Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 164 (2004) 209–219

Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Light and energy—dye solar cells for the 21st century

Gavin E. Tulloch[a,b,*]

[a] *Sustainable Technologies International Pty. Ltd., P.O. Box 6212, Queanbeyan, NSW 2620, Australia*
[b] *Greatcell Solar S.A., Lausanne, Switzerland*

Received 26 November 2003; received in revised form 20 January 2004; accepted 20 January 2004

Abstract

Dye solar cells (DSC) are the first commercially available third generation solar cell technology. DSC have been subject of increasing laboratory research since first reported by Grätzel in 1991 [Nature 353 (1991) 737]. Much of that work has been involved with laboratory scale cells of less than 1 cm^2. The knowledge resources required to undertake research in DSC are much broader than those necessary for traditional solar cell technologies such as silicon. These elements are discussed and related to the operation of the DSC, from which the relative advantages of DSC are gleaned.

The experience gained from laboratory work has formed the basis for market expectations concerning performance and stability of DSC in commercial applications. However, it has been found that there is a new set of variables to be addressed when taking the technology from the laboratory cell level to the module and product level. This paper describes the background cell technology and the module designs considered for the first production DSC modules and explains the reasons for selection of the preferred design for outdoor applications. A number of alternative product designs that are expected to be commercially viable in the next several years are discussed. In conclusion some tandem designs demonstrate the potential of DSC for integrated products to serve the energy market.

Keywords: Dye; Solar; Module; Product; Sustainable; Electrochemical

1. Introduction

Dye solar cells (DSC), first disclosed by O'Regan and Grätzel in 1991 [1], have promised to provide a 'leapfrog' in solar cell cost effectiveness and the field has attracted an increasing number of academic and industrial research teams [2,3], especially in the past 5 years since Grätzel and his team at EPFL were able to demonstrate the first 10% efficient cell at NREL in USA. Since 1993, industrial researchers have led the way with teams from Germany, Australia, Switzerland and, more recently, Japan at the forefront of the pioneering collaborative research with EPFL. Based on licenses to the core patents held by EPFL, these teams built strong bases for product development. In Australia, the team led by Sustainable Technologies International (STI), built its expertise on a solid grounding in sol–gel, synthetic chemistry, solar cell devices, optics and electrochromic device technology. The history of that development is summarised in Fig. 1.

2. Cell research

There are three key features to a dye solar cell:

- *Photoelectrochemical*: Charge separation occurs at the interface between the titania, a wide band gap semiconductor, and the distinctly different material, the electrolyte.
- *Nanoparticulate*: The surface area of the titania film is about 1000 times its apparent area. The device comprises essentially transparent crystalline nanoparticles in a 'light sponge' with nanopores.
- *Dye-sensitized*: The dye absorbed as a monolayer to the titania is the primary absorber of light—the capturer of the photons. Because the titania is inherently transparent, there is an increased chance of photon capture by the dye as the angle of the light moves away from normal.

The following subsections describe different aspect of the cell research to optimise these features.

2.1. Substrates

The early work on cell design produced the evidence that to achieve higher efficiency better conductive substrates would be necessary. Previous research and product

---

[*] Tel.: +61-2-62991592/+41-21-6012563; fax: +61-2-62991698.
E-mail addresses: gtulloch@greatcell.com, gtulloch@sta.com.au (G.E. Tulloch).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.photochem.2004.01.027

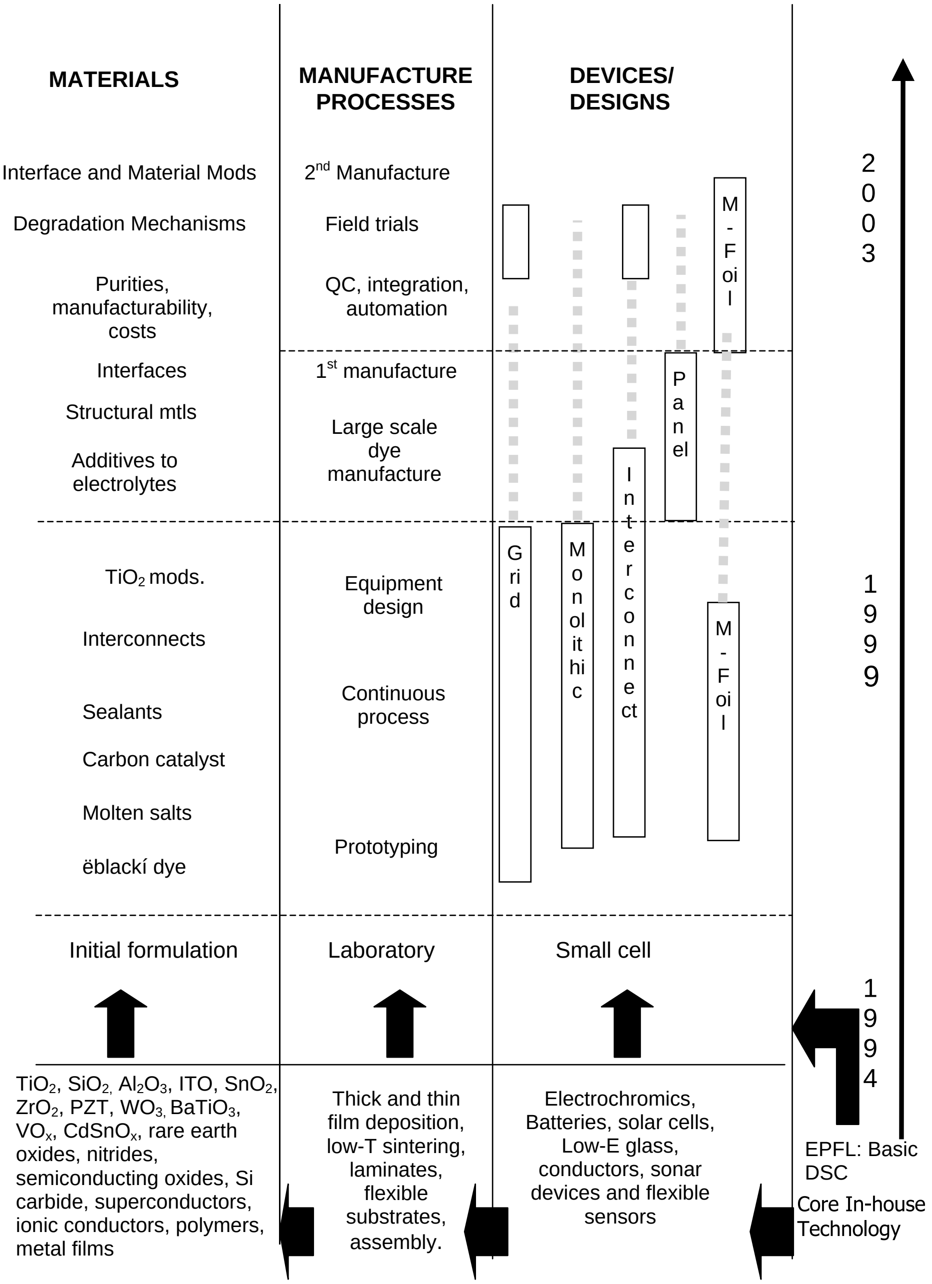

Fig. 1. History of DSC development at STI.

development of sol–gel-based conductive coatings and electrochromics at STI had shown the limitations of the transparent conductive coatings then available (1994) on glass, and even greater resistivities, coupled with higher cost and thermal instability of conducting coatings on plastics. At the outset, plastic substrates were rejected except where the plastic was laminated with a metal in the form of a film or grid. In 1995, STA commenced a collaborative program with BHP (then Australia's leading steel company) to demonstrate the application of DSC on flexible metal substrates, including, among others, titanium, steel and alloys. This resulted in demonstration of the feasibility and practicality of this concept and a patent application by BHP that has since been abandoned [4]. Key features of this program were the realization that the process must be continuous and that most metals (except particularly titanium and platinum) must be protected by a corrosion resistive conducting coatings. It has also been realised that if a substrate is selected in a form of thin metal foil, the foil must be encapsulated by plastic to provide mechanical integrity. However, as will be discussed later, work on all flexible substrates was put on hold in 1997 and the program subsequently concentrated on glass and thicker metal substrates.

2.2. Titanium dioxide

A significant project was carried out for 2 years, involving preparation of the titanium dioxide nanoparticle colloid by the autoclave route, in collaboration with ANSTO, wherein the conditions were optimised for small batches of colloid using the acidic precursor. The team also developed independent paste preparation and studied a range of processes for deposition. The two selected deposition processes were doctor blading and screen printing, though ink-jet printing was also a preferred option, but was not taken to the development stage because of the potential high technical risk at that time for high viscosity inks. Ultimately, screen printing was selected due to the potential for better definition. Methods to increase interconnection between titania nanoparticles have been subject of on-going research at STI since early 1995, based on STIs extensive expertise in science and technology of sol–gel. These materials have included the well-known $TiCl_4$ treatment as well as addition of titanium alkoxides and other ‘polymeric’ network forming titanium chemicals. Other cations have also been trailed. In summary, the addition of a network forming chemical (or ‘cement’) improves the performance of titania films that have been poorly ‘sintered’, i.e. those that do not have adequate ‘necking’ between particles as a result of the heat treatment process. It has been found that the capability of the titania particles to form an effective network is related to the preparatory conditions of the colloid and the paste.

Other modifications of the titania layer have been proposed including addition, predominantly by sol–gel means, of zirconia, antimony oxide, alumina, silica and niobia but the results have been inconclusive.

Core-shell techniques have been the subject of more recent studies based on electronic modifications to the titania. Separately, Kay and Grätzel [5] developed a technique to coat tin oxide particles with titania and other oxides to improve the dye absorbance and hence photocurrent of the more conductive tin oxide.

2.3. Dye

Dye development, in collaboration with Monash University, predominantly involved reproduction of the EPFL formulations modified to improve ease of processing and purity. Some ligand developments were trailed but did not yield improvements. To a similar extent, trials of dye co-adsorbents involving organic acids with a view to produce titanate ester blocking layers yielded only temporary improvements in performance. Sixteen different acid and salt additions were trailed from C7 to C17 chain lengths with a view to reduce dark current and substantial temporary voltage improvements were achieved. These studies, that showed the importance of long-term high insolation and high temperature testing, provided the impetus for development of automatic multi-cell testing equipment at STA and the use of a range of stresses to evaluate stability and performance. Subsequently Wang et al. [6] at EPFL derived an amphiphilic dye referred to as Z907 that has shown very good high temperature stability while retaining good performance.

2.4. Electrolyte and counter electrode

Electrolyte development was based on modifications of the solvents and redox couple. Some solvents such as acetonitrile were rejected early in the program due to toxicity considerations and difficulty with long-term sealing due to high vapour pressure and chemical reactivity. Others, such as valeronitrile were rejected because of low boiling point and high vapour pressure at anticipated operating temperatures (>70 °C). All simple solvents were found to suffer from one or more limitations, including toxicity (e.g. glutaronitrile which also required purification), cost (e.g. methoxyacetonitrile), stability (e.g. γ-butyrolactone under UV radiation), reactivity with other cell components, or purity. Ultimately, it was necessary to develop a proprietary solvent mixture based on low cost solvents that would be effective at the anticipated operating temperatures.

Trials of alternative redox couples (ferrocenes, $(SCN)_2/SCN^-$, Br^{3-}/Br^-) provided no enhancement over iodide/triiodide and in some cases introduced adventitious water (as in the case of ferrocenes). The high insolation trials demonstrated that water additions cannot be sustained for full sun conditions due to either or both of dye desorption and iodine consumption (in the case of the iodide/triiodide redox couple). The early studies used molten iodide salts such as 1-methyl 3-hexyl imidazolium iodide (MHII) or 1-methyl 3-propyl imidazolium iodide (MPII), produced in STI laboratories, with addition of lithium iodide and iodine. Later in the program (1997), the molten salt was changed to the solid 1,2-dimethyl 3-propyl imidazolium iodide (DMPII). It was recognised that all these imidazolium-based iodide salts are hygroscopic and must be stored under appropriate dry conditions. A range of buffers were trailed with the objectives to improve cell performance and to ensure that local conditions in the cell did not cause desorption of the dye. Some buffers (such as 4-*tert*-butyl-pyridine (TBP)) suffered from purity variations that were considered disadvantageous for long term stability. Buffer concentration had to be optimised for each electrolyte formulation (e.g. solvent, iodide/triiodide concentration).

The counter-electrode options for dye solar cells are limited due to the requirement for mechanical and electrochemical stability. Except for the monolithic design (see Section 3.2), dispersed micro-platinum crystals is the material of choice. The key issue was found to be control of the deposition process to ensure an even dispersed coating. Trials of a range of coating methods and concentrations were carried out to select the optimum ranges for different light conditions. Ultimately, the preferred deposition method is screen printing for the designs being utilised by STI. Spraying (either two stage or spray pyrolysis) and doctor blading are also acceptable. The precursor hexachloroplatinic acid and the paste, must be kept away from strong illumination to enhance shelf-life.

2.5. Sealants

In the period to 1999, trials of a range of thermoplastic and two part sealants were carried out. The aggressive corrosive properties of the nitriles reduced the list of acceptable polymeric materials to polyolefin thermoplastics, some epoxies and additive silicones for sealants in contact with the electrolyte. The option of glass seals was rejected due to perceived difficulties in scale-up. In practice, all these sealants are still used in various applications in DSC products.

3. Module development

Three quite separate module designs were considered. The parallel grid module (mentioned above) was the initial selection to maximise active surface area. As a result of problems with this design, EPFL conceived two alternatives being the series monolithic (or Kay cell) and the series interconnect.

3.1. Parallel cell modules

The first module design trailed in 1995—the parallel grid—utilised conductive fingers to collect current in a 100 mm × 100 mm glass substrate module. It was recognised that the parallel modules would have to be connected in series to obtain an acceptable panel voltage, but it was also reasoned that the highest active surface area would be obtainable in a parallel grid cell. Metals trailed for the grid to reduce resistive losses of the conducting coating on the glass included Ag, Au, Cu, Al, Ni, but, all of these metals were corroded by the iodide electrolyte, even when protected by polymer or ceramic glazes, due to pinhole and leakage at the interface of the overcoating with the substrate. To ensure satisfactory sealing multi-layer thick overcoats were required that increased the cell thickness to over 100 μm resulting in reduced fill factors and currents, especially under full sun conditions. These results were presented in various forms in 1996. These issues have since been solved at a production module level, but not yet commercialised. The option to use platinum and other similar metals was rejected due to cost, while titanium and tungsten were considered too resistive and difficult to utilise despite good resistance to corrosion. For example, the use of micro-wires was rejected due to difficulties with ensuring electrical contact under thermal expansion conditions. Carbon was trailed but the resistivity was too high.

Consequently, in 1997 work on the parallel module was suspended and not recommenced till 2001, when, following the identification of new protective coatings for the silver grid, a design was produced that yielded over 6% active area efficiency at the module level (180 mm × 100 mm). The challenge still is to increase fill factor by reducing the thickness of the cell. Laser or saw grooving of the glass for the grid lines to reduce the height of the grid/overlayer laminate was rejected due to additional costs of manufacture.

3.2. Series interconnect Z and W designs

There are two options for series interconnected two glass substrate modules.

3.2.1. W-series design

This design accumulates all current on each substrate and should have identical output when illuminated from either side. It avoids interconnects but entails each cell being alternate bias (i.e. working electrode/counter-electrode) and still requires separation of the cells by an effective seal. The design has apparent advantages in simplicity and avoids the reduction in fill factor resulting from additional resistance of series interconnects, but has some manufacturing and performance weaknesses. In manufacturing of this design, it is necessary that the counter-electrode and working electrode are each processed on the one substrate. This introduces processing complexities in deposition and curing. In addition it decreases the options for post-treatment of the titania electrode and requires masking for pre-treatment of the substrate. Unfortunately, the width of the electrodes must be different as the current of the cell from the counter-electrode side is approximately 80% of that from the working electrode side due primarily to absorption of light by the triiodide ion but also due to increased recombination. There are also potential issues of imbalance under differing light conditions, so it is essential that this design be optimised for full sun condition. Because of the lower performance from the counter-electrode side, this design provides about 80% of the performance of a similar Z interconnect module. Other factors described above (e.g. post-treatment) may reduce performance by a further 10%.

3.2.2. Z-series interconnect

The Z-series interconnect, which can also be used for glass/metal, plastic/metal, glass/plastic and plastic/plastic substrates, comprises two opposing electrodes with the connection between cells consisting of a conducting medium. This medium may also act as the barrier between cells, as disclosed in of STI Patent [7], it may be a filament with a separate barrier, or it may be comprised of composite materials. The advantage of this design is high voltage output at relatively small IR losses and facility for pre- and post-treatment of the working electrode. The disadvantage, as stated above, is the risk of lower fill factor resulting from the series resistance of the interconnect. STI selected this design on the basis of invention of an interconnect design with low resistance. The working electrode and counter-electrode can be separately optimised and there is no requirement to mask the counter-electrode or preseal the module when applying the dye. Consequently, the dye uptake can be more carefully controlled. On the basis of manufacturing cost analysis and reproducibility, STI had rejected any module design, such as the ‘masterplate’ concept commonly used in several European projects, that required application of the dye by pumping after sealing. The requirement to pump also utilises more dye and there is a risk of dye adsorption on the counter-electrode. The curing of the interconnect and the primary seal are carried out in one operation. It is essential to ensure that the module thickness is uniform from cell to cell to avoid mismatch. This is common for all series connected modules except the monolithic (see below). This curing is followed by injection of the electrolyte and final sealing.

The design selected for the first module product consists of six cells in series. The substrates are offset to provide for electrical connection from silver buses on either side. The resulting series interconnection can then be ‘tongue and groove’.

3.3. Monolithic series interconnect

The monolithic module (or Kay cell named after the inventor Dr. Andreas Kay), is an alternative design that has significant advantages for volume production and for relatively small cells. It effectively eliminates one substrate by connecting both electrodes to the one conductor substrate and effecting the cell by electrical isolation on that substrate. It consists of three printed layers, so thickness (and uniformity) is controlled by the printing process. The novelty was in the selection of a suitable insulator between the working electrode and the counter-electrode/back substrate, and selection of the back substrate material to enable both catalysis function for the redox reaction, connection to the substrate and low-ohmic losses. The insulator can be zirconia or any similar electrical insulator that can be printed on top of the titania working electrode. The material must be porous to facilitate ionic transport. The back electrode of choice is carbon in different morphological ratios and doped to enhance bonding to the substrate. The dye is usually applied after all materials are printed so the dye usage is higher than in the Z-series interconnect, and fill factor has been a limiting factor for high solar insolation conditions. At STI the research activities did not succeed in perfecting the bond of the carbon electrode to the substrate or ensuring adequate high light performance. Consequently, work was suspended in 2000, subject to identification of alternate materials. There are new concepts in structured nanomaterials (e.g. nanochannels) that could make this design more viable. This is the preferred design for flexible substrates as it does not required separators to maintain constant cell thickness.

4. Panels

4.1. Design considerations—DSC advantages

On the basis of the development and testing of the modules, the advantages of and challenges for DSC became more apparent. Whereas, in early projections it had been forecast that the product would initially perform well in strong solar conditions compared to crystalline silicon, the practical efficiency of the modules at this stage of development (4–5%) is not competitive for the full sun roof market. In addition, calculations were carried out to show that a throughput of at least 40,000 m^2 per year would be required to be cost competitive with standard silicon panels. Fortunately, the DSC modules have exhibited a number of strategically important advantages over other solar cell technologies. These are:

- the ‘natural’ colours and option for inherent transparency;
- performance enhancement at low light;
- performance retention at high angles of solar incidence;
- very low added energy to the basic glass substrates;
- clean manufacturing processes;
- capacity to produce tandem products such as photoelectrochromics built on the inherent transparency of the DSC device (see Section 7).

Consequently, it was decided to direct the product development to a market that would be receptive to these advantages and for which current price was not the major driver. The selected market is building facades, and the means of addressing the market was decided to be through supply of façade elements isostructural with glass, stone or similar façade panels.

4.2. Panel design

There are three elements of panel design, mechanical, electrical and asthetic.

4.2.1. Mechanical

For the panel to be a replacement for another façade element it must comply with standard building practice in terms of size and mechanical properties. It was decided that the first panel design should fit a standard 600 mm × 900 mm envelope. This required that the external pane of glass should be 4 mm thick and toughened. The number of modules to fit the 600 mm × 900 mm envelope is 24, in three rows of eight modules. The requirement for the series connecting material is to provide a flexible connection between modules to reduce the risk of breakage. The design also incorporates provision for an edge sealant similar to that used in DGU construction and a laminating encapsulant between the outer glass panes and the modules. This encapsulant fulfils four roles:

- laminate for mechanical toughness (panel is tested to the equivalent of 200 km/h winds);
- UV protection;
- high visible light transmission;
- acoustic reflection at interface.

The selection of the encapsulant is limited by the requirement that, in manufacture, the modules not be heated to over 100 °C for more than a few minutes.

4.2.2. Electrical

A combined series parallel design was selected with each row of three tiles in parallel and the line of eight tiles in series with V_{oc} of between 27 and 30 V. The electrical series connection is a flexible conducting polymer. The external leads are soldered and provision is made for thermal expansion. Modules are selectively matched for V_{oc}, I_{sc} and fill factor to prevent mismatch. The module measurement is carried out on aged modules as the ageing rates may vary in the first few days after manufacture from batch to batch.

Electrical wiring is effected via independent connectors at each panel using channels designed into the frame sections.

4.2.3. Aesthetic

For architectural applications the panels must have aesthetic acceptance. The architectural options are:

- colour shade and density;
- transparency, translucency, opacity;
- colour shade of outer pane;
- back reflectors/refractors;
- outer pane patterning;
- intra-module patterning.

There is a trade-off between performance and architectural effects. Increasing opacity increases performance. For a transparent panel, use of reflectors increases performance by 15–20%. Modification of apparent array colour by utilising a coloured outer pane reduces performance proportional to the light absorbed by the outer pane in the blue/green spectral range. Patterning only affects performance to the extent that active PV area is reduced.

The final element to create the desired aesthetic effect involves the selection of framing materia, style and colour.

5. Façade systems

5.1. The façade environment—outdoor factors

There are several factors that must be considered when installing solar panels, and specifically on a façade, and for some of these, the response by DSC panels differs significantly from that of silicon panels.

5.1.1. Temperature variation

In a similar manner as any large glass module, differential thermal expansion must be recognised in the design of the panel and the design of the façade. The key difference between DSC and silicon wafers is that the DSC modules are comprised of glass, as are the outer panes, so thermal expansion mismatch only occurs ‘front-to-back’ due to temperature gradients. Nevertheless, the DSC panels do show performance degradation above 60 °C due to thermal expansion of the modules resulting in increased gap between the electrodes and lower fill factor and current. This effect is being quantified, and engineering modifications introduced to increase the onset temperature for thermal expansion effects.

5.1.2. Internal device stability at high temperature and light

Because DSC is an electrochemical device, the electrochemical balance must be maintained at the maximum operating conditions of temperature and insolation, i.e. the point of maximum stress for secondary corrosion mechanisms. The selection of electrolyte and quality of the counter-electrodes are key to achieving stability. In addition, any mismatch in cells or modules that could cause significant reverse bias will be exacerbated under these conditions.

5.1.3. Cell electrochemical balance versus time

The long term ageing characteristics of large DSC panels in real time are not yet fully understood due to the early stage of commercialisation. Consequently, until such data is available, a design criterion has been implemented to utilise matched modules from the same batch group in any set of panels, and to age panels before matching for array installation. The criteria for matching are similar to those for rechargeable NiCd cells.

5.1.4. Shadowing and solar range effects

Whereas the performance of silicon solar panels and array sections is significantly affected by shade (especially temporary shade that results in inverter shutdown), DSC performance reduces approximately proportionally to the average light level, so there are less instances of inverter shutdown. A similar effect is evident at low light (whether due to angle, haze/mist or general cloud cover). Fig. 2 shows the dc output comparison between two side-by-side north facing solar panels—DSC and amorphous silicon—on a test bed at STI. This graph shows the significant advantage of the DSC panel in periods on either side of the peak solar insolation period in the middle of the day. The extent of this benefit requires further quantification.

5.1.5. Mechanical stability

There are two elements of mechanical stability, mechanical loading and water ingress. The DSC panels are mounted in a frame that is designed to provide additional impact and flexure loading to the mechanical integrity of the panels. In the case of physical damage to a pane, the toughened glass is held in place by the encapsulant, it is not possible for a pane to become dislodged. The design of the frame also eliminates direct water ingress to the panel. There is, as yet, no statistical evidence for water ingress as a cause of failure. Results of laboratory humidity trials will be published when available.

Both modules have the same peak-Watt power. Ratio of instantaneous power outputs is presented versus time during 24 August 2003. Periods 1 and 3 (morning and afternoon hours) are characterised by high angles of incidence and relatively low sun irradiation. During the Period 2, solar angle of incidence is closest to 90° and irradiation is the

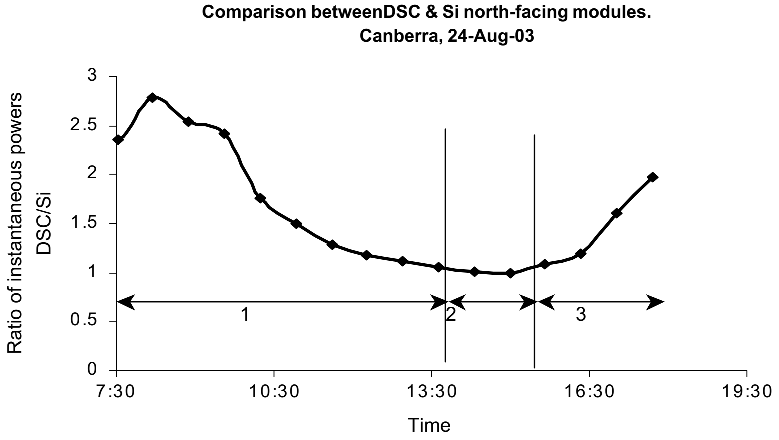

Fig. 2. Comparison between DSC and Si modules.

highest so conditions during the Period 2 are closest to the standard testing conditions. Although, the two modules have similar peak-Watt power, total energy output of DSC module is higher than that of Si module.

5.2. Façade systems—characteristics of DSC arrays

5.2.1. Transparency

The design of the module elements provides about 65% active area, 15% transparent glass, 5% translucent area and 15% opaque area. The visual impact of a panel from a distance of several metres is that of a transparency with the colour shades being bands of ochre and gold in transmission and magenta in 'reflection'. Architects have provided positive feedback to the architectural effect both from the outside as an architectural feature and from the inside for the lighting effects.

5.2.2. Energy efficiency

The DSC panel consists of effectively four panes of glass with polymer and ceramic material between each pane. According to the numbering protocol for glazing structures, where the surfaces are numbered from the outside, surfaces 4 and 5 each have 'super' low-*e* properties arising from the transparent conducting oxide layers. These layers provide for IR reflection from both sides. Nevertheless, the DSC panel absorbs a significant amount of energy, typically a panel will experience a temperature of 20 °C above ambient. Consequently, the DSC panel will inject heat into a building if mounted as a flush element of the building envelope. This characteristic can be used for convective energy management. For hot climates it is recommended that the array be mounted to maximise draft on the outer surface. The *U* value (thermal conductivity) will be reported separately, once independent tests have been performed.

5.2.3. Acoustic performance

The double laminate structure of the DSC panel provides multiple acoustic interfaces that reduce sound transmission. The use of low modulus laminate further enhances the noise reduction. Total sound transmission will depend on the overall thickness of the panel, but for a 16–18 mm panel, with noise isolation mounts, the calculated reduction of transmission through the panel is >40 dB.

5.2.4. Power availability

One issue that has reduced the introduction of façade mounted BIPV arrays in all but the more northern climates of the northern hemisphere is power availability. Silicon arrays lose conversion efficiency when the angle of incidence of the solar radiation increases with more dramatic fall-off at about 70° due to increasing reflection from the glass surface. The power of the incident solar radiation per unit area of panel is dependent on $\cos\theta$ with respect to normal incidence. For this reason, expensive structures are used to modify the light or angle the silicon array when used in lower latitudes. DSC has two advantages over silicon in this operational mode. The first is the 'light sponge' effect whereby the percentage of photons converted to electrons increases with increasing non-normality of the light. This effect is enhanced through reflected and refracted light. The second effect is the bifaciality of DSC. DSC panels provide about 80% of standard output from illumination from the rear surface.

Consequently, in arrays where light can be captured from both sides, the power availability is very high. Fig. 3 shows the output for a specific period from a demonstration array. The increased power availability reduces balance of system costs in terms of inverter rated power per delivered kW h, and improves array/grid interface management.

5.3. Façade system advantages

There are specific general advantages in façade BIPV compared to stand-alone grid PV. These are:

- do not require any extra land area;
- do not require additional mountings when designed as a façade product;

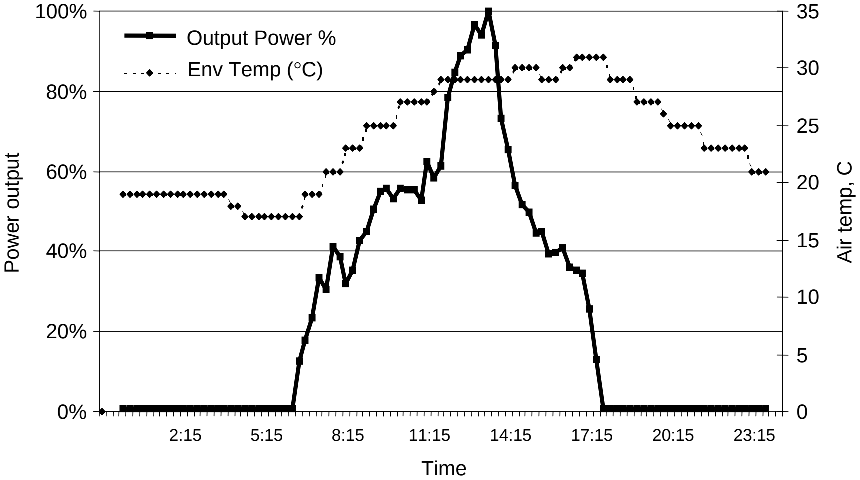

Fig. 3. Power availability of bifacial DSC array.

- replace conventional wall materials, which reduces payback period;
- provide an aesthetic design element;
- provide electricity with minimum transmission/distribution losses;
- reduce demand for additional distribution cable;
- provide a visible demonstration of the ESD credential of the building.

6. Roof and stand-alone products—low cost future

For at least the next 5 years, crystalline silicon will outperform DSC in sunbelt roof and stand-alone applications. Consequently, for DSC to compete in those markets (that are not driven by architectural and engineering considerations or by value of multi-use attributes), low cost modules must be developed that can be manufactured in relatively low volumes in distributed regions. Among the several designs that have been considered for this application, two are discussed here.

6.1. Large sheet DSC

The thickness of a DSC device must be no more than about 50 μm to obtain good performance. Experimental evidence from comparison of three different thicknesses of cells separated with surlyn (35, 54, 81 μm) showed that the thickest cell had reduced power resulting from lower current and fill factor especially under strong solar radiation. This limitation on thickness creates a problem for manufacture of large area modules. The limiting factor is the glass. Flatness of glass coated by transparent conducting oxide (TCO, typically: fluorine doped tin oxide) has been measured on a 200 mm length to be ±5 μm. However, after heat treatment this variation can be ±10 μm, due to the differential thermal expansion of the two sides arising from the increased IR absorption by the TCO coating. While it is possible to reduce this variation, it has been considered undesirable to base a manufacturing operation on the assumption of assured flatness of the glass. Obviously, if the thickness of a module were to vary 50 ± 20 μm, the performance of cells would differ significantly and the module would be mismatched at high insolation, resulting in significant reduction of performance and possible degradation.

STI scientists devised a design (Patent Pending) shown in Fig. 4, that reduces the impact of variation of glass flatness and is easier to manufacture. This design consists of a single pane (say 600 mm × 900 mm) isolated for series interconnection on which the titania (or other semiconductor) is deposited and heat treated and possibly toughened. The titania is then preferably dyed prior to assembly of the

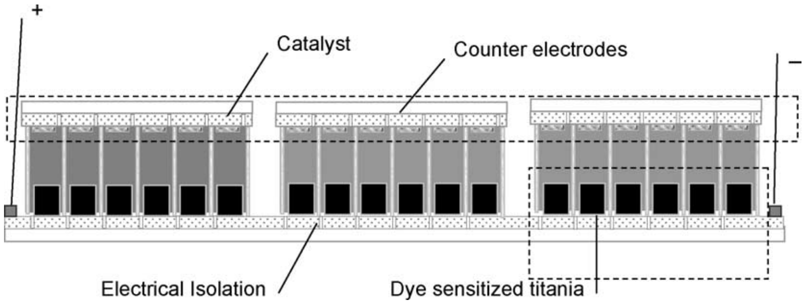

Fig. 4. Large sheet DSC.

counter electrodes (say 150 mm × 220 mm) with interconnect and sealant onto the working electrode. The structure is backfilled with encapsulant and a back pane, normally metal sheet or plastic (rigid or flexible) is applied.

This design has an advantage for lower weight applications, such a roofing, and will be significantly cheaper than the façade panels.

6.2. Monolithic large sheet DSC

An alternate solution to the construction of larger panes is the use of the monolithic design. In this design (see Section 3.3), all electrical connections are made on the base substrate and the overall panel thickness may vary (control of encapsulation is not critical). The unique feature of this design is the means of providing electrical connection at any position on the module. This is achieved by use of a feed through pin connector that is hermetically sealed on the rear side of the panel.

6.3. Flexible designs

Flexible designs are not novel and were considered very early in the development of DSC (see Section 2.1). The concept of a metal foil laminated with polymer as an alternative to ITO on polymer is well known and the use of mesh as a means of implementing the metal surface was first proposed to STI in March 1998 [9]. A design development at STI is shown in Fig. 5.

The difficulty with implementing these designs has been two-fold—temperature for heat treatment of the titania is limited to about 250 °C for thin metal films, so this necessitates utilising the lower efficiency ‘cemented’ titania films (e.g. addition of sol–gel-based binders). In addition, the use of titanium foils or thin sheet adds material cost. In order to reduce cost, STI developed a process to enable the use of other metals as the flexible substrate while avoiding corrosion from the iodide. This process, which is subject of a Patent Pending, enables the use of materials such as stainless steel and other metal foils and a wide range of mesh metals. Fig. 6 shows the stability of cells using STI standard manufacturing processes and materials but with a stainless steel substrate. The process for continuous manufacture of the cells and modules is subject of a patent granted in USA [10].

7. Tandem designs

The capability to produce transparent DSC provides the opportunity for two types of tandem devices.

In the first type the dye solar cell is in series or parallel with another device such as the electrophotochromic devices patented by STI [8]. In the series device, the DSC operates in power limited mode (with low iodide concentration for high visible light transmission) in series with an electrochromic smart window based on tungsten oxide and vanadium oxide. One key element of the STI invention was the ability to deposit the coatings on opposing sides of the inner glass pane. The parallel design incorporates a smaller standard DSC device deposited on one section of the window providing the 0.05 W h at up to 2 V for each switch. The absorption spectrum of the dye is optimised with respect to the spectrum of the light required for the other device. The power is delivered by either feed-through or wrap-around electrodes.

The second type is a related, but later invention, that draws for some of its implementation on the first type. In this device there are three elements rather than two. It is a chemical conversion device that, in the STI design, utilises photocatalytic properties of a material (typically tungsten oxide) on surfaces 2 or 3 to split a chemical compound such as water to produce hydroxide radicals. The light not absorbed in this cell is passed to the dye solar cell (in series—and, in

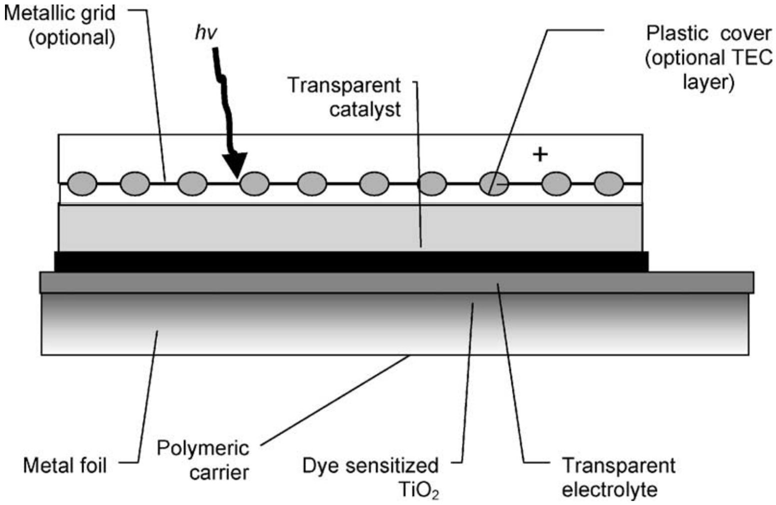

Fig. 5. Flexible metal/polymer DSC design.

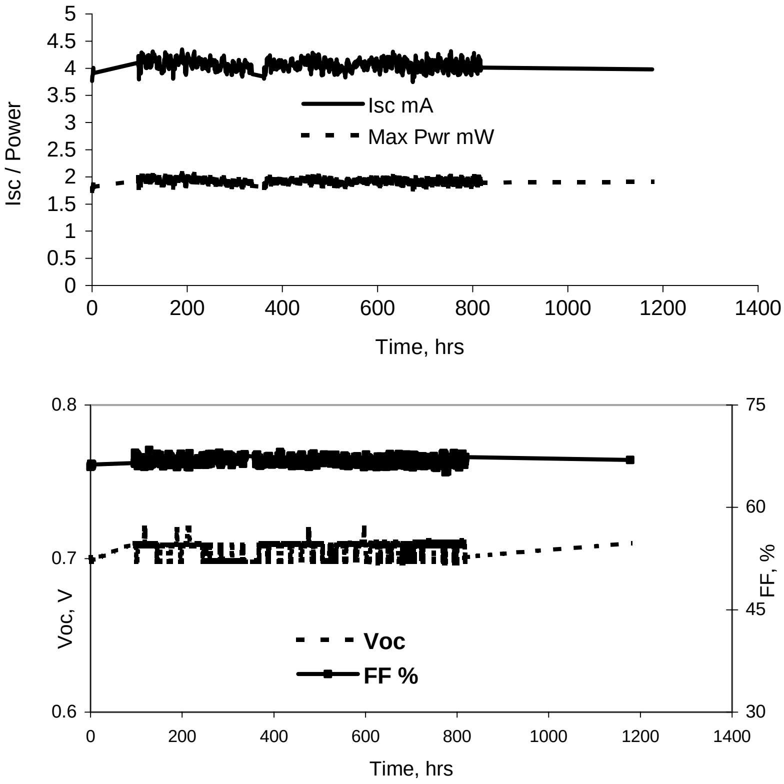

Fig. 6.

the case of the EPFL patent—integrated) where it produces power to produce hydrogen from a platinum or similar catalytic surface (typically surface 6). The challenges to this device include efficiency, materials stability, ionic conductivity of the electrolyte and capture of generated hydrogen. In an embodiment of this design, a patent application has been filled that may incorporate these types of tandem device as integrated building structures [11].

8. Conclusion

In the 12 years since the dye solar cell was invented, many unique opportunities have been realised for the application of these cells in products. In the near future, DSC panels that have outstanding architectural appeal are forecast to be in wide use in the commercial façade market. Within a few years, lower cost rigid and flexible products will become available. Later in the decade, electrophotochromic windows should be commercialised. During the next decade, the introduction of tandem water-splitting devices is possible.

However, to address the low cost product markets and to compete with the silicon industry, it will be necessary to increase delivered power of the products. At STI, a program was initiated in 2002 to progressively enhance the performance of standard products (this compares to performance enhanced products resulting from special designs). The program goals are for performance doubling by

- application of semiconductors with lower trap densities;
- increasing spectral response of dyes and use of composite dyes;
- modifications to the electrolyte for interface management;
- closer tolerance manufacture.

The outcome of this program will enable the commitment to automated continuous manufacturing facilities, for flexible product, that could not be economically justified at the current stage of maturity of the technology.

DSC has great promise for the future to provide a combination of energy and natural light for prosperity, particularly in the built environment.

Acknowledgements

The work presented here is the result of many years of effort by the team at STI without whom the technology and product advances would not have been possible. The scientific discussions with Dr. Igor Skryabin proved most helpful. Assistance of Sylvia Tulloch in preparation is recognised. This work has been primarily privately funded, however, the assistance of the Australian Greenhouse Office during establishment of manufacturing facilities and IR&D

START during the first phase of the Performance Enhancement Project in 2003 are gratefully acknowledged. The opportunity to present this work would not have been possible without the encouragement of and generous assistance arranged by Professor Shozo Yanagida and Dr. Hironori Arakawa.

References

[1] B. O'Regan, M. Grätzel, Nature 353 (1991) 737–740.

[2] A. Hagfeldt, M. Grätzel, Acc. Chem. Res. 33 (2000) 269–277.

[3] A. Hinsch, J.M. Kroon, R. Kern, I. Uhlendorf, J. Holzbock, A. Meyer, J. Ferber, Photovoltaics 9 (2001) 425–438.

[4] S.G. Brodie, I.C. Hamilton, E.M. Boge, P.J. Riley, International Patent WO98/05084.

[5] A. Kay, M. Grätzel, Chem. Mater. 14 (2002) 2930–2935.

[6] P. Wang, S. Zakeeruddin, R. Humphrey-Baker, J. Moser, M. Grätzel, Adv. Mater. Commun. 15 (2003) 2101–2103.

[7] J.A. Hopkins, G. Phani, I.L. Skryabin, US Patent 6,555,741.

[8] G.E. Tulloch, I.L. Skryabin, US Patent 6,297,900.

[9] Proposal from Superconducting Ceramic Inc. to STA re-Project Proposal to NIST, STI, 1987.

[10] G. Phani, A.J. Hopkins, D. Vittorio, US Patent 6,652,904.

[11] I.L. Skryabin, G.E. Tulloch, International Patent WO03066993A1.