# FABRICATION OF SCREEN-PRINTING PASTES OF CARBON POWDERS FOR DYE-SENSITIZED SOLAR CELLS

**J. O. Ozuomba[1], L. U. Okoli [2], A. J. Ekpunobi [3], and P. I. Ekwo[3]**

*[1]Department of Industrial Physics, Madonna University, Elele, Rivers State, Nigeria*
*e-mail: okanandu@yahoo.com; 08033267967*
*[2]Department of Physics, Federal College of Education, Technical, Umunze, Anambra, Nigeria*
*[3]Department of Physics and Industrial Physics, Nnamdi Azikiwe University, Awka, Nigeria*

(Received 3 April 2012)

## Abstract

A preparation technique of screen-printing pastes of carbon has been disclosed in order to fabricate nanocrystalline layers without cracking and pealing-off over 6.8-µm thickness for the counter electrodes of dye-sensitized solar cells (DSSCs). A well blended mixture of powdered activated carbon, natural graphite powder, and a colloidal sol produced the screen-printing pastes. A DSSC fabricated with the carbon electrode whose $TiO_2$ photo-electrode was sensitized with *anthocyanin* local dye gave a photoconversion efficiency of 1.01%.

## 1. Introduction

Dye-sensitized solar cells (DSSCs) are currently attracting academic and commercial interest as regenerative low-cost alternatives to conventional solid state devices [1, 2]. A DSSC is composed of a dye-sensitized nanocrystalline titanium(IV) oxide photoelectrode, a counter electrode, and a redox electrolyte in between [3]. Light incident on the transparent photo-electrode excites the dye in the cell from the ground state, whereby an electron is formed [4]. The photo-excited dye molecules inject electrons into the conduction band of $TiO_2$, whereby the combined action of redox species in the electrolyte and the counter electrode reduce the oxidized dye molecules back to their original state [4, 5]. Generally, DSSCs consist of platinized counter electrodes fabricated by deposition of platinum on a transparent conducting oxide (TCO) substrate using thermal decomposition, sputtering, or electrodeposition of $H_2PtCl_2$ [3, 6, 7]. Platinum is relatively expensive, and the deposition techniques usually employed are costly and sophisticated [7].

Carbonaceous materials are quite attractive to replace platinum due to their high electronic conductivity, low cost, high total surface area, porosity, high temperature stability, and chemical resistance [6-9]. The development of simpler deposition methods will lower the cost of DSSC and enable the fabrication of large-scale DSSC devices.

Hence, we have developed a procedure which takes less than 24 h to fabricate and deposit high quality screen-printing carbon paste electrodes. Optimization of the electrical properties of the carbon electrodes was achieved through doctor blading and DSSC fabricated with the carbon electrode achieved a photoconversion efficiency of 1.01%.

## 2. Material and Methods

### 2.1. Reagents and solutions

Tin(II) chloride, carboxy ethyl cellulose (NATROSOL), 25% hydrochloric acid, powdered activated carbon (PAC) and a kind of natural graphite powder (NGP) were used. High purity de-ionized water was used to prepare the solutions at a temperature of $25\pm2^0$C. The chemicals were of analytical grade and used without further purification.

### 2.2. Apparatus

Ainsworth DE – 100, Max 100g, e = 0.0001g chemical balance, electric hot plate, Carbolite 201 tubular furnace, wooden clamp, 500 W electric bulb, no. 90 polyester mesh and its mounting frame, blue emulsion, sensitizer, squeegee, fluorine-dope tin oxide (FTO) glass substrate, substrate holder, film, UV filter, hot air blower, carbolite 201 tubular furnace, acetone and methanol.

### 2.3. Fabrication of screen-printing pastes through sol-gel technique

We dissolved 12 g of tin(II) chloride in 50 ml of deionized water and titrated with about 1 ml of 25% HCl. The solution became colourless and there was a noticeable fall in temperature. Then 2 g of Natrosol was dissolved in 50 ml de-ionized water and stirred properly. We mixed the two solutions under permanent stirring. This mixture was heated to $300^0$C using a hot-plate technique. The stirring continued as the heating lasted for about 39 s. The resulting solution (about 16 ml) was allowed to stay for about 12 h at room temperature. It was further heated on the following day for about 7 min to get a polymeric colloidal sol of about 12 ml. The resulting solution was our "binder." Eighteen grams of powdered activated carbon PAC were ground in a porcelain mortar for about 30 min. The screen-printing carbon pastes were obtained by hand mixing certain proportions of the well-blended PAC and the binder.

### 2.4. Deposition of carbon electrode through screen-printing

The first step was to prepare the photoresist by hand mixing the blue emulsion and sensitizer in the ratio of 2 : 1. Then we applied the photoresist onto a small portion of the mesh. The squeegee was used to rub it uniformly (front and back) on the mesh and it was allowed to stay for 2 min. A hot air blower was used to fasten the drying process. The film in form of a dark image imprinted on a sheet of tracing paper has been designed. The shape of the film determines the shape of the screen and, hence, that of the electrode. We placed the tracing paper on the top of the photoresist and set the mesh 40 cm below the source of radiation. The ultraviolet radiation filter (glass shield) was placed on the top of the film, while a 500-W electric bulb was switched on. After about 5 min, the UV filter and the film were removed and the mesh was placed beneath a water tap. The tap was slightly opened and water was allowed to gently run on the top of the photoresist. The spot covered by the dark image on the tracing paper was washed away by the water thereby forming a sharp image (screen) on the mesh. The mesh can be allowed to dry naturally, but we used a hot air blower to fasten the drying process.

The photoresist is soluble in water, but when radiant light passes through it for some time, it will become insoluble. Hence, it was possible to wash off the area that formed our screen because the dark design on the tracing paper served as an absorber surface. With the help of the substrate holder, we positioned the FTO at a short distance beneath the screen with the conducting side facing upward. A small amount of the carbon paste was dispensed onto the upper surface of the screen using the squeegee, and the squeegee was used to squeeze the paste across the screen surface. This is a single layer deposition. Double layer deposition can be achieved by

running another stroke of the carbon paste using the squeegee, and the thickness of the deposited carbon electrode increases with multiple deposition. Before deposition, the glass substrate was cleaned with acetone, then methanol and etched through plasma treatment for 1 min. The entire mesh was washed with acetone at the end of screen printing and the entire process can be repeated. Meanwhile, the particular screen can be washed with water after usage so that it can be used again but it is advisable to imprint many dark films on a sheet of tracing paper so as to obtain many screens.

### 2.5. Thermal treatment

A hot air blower was used to dry the carbon counter electrode for about 3 min immediately after deposition. Using an electric hot plate, the carbon electrode was subjected to thermal annealing at $150^0$C for 5 min. Immediately after annealing, the electrode was sintered at $200^0$C for about 15 min using a carbolite 201 tubular furnace.

### 2.6. Optimization of electrical properties

The sheet resistance of the carbon electrode was reduced to a very low value by preparing another carbon paste using equal mixtures of PAC and NGP and applying doctor blading deposition technique [10]. This method is very similar to screen-printing, except that the mesh has no role to play. The carbon paste was deposited directly onto the FTO glass substrate using a squeegee. The thickness of the film was determined by covering the four edges of the glass substrate with a masking tape, while thicker films were obtained using multiple layers of the masking tape. Carbon films prepared through this blade method were subjected to the same thermal treatment.

## 3. Results and discussion

The quantity of carbon and binder which formed our carbon paste was varied in the ratio of 0.133 g/ml to 1.2g/ml, while the sheet resistance of the fully sintered electrode varied from 1.99 x $10^4$ Ω /square to 543.35 Ω /square (Table 1). It is true that we achieved a significant reduction in the sheet resistance, but there was need for further reduction since we obtained the sheet resistance of the FTO glass substrate of14.55 Ω/square. The carbon concentration must be further increased, but a bottleneck would be the ability of the thick carbon paste to pass through the mesh. At this stage, we resorted to the blade deposition technique.

**Table 1.** Electrical characterization of carbon electrode deposited through screen printing

| Quantity of carbon (g) | Quantity of binder (ml) | Concentration (g/ml) | Sheet resistance (Ω/square) |
|---|---|---|---|
| 0.20 | 1.50 | 0.133 | $1.99x10^4$ |
| 0.30 | 0.40 | 0.750 | $1.02x10^3$ |
| 0.80 | 1.00 | 0.800 | 893.75 |
| 0.50 | 0.50 | 1.000 | 599.47 |
| 0.30 | 0.25 | 1.200 | 543.35 |

The results of electrical characterization of carbon electrode deposited through the blade method are shown in Table 2. The quantity of carbon and binder which formed our carbon paste was varied from 1.2 g/ml to 4.0 g/ml, while the sheet resistance of the fully sintered electrode

varied from 212.137 to 60.713 Ω/square. This was another breakthrough in the sheet resistance reduction, yet further optimization was required taking into account the low resistivity of the FTO glass substrate. We found that the 4.0 g/ml carbon electrode was pealing after sintering, so we considered 3.0g/ml for further optimization since it was stable.

**Table 2.** Electrical characterization of carbon electrode deposited through blade method

| Quantity of carbon (g) | Quantity of binder (ml) | Concentration (g/ml) | Sheet resistance (Ω/square) |
|---|---|---|---|
| 0.60 | 0.50 | 1.20 | 212.137 |
| 1.00 | 0.50 | 2.00 | 139.520 |
| 1.40 | 0.50 | 2.80 | 90.289 |
| 1.50 | 0.50 | 3.00 | 66.594 |
| 1.00 | 0.25 | 4.00 | 60.713 |

The carbon paste electrode comprising 3.0 g of powdered activated carbon per milliliter of binder was considered for further optimization through multiple layer deposition by doctor blading. We obtained the sheet resistance for double and triple layer deposition of 50.998 Ω/square and 36.954 Ω/square, respectively (Fig. 1). This was another breakthrough in our research work, which implies that the thicker the electrode, the lower the resistivity [3, 4, 9]. Meanwhile, we observed little cracks on the three-layered electrode, and we still need to go further to match the impedance of the counter electrode with that of the FTO glass substrate.

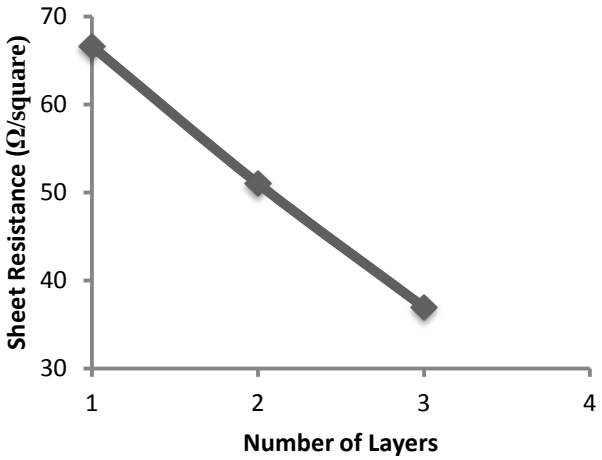


**Fig. 1.** Sheet resistance versus number of layers for 3.0g/ml PAC electrode

Since we need a carbon counter electrode with a lower sheet resistance, we fabricated another carbon paste with a well blended mixture of equal amount of PAC and NGP. The effect of graphite on the sheet resistance is shown in Fig. 2. The single, double, and triple layer deposition gave stable electrodes. The triple layer deposition was able to reduce the sheet resistance to 15.400 Ω/square. This result confirmed not only the fact that the thicker the electrode, the lesser the sheet resistance, but also that graphite has high electrical conductivity [7, 10].

So, we were successful in matching the sheet resistance of the counter electrode to that of

the FTO glass substrate which is 14.55 Ω/square. The electrode is expected to exhibit optimal performance when deposited on the substrate. Electrode characterization using a Dektak stylus 7.0 surface profiler gave the film thickness for the single, double, and triple layer PAC-NGP electrodes to be 5.26, 6.31, and 6.82 μm, respectively.

A DSSC of active surface area 1.8 $cm^2$ was fabricated with a titanium dioxide photoelectrode and sensitized with *chlorin* dye. *Chlorin* is a local dye fabricated from bahama grass [9, 11]. Figure 3 depicts the current-voltage characteristics of the DSSC at the illumination intensity of 100 $W/m^2$ using an Oriel class A solar simulator. The cell parameters were the following: open circuit voltage (0.44 V), short circuit photocurrent (3.9 $mA/cm^2$), fill factor (0.59), and photoelectric conversion efficiency (1.01%) [9]. The results can be compared to those obtained by Waita *et al.* using platinum as the counter electrode [3].

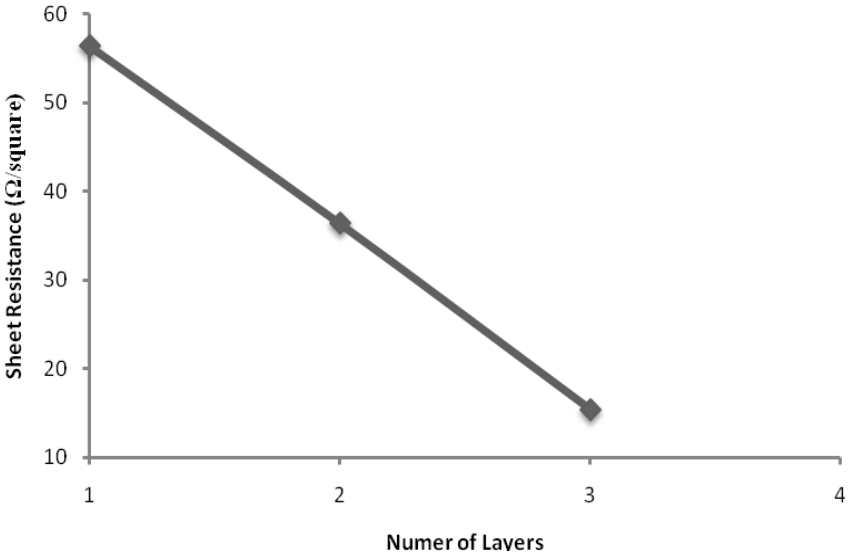


**Fig. 2.** Sheet resistance versus number of layers for 3.0g/ml PAC-NGP eletrode

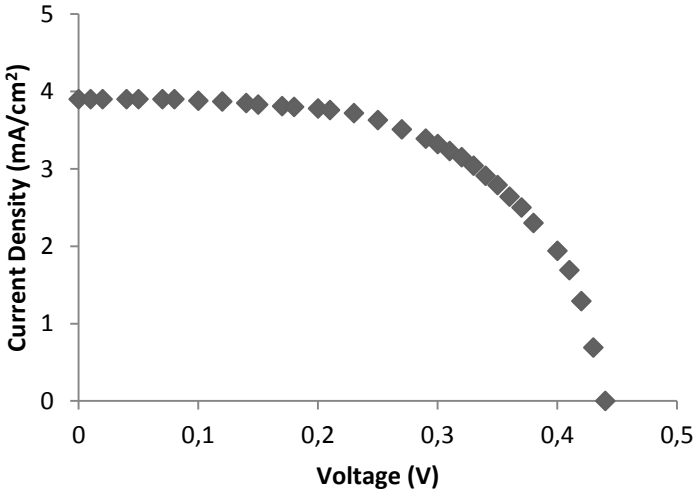


**Fig. 3.** The I-V curve for cell sensitized with *chlorin* dye

## 4. Conclusions

Screen printing pastes from carbon powders were successfully fabricated through a sol-gel technique. Stable carbon paste electrodes with a very low sheet resistance were obtained. A DSSC fabricated with the carbon electrode achieved a photocurrent conversion efficiency of 1.01%. This methodological investigation can contribute not only to the development of cheaper DSSCs, but also to the encouragement of production of large-scale DSSC devices.

## References

[1] B. O'Regan and M. Gratzel, Nature, 353, 737 (1991).
[2] M. Gratzel, Nature, 414, 338 (2001).
[3] S. M. Waita, J. M. Nwabora, B. O. Aduda, G. A. Niklasson, S. Lindquist, and C. Granqvist, African J. Sci. Technol. l 7, 106 (2006).
[4] J. O. Ozuomba, A. J. Ekpunobi, and Ekwo P. I., Dijest J. Nanomater. Biostruct. 6, 1043 (2011).
[5] N. R. Neale, N. Kopidakis, J. van de Lagemaat, and A. J. Frank, Tailoring the Interface to Improve $V_{oc}$ in Dye-Sensitized Solar Cells, Conference paper NREL/CP-590-37056, Colorado, 1-2 (2004).
[6] Z. Huang, X. Liu, K. Li, D. Li, Y. Luo, H. Li, W. Song, L. Chen, and Q. Meng, Electrochem. Commun. 9, 596 (2007).
[7] G. Wang, L. Wang, W. Xing, and S. Zhuo, Mater. Chem. Phys. 123, 690 (2010).
[8] Z. Kavaliauskas, L. Marcinauskas, and P. Valatkevicius, Enhanced Capacitance of Porous Carbon Electrodes through Deposition of Small Amounts of NiO, Proceedings of the VII International Conference ION, Poland, 66 (2010).
[9] J. O. Ozuomba and A. J. Ekpunobi, Res. J. Chem. Sci. 1, 76 (2011).
[10] E. Sabio, E. Gonzalez, J. F. Gonzalez, C. M. Gonzalez-Garcia, A. Ramiro, and J. Ganan, Carbon 42, 2285 (2004).
[11] J. O. Ozuomba, A. J. Ekpunobi, and P. I. Ekwo, Chalcogenide Lett. 8, 155 (2011).