

Dye solar cells: A different approach to solar energy

LJ LE ROUX, S HIETKAMP, F CUMMINGS

*CSIR Materials Science and Manufacturing, PO Box 395, Pretoria, 0001

Email: lleroux@csir.co.za

Abstract

An attractive and cheaper alternative to silicon-based photovoltaic (PV) cells for the conversion of solar light into electrical energy is to utilise dye-adsorbed, large-band-gap metal oxide materials such as TiO₂ to absorb the solar light. These devices, known as dye solar cells (DSCs), have a visible difference to conventional PV cells, in that they are semi-transparent. Hence they could be installed in place of glass windows in buildings and perform the dual tasks of providing shade for the occupants of the building and generating electricity.

Our research includes the synthesis of TiO₂ nano particles, the synthesis of a specific ruthenium dye, the preparation of the screen printable TiO₂ paste and the assembly of complete cells ready for testing. Further research includes the testing of cells under reverse bias to determine the extent to which cells recover from adverse operating conditions, a characteristic that will be essential for the commercial application of the cells. In addition to chemical analysis, techniques such as impedance spectroscopy (Nyquist and Bode plots), cyclic voltammetry and I-V measurements by means of a PC-interfaced solar simulator are used to determine the stability of the cells. Further work includes research into the improvement of the efficiency of DSCs by utilising nanotechnology (TiO₂ nanotubes).

DSCs also generate electricity in diffuse light, i.e. cloudy days and in the shade. Results published by Japanese researchers (Toyoda *et al.*, 2006) lead to comparative studies being conducted under South African conditions between DSCs and conventional silicon-based PVs. They found that the DSCs outperformed the crystalline silicon cells by ~20% per month over a six-month period, even though the DSC has a lower peak efficiency (~7.5 % vs. 15 %).

1. Introduction

The dye-sensitised solar cell is a photoelectrochemical solar cell that uses a liquid

electrolyte or other ion-conducting phase as a charge transport medium. The process is similar to photosynthesis in plants, the major difference being that electricity is produced (with the aid of a ruthenium dye) whereas plants produce oxygen and 'sugar' (with the aid of chlorophyll). This is different compared to the conventional semiconductor solar cells that work on a p-n junction principle. The research interest in the DSC technology grew rapidly during the 1990's due to increased efficiencies and good long-term stability reported (Kern *et al.*, 2001). Numerous research groups explored the replacement of the original materials with new ones, especially the replacement of the liquid electrolyte with solid or less volatile products (Grätzel, 2000).

Advantages of DSC vs. Silicon Cells

- Low cost and ease of production
- Performance increases with temperature
- Bifacial configuration - advantage for diffuse light
- Transparency for power windows
- Colour can be varied by selection of the dye, invisible PV-cells based on near-IR sensitizers are feasible
- Outperforms amorphous Si
- Performance retention at high angles of solar incidence
- Short energy payback time
- Clean manufacturing processes
- Capacity to produce tandem products such as photoelectrochromic devices, built on the inherent transparency of the DSC device (Tulloch, 2004).

At this stage the product is directed to a market that would be receptive to these advantages and for which the current price is not the major driver. Advantages of the idea of incorporating a DSC in a building facades are:

- They do not require any extra land area

- They do not require additional mountings when designed as a product.

TiO₂ is a low cost, widely available, non-toxic and biocompatible material, and as such is even used in healthcare products (sun tan lotion) as well as domestic applications such as paint pigmentation. (Grätzel, 2000).

Some disadvantages are the relative low conversion efficiency of modules (~7%) and the liquid electrolyte causes sealing problems. The ITO in the glass has a relatively high resistivity when compared with metal conductors.

The working mechanism and components of a DSC

The dye-sensitised solar cell (DSC) comprises a transparent conducting glass electrode (Indium tin oxide – ITO) coated with porous nanocrystalline TiO₂. Dye molecules are chemically adsorbed to the surface of the TiO₂ and this configuration acts as the working electrode. Figure 1 shows a diagram of the cell configuration. A redox electrolyte couple (I⁻/I₃⁻) and a counter-electrode consisting of a Pt catalyst coated on an ITO/glass substrate, makes up the rest of the configuration. During illumination the cell produces a voltage over and current through an external load that is connected to the electrodes.

The absorption of light in the DSC occurs in the dye molecules. The charge separation by electron injection from the dye to the TiO₂ occurs at the TiO₂/electrolyte interface (figure 1). Figure 1 also shows schematically the relative energy levels of a working DSC as well as the regenerative working cycle of the cell.

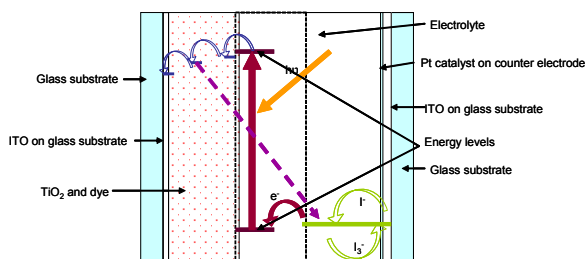


Figure 1: Diagram of the cell configuration

2. Current research

2.1 TiO₂ nanotubes

One of the main causes for the low efficiencies reported for the DSC is the ineffective transport of electrons through the cell. This is caused by the rough surfaces and disorder at the interface of two TiO₂ nanoparticles (Peng et al., 2003).

Our research, aims to overcome this problem by synthesising smooth surfaced, highly-ordered TiO₂ nanotubes. These structures are of particular interest because their predominantly one-dimensional nature creates a vectorial route for electrons to travel from their point of generation, at the dye/TiO₂ surface interface, unhindered to the conducting glass substrate (Paulose et al., 2006).

In addition, enhanced surface area of the nanotubes, combined with its much more open structure allow for more dye molecules to be chemically adsorbed onto the surface, whilst simultaneously facilitating the penetration of the electrolyte, thereby improving the iodide diffusion inside the cell. These distinct advantages of TiO₂ nanotubes over nanoparticles hold great potential for future research and development of DSCs. Initial reports have shown that DSCs employing nanotubes outperform traditional nanoparticle-based DSCs in terms of charge transport and ultimately light-to-electricity conversion efficiency (Mor et al., 2006).

2.2 Dye synthesis

Figure 2 shows the different steps for the synthesis of the ruthenium dye [*cis*-dithiocyanato-bis-(2,2'-bipyridyl – 4,4'-dicarboxylate)ruthenium(II)], also known as the N3 dye, to be used in the DSCs.

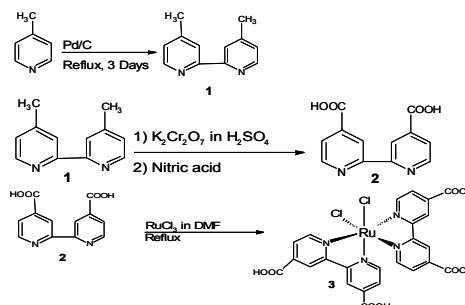


Figure 2: Diagram of the chemical steps for the synthesis of the N3 dye

2.3 Reverse bias and recovery

When a solar module is designed, diodes are incorporated to prevent damage due to shading that causes reverse bias. The DSC is not as susceptible to damage from reverse bias but the boundary conditions should be clearly understood and defined. Modules can then be built at even lower cost. During this research DSCs were submitted to various reverse bias voltages and their efficiencies were monitored with time. The degradation as well as the regeneration were plotted against time.

2.4 Comparative studies

Performance of DSC vs. crystalline Si in Japan

Comparative studies (actual atmospheric conditions) that were done by Toyota R&D have concluded that the DSC outperformed the Si cells by ~20% per month over a six-month period (Toyoda et al., 2004). A similar project has started in South Africa. It should be noted that South Africa has significant more sunshine than Japan.

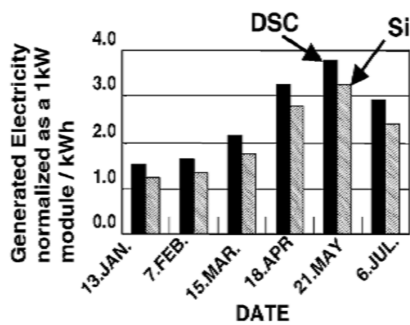


Figure 3: Results of comparative studies by Aisin Seiki, Inc. Toyota R&D in Japan (Toyoda, 2006).

3. Research outputs/findings

3.1 TiO₂ nanotubes

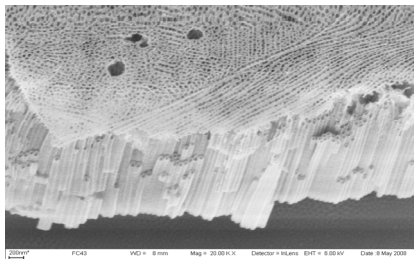


Figure 4: SEM micrograph of the TiO₂ nanotubes

Figure 4 shows a micrograph of the TiO₂ nanotube material synthesised the anodisation technique. A study is currently in progress to determine the extent of the effect of the anodisation parameters (voltage, time and electrolyte) on the morphology of the structures shown in figure 4. Preliminary results up to date show that it is capable to control the outer diameter, wall thickness and length of these nanotubes by simply having accurate control over the experimental parameters, i.e. voltage, time and electrolyte.

Future research will be aimed at investigating the effect of the structure of the TiO₂ nanotubes (diameter, length, etc.) on their optical and electric properties, which is crucial in determining whether or not they will be suitable for use within a DSC.

3.2 Dye synthesis

The N3 dye was synthesized successfully by utilising ruthenium residues that accumulated over years of research. The final purification step is currently being optimised. The product will be tested in cells that are assembled in our laboratories against commercially available dyes from Switzerland and Australia.

3.3 Stability tests under reverse bias and recovery of cells.

DSCs were subjected to various reverse bias voltages and the efficiencies were monitored with time. The degradation as well as the regeneration were plotted against time. The cells were analysed by impedance spectroscopy (Bode- and Nyquist plots) and cyclic voltammetry. Chemical analysis on the cells are currently underway to determine the chemical changes that the cells underwent during the reverse bias experiments.

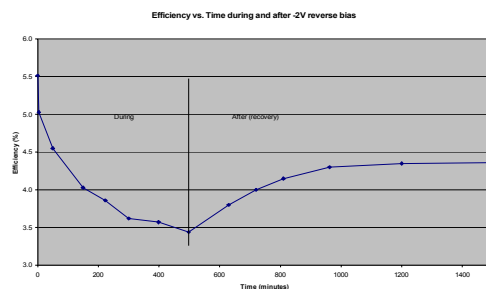


Figure 5: Efficiency vs. time after subsection to a reverse bias voltage of 2V.

The Nyquist and Bode plots give information regarding the charge transfer resistance at the electrode interfaces as well as the ionic movement inside the cells. Bode plots are where the impedance and phase change is plotted against the frequency. Nyquist plots are obtained where the real impedance is plotted against imaginary impedance and can give up to three semi circles for the DSC, depending on external conditions.

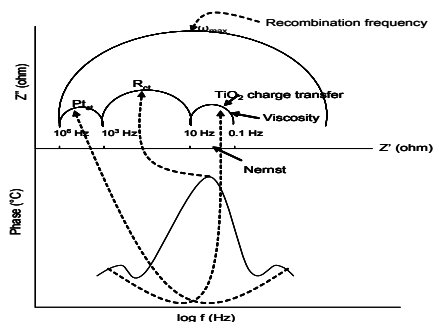


Figure 6: Bode- and Nyquist plot and the relation between the different zones

A further technique that is used for the electrochemical characterisation of the electroactive species in the cells is cyclic voltammetry. The working electrode potential is ramped linearly versus time. When a set potential is reached, the scanning potential of the working electrode is inverted. The potential is then plotted versus the

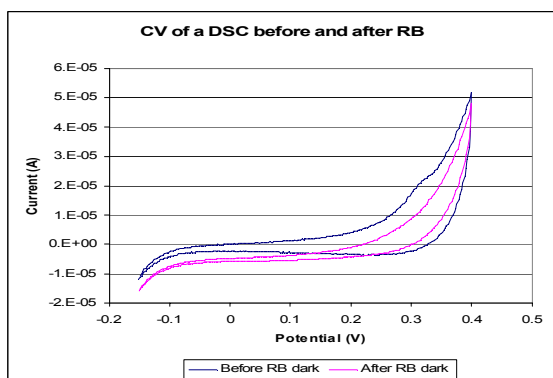


Figure 7: A cyclic voltammogram of a cell before and after it was subjected to reverse bias.

current. A cyclic voltammogram can give information regarding oxidation potentials, energy measurements between the 'highest occupied molecular orbital' (HOMO) and 'lowest unoccupied

molecular orbital' (LUMO), capacitance, half cell potentials. Figure 7 gives a typical cyclic voltammogram.

3.4 Comparative studies

Parameters such as the effect of temperature, humidity, wind speed and light intensity will be logged to determine their effects on the efficiency of the cells. The equipment and programming of the equipment has commenced. It is expected to get the first results by the end of September 2008.

4. References

Longo, C. and De Paoli, M. (2003). Dye-sensitized solar cells: a successful combination of materials. *J. Braz. Chem. Soc.* vol.14 no.6

Grätzel, M. (2000). Perspectives for Dye-sensitized Nanocrystalline Solar Cells. *Prog. Photovolt. Res. Appl.* 8, 171-185

Mor, G.K., Varghese, O.K., Paulose, M., Shankar, K. and Grimes, C.A. (2006). A review on highly-ordered, vertically oriented TiO₂ nanotube arrays: fabrication, material properties, and solar energy applications. *Solar Energy Materials & Solar Cells* 90, 2011-2075

Kern, R., Ferber, J., Hirsch, A., Kroon, J., Luther, J., Meyer, A., Sastrawan, R., Uhlendorf, I., 2001. Investigation of the long-term stability of dye-sensitized solar cells by optical and electrochemical impedance spectroscopy. *Proceedings of the 13th Workshop on Quantum Solar Energy Conversion - (QUANTSOL)*

Paulose, M., Shankar, K., Varghese, O.K., Mor, G.K. and Grimes, C.A. (2006). Application of highly-ordered TiO₂ nanotube-arrays in heterojunctiondye-sensitized solar cells. *Journal of Physics D: Applied Physics* 39, 2498-2503

Peng, T.Y., Hasegawa, A., Qui, J.R. and Hirao, K. (2003). Fabrication of titania tubules with high surface area and well-developed mesostructural walls by surfactant-mediated templating method. *Chemistry of Materials* 15, 2011-2016

Toyoda, T., Sano, T., Nakajima, J., Doi, S., Fukumoto, S., Ito, A., Tohyama, T., Yoshida M., Kanagawa, T., Motohiro, T., Shiga, T., Higuchi, K., Tanaka, H., Takeda, Y., Fukano, T., Kato, N., Takeichi, A., Takechi, K. and Shiozawa, M.(2004). Outdoor performance of large scale DSC modules.

Journal of Photochemistry and Photobiology A: Chemistry 164, 203–207

Tulloch, G.E. (2004) Light and energy—dye solar cells for the 21st century. *Journal of Photochemistry and Photobiology A: Chemistry* 164, 209–219

CLOSE