$_2$S·9H$_2$O solution and finally washed again. This sequence corresponds to one SILAR cycle. Ten SILAR cycles were performed in all studied cases. Finally, the electrode with deposited CdS–ZnS@nc-TiO$_2$ film was first left to dry in a N$_2$ stream and then it was put for a few minutes in an oven at 100 °C.

2.3. Fabrication of the cathode electrodes

2.3.1. Fabrication of epoxidized MWCNT buckypapers

Epoxidation of MWCNTs was carried out as follows: 7 g of 3-chloroperoxybenzoic acid was dissolved in 150 ml CH$_2$Cl$_2$. Then, 1.5 g of multi-walled MWCNTs was added, and the solution was stirred for about 20 h at room temperature. The reaction mixture was filtered through a 0.2 μm PTFE membrane filter and washed with excess CH$_2$Cl$_2$. The epoxidized MWCNT were dispersed again in 150 ml CH$_2$Cl$_2$ by sonication, filtered and dried under vacuum at 80 °C. Stable epoxidized CNT suspensions in CH$_2$Cl$_2$ at a concentration of 1 mg mL$^{-1}$ were prepared by tip sonication for 16 min. The mass of the MWCNT material was 250 mg. These dispersions were then vacuum-filtered through PTFE filters respectively of 0.2 μm pore size. After drying with hot air, MWCNT films were peeled off from the filtration membrane. The average thickness of the produced buckypapers was approximately 230 μm and their diameter 7 cm. In order to make electrodes, pieces were cut at a size of 3.5 cm x 2 cm. Contacts were made by using an adhesive copper ribbon. The effective electrode size in contact with the electrolyte was 5 cm$^2$ (2.5 cm x 2 cm).

2.3.2. Deposition of NiO on buckypaper or carbon cloth electrodes

NiO has been deposited on buckypaper or carbon cloth electrodes by utilizing a surfactant template for nanoparticle formation and by modifying a procedure employed elsewhere [19]. 1 g of anhydrous NiCl$_2$ was mixed with 1 g Triton X-100. Then we added 3 ml water and 6 ml EtOH and magnetically stirred until a green
clear solution was obtained. This solution was cast on a buckypaper or on a plain carbon cloth electrode, covering the entire active area of 5 cm$^2$ (2.5 cm $\times$ 2 cm). Then it was dried in a hot air stream and a second layer of the above mixture was subsequently applied. Finally, it was dried and calcined in the air at 400 $^\circ$C for about 30 min. The same procedure applied to buckypaper and to carbon cloth electrodes.

2.3.3. Deposition of Pt/carbon black on carbon cloth electrodes

0.246 g of carbon black was mixed with 8 ml of distilled water by vigorous mixing in a mixer (about 2400 rpm) until it became a viscous paste. This paste was further mixed with 0.088 ml polytetrafluoroethylene (Tefton 60 wt% dispersion in water) and then applied on a carbon cloth cut in the necessary dimensions. This has been achieved by first spreading the paste with a spatula, pre-heating for a few minutes at 80 $^\circ$C and finally annealing also for a few minutes in an oven at 340 $^\circ$C. Subsequently, the catalytic layer was prepared as follows: 1 g of Pt/carbon black electrocatalyst (30% on Vulcan XC72) was mixed with 8 g of Nafion perfluorinated resin (5 wt% solution in lower aliphatic alcohols and water) and 15 g of a solution made of 7.5 g H$_2$O and 7.5 g isopropanol. The mixture was ultrasonically homogenized and then applied on the previously prepared carbon cloth bearing carbon black. The electrode was then heated at 80 $^\circ$C for 30 min and the procedure was repeated as many times as necessary to load about 0.5 mg of Pt per cm$^2$. The active area of the electrode was again 5 cm$^2$ (2.5 cm $\times$ 2 cm).

2.4. Description of the reactor

The reactor was made of Plexiglas and comprised two compartments of orthogonal shape (cf. Fig. 1) separated by a silica frit (ROBU, Germany, porosity SQG 5, diameter 25 mm, thickness 2 mm). Both compartments contained the same aerated electrolyte. The capacity of the anode compartment was 10 ml and that of the cathode compartment was 2 ml. The fuel (ethanol) was added only in the anode compartment. The combination of the glass frit with the alkaline electrolyte plays the role of an alkaline transfer membrane. Irradiation by simulated solar light was made by employing an Osram XBO 450 W Xe source. The incoming light was filtered for the IR radiation using a circulating water filter. The intensity of radiation at the position of the photocatalyst was 75 mW cm$^{-2}$.

In all cases, the exciting radiation passed through the glass-FTO electrode, which played the role of window. The active area of the photoanode was 1 cm$^2$. Electrical connections were made by means of an auto-adhesive copper ribbon and wires soldered on the ribbon.

2.5. Methods

Electrochemical measurements were carried out with an Autolab potentiostat PGSTAT128N. All current–voltage curves were traced at 5 mV/s. FE-SEM images were obtained with a LEO SUPRA 35 VP Scanning Electron Microscope and the porosity of the buckypaper was examined with a Quantachrome PoreMaster 60 Hg Porosimeter.

3. Results and discussion

The purpose of the present work is to demonstrate the applicability of a Pt-free buckypaper electrode producing equivalent data as those obtained with a standard gas-diffusion electrode (GDE) made of carbon cloth, carbon black and Pt nanoparticles. Characterization of such a standard electrode has been made previously [10].

![Fig. 2. FE-SEM images of a plain buckypaper (A) and a buckypaper with deposited NiO (B). The scale bar is 200 nm. The size of the NiO crystallites is around 70 nm.](image)

3.1. Characterization of buckypaper

Field Emission Scanning Electron Microscopy (FE-SEM) was used to investigate the surface morphology of the MWCNT network of the buckypaper. A FE-SEM image of a cross section is shown in Fig. 2A which illustrates clearly the buckypaper structure. The film surface consists of randomly oriented entanglements of nanotubes. In addition, it is clear that all films are porous, forming a random heavily interconnected network having a broad distribution of pore sizes. The textural characteristics (porosity) of neat buckypapers were examined by mercury porosimetry analysis. Mercury intrusion curves of the studied CNT sheets were obtained. The frequency distribution of pore diameters is shown in Fig. 3. The solid line corresponds to a bimodal distribution of two components of log-normal function, which has been fitted to the raw data. The epoxide-modified buckypapers show a broad pore size distribution. The profile in the mesopore region (2–50 nm) has a maximum at 12 nm, whereas the majority of porous structure consists of small macropores, which mainly lie in the range between 50 and 2000 nm (maximum at 300 nm). The mesopores and small macropores are formed between entangled adjacent tubes crisscrossing each other. Conductivity characteristics were obtained with a conventional four probe method. The conductivity curve is shown in Fig. 4 and corresponds to a surface conductivity value of 6.66 S/cm. Corresponding measurements with the carbon cloth used in the present work, for reasons of comparison, produced data also shown
in Fig. 4. The conductivity of the carbon cloth was substantially larger, reaching 19.6 S/cm.

Fig. 2B shows a buckypaper with NiO deposited on the top. NiO consists of nanocrystals of size around 70 nm. They crystallized in the form of square bipyramidal (octahedral) structure. A similar picture was obtained for NiO on carbon cloth.

3.2. Voltage–current behaviour of a cell employing various cathode electrodes

Photoactivated fuel cells (PFCs) were made in the standard configuration described in Section 2 by employing a FTO photoanode carrying a double-layer of nc-TiO2 sensitized with ZnS–CdS quantum dots. This combination produces more current and gives a more functional cell than with pure CdS sensitizer. There are a few reasons for the superiority of the combined material. The presence of the minority component helps passivation of defects, which otherwise become electron–hole recombination sites. Combined materials facilitate dispersion of the photogenerated charge carriers thus impeding recombination. Furthermore, ZnS has a lower-lying valence band and a higher-lying conduction band than CdS [2], and it can act as a blocking layer for back reactions involving both electrons and holes. Finally, the presence of a material with higher oxidative power than CdS, i.e. with lower lying valence band [2], increases the phodegradation capacity of the combined photocatalyst towards ethanol. Thus in the present work, the photoanode composition was always 75% CdS–25% CdS@nc-TiO2/FTO. The electrolyte was in all cases 0.5 mol L−1 while 5% volume ethanol was added in the anode compartment. Functioning of the cell was studied with the help of linear JV plots using two electrodes, as a function of the composition of the cathode electrode. Use of QD sensitizers has raised some concern, since these materials are known to suffer photoinduced oxidation. However, in the presence of a sacrificial agent, ethanol in the present case, QDs demonstrate a satisfactory stability. Stability tests have been separately run and they are presented as Supplementary material. They show that photoanode was stable enough to ensure that the present data are not affected by any sensitizers’ corrosion.

Fig. 5 shows the JV plots for five different cases and Table 1 shows the corresponding extracted data. A cathode made of pure carbon cloth (trace 1) gave the poorest behaviour offering the lowest open-circuit voltage $V_{oc}$, the lowest short-circuit current density $J_{sc}$ and the worst fill factor (cf. Table 1). A substantial improvement was obtained (trace 2) with a cathode made of carbon cloth on which NiO was casted, as described in Section 2.3.2. NiO is a p-type semiconductor with a large energy gap (3.6–4.0 eV [19–20]) and ionization potential (vs. vacuum) 5.4 eV [19]. NiO has been frequently used in p-type dye sensitized solar cells as a hole acceptor photocathode (i.e., electron donor from its valence band) [19–21]. For this reason we have tested its applicability as reduction electrocatalyst. Trace 2 of Fig. 5 shows that it can indeed function in this purpose. Plain buckypaper cathode gave a greatly improved behaviour, as seen by trace 3. Both $V_{oc}$ and $J_{sc}$ reached almost the highest values observed in this work, indicating that the presently used epoxidized buckypaper can satisfactorily function as oxygen reducing cathode. NiO casting on the buckypaper slightly further increased $J_{sc}$ and greatly improved the fill factor (trace 4). Finally, a further improvement of the fill factor was observed in the case of trace 5, which corresponds to a cathode made of carbon cloth, bearing carbon black and 0.5 mg cm−2 Pt (see Section 2.3.3), i.e., it corresponds to a standard cathode bearing Pt/carbon-black electrocatalyst. Finally, the last column of Table 1 shows the corresponding photovoltaic efficiency of the cell. It is seen that the maximum efficiency was obtained with the standard Pt/carbon-black/carbon-cloth electrode.
Table 1
Data extracted from the plots of Fig. 5. The intensity of the incident radiation was 75 mW cm\(^{-2}\). These data treat the cell as a photovoltaic cell, exclusively for comparison purposes.

| Type of cathode electrode | \(J_w\) (mA cm\(^{-2}\)) | \(V_{oc}\) (V) | Maximum power output (mW cm\(^{-2}\)) | \(\eta\) | \(\eta\) (%) \\
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<td>Plain carbon cloth</td>
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<td>1.0</td>
<td>0.25</td>
<td>0.12</td>
<td>0.3</td>
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<td>NiO/carbon-cloth</td>
<td>3.6</td>
<td>1.2</td>
<td>0.91</td>
<td>0.21</td>
<td>1.2</td>
</tr>
<tr>
<td>Plain buckypaper</td>
<td>4.8</td>
<td>1.2</td>
<td>1.90</td>
<td>0.33</td>
<td>2.4</td>
</tr>
<tr>
<td>NiO/buckypaper</td>
<td>4.9</td>
<td>1.3</td>
<td>2.55</td>
<td>0.40</td>
<td>3.3</td>
</tr>
<tr>
<td>Pt/carbon-black/carbon-clot</td>
<td>4.7</td>
<td>1.2</td>
<td>2.76</td>
<td>0.49</td>
<td>3.7</td>
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</table>

4. Conclusions

The present work has shown that buckypaper can be employed as Pt-free cathode electrode in PFCs. When enriched with NiO, it is practically equivalent to a standard Pt/carbon-black/carbon-clot cathode. A device bearing a ZnS-CdS@nc-TiO\(_2\)/FTO photoanode, a NiO/buckypaper cathode, an alkaline electrolyte and ethanol as fuel, when activated by simulated solar light yielded a \(J_{sc}\) equal to 4.9 mA cm\(^{-2}\) and \(V_{oc}\) equal to 1.26 V at a fill factor of 0.4. This is a satisfactory yield while there is ground for further improvement. Ethanol is used as a model fuel but aqueous wastes can be employed as well, since photocatalytic oxidation is not specific to the organic fuel used.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2012.07.046.

References