dti

GENERATING HYDROGEN FROM SUNLIGHT AND WATER USING PHOTOVOLTAIC TANDEM CELL

CONTRACT NUMBER: S/P2/00470/00/00

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dti

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Hydrogen Solar Ltd

EXECUTIVE SUMMARY

Realising a sustainable hydrogen economy requires a breakthrough in the production of hydrogen. Photoelectrochemical conversion of solar energy to energy in hydrogen at viable efficiency is a long term goal needed to usher in the Hydrogen economy worldwide. The twin cell technology based Tandem Cell™ tackles a number of challenges faced by single photoelectrochemical cell based water splitting and offers a novel way of utilising complimentary parts of the solar spectrum in two cells. The overall process results in a complete system driven by solar energy that splits water into hydrogen and oxygen.

Hydrogen Solar Ltd is a UK based enterprise that is working towards commercialisation of this Tandem Cell™ technology.

One of the main project activities involved the development and optimisation of methods for preparation of larger scale photocatalytic electrodes using reproducible low cost industrial processes, with efficiencies equal to or greater than those from small scale samples made experimentally in University laboratories. Stability is also an important issue and endurance testing was performed on some samples. Spray pyrolysis methods offer considerable promise as for preparation of metal oxide semiconductor films at low cost, reproducibly. The work carried out in task 1 focused on this area. This task included optimisation of spray nozzle parameters and glass substrate temperature for metal oxide films able to crystalise into nanocrystalline structures. Optimisation of the solution parameters is also important for the overall coating process and was the subject of task 3. For certain types of metal oxide films, doctor-blading and screen printing methods are preferred. Optimisation was required to produce the most photocatalytically active electrodes and this was addressed in tasks 4 and 5. Having achieved this for larger scale, the effects of significant scale-up were studied in task 6.

This programme also investigated the preparation of alternate photo-catalytic semiconductor material electrodes for task 7. Studies were also done on alternative electrolytes in task 8. Desk and bench studies were conducted with the aim of identifying new, alternate low cost substrate materials with demonstrated durability in tasks 9 and 10 respectively. Alternate designs for the Tandem Cell were carried out based on the findings of these activities, with the aim of optimising the efficiency and cost of the Cell. This was the focus of task 11. Quality control procedures were developed for fabrication of Tandem Cells in a repeatable way at industrial scale. These studies lead to optimised designs for Tandem Cells, resulting in construction of an array of 12 Tandem Cells. This was field tested at a UK site as task 12. The findings of this array work, in particular

engineering issues were very significant. Based on this work it is intended to build another 2 array systems that consists of 24 Tandem Cells which will be tested for light to chemical conversion efficiency, to determine what efficiency has been achieved overall.

The main conclusions resulting from this DTI-assisted project were as follows.

- Semiconductor metal oxide spray deposition parameters such as nozzle height and liquid flow rate were optimised in order to improve the photocurrent performance.
- A number of dopants that improve the performance of photocurrent density over 50% over undoped samples were discovered by a systematic study.
- A semi-automated method was developed for the production of metal oxide coated electrodes that is suitable for producing larger scale plates, up to 25 x 25 cm^2. The method would be suitable for further scaling to produce 5m^2 Tandem Cells/day.
- A new annealing regime capable of producing crack-free larger scale semiconductor electrodes was introduced.
- Some new photocatalytic semiconductor materials were highlighted with good potential
- An extensive study on alternative electrolytes was conducted and some new electrolyte systems were discovered.
- A desk and lab study on alternative substrates was conducted.
- Alternative Tandem Cell design configurations were studied.
- Quality control procedures were developed for each step of the Tandem Cell production process.
- An array of 12 Tandem Cells was constructed. This was set up as a demonstration unit in a UK site and produced gas.

In overall, considerable progress was made in characterising the factors that affect photoelectrode performance efficiency but that, losses in efficiency when increasing the area of photoelectrodes was greater than expected and optimisation of efficiency at practical device scale needs more work.

Based on the outcome of this work program the following recommendations are made for future work.

- New methods should be investigated for production of current metal oxide semiconductor electrodes at industrial scale.
- An extensive study is required to identify new semiconductor materials for solar water splitting process.
- Scale up process needs further optimisation.

- Further studies required in order to investigate alternative electrolytes and substrate materials.
- The engineering issue related to Tandem Cell array should be thoroughly investigated to prepare optimised large scale cells.
- The Cell performance delay mechanisms need to be identified to improve the stability.

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1. INTRODUCTION

The project titled 'Generating hydrogen from sunlight and water using photovoltaic Tandem Cell™' is a DTI assisted 2 year program that aimed at developing Tandem Cell™ technology in order to produce hydrogen by solar energy driven water splitting.

Solar-driven hydrogen production has an advantage over hydrogen production methods such as steam reforming of natural gas and gasification of coal due to the fact that it is a carbon emission free method and uses sunlight as the energy input. It has the potential to become a cost-effective way of producing hydrogen fuel from solar energy while preventing environmental pollution. The direct approach to solar-induced water cleavage for hydrogen production is to generate electricity using PV cells and then use this electricity to power an electrolyser to split water. This is based on PV cells made from expensive semiconductors that are costly to scale-up and requires a separate electrolyser potentially halving the efficiency. The Hydrogen Solar Tandem Cell™ configuration has been proposed as a more efficient alternative. The Tandem Cell™ approach simplifies the overall process by combining PV material and electrolyser into a single monolithic device known as a photosynthetic cell. Due to the nature of energetic mismatch between semiconductor materials and H_2 and O_2 redox potentials an additional applied voltage is required to complete the overall process. This is provided by a second PV cell which is electrically connected to the photosynthetic cell. Therefore, the Hydrogen Solar Tandem Cell™ comprises two cells. The beauty of this approach is that each cell absorbs complimentary parts of the solar spectrum thereby harnessing the full spectrum of sunlight.

The key to the performance of the Tandem Cell™ is the light harvesting efficiency which is determined by light absorption, photo-induced charge separation, charge transport within the semiconductor thin-film electrode, charge transfer kinetics at the semiconductor photoanode/electrolyte junction, ionic transport in electrolyte, and charge transfer kinetics at the cathode.

This DTI assisted project was aimed at the development of Tandem Cell™ technology. The program included 12 technical tasks as follows:

1. Studies on spray nozzle parameters
2. Studies on spray solution parameters
3. Investigation of the mechanised doctor blading technique
4. Investigation of spray pyrolysis techniques
5. Performance of scale-up electrodes in Tandem Cell™
6. Alternate photocatalytic materials

7. Alternate electrolytes
8. A desk study on substrate materials
9. A lab study on substrate materials
10. Alternate design configuration
11. Quality control procedures
12. Fabrication of Tandem Cells

In the following sections each of the 12 technical tasks are described in order, separated into experimental method description, results and discussion of results. Finally the overall conclusions are summarised. It includes an assessment of further work that is required to perform in order to exploit the outcome of this project and how Hydrogen Solar intends to progress these activities.

2. EXPERIMENTAL WORK

The primary characterisation tool for the entire set of semiconductor electrodes prepared within this research and development program was the recording of the steady-state current-voltage (the I-V test). Figure 1 shows the current-voltage characterisation test set up used. It was designed to measure the current at a chosen voltage range for a standard size test sample when illuminated by a calibrated light source. It is a three electrode set-up incorporating a standard Ag/AgCl reference electrode. The light input was from zenon and metal halide light sources and was determined as 1 sun using a set-up method advised by Hydrogen Solar expert partner at the University of Geneva, Professor Augustinski. Unfortunately towards the end of the programme Prof Augustinski advised Hydrogen Solar of an error in his set up approach which is likely to have had the effect of meaning that the light input was nearer to 1.5 or in some cases 2 sun rather than 1 sun. However since this is a systematic effect it does not invalidate the methods, results or conclusions regarding the effects investigated in the 12 technical tasks. Hydrogen Solar has since been in direct contact with experts at NREL in the USA and it emerges that there is in practice considerable variation around the laboratories in the world in this field regarding the set-up characterisation of 1 sun. There is work in hand to develop an improved standardised method that would avoid these difficulties in the future.

2.1 Spray nozzle parameters

In task 1, the effect of spray nozzle parameters was investigated. Figure 2 shows that spray pyrolysis rig used. This incorporates a hotplate on which the glass substrate is placed prior to spraying on the metal oxide precursor solution. The spray is applied through a nozzle which atomises the liquid stream into small droplets that contact the preheated glass plate. The nozzle

parameters control the spray plume and this is an important factor in the development of the crystalline metal oxide on the glass surface. All of the glass used in this study was Tech 8 glass from Pilkington which was coated in a layer of fluorine doped tin oxide.

In this study the surface temperature of the glass substrate was first varied in the range of 400 to 525C. In each case the resulting I-V test was performed on samples. The samples were sprayed in a X-Y scanning frame with a 300mm traverse, with speed variable from 1-300mm/s was produced. The frame size was 925mm wide, 780 mm deep, 807 mm high. The scanning frame was fully computer controlled to allow automated spray coating of the samples.

The spray nozzle height was varied at the optimised surface temperature and fluid flow rates were also adjusted. As plume of droplets flows to the glass plate there is evaporation of the liquid. Thus there is an expected interaction between flow rate and nozzle heights. Flow rate was controlled with a valve set-up and bottled gas supply which drives the precursor solution. The spray nozzle scans the surface controlled by a computer programme. This equipment was not developed as a part of this programme.

The spray nozzle height was adjusted from 40-200mm above the hotplate. That allowed us to study the effect of the spray nozzle height on the performance of sprayed metal oxide semiconductor electrodes. Heated conducting glass plates were sprayed with the precursor solution. At each height the flow rate of atomising gas was also adjusted. The idea is to investigate the effect of liquid flow rate at various nozzle heights on photocurrent performance. Single spray layers were also investigated to determine whether there was an advantage to using fewer coatings. A series of experiments were conducted to determine the effect of the speed at which the nozzle scans on the photocurrent performance.

After the metal oxide coating has been applied it is possible that the crystal structure would be affected by annealing. The post annealing effect was studied at different annealing temperatures.

2.2 Spray solution parameters

The effects of spray solution parameters on photocurrent performance were investigated as task 2. Studies on precursors and preparation techniques were also a part of this work. Two different precursors were utilised. Solutions containing doping agents were sprayed at the standard flow rate using the lower established substrate temperature. Solvent effects were also studied.

The effect of preheating the gas supply was investigated.

2.3 Mechanized doctor blading

Task 3 consisted in studying the doctor blading technique. This consists in applying a thicker layer than from the spray pyrolysis method used in tasks 1 and 2 above.

In addition, the annealing condition that was designed for calcinations of token electrodes was optimised to account for thermal distribution effects on larger electrode plates. Annnealing methodology was altered in order to prevent bending and cracking of 10 x 10 cm^2 electrodes.

For process optimisation, different applicator methods were considered for the doctor blading equipment including K Lox, K bar and micrometer adjustable applicators. K Lox applicators were not found beneficial in producing crack free films. K bars also proved problematic, due to the requirement for application of a number of coatings. Meter wires produced scratched coatings and hence micrometer adjustable applicators were studied. After further investigations, a K202 control coater was obtained from RK. This was sized to enable automated coating of 25 x 25 cm^2 plates. The technique was optimised using the micrometer adjustable applicator to spread metal oxide semiconductor sol uniformly on conducting substrates. After coating, the electrode was annealed at an elevated temperature for 1 hour; this resulted in a layer of 3-4μm in thickness. Tokens prepared from the 10 x 10 cm^2 films were tested for the photocurrent and film thickness and the uniformity established. Characterisation of the films was studied by SEM and XRD.

2.4 Investigation of spray pyrolysis techniques

Task 6 consisted in investigating spray pyrolysis techniques for the deposition of metal oxide. Spraying and droplet dispersion techniques were investigated using different precursors, including the standard nanoparticle sol suspension. Surface temperature and film thickness were investigated for each technique and precursor.

2.5 Performance of scale-up electrodes in Tandem Cell™

Task 6 involved scale-up of the doctor-blading technique from 10 x 10 cm^2 electrodes to 25 x 25 cm^2 working electrodes. Also within the task, spray pyrolysis methods was investigated. This task progressed further the methods that were developed in earlier tasks. The photoelectrochemical performance of electrodes produced by spray pyrolysis and the steel bar

doctor blading method were compared to assess their suitability for scale-up.

It was not possible to produce scratch-free coatings using the K-bar in the semi-automated doctor-blading equipment. However, uniform and crack free films were prepared by replacing the K-bar with home made applicators in the equipment. The coating effectiveness of films produced in this manner was established.

For the spray pyrolysis technique, the process was developed from that defined for small 5 x 2 cm^2 electrodes reported in the previous milestone. 200 layers were applied to a 25 x 25 cm Fluorine doped tin oxide (FTO) glass substrate. The thermal annealing methodology was also investigated as a part of the work package for this task.

2.6 Alternative photocatalytic materials

Task 6 evaluated alternative photocatalytic materials for Tandem Cell™ working electrodes (WE). The photoelectrochemical performance of tungsten and ferric based nanocrystalline materials are limited by a light absorption and photogenerated charge recombination. Candidate materials were identified by surveying other semiconductor materials for band gap and band edge values. Some of the materials reported in literature were not available. The materials investigated were doped-oxides, metal chalcogenides and binary metal oxides.

2.7 Alternative electrolytes

Task 7 evaluated alternative electrolytes and compared their performance under the same test conditions. In addition, the effects of small amounts of additives in standard electrolyte were also investigated. Both acidic and alkaline electrolytes were studied.

Hydrogensolar nanocrystalline metal oxide semiconductor electrodes were tested in following strong electrolytes shown in Table1. Prior to that all metal oxide semiconductor electrodes were tested for quality control in Hydrogensolar standard electrolyte.

Table 1 - X, Y and Z Electrolytes Tested

X	Y	Z
A	F	K
B	G	L
C	H	M
D	I	N
E	J	O

All of the electrolytes were aqueous solutions. X, Y and Z salts all produced a range of strong electrolytes, with the Y family including the currently used standard electrolyte. Each electrolyte was tested at 2, 1, 0.5 and 0.1M concentrations.

2.8 A desk study on conducting substrate materials

For task 8, a desk study was conducted on substrate materials that would be suitable to replace the conductive glass substrate. Standard conductive glass substrate is liable to cracking both during photoelectrode production and shipping. Alternate substrate materials considered included different types of glass, polymer materials and metals. Alternatives to Pilkington glass including Asahi, St Gobain, Central, GfE Metalle und Materialen GmbH and Solaronix were considered. Although Central produces materials having conductivity and transmissivity comparable to Pilkington their products suffer lack of important technical information such as conducting material data and it's thickness. GfE Metalle und Materialen GmbH does offer coated glasses having a 10x improvement over standard F-doped Sn oxide glass. The cost is however dependent on volume supply and it is believed that some of the coating materials are not stable in acidic and basic electrolytes. For polymer materials, a number of options exist. Some polymers are available coated with electrically conductive layers; potential materials include polycarbonates, polyethylene terephthalates and polyetherimides. The sputtered coating of choice for conductivity is Indium Tin Oxide (ITO). Materials can additionally be coated with metals such as Ti, Al, Cu, Ag, Zr and others. Alloys such as stainless steel, nichrome, inconel and others and oxides such as tin oxide, ITO, SiO_2 and others. ITO coatings are less robust than FTO and not as suitable for volume manufacturing. Fluoropolymers are another alternative and may be important in photovoltaic devices. Materials include Dupont Teflon and Asahi's CYTOP. These materials are however expensive compared with the cost of PET. Electrically conductive polymers such as polypyrrole, polyaniline, polythiophene and polyacetylene are possibilities. Doping of electrically conducting polymer materials is an approach but currently only in the research phase. Electrically conductive dopant materials are also

being investigated for inclusion into the polymer matrix. The hybrid material formed can be produced with electrochemical, photochemical or photocatalytic properties of the metal. Incorporation of a conductive filler material is also an alternative means to enhance the conductivity of inert polymer substrates. Materials such as carbon are utilised, but this material area is still under development. Metals are generally available at low cost; however a more limited number of speciality porous materials are available. The substoichiometric titania produced by Atraverda can be utilised with an electrocatalyst coating as an anode. Costs may however be higher for these materials. The task 8 desk study resulted in alternate glass, polymer and metal material options for substrate supports for photoanode/cathodes.

2.9 A lab study on substrate materials

Task 9 consisted of studying alternate glass materials, conductive polymers and metallic materials identified as potential replacements for the Pilkington glass substrates currently utilised. This is a continuation of task 8 and involved lab testing of alternate substrate materials identified in the desk study. These were sourced and coated with fluorinated tin oxide prior to testing as Tandem Cell™ working electrodes. The characteristics of these materials follow.

Pilkington TEC 8 and TEC 15
TEC 8 and TEC15 are manufactured by Pilkington Glass as a speciality product. They are commonly used in optoelectronic industries including solar cells, smart windows and liquid crystal displays. Some of the main physical properties that are associated with TEC glass are shown below;

- Good flatness and surface quality associated with the plate glass production process
- Optically clear, with a very low number of occlusions
- Available on a short timescale and at a reasonable cost
- Delivered pre-coated with a very thin electrically conductive coating
- Good UV/Visible transmission properties

Various Borosilicate
Borosilicate glasses (including Corning 1737, Schott borofloat and D263) have been considered as an alternative to substrate glass currently available at commercial producers. The physical properties of borosilicate glass include;

- High performance load capacity
- Low thermal coefficient of expansion
- High thermal shock resistance
- Clear and colourless in appearance

- High UV transmission
- High chemical resistance against acids, bases and organic substances
- Low alkali content in glass composition

Pilkington K-Glass
Pilkington K-Glass comes with an electrically conductive FTO coating already in place. A few of its main properties are shown below;

- High thermal insulation properties
- High light transmission
- Clear float glass appearance
- Electrically conductive thin film on surface
- Low cost
- Available in very large volumes

Various Fused Silica, Synthetic Quartz Glass, Reclaimed
The main properties of this material are shown below;

- Very high UV transmission
- Low thermal expansion
- High temperature resistance
- High temperature change resistance
- High thermal shock resistance
- High material purity

Various Titanium Foil
A few of its main properties are shown below;

- Unalloyed titanium foil has a high ductility and cold formability
- High impact toughness and forms very strong welds
- Resistant to sulphuric and hydrochloric acid, most organic acids, and chloride solutions
- High material purity
- High heat transfer capability

Titanium metal foil is produced around the world in very high purity sheets. These sheets possess very low coefficient of expansion, a property that allows titanium to be more compatible with ceramic or glass. It also possesses an inherent electrical conductivity (54 μΩcm) not present in any glass based substrates.

Coating of substrates
The above discussed materials (except Pilkington TEC 8 and TEC 15 and Pilkington K) were coated with conductive fluorinated tin oxide. The sheet resistance was measured using 4 point probe method. A semiconductor metal oxide photoactive layer was deposited on each substrate. The coatings were characterised for light transmission and photocurrent was

recorded. The recorded photocurrent was compared with the photocurrent obtained for Hydrogensolar standard electrode prepared on Pilkington TEC 8 and 15 glasses.

2.10 Alternate design configuration

The work on task 10 involved research into a concept for an alternate design configuration, based on a Tandem Cell™ supported on a metallic substrate. The idea was to design a Tandem Cell™ in which the two cells were mounted optically parallel.

This alternative design based on an "elementary unit" consisting of the photoactive semiconductor material coated metal sheet electrode. This was made by depositing a precursor solution onto a moderately heated metal foil, followed by heating to higher annealing temperature. A counter electrode was designed that allowed light incident on the semiconductor layer. It was made by applying the precursor solution, followed by heating to higher annealing temperature.

The solar modules are laminated in order to protect from possible damage caused by the electrolyte solution in contact. The module is situated above the centre hole in the metallic sheet to allow unhindered ionic current flow to the counter-electrode.

2.11 Quality control procedures

The objective of this task is to develop quality control procedures for photoelectrodes. Separate quality control procedures were prepared for;

(1). cleaning conducting glass substrates

(2). preparation of metal oxide semiconductor

(3). deposition of semiconductor films

(4). characterisation of semiconductor photoelectrodes for current - voltage performance

(5). coating metal oxide semiconductor thin films on 25 x 25 cm^2 scale electrodes

(6). assembly of 25 x 25 cm^2 Tandem Cells.

(1). Preparation of metal oxide semiconductor

The procedure for metal oxide semiconductor preparation has been developed and is documented. For each batch preparation the quality control procedure involves

- documentation of the preparation method including
    - chemicals
    - suppliers
    - catalogue numbers
    - batch numbers
    - quantities

This information was logged for all the components of material preparation. In addition certificates of analysis have been received and logged for some of the materials used in preparation. Five photoelectrodes were prepared from the batch for quality control testing. Details including

- type of substrate used
- electrode size
- application method

were also logged. Annealing procedure and temperature were also documented. This procedure was followed for each metal oxide semiconductor preparation and records of the batch results were documented.

(2). Glass cleaning

A procedure for cutting and a rigorous cleaning process for conducting glass has been documented. This procedure was followed for all glass substrates materials prior to coating deposition.

(3). Film deposition

For quality control of the batch preparation, a procedure has been documented for film deposition. Precise records of annealing temperature were also recorded. This procedure was repeated as required. The procedure was followed for semiconductor film deposition at all times.

(4). I-V characterisation

For each material batch, five token electrodes were prepared and tested for quality assurance. The test procedure involved setting up the current-voltage measurement equipment, calibration of the light source, preparation of the photoelectrochemical test cell and cell positioning. Prior to the start of test measurements, the lamp was allowed a specific warm up time to reach maximum intensity. A computer programme was used to record the test data for all samples. The I-V characteristics for semiconductor photoelectrodes were recorded and the data saved.

Of direct importance to the quality control procedure was the level of light intensity provided by the test lamp. Since this is susceptible to degradation

with time, illumination level was measured each time the lamp was used. A log of light intensity vs time and number of ignition was maintained.

(5). 25 x 25 cm^2 photoelectrode production
A method for production of 25 x 25cm electrodes has been documented and involved recording both of substrate details and details of the semiconductor photoelectrode material and number of layers deposited.

The substrate details including
- type of substrate
- producer
- size
- thickness
- type of conductive coating
- where the conductive coating was deposited

were all recorded. Details of the semiconductor photoelectrode layer are also documented during the coating application method including
- material used for coating
- material batch number
- deposition temperature.

Details of the layer deposition including
- method of application
- amount of material applied
- annealing temperature and duration

were also recorded. The details of oven used for annealing was also noted. Visual inspection notes of the quality of the films produced were documented. This procedure was utilised each time an electrode plate was produced.

(6). 25 x 25 cm^2 cell production
A quality control procedure was developed for cell production. The main cell components include the working electrode, membrane and counter electrode. The cell frame components (frame, bezel and tubes) have been machined to specific drawing designs and have certificates of conformity to specification. O-rings were visually inspected for quality prior to installation of the working electrode. These O-rings are normally sized to prevent leakage but provide adequate cushioning of the working electrode against the outer frame. Quality control checks were performed on new batches of membrane material to determine optical clarity and robustness in the electrolyte solution. Each cell membrane was perforated to allow electrolyte passage. Hole sizes and frequency were maintained for each

individual membrane by the use of a template and sizing tool. Similar checks were in place for the O-ring sealing the counter electrode. A procedure was prepared for making counter electrode. A quality control procedure was developed in order to verify the uniformity of each 10 x 10 cm^2 counter electrode coating. All completed cells were leak tested using water, prior to filling with electrolyte. This procedure was utilised for each cell produced.

2.12 Fabrication of Tandem Cells

This task consisted in the construction and testing of a Tandem Cell array. A module of a 12 cell array was built. The module performance was investigated over 112 hours of outdoor trials.

Construction of 12 cell array
In order to demonstrate the potential of the Hydrogensolar Tandem Cell™, an array structure was designed and then set up. A modular form of panel was developed. This array was capable of housing three 12 cell modules and this report summarises the construction of the first 12 cell module. Balance of systems comprised; a gas collection facility and electrolyte handling. In addition, various functions were monitored for performance analysis

Module construction:
Each cell contains a photo active material layer that is coated onto fluorinated tin oxide coated glass. Conductive patterns were used to minimise sheet resistance losses. A 250 μm microporous membrane was employed as a gas separating membrane. Behind this was the hydrogen evolving electrode. The module was constructed from a pair of uPVC machined frames which carry the photo electrode, counter electrode and also the gas outlet connections.

The electrical connection to external bias supply was made at the lower edge of the device, through a specially devised potting arrangement. A flying lead was provided of suitable length to connect to the chosen external bias. High efficiency silicon single crystal screen printed cells were used as the bias source in the array.

Array:
A modular design was used, each carrying twelve modules in an array of three cells high by four wide. Each of the middle rows was interspersed by the bias PV cells, which also concealed the gas connections. The general array structure was of welded steel tube, with the array inclination set to forty five degrees at fabrication. This was selected as a simple compromise of optimum angle of inclination for the site latitude versus the need to have

a suitable angle of inclination to facilitate gas evolution and the subsequent flow of gas and some electrolyte to the gas collector unit.

Gas collection:
The gas collector was a series of vertical vessels linked by a dip tube into the top of the lower vessel, the top vessel acts as a holder for electrolyte displaced by collected gas and expansion; it also acts to control the discharge pressure. Alongside the hydrogen collection apparatus was a simplified oxygen tower which maintains a similar head, to avoid any pressure differential across the membrane in the modules. Both vessels had separate vent lines which exit to each side of the enclosure to ensure that no significant mixing can occur.

The vessels of the hydrogen collector were instrumented with a series of reed relay type float switches which indicate to the controls system the status of liquid levels. In the hydrogen collecting vessel the difference was arranged to be a displacement of 250 mls, so that gas was allowed to collect in batches of 250 mls. Having collected a suitable volume of gas, a solenoid valve is opened to dispense the gas to systems supplied by the user, but typically a compressor and collection arrangement.

Durability testing
A selection of 10 x 10 cm^2 Tandem Cells were constructed from the same set of electrodes used to assemble 25 x 25 cm^2 Tandem Cells assembled for array. The illumination area of each electrode was 70.5 cm^2. In order to minimise heating of cells during the stability tests, a quartz window water filter was employed in front of each cell. The light source was the Hydrogen Solar metal halide lamp. The incident light intensity on each cell was monitored. The spectral response in front of each cell was recorded by using StellarNet fibre optics radiometer.

1.2 V applied voltage was maintained for each cell during these tests. The electrolyte pH of each cell was tested at the beginning and the end of durability tests. The temperature just in front of cells and inside the room was recorded. The electrolyte of each cell was topped up with original electrolyte solution and records were kept. Dark and illuminated I-V curve of each cell was recorded at the start and after 37 hours of the test using Hydrogen Solar standard method.

3. RESULTS

3.1 Studies on spray nozzle parameters

It was found that there was a linear relationship between the glass surface temperature and the hotplate set temperature with a lag of about 50 °C. The lag depended on the flow rate since the glass surface was cooled by the spray plume.

Precursor solution was sprayed onto glass substrates held at a range of temperatures from 350 to 510°C. The photoelectrochemical performance steadily declined as the temperature was reduced. However, there was a plateau in the temperature around 400°C.

The results shown in Figure 3 show that it was found that increasing nozzle height had a beneficial effect on photocurrent. This was in fact a larger effect than increasing the number of coating layers which also increased the photocurrent.

The scanning speed was not found to have a significant effect as illustrated by Figure 4. The post annealing at 600 °C was not found to improve the photocurrent performance. Figure 5a, b, c show the SEM micrographs of metal oxide semiconductor electrodes prepared by spray pyrolysis method at temperatures 350, 425, 510 °C respectively.

3.2 Studies on spray solution parameters

Acetylacetone was used as an alternative solvent. The initial work encountered partial blocking of the spray nozzle during the spraying process. As a result the coated metal oxide films were rather thin. To prevent the precipitation at the tip and subsequent blocking of the spray nozzle the solution was diluted and re-sprayed at half speed to maintain the coating thickness. This solved the nozzle blocking problem but did not improve the photoelectrochemical performance of coated electrodes.

Studies on precursors and preparation techniques were initially studied within this task. Two different precursors were utilised to have a composite type photoelectrode material. This electrode only had a photocurrent density of 0.5mA/cm^{-2} and showed no improvement over the performance of undoped electrodes.

Thin film electrodes made using aqueous based precursors shown photocurrent density up to 0.84mA/cm^{-2}. Some particles of the dopant however failed to dissolve in all solvents considered in this study. As shown

in the Figure 6, SEM analysis of the surface of the coating showed the appearance of specks on the final sprayed sample.

Some experiments were performed using a heated gas supply to atomise the coating solution. This resulted in electrodes having photocurrents of 3.41mA/cm^{-2}, 4% higher than the sample sprayed without a heater. No further improvements resulted from spray solution investigations in this task.

3.3 Investigation of the mechanised doctor blading technique

Several 5 x 2 cm^2 metal oxide semiconductor electrodes were prepared by cutting randomly selected areas of a 10 x 10 cm^2 film that prepared by mechanised doctor-blade technique. 5 x 2 cm^2 size token electrodes were investigated by field emission scanning electron microscopy (FE-SEM). Figure 7 shows a SEM micrograph of the resulting morphology. Figure 8 shows the XRD analysis of the metal oxide sample.

3.4 Investigation of spray pyrolysis techniques

The current-voltage plots of semiconductor photoelectrodes prepared by spray deposition using various precursor solutions showed a temperature dependance. This is illustrated in the resulting I-V curves shown in Figure 9. For chloro-metal precursors, eight spray cycles were required to produce optimum film thickness which is 4-5μm for optimum light absorption

The drop dispersion technique was studied as an alternative technique and the current-voltage results of metal oxide photoelectrode.prepared by this technique are given in Figure 10.

3.5 Performance of scale-up electrodes in Tandem Cell™

Scale-up of the doctor-blading technique from 10 x 10 cm^2 electrodes to 25 x 25 cm^2 working electrodes was the focus of this task. The scaled-up electrodes were tested under 1 sun illumination with PV bias cells. The resulting Tandem Cell™ tested under illumination and hydrogen generation for a 25 x 25 cm^2 cell are shown in detail in Figure 11.

3.6 Alternate photocatalytic materials

The I-V performance of alternative semiconductor photoelectrodes is given in Appendix.

3.7 Alternate electrolytes

The results of alternative electrolyte study are illustrated in Figure 11. At 2M concentration the X electrolyte family A, B, C, D and E showed differences both in height of I-V peak and in position of I-V peak.

3.8 A desk study on substrate materials

Glass

Pilkington are the largest and best known of the general and specialist glass companies. They supply a range of specialist optically conducting TEC Glass. This is supplied in a variety of thicknesses with varying optical transmission properties. In their standard range, the glass most commonly used are the TEC 8 and TEC 15 materials which have different optical and conductivity characteristics.

Alternatives to Pilkington glass include Asahi, Saint-Gobain, Central, GfE Metalle und Materialen GmbH and Solaronix. Some of these suppliers provide specially coated glasses in which properties have tuned to the specific demands. However, the problem with speciality coated glasses is the cost. Typically a $1m^2$ piece of TEC8/3 costs $100.

Polymers

(a) Coating with a conductive thin layer

There are a number of commercial suppliers of polymeric materials having sputter-coated electrically conductive layers. The polymers of choice for coating with a metallic material are polycarbonates (PC), polyethylene terephthalates (PET) and polyetherimides, as they are all highly transparent to visible light. These polymers can be sputter coated with metals such as titanium, aluminum, copper, silver, zirconium and others, alloys such as stainless steel, nichrome, inconel and others and doped oxides such as FTO and ITO. Typical coating thicknesses are 10 to 5,000 A and light transmission is around 70% (wavelength dependent). The optical density ranges from 0.15 to 4.0 and the resistivity is between 0.03 and 2,000 Ω/square.

(b) Electrically conducting polymers

The optical characteristics inherent to inorganic semiconductors, such as photoemission, photocurrent and optical transmission have been observed in a class of conjugated polymers. These polymeric materials present easy process fabrication and are a potential low cost substrate material. Their use as materials with which to assemble polymer based photochemical

devices offer an exciting new technological route. They also offer the possibility of controlling the electronic and optical properties of the polymer material by tailoring the organic molecular structure before final fabrication. The photovoltaic effect has been observed in conducting polymers and the electrolyte interface by irradiating with an energy higher than the polymer band gap, and should it is proposed, produce low cost photoelectrochemical cells (PEC). However, at the present time the efficiency of these devices is low.

A range of polymeric species, such as polypyrrole, polyaniline, polythiophene and polyacetylene are being investigated for this application. Of particular interest are polythiophene and related derivatives. These materials offer the possibility of obtaining a family of low band gap materials. Alternatively, by combining different polymers, at the molecular level, it may be possible to adjust their band gap energy and obtain a more efficient light harvesting material.

(c) Doped electrically conducting polymers

It has been established that polymeric materials can become electronically conducting if the polymer backbone consists of conjugated bonds. While conjugated materials such as polyacetylene show significant conductivity, this is raised by several orders of magnitude when the polymer is doped chemically or electrochemically with additional compounds such as iodine. These polymeric materials have been given the name electronically conducting polymers (ECP) and either on their own or deposited on an electrode material open up number of interesting applications. However, these materials are currently in the research phase and are not available commercially.

(d) Dopant inserted polymers

An area of considerable research at the present time is the inclusion of an electrically conducting compound into the matrix of the polymer at a physical level. One route to a composite conducting material involves the inclusion of a metal directly into an inactive polymer matrix. Metallised or redox polymers result. This is of interest since the hybrid material can be produced with electrochemical, photochemical or photocatalytic properties of the metal.

For example, NASA has developed a family of such metallised, highly reflective and conductive surfaces on polymer films which they claim will enable advancements in high end technology applications such as solar cells, flat panel displays, flex electronics, and radiation shielding. This metallised surface provides superior adhesion over commercially available

deposited films from which the metallised coating can be easily removed. These materials create films and coatings that have an optically clear, semiconductive metal oxide surface. This technology enhances the thermal and dimensional stability of the base polymer. The incorporation of metal ions lowers the base polyimide coefficient of thermal expansion by as much as 30%. These materials can be conducting or light reflecting.

(e) Incorporation of conductive filler

An alternative and not so elegant route to inducing conductivity into an inert polymer substrate is the inclusion of a cheap readily available source of conducting material. This could be the inclusion of a metal in sufficient quantities to conduct throughout the polymer or more likely the inclusion of an inert material such as carbon. This particular area is still under development and is not seen as a short term answer to the problem of electrical conductivity in the substrate material for photovoltaic and photoelectrochemical cells.

Metals

Whilst metals are generally widely available at low cost, a more limited number of producers supply specialist porous metals. They can be used in optoelectronic devices with cleverly designed configurations.

3.9 A lab study on substrate materials

Commercially available Borofloat, 1737, D263, Fused Silica and plain glass substrate materials were tested for light transmission. A comparative study of light transmission was performed. They were coated with conductive fluorinated tin oxide. The average resistance of coating on each substrate is compared.

3.10 Alternate design configuration

This alternative design based on an "elementary unit" consisting of the photoactive semiconductor material coated metal sheet electrode. The size of the module is optimized to deliver the maximal power at the range of 1.1 - 1.3 V when illuminated under simulated sunlight.

3.11 Quality control procedures

Record sheets for metal oxide semiconductor electrode preparation, I-V measurements and electrode production were developed. A central quality control record is maintained of all batch preparations, characterisation measurements of individual batches and electrodes produced.

3.12 Fabrication of Tandem Cells

A 12 cell array (25 x 25 cm^2 panels) was constructed at a UK demonstration site, with associated balance of cell systems. Photographs of the array are shown in figures 13a and 13b. Cells for the remaining two 12 cell modules are in the process of construction.

A detailed summery of the results obtained in this whole program is given in Appendix.

4. DISCUSSION

4.1 Studies on spray nozzle parameters

Effect of variation of glass surface temperature

The plateau allows a significant reduction in the substrate temperature from 510 to 425°C, while maintaining the photocurrent performance at 75% of its peak value. Further enhancements in photocurrent density can then be achieved through modification of nozzle parameters. After spraying the samples were checked for coating adherence; all coatings were intact.

The surface morphology of metal oxide semiconductor particles spray coated at various surface temperatures was studied using SEM. The coatings were prepared at low temperatures showed particles with a rounded morphology. The oxide particles sprayed at high temperature (>425°C) were platelet like in shape. After considering the photoelectrochemical performance it was decided to optimise the system in terms of spray nozzle height and spray nozzle parameters at 425°C.

Annealing

Annealing is not thought to improve crystal structure as it relates to photochemical performance.

Optimisation of spray nozzle height

Whilst reduction in the number of spray passes from five to one reduced the photocurrent density, this reduction was only ~25% and was the same irrespective of nozzle height. Therefore, it may be possible to standardise a number of coatings lower than five (e.g three) to reduce costs in production.

Optimisation of liquid flow rate

Both spray height and gas flow rate have a significant effect on the photocurrent. Reducing the gas flow rate and increasing the nozzle height both improved the performance. The results indicate that there is an interaction between these two parameters that is explained by the way the spray plume is formed and the shape it has when it contacts the preheated glass surface. It is expected that a lower gas flow rate results in larger droplets in the spray cone and potentially larger particle sizes. Spray plume imaging was performed to confirm this. For the larger scale process a lower gas flow rate is also clearly preferred.

Scanning speed trials

Spraying at half the speed with half the liquid flow or at twice the speed with twice the liquid flow both had little effect on the performance. It would therefore seem the photocurrent is not very sensitive to the scanning rate. Spraying twice as many layers at twice the speed was detrimental with a drop in performance of 30%. The standard scanning speed produced the best samples.

4.2 Studies on spray solution parameters

Alternative solvents

It appears that aqueous solutions suffer from adhesion problems compared to non-aqueous solutions

The aqueous solution with additives produced a thick coating when sprayed, which was opaque and could easily be rubbed off the glass substrate. Thinner coatings were produced both by reducing the liquid flow rate and by diluting the solution to half strength with water. In both cases the coating could be rubbed off the substrate. Photocurrent – voltage performance could not be recorded for these electrodes due to poor adherence. Due to the differential thermal expansion coefficients the aqueous solvent could not be used as spray solvent.

Effect of dopants

A number of dopants were studied with the aim of improving the photocurrent of metal oxide semiconductor electrodes. Some dopants were found to be detrimental to the performance of the coating. Others were beneficial, with one dopant increasing the photocurrent 250% over the undoped sample. It appears that some dopants improve the charge mobility within the semiconductor photoelectrode.

Effect of gas temperature

Preheating of the coating solution may be slightly beneficial but a 4% difference may be within the margin of error.

4.3 Investigation of the mechanised doctor blading technique

Characterisation of the uniformity of metal oxide semiconductor coated films by I-V properties

Several 5 x 2 cm^2 metal oxide electrodes were prepared by cutting randomly selected areas of a 10 x 10 cm^2 film and recorded the I-V characteristics. I-V properties of two 5 x 1 cm^2 electrodes made from two different sites of a 10 x 10 cm^2 coated film were compared. Results suggested uniform photocurrent densities. This confirms that the 10 x 10 cm^2 coating is fairly uniform.

Characterisation of metal oxide semiconductro coated films by FE-SEM

No morphological differences are evident in the SEM micrographs. The SEMs show that the oxide film is a nanostructured porous 3-dimensional interparticle network. The particles look uniform with the average particle size being about 20-30 nm.

Characterisation of metal oxide coated films by X-Ray Diffraction technique.

XRD diffraction patterns of oxide film coated fluorine-doped tin oxide conducting glass were compared with JCPDS indexing data of relevant metal oxide and cassiterite-synthetic SnO_2. The X-RD analysis shows that the metal oxide particles are crystalline. Majority of characteristic peaks of the coated sample are related to metal oxide and cassiterite-synthetic tin oxide (SnO_2) crystals. There is no concrete X-RD evidence for the presence of any contaminants in the final annealed film.

Characterisation of the semiconductor film thickness by SEM.

The coated metal oxide film thickness was characterised by SEM. The measured coating thickness was confirmed as 3-4μm and no morphological differences were evident. There was a slight variation of the thickness of the coated film throughout the 10 x 10 cm^2 electrode.

As a result of this task, an automated method of production of metal oxide semiconductor sol coated electrodes was developed that is suitable for producing larger scale plates, up to 25 x 25 cm^2.

4.4 Investigation of spray pyrolysis techniques

Spraying chloride-I solution

I-V characteristics of metal oxide films made by spraying chloride-I precursor solution at different surface temperatures, 100 °C, 160 °C and 200 °C on F-SnO_2 glass were compared. In order to make the comparison all electrodes were prepared by spraying an identical number of layers (in this case each electrode was prepared by repeating the deposition cycle 8 times). It seems that the current-voltage performance of metal oxide thin film electrodes prepared at 100 °C is better than the electrodes prepared at higher temperatures.

Droplet deposition of chloride-I solution

Photocurrent-voltage performance of metal oxide electrodes prepared by 2 and 4 drop dispersion cycles are compared. Since the same solution was used to prepare spray deposit and drop dispersed electrodes the different electrode performance must have resulted from deposition technique. Electrodes prepared by spray deposition have lower performance than those made by the drop dispersion technique. In fact, during the film preparation in the drop dispersion method the solution flow is relatively slow compared to the spray method. This might allow the solution to slowly permeate into the porous network and gradually forming a well connected inter-particle network. A continuous inter-particle network is very important for charge transport within the film.

Spraying chloride-II solution

The photocurrent-voltage performance of metal oxide electrodes prepared by spraying chloride-II precursor solution at different temperatures is compared. In contrast to the chloride-I precursor, electrodes prepared at 200 °C had better performance. This may be due to the different decomposition mechanisms of chloride precursors.

Droplet deposition of chloride-II solution

The photocurrent-voltage performance of metal oxide thin film electrodes prepared by the drop dispersion technique at 100°C was studied. Comparison of the performance of electrodes prepared by following this technique with those prepared by spray pyrolysis clearly shows that the drop dispersion technique is better.

Spraying metal oxide colloidal suspension

The I-V characteristics for electrodes produced by spraying diluted sol-gel metal oxide colloidal suspension were investigated. It is evident that the I-V characteristics are improved with film thickness, approaching an optimum for 150-200 sprays. Considering the importance of preventing particle agglomeration, another part of colloidal spray solution from the same batch was used to spray and make a second set of thin film electrodes but this time the spray solution was treated prior to spray deposition. As expected the treated solution sprayed films performed better when the films are relatively thin (e.g. 50, 100 sprays). Photocurrent-voltage performances of relatively thick films (e.g. 150, 200 sprays), were poorer.

This task demonstrated the feasibility of utilising drop dispersion technique to prepared metal oxide semiconductor photoelectrodes.

4.5 Performance of scale-up electrodes in Tandem Cell™

Several 25 x 25 cm^2 electrodes were prepared by the doctor blade and spray pyrolysis processes. Both coating processes produced fairly uniform and repeatable films. For larger scale plates annealing on a ceramic hotplate caused problems with electrode cracking. This problem was overcome by developing an alternative annealing method in box furnace. However in order to prevent electrode bending the heating and cooling rates were required to be adjusted to significantly lower levels, and this effectively increased the electrode preparation time and cost, which was not ideal for the production of larger electrodes. Alternatives methods including use of a metal hotplate and an oven protocol were investigated. Electrodes were made using a thermal annealing procedure utilising a combination of both methods. Occasional warping was rectified using a blanketing technique. Fairly uniform 25 x 25 cm^2 electrodes were prepared by the doctor blade and spray pyrolysis processes. The I-V characteristics of the films were also compared.

The scaled-up electrodes produced by both doctor-blade coating technique and spray pyrolysis were tested under 1 sun illumination with PV bias cells. Hydrogen generation was detected for both 25 x 25 cm^2 cells each one producing gas at about 9 ml/min rate.

This task resulted in the further development of an automated doctor blading method for larger scale 25 x 25 cm^2 electrodes. A semi-automated method of spraying electrodes was also developed. The work within this task also resulted in developing a new annealing regime that is capable of producing crack-free larger scale electrodes.

4.6 Alternate photocatalytic materials

The semiconductor metal oxides currently used in thin film electrodes form in Tandem Cell™ absorb only at the high energy end of the solar spectrum which limits the harnessing of sunlight. The work in this task focused on searching for alternative semiconductor materials with large enough band gaps to split water under the irradiation of sunlight, and small enough to collect a significant fraction of solar radiation.

One of the major draw backs of the performance of some oxide semiconductors is the very high recombination of photogenerated carriers. Potential candidate materials were identified by literature surveying for other semiconductor materials with suitable band gap and band edge values. The materials studied included doped-oxides, metal chalcogenides, and binary metal oxides.

Effort focussed on extending the light absorbance of metal oxides such as TiO_2 into visible region by doping with various anions and cations such as C, N, Cu, S etc. Nitrogen doped TiO_2 is well known as a visible solar spectrum sensitive photocatalytic material and has already been tested for photoelectrochemical water splitting. The photocurrent density was very low and about 0.8 $mAcm^{-2}$ for the new doped metal oxide photoelectrode that studied; this low performance was believed to be the result of recombination of photogenerated electrons and holes. The metal chalcogenide semiconductor that studied is an ideal photoanodic material for water splitting because it straddles the water reduction potential, $E_F(H_2/H^+)$ and the water oxidation potential, $E_F(H_2O/O_2)$. Photocurrent density of 3 $mAcm^{-2}$ was seen, but a rapid decay in photocurrent was observed due to fast photocorrosion in aqueous electrolytes. The binary metal oxide photoelectrode that studied showed only a maximum photocurrent density of 0.7 $mAcm^{-2}$ at 1.2V vs Ag/AgCl.

This task highlighted some potential photocatalytic materials, however to date no material has demonstrated higher efficiency than that of tungsten and ferric based semiconductor oxide systems.

4.7 Alternate electrolytes

X Electrolyte family

Photocurrent-voltage performance of a known metal oxide semiconductor electrode was recorded in all A, B, C, D and E electrolytes at 2M, 1M, 0.5M and 0.1M concentrations. In terms of I-V performance D was delivered the best results (5.4mA/cm^2 at 1.2 V vs RHE). Both E and B electrolytes showed reasonable photocurrent performances (~4.4mA/cm^2 at 1.2V vs RHE).

However, electrolyte B reaches the photocurrent maximum and plateau at a significantly lower applied voltage compared to E due to low pH. The performance order of the X electrolyte family in terms of the photocurrent density at 1.2 V vs RHE was therefore; D > B > E > C > A. However, in terms of solar conversion efficiency the performance order is B > D > E > C > A.

Y Electrolytes family

With respect to Y electrolytes family, F is the best performer (5.21 mA/cm^2 at 1.2V vs RHE) at higher concentrations, however at lower concentrations (0.5 and 0.1M) there was little to choose between all electrolytes. A photocurrent density of 4.6 mA/cm^2 (at 1.2V vs RHE) was recorded for the tested semiconductor electrode in electrolyte G at the same applied voltage and same illumination condition. Though for the tested electrode the photocurrent onset is around 0 V vs Ag/AgCl for H electrolyte the average photocurrent density remains low for all concentrations studied. The low onset for H electrolyte may be attributed to low pH. Compared to F, G and H, the photocurrent-voltage performance of semiconductor electrodes tested in I and J electrolytes were very poor. In general the performance order of F, G and H electrolytes in Y electrolyte family is; F > G > H. This could be mainly due to the difference in size of solvated cation in Y family. Both onset potentials and photocurrent maxima were generally low for X electrolyte family compared to Y counterparts.

Z Electrolytes family

Under Z electrolyte family, K, L, M, N and O were investigated. However, the photocurrent performance of tested electrode in M, N and O were negligible. Therefore, only the performance of electrolytes K and L were discussed in this report. Photocurrent-voltage performance of a known metal oxide semiconductor electrode was recorded in K and L electrolytes at 2M, 1M and 0.1M concentrations. For all concentrations L electrolyte delivered the highest current density of 3.47 mA/cm^2 at 1.2V vs RHE. However, this value is notably low compared to photocurrent densities recorded for X and Y electrolyte families. K not only has lower photocurrent performance compared to that of L but also higher photocurrent onset requiring higher applied voltage in Tandem Cell™ operation.

As part of this milestone work combined electrolyte systems were studied. However, the photocurrent-voltage measurements recorded for known metal oxide semiconductor electrode in combine electrolytes did not show any advantage.

4.8 A desk study on substrate materials

The current conductive substrate material utilised in the Tandem Cell™ is F-doped tin oxide. The characteristics of this material are such that the large area devices suffer in the process of scale up due to low conductivity. The material is also relatively expensive (1m^2 costs $100), and fragile, liable to cracking during electrode production and shipping. For these reasons identification of a more highly conductive glass substrate or a more robust and cheaper material with improved conductivity would be an advantage. Substrate materials considered were different types of glass, polymer materials and metals.

Glass
The chemical and physical properties of glass can be altered extensively by modifying the composition and production techniques. In any one glass material, the mechanical, chemical, optical, and thermal properties contribute to material characteristics. Some of the more critical characteristics for the performance glass substrates include electrical conductivity, light transmission properties and chemical, electrochemical and photochemical resistance. These properties are particularly apposite when considering a glass for use as a conducting substrate in a photoelectrochemical cell, where light harness and charge collection and transport are vital. Since glass is typically a silicon oxide insulator, electrical conductivity is achieved by coating with conductive ITO or FTO or incorporation of conductive filler during production. For a photoelectrochemical device, high optical transmission over the range from UV to IR is required with minimal reflection. High resistance to corrosion is particularly important in the cell where acidic or alkaline environment prevails dependent on electrolyte. These characteristics have been reviewed for materials from different suppliers.

Polymers
Polymer materials have long been considered as alternative substrate materials in photoelectrochemical cells. Using a polymeric based substrate opens the way to attractive roll to roll continuous production processes. It also opens the way to applications in which flexibility of the final product is a desired requirement. Polymers offer unique advantages in the area of building integration, where they can be laminated onto low cost roofs or facades. Furthermore, the processing, transport and handling of devices constructed out of polymer based substrate materials are in general, less problematical than the equivalent glass based versions.

Polymers in principle would appear to be ideal materials for use as substrates in a photoelectrochemical device. They are optically transparent in the visible region of the spectrum, highly durable, easily manufactured

into a variety of forms and are relatively inexpensive. However, as with all materials there are a number of fundamental material problems, which have to be overcome. As with glass based substrates, the most pressing of these problems is their low or non-existent electrical conductivity. To some extent, this problem has been minimised by the introduction of new chemical breakthroughs and process techniques. These include advances, such as the inclusion of electrically conducting dopants and the development of new classes of polymer, the electrically conducting polymer.

The main areas of technological development presently available in conducting polymers include coating of an optically transparent polymer with an electrically conducting film, the inclusion of electrically conducting materials to improve the overall conductance of the polymer and more recently, technological development of polymeric based materials designed from first principles, with an inherent electrical conductivity. Of these three main techniques, only the sputtering of polymer surfaces with an electrically conductive material is available on anything approaching a commercially viable scale.

Polymers need to be both optically transparent in the required frequency range (UV/Visible) and electrically conductive. There are already a wide range of polymers, which are readily available from a variety of sources, which are optically transparent in the required range. However, there are a very limited number of polymeric materials which are both optically active and electrically conductive. A variety of possible polymeric materials are discussed in addition to process routes which are presently available to overcome these problems.

Metals
Metals are a serious alternative to the presently available glass substrates due mainly to their inherent electrical conductivity. A metallic substrate offers a number of advantages and disadvantages over the glass and polymeric systems.

Metals are very readily available in relatively large quantities, at reasonable cost, with a robust and mature supply infrastructure. The process technology and techniques, which are used in metallurgy, are well developed and documented.

4.9 A lab study on substrate materials

Commercially available Borofloat, 1737, D263, Fused Silica and plain glass substrate materials were tested for light transmission. The comparison of light transmission showed that UV grade fused Silica has the best light

transmission properties. At visible and IR region all the substrates were shown similar light transmission profiles. Except quartz substrates all the others substrates were started to lose light transmission at about 250 – 300 nm region. However, light transmission properties of 1737 Corning and Borofloat were also at an acceptable level for many optoelectronic applications including Tandem Cell™ when it takes into account the photon density of AM 1.5 standard illumination at high energy end. The order of light transmission with the best performing substrate at first is quartz > Borofloat® > 1737 Corning > C263 > Plain glass.

Even after coating with a conducting FTO layer the 1737 Corning showed very high light transmission. Pilkington TEC 15 also showed light transmission properties similar to that of FTO coated 1737 Corning substrates. In fact, each FTO coated substrate material retained 90% of light transmission well into the UV region, with transmission only dropping off at about 300nm. Generally, all FTO coated substrates investigated exhibited dropping of light transmission within the range of 300nm to 350nm due to absorption of fluorinated SnO_2.

The comparative study of sheet resistance on all FTO coated substrates materials investigated confirmed that the coatings were equivalent to those deposited on Pilkington TEC substrates. This was very encouraging. In fact, it allowed comparing the photocurrent – voltage performance of electrodes made on FTO coatings on various substrate materials that were subjected to investigation within this milestone.

Relatively low photocurrent was observed for all the photoelectrodes made from various substrate materials at 10 x 10 cm^2 scale. In terms of photocurrent density the highest performance was shown by the Borofloat and the GB quartz samples. The comparative photocurrent values attained were ~100% higher than those achieved on the standard TEC substrate. These results qualified the choice of borofloat as a suitable replacement for the TEC glass.

The reason for the rather low values observed at 10 x 10 cm^2 scale was due to poor current collection across the surface of the substrate. This is being addressed by a separate in-house programme.

4.10 Alternate design configuration

Task 10 investigated an alternate design configuration in which a Tandem Cell™ is based on a metallic substrate

Concept
An optically parallel tandem cell system for hydrogen generation combines a commercially available high efficient solar cell and a solar water splitting cell so that both elements are lit directly, while matching the photocurrent in both cells. Though it is optically parallel in the new configuration, the purpose of using a solar cell is to provide the appropriate bias voltage.

This Tandem Cell configuration consisted of a photoelectrode coated on a metal sheet with solar cells fitted as the counter-electrode, forms a stand-alone elementary unit that plunges into the electrolyte bath. The cell is closed by a simple plastic or glass window. Later-on, the multiplication of such elementary units i.e. in the form of a large metal sheet allows for increased area Tandem Cell systems.

Performance of early prototypes of newly designed Tandem Cell

For an early prototype cell with an active surface area of 20.8 cm^2, the photocurrent performance at 1.2 V applied DC bias voltage under 0.7 Sun illumination condition was similar to that observed for the same semiconductor material in current Tandem Cell configuration. Therefore, the new design system has achieved its objective at very early stage of design.

4.11 Quality control procedures

As far as standardisation of each step of Tandem Cell™ manufacture process concerned the work of this milestone is very important. This work allowed formulating a quality control process for each step given below.

(1). cleaning conducting glass substrates (wet chemical process)

(2). preparation of metal oxide semiconductor (wet chemistry dominant process)

(3). deposition of semiconductor films – (the type of the process depends on semiconductor)

(4). characterisation of semiconductor photoelectrodes for current - voltage performance (photoelectrochemical process)

(5). coating metal oxide semiconductor thin films on 25 x 25 cm^2 scale electrodes (large scale production process)

(6). assembly of 25 x 25 cm^2 Tandem Cells (engineering process).

The work resulted in logging a set of data systematically on day-to-day basis that covers whole Tandem Cell™ manufacture process. In fact, it simplified the data recording, maintaining test results on a database, data analysis, generating short reports.

4.12 Fabrication of Tandem Cells

During this task 12 Tandem Cells were produced and assembled into an array construction.

For the 25 x 25 cm^2 cell used in the array, 500 mA, photocurrent was achieved at 1.2V applied voltage. The active area is calculated as 438cm^2, accounting for substrate design, corresponding to a photocurrent density of 1.14mAcm^{-2}. Efficiencies of ~2% result.

5. CONCLUSIONS

The main conclusions resulted from this DTI-assisted project were as follows.

- Semiconductor metal oxide spray deposition parameters such as nozzle height and liquid flow rate affect the photocurrent performance.
- Dopants can improve the performance of photocurrent.
- A semi-automated doctor blading method for the production of metal oxide coated electrodes is suitable for producing larger scale plates, up to 25 x 25 cm^2.
- A new annealing regime capable of producing crack-free larger scale semiconductor electrodes was introduced.
- Some potential new photocatalytic semiconductor materials were highlighted.
- An extensive study on alternative electrolytes was conducted and some new electrolyte systems were discovered.
- A desk and lab study on alternative substrates was conducted.
- Alternative Tandem Cell design configurations were studied.
- Quality control procedures were developed for each step of Tandem Cell production process.
- An array of 12 Tandem Cells was constructed. This was set up as a demonstration unit in a UK site and succeeded in producing gas.

In overall, considerable progress was made in characterising the factors that affect photoelectrode performance efficiency but that, losses in efficiency when increasing the area of photoelectrodes was greater than

expected and optimisation of efficiency at practical device scale needs more work.

6. RECOMMENDATIONS

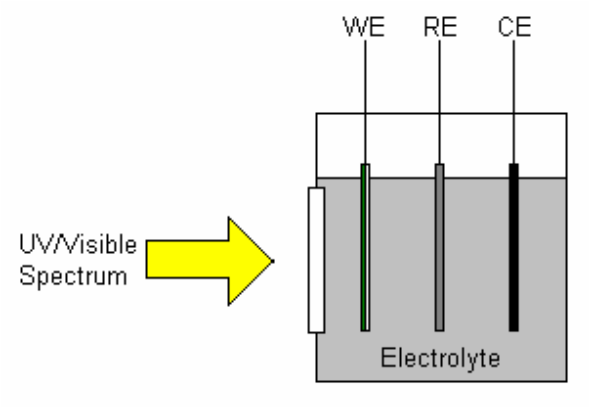
Based on this work program the following recommendations were made for future work.

- New methods should be investigated for production of current metal oxide semiconductor electrodes at industrial scale.
- An extensive study is required to identify new semiconductor materials for solar water splitting process.
- Scale up process needs further optimisation.
- Further studies required in order to investigate alternative electrolytes and substrate materials.
- The engineering issues related to Tandem Cell array should be thoroughly investigated to prepare optimised large scale cells.
- The Cell performance delay mechanisms need to be identified to improve the stability.

7. ACKNOWLEDGEMENTS

The department of trade and industry is acknowledged for assisting to conduct this extensive development program. Hydrogen Solar Ltd has immensely benefited from the work carried out in this program in order to meet its various commercial targets. E-Synergy Ltd, EPFL, University of Geneva, CERAM Ltd and Solaronix SA are also acknowledged for their collaboration at various parts of this program.

Figure 1 – Photoelectrochemical testing equipment



WE = working metal oxide electrode under study
RE = reference electrode
CE = counter electrode (platinum)

Figure 2 - The Spray Pyrolysis rig

Figure 3 – Effect of nozzle height and number of spray passes on coating photocatalytic performance

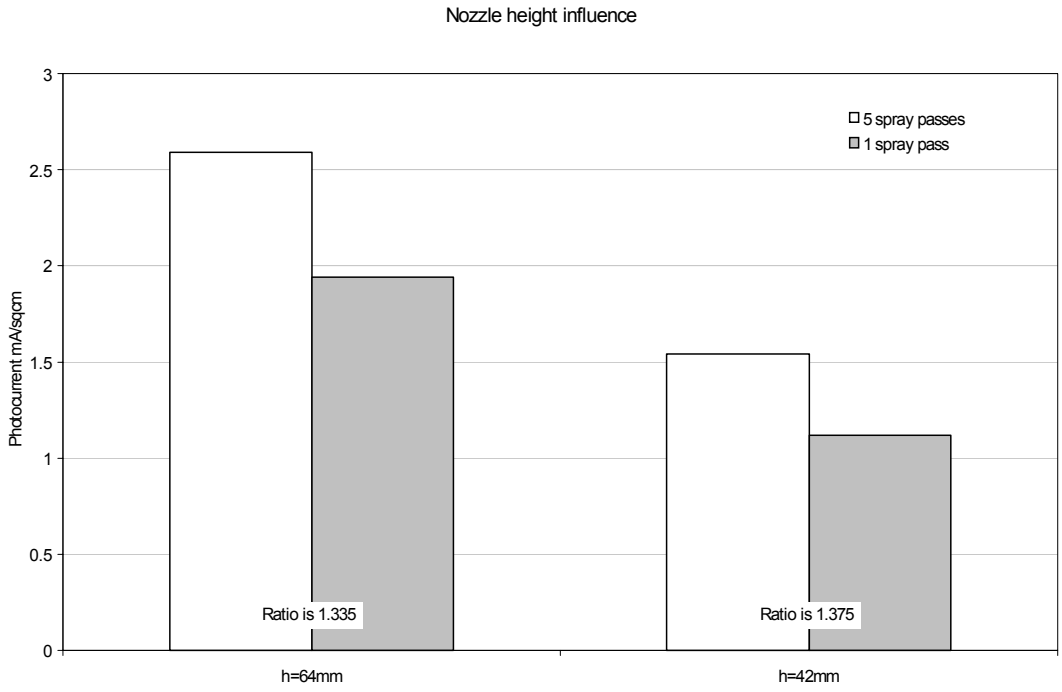


Figure 4 – Effect of substrate scanning on photocurrent density

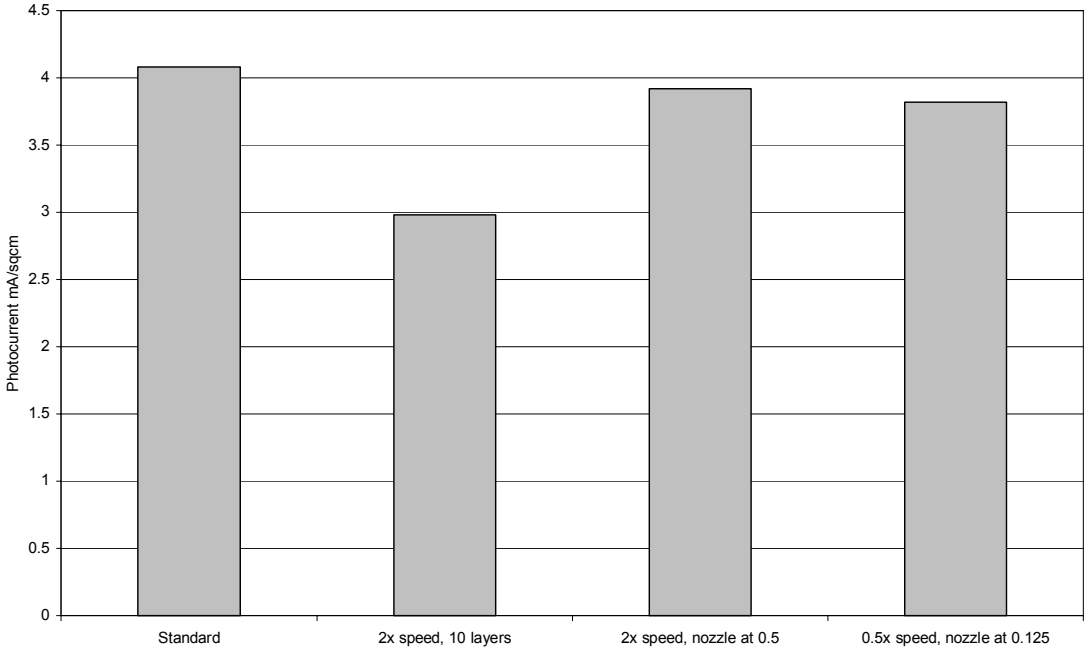
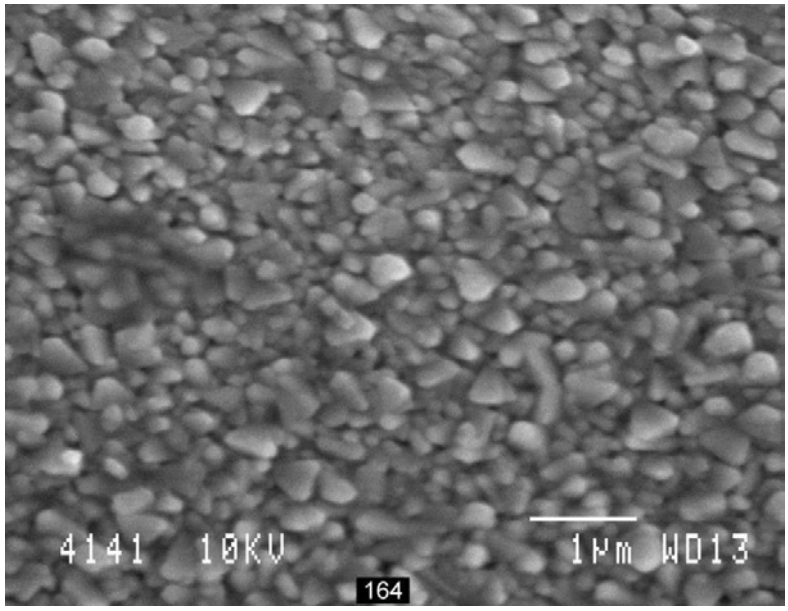


Figure 5 – Effect of temperature on morphology (a) 350°C, (b) 425°C (c) 510°C

(a)



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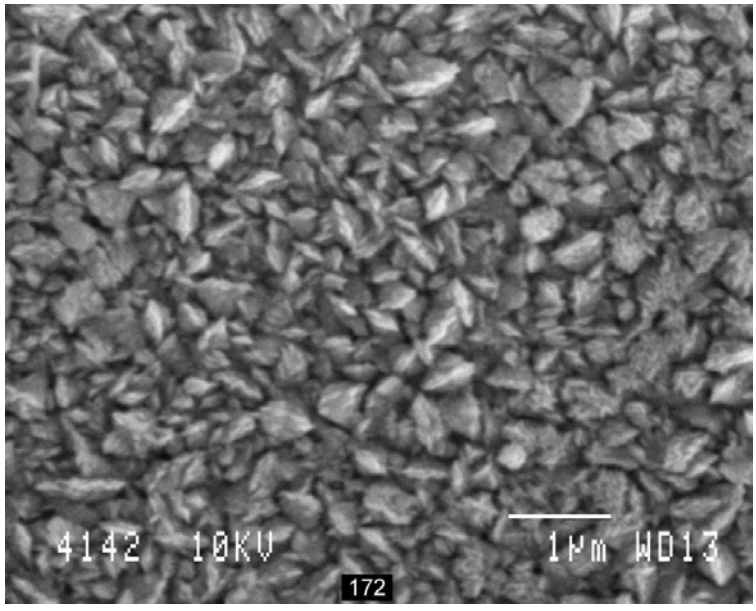

c)

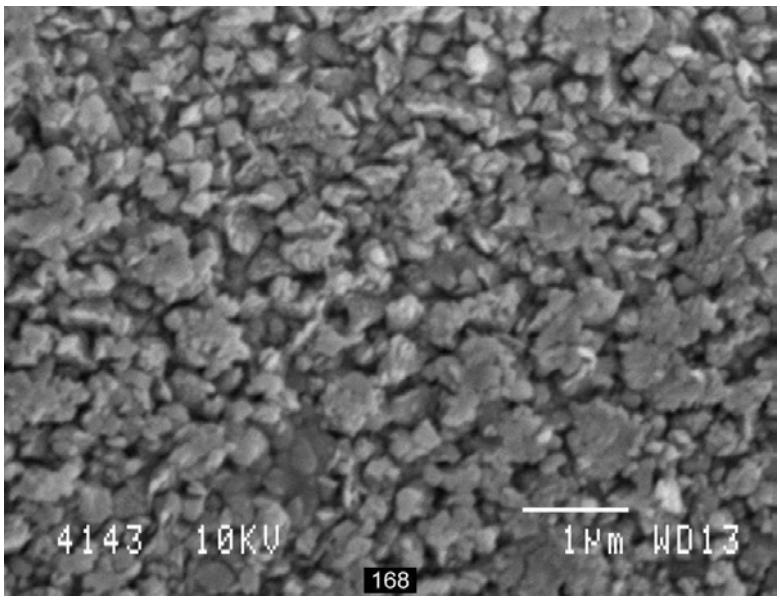

Figure 6 – The SEM provides evidence for the presence of insoluble dopant species in some spray solvents

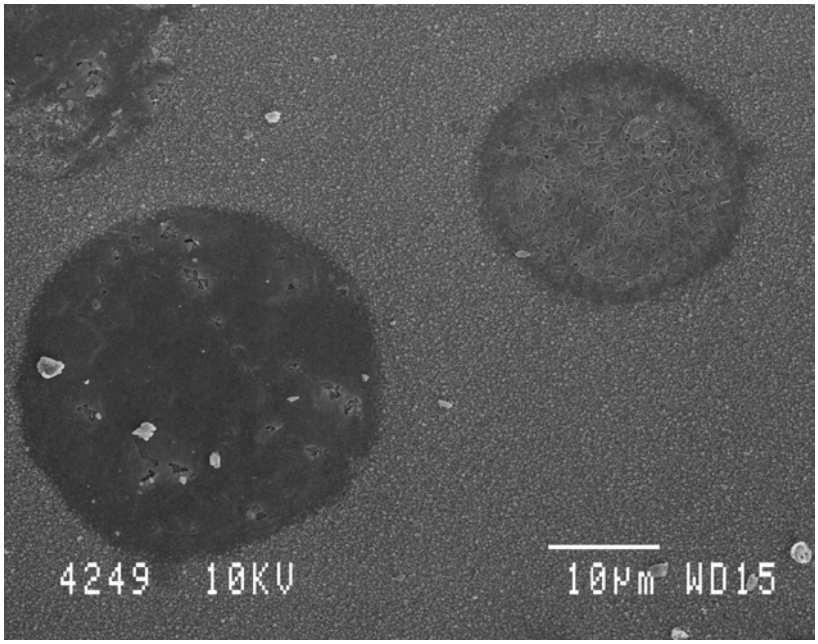

Figure 7 – FE-SEM micrograph of a mechanised doctor-bladed metal oxide electrode

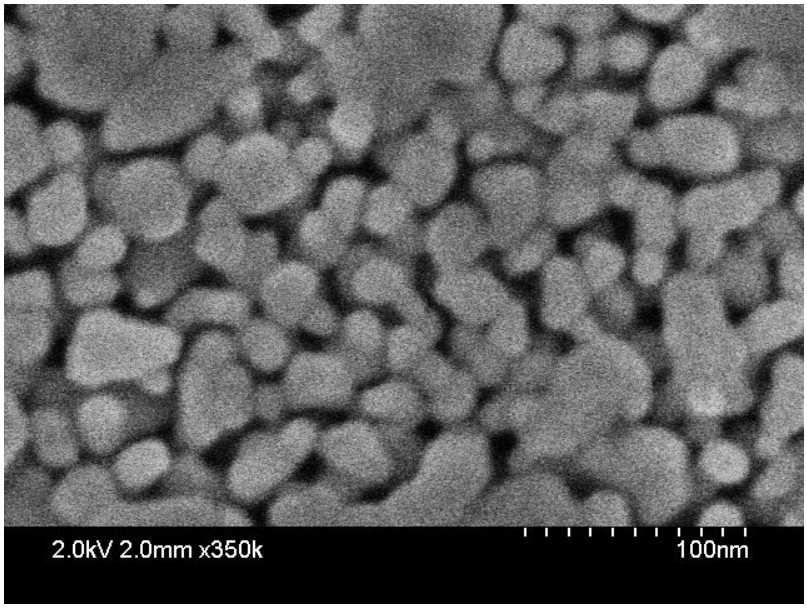

Figure 8 – XRD analysis of a metal oxide electrode

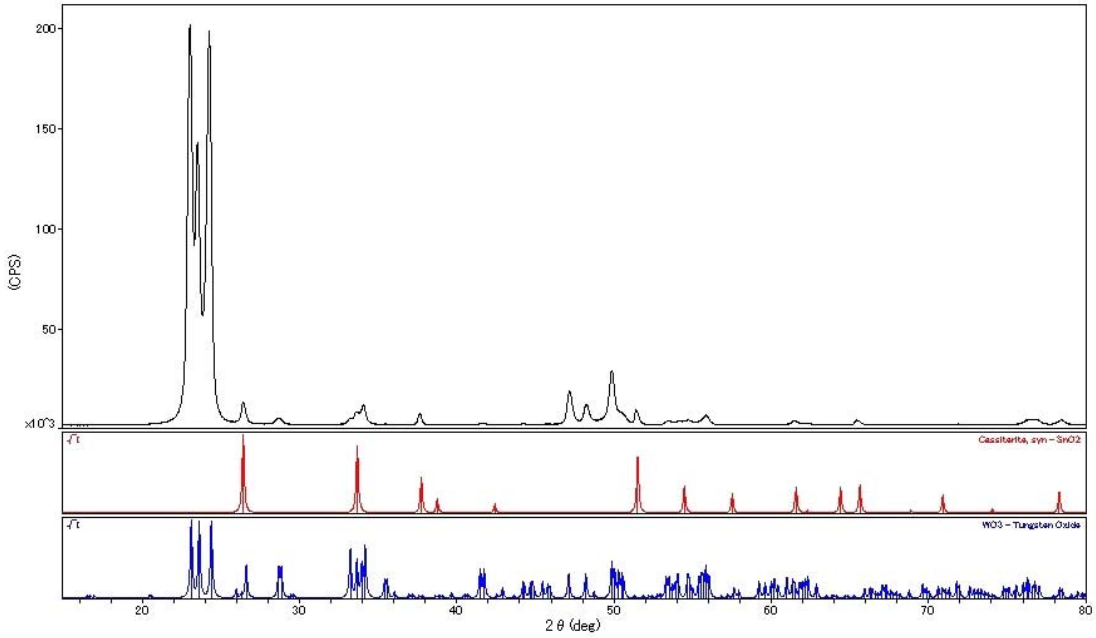

Figure 9 – I-V characteristics of metal oxide films made by spraying isopropanolic precursor solution at different surface temperatures

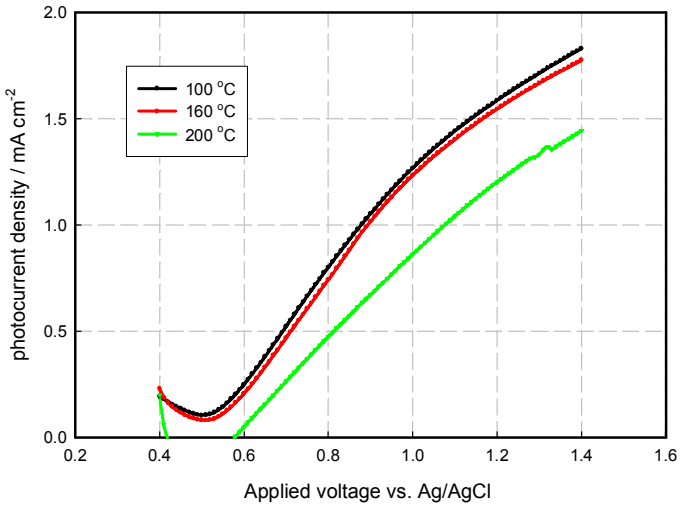

Figure 10 – Comparison of current-voltage performance of metal oxide thin film electrodes prepared by spray deposition.

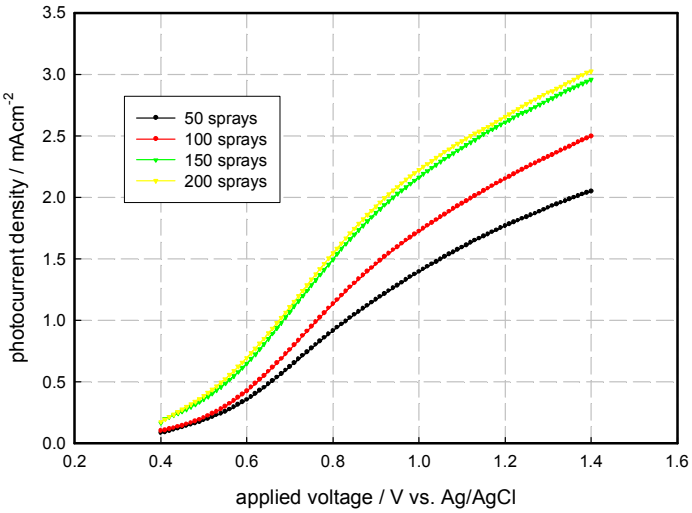

Figure 11 – Generation of hydrogen from 25 x 25 cm^2 scale Tandem Cell

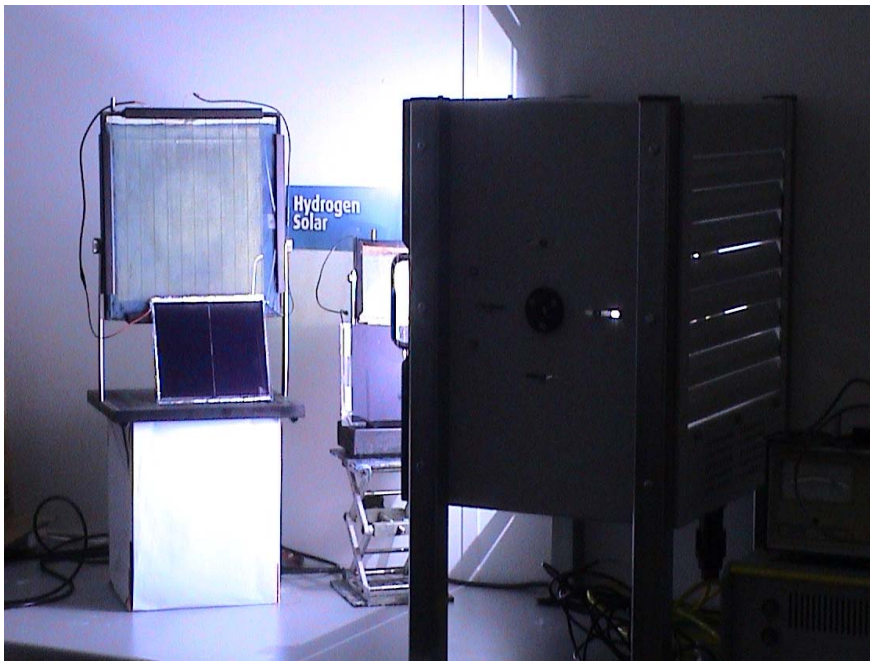

Figure 12 – X electrolyte family A, B, C, D and E at 2 M concentration

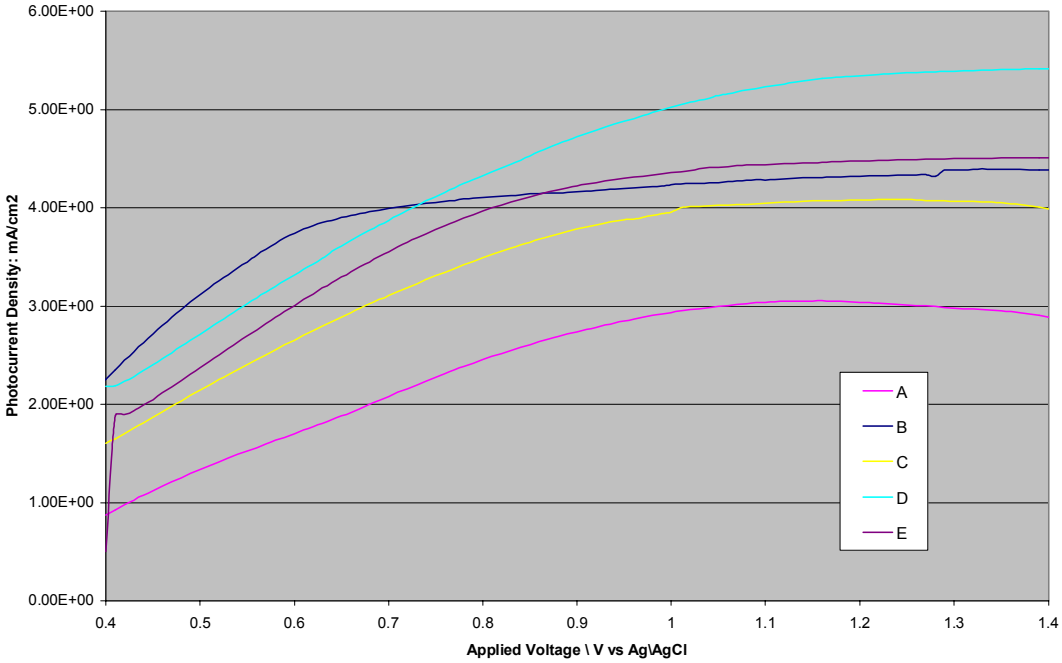

Figure 13 – 12 Cell array assembled at UK outdoor demonstrator site
(a) Frame assembly constructed for three 12 cell modules

(b) 12 cell module with associated balance of cell systems shown in Figure 1