Solar flair – generating electricity from toothpaste

The latest research into generating solar electricity is replacing complex, expensive solar cells reliant on semiconductor technology in favour of 'dye sensitised' cells built on...toothpaste? Simon Hodgson and James Wilkie shed some light.

The big problem with current technology for converting solar energy into electricity is scale, or rather the lack of it. The classical semiconductor devices produced by the industry are expensive, complex and require exacting standards of manufacture, all of which make producing them in the large area sizes that would be truly useful extremely difficult. In order to generate significant amounts of electricity, hundreds of square kilometres of cells need to be produced every year, and this demands photovoltaic materials that are readily available, can be applied to very large area arrays and are tolerant to the presence of impurities or manufacturing defects. Enter toothpaste, or rather titanium dioxide, its white ceramic pigment.

Generating environmentally-friendly electricity directly from sunlight using solar cells is currently the basis of a world-wide industry growing at around 20% per year. In 1999 the total area of solar panels shipped was about two square kilometres. This area can generate around 200MW of electricity – about the output of a small power station. Most of these solar panels are based on connecting many individual crystalline silicon solar cells together, and the cost of the silicon and the complexity of their assembly makes them expensive. The search for cheaper technology has led to an alternative approach in which a carrier (usually glass, stainless steel or a polymer) is coated with an extremely thin layer of photovoltaic material (such as amorphous silicon or cadmium telluride), but this is also a classical semiconductor device and impurities or crystallographic defects can destroy its working properties.

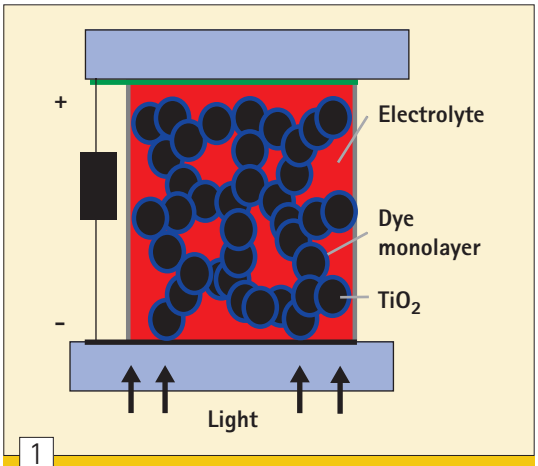
The solar power industry has to develop solar panel technologies that are capable of being scaled up to levels comparable with, or even greater than, the hundreds of square kilometres shipped each year by today's coated glass or photographic film industries. This is a very tall order – we know of no other application that currently depends upon the manufacture of 'smart' materials on this scale. Fortunately, there is a way forward.

In November 1991 two scientists, based at the Swiss Federal Institute of Technology in Lausanne, published an article in Nature in which they described a 'dye sensitised' nanocrystalline ceramic photovoltaic cell based on titanium dioxide. It had a light-to-electricity conversion efficiency of around 12%, a level of performance that, combined with the intrinsically low costs of such systems, represented a remarkable breakthrough and led to an explosion of interest in the field.

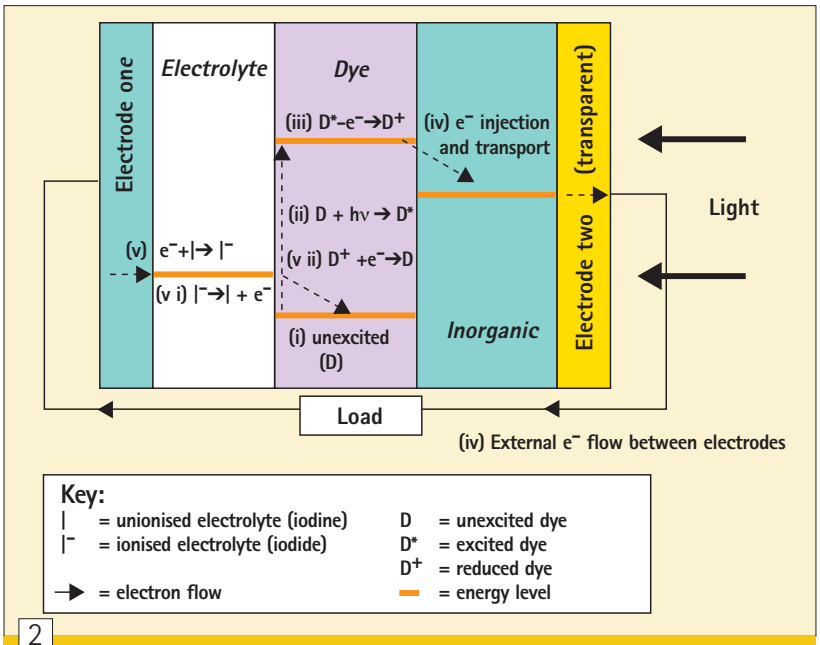
The concept of generating electricity from dye sensitised metal oxides was actively considered from the early 1970s, with a number of workers investigating principally ZnO-based ceramics sensitised by chlorophyll and other organic dyes. However, such systems generally resulted in low conversion efficiencies because the flat dye coated surfaces didn't have enough cross section to interact with more than a small amount of the incident light – incoming light energy effectively encountered a bottleneck. The dyes also degraded rapidly when illuminated.

What the Swiss researchers did was to replace flat oxide films with a 'nanocrystalline' form of titanium oxide to give a material with an extremely high surface area (60-100 square metres per gram). They then coated this with a new dye that was well matched to the oxide and did not degrade so much.

The principle of dye sensitisation forms the basis of colour photography. The essential concept is that a semiconducting material can be made to absorb light outside its normal range of photoresponse by coating it with an optically absorbing organic dye. If the energy levels of the dye and semiconductor are appropriately matched then a dye molecule excited by light can transfer an electron



1 Schematic diagram of cell design for high efficiency dye sensitised solar cell (not to scale)



2 Schematic diagram of the principle of dye sensitised PV device operation

into the semiconductor across the interface between the two materials. In this way, the same semiconductor (silver halide in the case of colour film) can be made to respond to red, blue or other wavelengths of light by the appropriate organic dye.

The main difference between the sensitisation process in a photographic application, and that in a photovoltaic cell, is that the process must be continuous, and thus the depleted electrons in the dye must be continuously replaced by completing the electrical circuit. In the Swiss case this was done by using a liquid electrolyte, figure 1.

Because the electrons are excited within a dye rather than a semiconductor, and then separated by an interface rather than an electric field, these devices are much less sensitive to the effects of low levels of impurities and structural defects than the conventional solar cells mentioned above. This relative insensitivity dramatically reduces the comparative cost and complexity of the manufacturing process and potentially opens the way to truly large area manufacturing.

3 Photograph Shell Solar / ECN dye sensitised solar cell (courtesy of Shell Solar and Energy Centre Netherlands)

The dye sensitised solar cell shown schematically in figure 1 is made from nanocrystalline particles of titanium dioxide (anatase) coated with a monolayer of dye, with the second electrode contact made via a suitable electrolyte. Operation of such a cell involves two main charge transfer reactions – injection of excited electrons from the dye to the semiconducting ceramic, and a 'redox' reaction, typically involving iodine and iodide species in the liquid electrolyte, which regenerates the dye after injection. A schematic diagram of the operational principles for such a cell, with regard to the respective energy levels of the electrolyte, dye and titanium dioxide phases, is shown in figure 2. Figure 3 shows such a cell, made in a joint programme between Shell Solar and the Energy Centre of the Netherlands.

Apart from its dental applications, titanium dioxide is familiar to us as the white pigment in paint. Paint fades in sunlight because of the photocatalytic action of the titanium dioxide. So we might also expect the sensitised dye cells to fade in UV light. However, much accelerated testing and outdoor exposure data has now been gathered and it turns out that this effect is not nearly so serious as one might expect, figure 4. Why is this?

When an electron is excited from the dye and transferred across the interface into the ceramic oxide it leaves behind a 'hole', which can either be filled by an electron from the electrolyte or transferred back from the oxide. This is known as 'interfacial recombination' and would both oxidise the dye and make the cell very inefficient since fewer of the electrons created by incident light would ever reach the external circuit. Recent research at Imperial College has shown that for the Swiss device, the interfacial recombination happens at speeds many orders of magnitude slower than transfer of the excited electron across the interface followed by its replacement from the electrolyte. This explains why the dye is not rapidly degraded in this system.

Despite their attractiveness for low cost photovoltaic generation, there remain a number of practical difficulties in exploiting these cells, and considerable international research effort is now focused on addressing these issues. Some of the main obstacles which remain are the long term stability of the cells, sealing or replacement of the electrolyte, cost and availability of the sensitising dyes and finding cheap lightweight alternatives to the conductive coated glass electrodes.

Research basically focuses on the three major elements – the dye, the electrolyte and the ceramic. The key to the performance breakthrough in dye sensitised cells was the development and use of new sensitising dyes. The demands on such dyes are very exacting, requiring high photo and chemical stability, a wide spectral response closely matching the solar spectrum, efficient and rapid injection of electrons into the ceramic phase, and correspondingly low rates of recombination of the electrons on the ceramic surface.

Recent work has suggested that low interfacial recombination rates are best obtained when the dye molecules have good chemical attachment and steric relationship to the surface of the ceramic. The most commonly used dyes are ruthenium complexes containing carboxyl functional groups that provide a chemical linkage between the surface of the ceramic

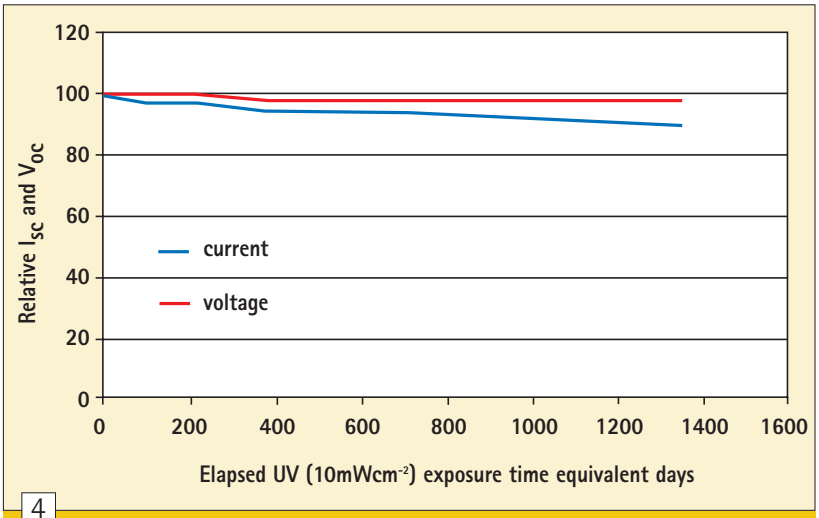
and the dye. However, such dyes are extremely costly, and present some concerns regarding their long term stability, so much work is being focused on the development of alternatives.

Almost from the inception of the dye sensitised cell, it was realised that the electrolyte poses a number of problems for practical device manufacture. Attempting to hermetically seal such cells adds significantly to their cost and presents an issue regarding their long term reliability. The race is now on to replace the liquid electrolytes with a solid state material such as suitably doped conductive polymers, for instance polyaniline or polyethylene oxide, or somewhat more exotic hole transport materials. These would open up the possibility of using simple printing techniques to make these types of solar cell extremely cheaply. The principal difficulty with solid-state electrolytes is that liquid electrolyte penetrates very well into the extremely porous interior of the ceramic, and also plays a significant role in minimising recombination losses. Consequently, at present the light conversion efficiencies obtained with such solid state cells remain substantially below those of the liquid electrolyte cells.

Of all the areas of the dye sensitised cell, the nanocrystalline ceramic remains the least well studied and understood. The majority of workers in this field use commercially available colloidal titanium dioxide in its anatase form, which is applied to the conductive-coated glass substrate and then sintered to provide an electrical contact. This heat treatment step rules out the use of low cost substrates such as conductive plastic, and also precludes direct incorporation of the dye in the ceramic, which would otherwise offer a number of advantages in terms of processing and performance.

Current research at Loughborough University is investigating the use of sol-gel and other chemical processing routes, in which two interpenetrating networks of conductive polymer and electrically continuous titanium dioxide are fabricated in situ. The aim is to produce an inorganic-organic hybrid or nanocomposite type material which will offer both improved mechanical properties such as flexibility and durability, and incorporate a suitable conductive polymer as the organic phase. The principal challenges are to achieve the required anatase crystalline form at low temperatures compatible with the conductive polymer component of the hybrid, to minimise the effect of surface defects and absorbed species on the electron injection efficiency, and to chemically locate a suitable sensitising dye at the organic/inorganic interface. Although these represent considerable technical challenges, such a material would open the possibility for a further step reduction in production costs, potentially leading to ultra low cost, lightweight cells in the form of suitably coated polymer films, which could be used 'off the roll'.

There are several commercial companies worldwide close to the launch of products using dye sensitised solar cells. Some of these are focusing upon novel applications such as light-powered pricing tags for supermarket shelves – price indicators which are linked by radio to the retailer's computer system. These are currently powered by small batteries and a better solution would be to power them from solar cells using the ambient illumination available in store. Dye sensitised cells are very sensitive to artificial light wavelengths and should be cheap enough to do this. Other companies (some with big corporate backers such as Shell, Johnson Matthey and Fuji) have targeted the outdoor solar power market where they expect to be able to substantially reduce the cost of solar panels using this technology.



4 **Lifetime testing results for dye sensitised solar cells (courtesy of Solaronix SA)**

As mentioned above, much work is being done to search for new dyes in order to increase the cell conversion efficiency still further. The interaction between the dye and the ceramic surface controls fundamental properties of the device such as its stability to UV light and the efficiency of electron transfer into the ceramic. Several solid state electrolytes have been used successfully but these cells remain less efficient than those using liquids. Much work is also going on to understand how the ceramic/dye system interacts and to devise new ways of getting the same effect, perhaps by mixing two ceramics, one of which would act as an inorganic 'dye'.

The dye sensitised ceramic solar cell offers the realistic prospect of truly affordable 'clean' electricity. However, improving the efficiency and practicality of the current nanocomposite cells is a problem for materials science since it cuts across disciplines as diverse as organometallic chemistry, ceramics, semiconductor physics and polymer processing. Successful approaches are likely to involve low temperature synthetic routes and self-organising systems such as sol-gel hybrids, surfactant templating and biomimetic approaches similar to those used by nature to fabricate composites such as bone.

The holy grail is a solar cell that is efficient compared to competing technology, while at the same time truly low-cost enough to open up new markets for solar power. In this 21st century vision, solar cells could be printed by equipment similar to that used by photographic film processing, applied to textiles or other flexible, low cost substrates or even applied as a 'self-ordering' paint to any appropriate surface.

Further reading

- B O Regain, M Grätzel, 'A low cost high efficiency solar cell based on dye sensitised colloidal TiO_2 films', *Nature*, 1991, **353**, 737-640

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