Working principles of dye-sensitised solar cells and future applications

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ABSTRACT

Invented in their high efficiency version in the early 1990s, dye-sensitised solar cells (DSCs) entered the global market in 2007 with the first commercial modules based on this versatile, hybrid (organic-inorganic) technology. The 6-7% efficiency of the first modules is a result of their good performance in diffuse light conditions, allowing for the production of electricity both under cloudy conditions and indoors. These low-cost solar cells are manufactured by highly productive roll-to-roll printing methods over rigid or flexible substrates affording modules coloured in widely different tones. These attributes render DSC a photovoltaic technology particularly well suited for BIPV applications and for electrification in developing countries, as discussed in this paper.

Introduction

Attempts to create photoelectrochemical solar cells by mimicking nature's photosynthesis started in the 1970s with early efforts involving the covering of crystals of semiconductor titanium dioxide with a layer of chlorophyll. However, owing to the electrons' reluctance to move through the layer of pigment, the efficiency of the first solar cells sensitised in this way was about 0.01%. In the late 1980s, scientists discovered that nanotechnology could overcome the problem [1]. Instead of using a single large titania semiconductor crystal, they worked with a sponge of small particles, each about 20nm in diameter, coated with an extremely thin layer of pigment. This method increased the effective surface area available for absorbing the light by a factor of one thousand, hugely increasing the efficiency on conversion of the sunlight into an electric current. The first system used a 10µm-thick, optically transparent film of TiO_2 particles of tens of nm in size with a photosensitiser dye chemically linked (usually by -COOH, $-PO_3H_2$, or $-B(OH)_2$ functional groups) to the semiconductor surface, a solution containing a redox mediator and a metallic counter electrode.

> "Beyond being highly effective, semiconductor TiO_2 is also abundant, low in cost, non-toxic and biocompatible."

Remarkably, even this first cell had 7.1% efficiency and photocurrent density up to 12mA/cm^2.

Working principles

The working scheme of a typical cell is illustrated in Figure 1, showing a TiO_2 layer deposited in a conductive ITO glass. The dye is placed over this semiconductor film, in contact with an electrolyte. The excitation of the dye upon irradiation is followed by injection of the resulting electrons into the CB of the semiconductor, from where they reach the cell anode (usually a conductive glass or plastic). Regeneration of dye electrons occurs through donation from a redox electrolyte in contact with the dye. This typically occurs through an organic solvent containing an iodide/triiodide couple. Triiodide is reduced in turn at the counter electrode, while electron migration from the anode to the counter electrode closes the circuit. The voltage generated is equal to the difference between the Fermi level of the electron in the solid TiO_2 and the redox potential of the electrolyte.

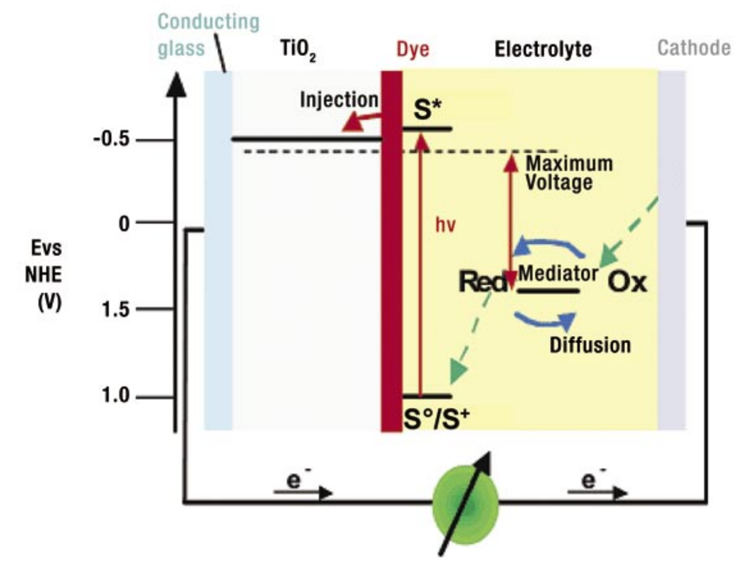

Figure 1. Working scheme of a typical dye-sensitised solar cell.

Image courtesy of [3].

Beyond being highly effective, semiconductor TiO_2 is also abundant, low in cost, non-toxic and biocompatible. Typically, nanocrystals of mesostructured TiO_2 in the anatase phase are prepared by sol-gel hydrothermal processing of a suitable titania precursor in the presence of a template such as Pluronic P123. The xerogel is isolated as thin film supported over a glass, further covered by another conductive glass [2].

The redox couple in the electrolyte, most commonly iodide/triiodide, functions well because the electron transfer from nanocrystalline TiO_2 to I_3^- is much slower than that from a counter electrode [4]. The $I_2^{-\bullet}/I^-$ couple potential determines the thermodynamic driving force for the electron transfer from I^- to the oxidised dye. Indeed, the mechanism of electron transfer from TiO_2 to I_3^- is preceded by a weak dissociative chemisorption of iodine on TiO_2:

$$I_3^- \leftrightarrows I_2 + I^- \qquad (1)$$

$$I_2 + e^-_{(TiO_2)} \rightarrow I_2^{-\bullet} \qquad (2)$$

Equation 1 has a very low equilibrium constant (~10^{-7} in acetonitrile), whereas the iodine radical is further reduced in a second-electron-transfer step:

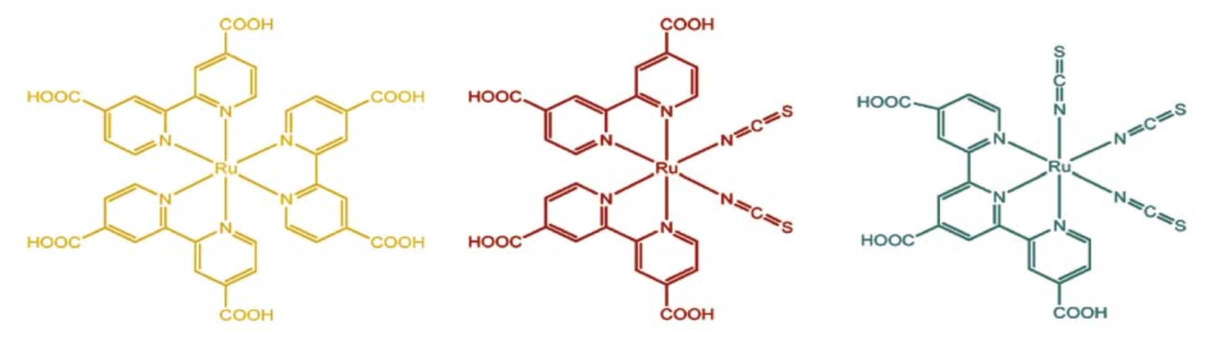

Image courtesy of [3].

Figure 2. Structure of the ruthenium sensitizers RuL_3 (left) cis-$RuL_2(NCS)_2$ (centre) and $RuL'(NCS)_3$ (right) where L = 2,2'-bipyridyl-4,4'-dicarboxylic acid and L' = 2,2',2"-terpyridyl-4,4',4"-tricarboxylic acid.

$$I_2^{-\bullet} + e^-_{(TiO_2)} \rightarrow 2I^- \qquad (3)$$

Regeneration of the dye ground state involves reduction of the oxidised dye by iodide:

$$\text{Ru(III)} + 2I^- \quad \text{Ru(II)} + I_2^{-\bullet} \qquad (4)$$

Sensitisers are generally based on polypyridyl complexes of Ru with an $RuL_2(X)_2$ structure (Figure 2). A monolayer is adsorbed over the deposited TiO_2 film; this is the device absorbing solar light at the beginning of the previously described cycle.

Current development – manufacturability

The Australian company Dyesol has pioneered the commercialization of DSC after obtaining a license from the inventors and has developed the technology in practically every aspect [5]. The company has recently introduced a flexible, foldable, lightweight and camouflaged solar panel for military applications which has been found to be superior to other PV technologies in maintaining voltage under a very wide range of light conditions, even in the dappled light under trees (Figure 3).

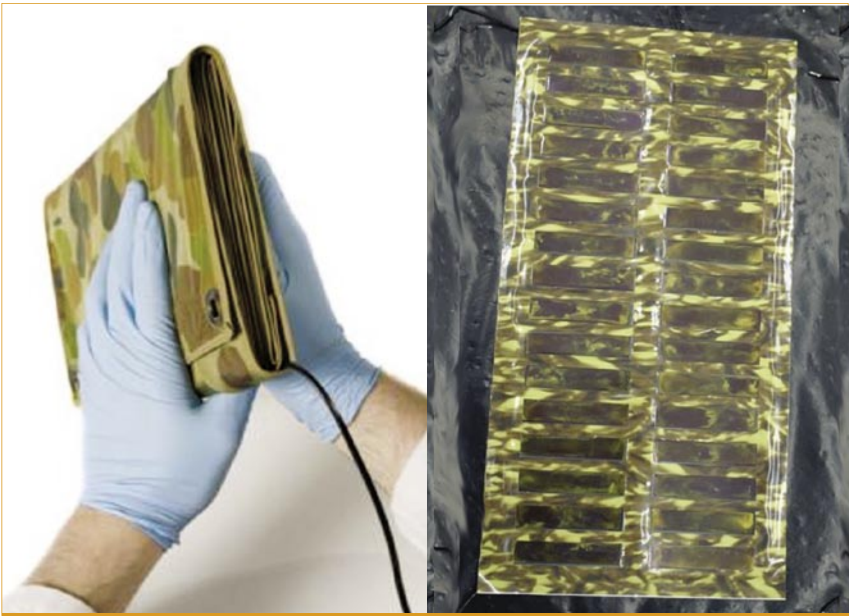

Photo courtesy of Dyesol.

Figure 3. The flexible DSC-based solar module developed by Dyesol for Australia's Army camouflages itself in trees from where it provides constant voltage under a wide range of illumination levels.

Photo courtesy of G24Innovations.

Figure 4. Roll-to-roll production of the first PV modules results into a flexible, lightweight PV material that can suit largely different applications.

Photo courtesy of OrionSolar.

Figure 5. Orionsolar dye cells have an additional advantage in that they are particularly suited to warmer climates.

On one other hand, the roll-to-roll production developed by G24Innovation easily allows the transformation of a roll of metal foil into a 45kg half mile of dye-sensitised thin film in less than three hours (see Figure 4) [6].

This material is rugged, flexible, lightweight and generates electricity even indoors and in low light conditions. In place of liquid electrolyte, solid or quasi solid-state hole conductors can be employed, but the reduction in efficiency currently precludes practical application.

The first and still the most efficient electrolytes were liquid, so cell and module designs that prevented electrolyte leakage had to be developed to prevent evaporation. Stability and lifetime of DSC modules have thus reached appreciable values, and rapid improvements are being made [7].

OrionSolar has developed inexpensive modules based on 15cm x 15cm dye cells, by using a low-cost method of depositing TiO_2 in a sponge-like array on top of flexible plastic sheets (Figure 5) [8]. This is only one of the many companies that are waiting for the best moment to start commercial activities to enter the market, as in the case of the Japanese Mitsubishi, Sony, Sharp and Aisin Seiki.

Applications

DSC technology is probably the most appropriate application for use in building integration. The wide range of available

Photo courtesy of CSIRO and Dyesol.

Figure 6. Dyesol manufactured the solar wall panels to supply and install in the CSIRO Energy Centre in Newcastle, Australia.

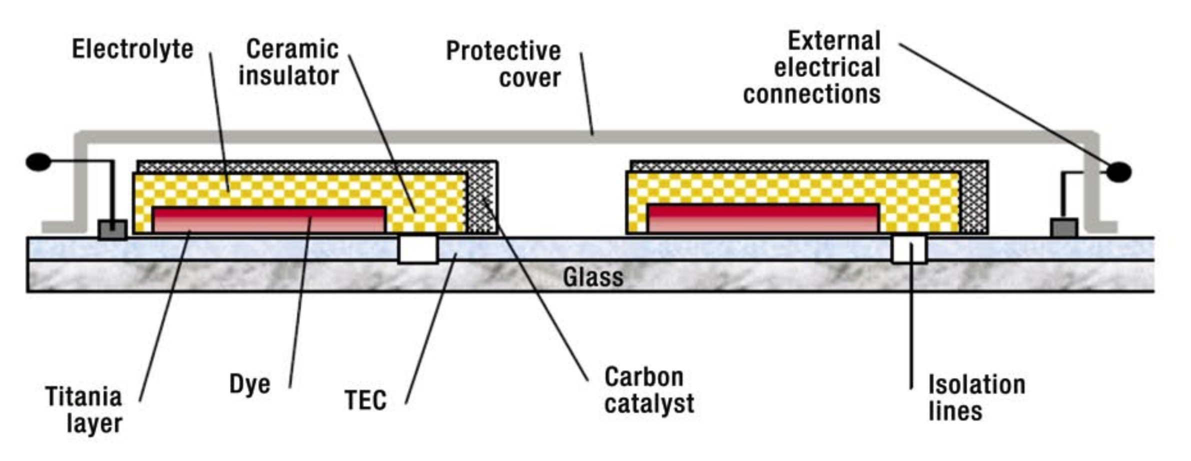

Image courtesy of Dyesol.

Figure 7. Integrated module design for a typical DSC module.

colours and transparency, along with the wide range of operation temperatures and the relative insensitivity to the angle of incident light make DSC modules very attractive. All these factors allow for building-integrated windows, walls and roofs of varying colour and transparency that will simultaneously generate electricity even in diffuse light or at relatively low light levels, in addition to whatever other function they serve.

A pioneering building integration took place in Australia in 2003 as the research body CSIRO commissioned a DSC BIPV system for the CSIRO Energy Centre in Newcastle, shown in Figure 6. The order was in April 2002, and Dyesol manufactured the solar wall panels to supply and install.

Solar wall panels are constructed in a laminated design, with the connected tiles sandwiched between two panes of glass, fully encapsulated in the UV-resistant transparent laminating polymer. Electrical interface can be typically via a short DC bus to a local area network for regulation and distribution or inversion to AC. The integrated module design comprises two sheets of conducting glass with the electrode deposited on one sheet and the counter-electrode deposited on the second sheet (see schematic in Figure 7).

Other applications, mainly developed by G24i, include efficient and lightweight solar power for extra talk time for mobile phones, solar stations consisting of an ecosystem of solar products to enable the use of mobile phones in areas not reached by the electric grid, and solar jackets with integrated battery supply for universal charging together with LED lights, as illustrated in Figure 8.

Roadmap

One of the major points of DSC technology is the technology's relative insensitivity to impurities. This, along with the intrinsically low cost of the constituents, allows for production costs much lower than those of conventional crystalline silicon.

Image courtesy of G24i.

Figure 8. Solar station (left) and jacket commercialized by G24i.

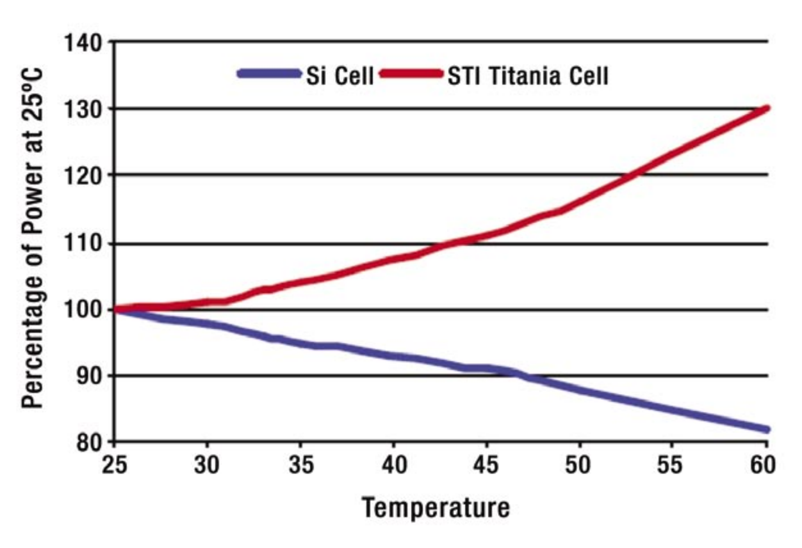

Image courtesy of [9].

Figure 9. The performance of dye PV modules increases with temperature, contrary to Si-based modules.

Advantages of the technology include its low cost - the materials are inexpensive, abundant and innocuous (titania is widely used in toothpastes, sunscreen, and white paint); ease of production; transparency; and compared to Si-based cells, DSCs boast easy bifacial configuration - advantageous for diffuse light - and colour, which can be varied by selection of the dye, including invisible PV cells based on near-IR sensitizers. Furthermore, contrary to Si-based modules, the performance of dye PV modules increases with temperature, as the graph in Figure 9 shows.

Hence, the global energy production of these modules is significantly higher than that of amorphous Si-based modules, despite their lower 5% efficiency. This was demonstrated during the 2005 Expo in Japan by analysis of the setup of the Toyota exhibition house, which was equipped with DSC modules consisting of wall-integrated 2.5m x 2.5m solar panels. Keeping a close eye on the energy produced, it was revealed that the

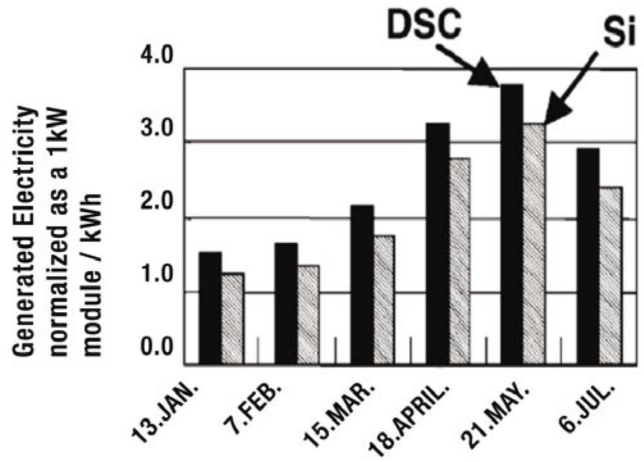

Image courtesy of [10].

Figure 10. Toyota's exhibition house at Aichi 2005 Expo was equipped with two large DSC modules whose output outperformed that of an a-Si panel.

DSC modules gave a faster output rise in the morning and a slower fall in the afternoon due to a different dependence on solar incident angle. The breakdown of the data collected is displayed in Figure 10 [10].

Stable and 10%-efficient cells are expected to become easily affordable in a very short time. These cells can surely give shorter pay-back times than other conventional and new PV technologies. As evidence of chemical and thermal robustness, recent accelerated aging tests showed that ≥8%-efficient laboratory DSCs retain 98% of their initial performance over 1000h when subjected to thermal stress (80°C) in the dark or when exposed to both thermal stress (60°C) and continuous light-soaking over 1000h. These results strengthen the technology's case for real investment, further proof of which is the evidence that suggests that and several companies are working toward commercializing [11].

As to the next few years' developments, it is expected that some companies will attain 10%-efficient modules that approach the criteria for solar module certification for thermal aging at 85°C for 1000h in the dark and for light-soaking in full sunlight for 1000h at 60°C. A realistic goal is that 20%-efficient laboratory-sensitised solar cells will be achieved by 2015.

Research on innovative dyes, for example, is expected to lead to considerable progress in the cell's efficiency. Mitsubishi, a manufacturer of traditional PV modules, has developed a whole new series of undisclosed, high-efficient new dyes. Progressively, the company makes its proprietary newly developed dyes available to Japan's scientific community engaged in PV research. Among such dyes, the early 2000s saw the first example of metal-free, entirely organic dye indoline, that (at the beginning of the 2000s) gave an 8% efficiency [12]. This is only one of the many developments made in the last few years that will surely bring DSC technology to the fore for many manufacturers as a viable processing method.

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About the Authors

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