

EH&S ANALYSIS OF DYE-SENSITIZED PHOTOVOLTAIC SOLAR CELL PRODUCTION

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ABSTRACT

Photovoltaic solar cells based on a dye-sensitized nanocrystalline titanium dioxide photoelectrode have been researched and reported since the early 1990's. Commercial production of dye-sensitized photovoltaic solar cells has recently been reported in Australia. In this report, current manufacturing methods are described, and estimates are made of annual chemical use and emissions during production. Environmental, health and safety considerations for handling these materials are discussed. This preliminary EH&S evaluation of dye-sensitized titanium dioxide solar cells indicates that some precautions will be necessary to mitigate hazards that could result in worker exposure. Additional information required for a more complete assessment is identified.

TABLE OF CONTENTS

ABSTRACT	v
LIST OF TABLES	vii
LIST OF FIGURES.....	vii
1. INTRODUCTION.....	1
2. EH&S CONSIDERATIONS IN MANUFACTURING.....	3
3. EH&S CONSIDERATIONS ASSOCIATED WITH PRODUCT USE.....	12
4. CONCLUSIONS.....	12
5. REFERENCES	15

LIST OF TABLES

Table 1 - Examples of Electrolytes and Iodides Used.....	2
Table 2 - Dye-Sensitized Solar Cell Production Calculations*.....	5
Table 3 - Chemical Substance Hazard Matrix	7
Table 4 - Summary of EH&S Issues in DSC Manufacturing.....	14

LIST OF FIGURES

Figure 1 Schematic Illustrating DSC Components (Adapted from www.sta.com.au).....	1
Figure 2 Process Flow Chart – Dye-Sensitized Solar Cells	4

1. INTRODUCTION

Dye-sensitized photovoltaic solar cells (DSC), a non-conventional PV technology, which was first reported in 1991, have shown electrical conversion efficiencies greater than 10% in laboratory testing. An assessment of the DSC's competitiveness with conventional solar cells is being conducted at NREL [1]. This report aims to provide input in this assessment regarding EH&S issues associated with this technology.

Brief Description of Dye-Sensitive Photovoltaic Solar Cells

The dye-sensitized photovoltaic solar cell (DSC) design represents a radical change from traditional solid-state, silicon-based solar cells, in that the photo-electrode is made from nano-scale particles of titanium dioxide (TiO_2 , and also referred to as titania) coated with a monolayer of a light-absorbing dye. Several variations have been developed [1-5], but those that are close to commercial development include nanoparticles of TiO_2 and a liquid electrolyte containing a redox couple completes the circuit. Figure 1 provides a schematic of DSC construction [3]. Other important features include a conducting glass support (usually fluorine-doped tin oxide, or $\text{SnO}_2:\text{F}$) for both the photo-electrode and counter-electrode, and a glass or reflective support substrate for the counter electrode.

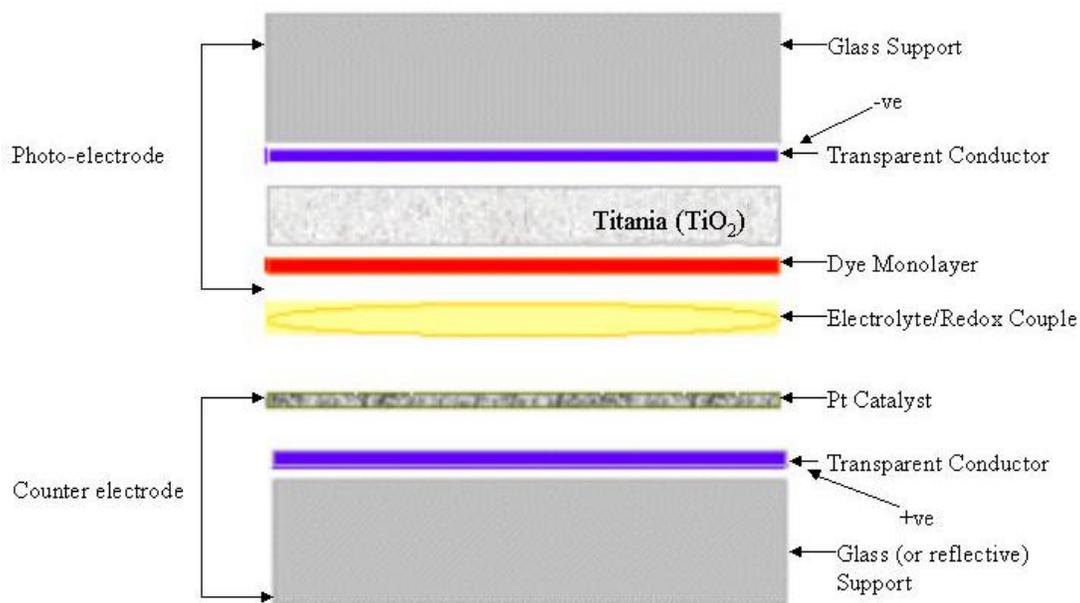


Figure 1 Schematic Illustrating DSC Components (Adapted from www.sta.com.au.)

Although Figure 1 illustrates the various components, it is misleading in that the TiO₂ photo-electrode is not a solid material, and the dye and electrolyte are not physically separate layers. The titania is a highly porous layer from 4 to 20 microns (μ) thick [5] with as much as 50% porosity, prepared by sintering nanocrystalline TiO₂ particles at 300°C. The sintering process takes place on the SnO₂:F transparent conducting electrode so that titania adheres to it. Dye is adsorbed onto the TiO₂ surfaces in the porous layer by soaking or dipping the layer in an alcohol solution containing the dye. This is then dried and the titania is baked again at 100°C. The preferred dye is cis-dithiocyano-bis-(4,4'-dicarboxy-2,2'-bipyridine) ruthenium (II) (also called N3), because it has demonstrated the best incident photon to current conversion efficiency and long-term stability. Another recently discovered "black" dye with better light absorbance properties ((tri(cyanato)-2,2',2''-terpyridyl-4,4',4''-tricarboxylate)-ruthenium (II)) may become used more, but its performance must be verified [6].

The organic liquid electrolyte containing a dissolved redox couple (I₃/I₂) fills the pores of the TiO₂ electrode. Usually acetonitrile or a higher boiling point analogue such as methoxy-acetonitrile, methoxy-propionitrile, or butyronitrile is used for the electrolyte. It is important that the titania layer and electrolyte be water-free, since water causes the dye to detach from the TiO₂ surface, degrading cell performance. The redox couple provides a means of replenishing electrons to the dye molecules (after the dye has absorbed light photons and transferred electrons to the TiO₂ conduction band). At present the I₃/I₂ couple is used, because it is stable, diffuses rapidly, and has low visible light absorption. The redox couple is added to the electrolyte as elemental iodine (I₂) and an iodide salt, such as lithium iodide, sodium iodide, or tetramethyl-ammonium iodide. Some examples of electrolyte/iodide combinations used and iodine/iodide concentrations are shown in Table 1 below.

Table 1 - Examples of Electrolytes and Iodides Used

Electrolyte, Iodide Combination	I ₂ Conc. (mole/L)	I ⁻ Conc. (mole/L)	Ref.
Acetonitrile, tetrabutyl-ammonium iodide	0.2	0.8	2
Acetonitrile/3-methyl-2-oxazolidinone (50:50 wt%) and lithium iodide	0.03	0.3	4
Acetonitrile/tertbutyl-pyridine (0.3 mole/L), lithium iodide	0.05	0.5	5
Acetonitrile/Ethylene carbonate (80 wt%), tetrapropyl-ammonium iodide	0.05	0.5	7

Contacting the electrolyte/redox mixture is the platinum (Pt) catalyst deposited on the SnO₂:F conducting counter-electrode. This completes the circuit. Platinum is usually deposited on the tin oxide by an electro-deposition process from a hexachloroplatinate solution, so that very small amounts (less than 0.1 g/m²) are used.

The final aspect of the cell design is that, once the various layers and substrates are in place and the electrolyte added, the edges of the cell must be sealed and electrode contacts installed. A good seal is necessary to prevent the loss of volatile organic electrolytes. The seal must withstand temperatures 60°C to 80°C, and be resistant to the organic electrolyte and the corrosive I/I₃ redox couple. Thermoplastic materials have been used, as has melted glass frit material.

One alternative design [2] incorporates an insulating porous layer of TiO₂ (rutile form) between the titania and counter-electrode. (The photo-electrode uses the anatase form of TiO₂.) In addition the counter-electrode was fabricated using porous carbon. The additional layers, like the titania, were spread on as a thin layer from a slurry and sintered at 300°C in separate process steps.

As noted above, several variations in dye-sensitized solar cells have been developed. Alternative dyes, electrolytes, redox couples, catalysts, and counter-electrode materials have been tested [6]. The design in Figure 1 [3] will form the basis of the ES&H analysis that follows, because it is currently the only one in commercial production. Some details of the design and manufacture were not available because they are considered proprietary. Even so, the analysis presented here is considered relatively complete, in presenting occupational and environmental hazards associated with manufacture and use.

2. EH&S CONSIDERATIONS IN MANUFACTURING

Overall, the production of dye-sensitized nanocrystalline titania solar cells can be envisioned as six steps:

1. Preparation of the titania photoelectrode on a fluorine-doped tin oxide support,
2. Application of dye monolayer to titania surfaces,
3. Preparation of the counter-electrode by deposition of platinum on a fluorine-doped tin oxide support,
4. Assembly of photoelectrode and counter electrode, including installing electrical leads for cell connections
5. Sealing the assembled cell(s),
6. Addition of electrolyte/redox mixture to titania pores and final sealing.

Addition of electrolyte could also be done before the cell is sealed, but may require special procedures to prevent evaporation of the electrolyte. This analysis assumes assembly and sealing is done first, and that ports for subsequent electrolyte addition have been included in the seal. This order of assembly is used in the single dye-sensitized commercial process now in operation [3]. The process flow chart in Figure 2 illustrates the manufacturing process.

In general, the production of DSCs is economically attractive because the processes used to produce them are relatively simple. The photo-electrode and counter-electrode support material, SnO₂:F, is available commercially and in various resistance values. Deposition of the titania layer can be accomplished rapidly and uniformly using screen printing [3] followed by heat treatment. Application of dye can be through a dip process or a wash

and rinse type process, again followed by heat treatment. Preparation of the counter-electrode would be conducted separately. Final assembly of the cell and sealing can be done before adding the electrolyte/redox couple mixture, in which case ports and a final sealing step would be needed. A vacuum (or possibly capillary action) would then be used to draw the electrolyte into the cell. If the electrolyte is added before the seal, then care would need to be taken to prevent evaporative losses before sealing the cell.

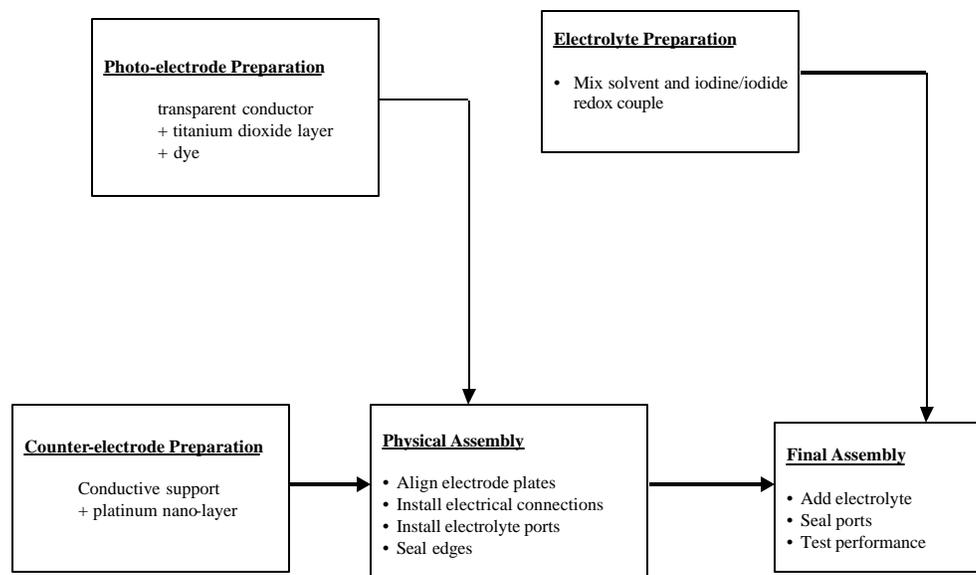


Figure 2 Process Flow Chart – Dye-Sensitized Solar Cells

A variety of organic and inorganic materials would be used in producing the cells. In order to provide focus on which process steps involve significant quantities of chemicals, some estimates of use per year are given in Table 2. The estimates are based on a cell similar to that shown in Figure 1, and on the assumption that solar cell production amounts to 100,000 m²/yr. Specific electrolyte and redox material quantities were obtained from the references indicated in the Table.

The largest quantities (greater than 10 metric tons per year) of materials requirements involve the SnO₂ conducting glass substrates for the electrodes, and ethanol solvent for the ruthenium dye. Intermediate amounts (between 1 and 10 metric tons per year) of titania and electrolyte will be required. Much smaller quantities (less than 0.5 metric ton) of dye, redox material, platinum catalyst, and the sealant to prevent electrolyte evaporation will be needed.

Table 2 - Dye-Sensitized Solar Cell Production Calculations*

Component	Quantity	Thickness	Vol/Area	Density	Percent fill	Use rate	Reference/Comments
		(micron)	(m3/m2)	(g/cm3)		kg/yr	
Conducting glass substrate (SnO2:F)		3,000	0.003	6.85	100	2,055,000	4
Photo electrode							
TiO2 (nanocrystalline anatase)		20	0.00002	4.23	50	4,230	1, 5
Dye	0.7 g/m ²					70	Calculated from Ru weight and molecular formula
Ruthenium - g/m2	0.1 g/m ²					10	Personal note from M. Graetzel
Dye Deposition solvent (ethanol)	700 g/m ²					70,000	Assume 0.1% by weight dye in ethanol (probably more dilute)
Electrolyte							
Propionitrile	50 mL/m ²					3,860	1
Redox - lithium iodide	0.635 g/m ²					64	Assume 0.05 moles/L
Redox - iodine	3.35 g/m ²					335	Assume 0.5 moles/L
Counter-electrode							
Platinum		0.05	5E-08	21.45	100	107.3	7
SnO2 substrate		3,000	0.003	6.85	100	2,055,000	4
Sealant							
Thermoplastic – 25 μm x 0.5 mm strip around 10 cm x 10 cm square			0.0000005	1.1	100	55.0	10, Density used is approximate
* Assumes Production Rate = 100,000 m2/yr							

This quantitative information combined with hazard data such as National Institute of Occupational Safety and Health (NIOSH) recommended exposure limits (RELs) will allow the estimation of risks associated with solar cell production. Table 3 lists available time-weighted average (TWA) threshold limit values (TLV) recommended by the American Council of Government Industrial Hygienists (ACGIH), NIOSH RELs, and OSHA permissible exposure levels (PELs) for assorted chemicals that are used in the current production facility, and some likely alternatives being developed in various research groups [1,6]. Lower explosive limits of the organic solvents are also included. RELs, TLVs, and PELs have not been developed for all chemicals, e.g. methoxypropionitrile, the solvent used in the Australian commercial venture [3]. Chemically similar substances that may serve as substitutes, in this case acetonitrile, are included in Table 3 for comparative purposes.

In the following sections, a more detailed discussion of hazards during manufacture of DSCs is given. Specific focus is on steps in the manufacturing process that could result in worker exposures or releases to the environment, primarily through spills.

Step 1 – Titania photoelectrode preparation

Further details of the solar cell production methods are the next consideration. It seems apparent that screen printing will be the preferred method for preparing the titania photoelectrode. This process has been used to mass-produce multicolor pictures and art, and more recently has been applied to industrial production of coatings on flat surfaces. The method is useful in that areas where a material (e.g. a pigment) is not wanted it can be masked. More importantly, uniform thicknesses of material, such as a pigment, can be laid down. The usual technique involves placing a screen on the substrate (the transparent conductor), applying a suspension (or slurry) of titanium dioxide, wiping off excess slurry, and then removing the screen. After this, the titania is sintered at 300°C. Since the titania suspension is aqueous there are no hazards apparent in this step. However, how TiO₂ is obtained may present some hazards.

Two means of obtaining nanocrystalline TiO₂ for use in solar cells are probable – preparation on-site from organometallic precursors, or purchase from commercial suppliers. If titania is purchased commercially, it may be a suspension or a powder. If it is purchased as a slurry, no hazards are apparent. (Currently, at the Australian pilot plant, it is purchased in the form of colloidal suspension.) If it is purchased as a dry powder, then handling it may be of concern. A TLV of 10 mg/m³ is listed by the ACGIH, and opening barrels or cans to prepare slurry could cause exposure if particles become airborne. The size of the powders (less than a micron) is well below the size of particles that can be inhaled and remain in the lung. Spills of the TiO₂ powders would present hazards to workers if dry methods were used to clean them up. However, wetting the powders with water, and spills of aqueous suspensions of titanium dioxide would not be expected to have a significant environmental impact, because the oxide is not reactive.

Table 3 - Chemical Substance Hazard Matrix

		ACGIH		NIOSH	OSHA	
	CAS Number	TLV	LEL	REL	PEL	Density
		Mg/m3	%	mg/m3	mg/m3	g/mL
Inorganics/Metals						
TiO2 - anatase - photo-electrode	13463-67-7	10				3.9
TiO2 - rutile - nano	1317-80-2	10			15	4.23
SnO2 (powder)	18202-10-5	2				6.85
SnO2:F (transparent conductor)						6.85
Platinum metal (catalytic trace)	7440-06-4			1	None	21.45
Hexachloroplatinate salt (Platinum precursor)				0.002	0.002	
Hexachloroplatinic acid	26023-84-7			0.002	0.002	2.431
Iodine (I2)	7553-56-2	1		1	1	4.93
Sodium iodide	7681-82-5					3.67
Lithium iodide	10377-51-2					3.49
Ammonium iodide	12027-06-4					2.514
Organics						
3-methoxypropionitrile	110-67-8					
Methoxy-acetonitrile						0.949
Acetonitrile	75-05-8	40 ppm	4.4	34	70	0.79
Propionitrile	107-12-0		3.1	14	None	0.772
Butyronitrile	109-74-0		1.7	22		0.794
Gamma-butyrolactone	96-48-0		1.4			1.128
Tetrabutyl-ammonium iodide	311-28-4					1.2
Tetramethyl ammonium iodide	75-58-1					
2,2'-bipyridine	366-18-7					
Pyridine	110-86-1		1.8	15	15	0.98
Ethanol	64-17-5		3.3	1900	1900	0.789
Organo-metallics						
Ru(II)(4,4'-dicarboxy -2,2'-bipy)2(SCN)2						
Titanium isopropoxide	546-68-9					0.955
Sealants						
Surlyn		15				

If titania is prepared on site, other hazards associated with reactive chemicals may apply. The preparation of nanocrystalline TiO₂ from the hydrolysis of titanium alkoxides has become a routine synthesis for research labs and for the commercial producers that use nanocrystalline TiO₂ in paint. Kay and Graetzel [2] describe a means of preparing anatase nanocrystals of TiO₂ by hydrolyzing titanium isopropoxide (Ti(OCH₂CH₂CH₃)₄), followed by peptisation with tetramethylammonium hydroxide, and hydrothermal treatment for several hours. Use of a similar process at a solar cell production plant will require the use of chemical process equipment capable of handling pressure, heat, and corrosive liquids. Using the figure for TiO₂ production of 4,230 kg/year, then 17,000 kg/yr of titanium isopropoxide would be required. Metal alkoxides are extremely reactive with water, and are sold commercially as alcohol solutions. Precautions for storage and handling would be necessary, and all equipment should be designed to prevent vapor release. Since the current commercial facility uses a colloidal suspension, there will be no further consideration of on-site TiO₂ production in this analysis, particularly with respect to potential environmental impacts. However, it is worth noting that the alkoxides present a more acute hazard because of their reactivity. Reaction products include alcohols and titanium oxide. Alcohols may have short-term environmental effects if released in large quantities, but are generally biodegradable. Titanium oxide is relatively non-reactive and is not considered a significant pollutant.

Step 2 – Application of dye monolayer to TiO₂ Surfaces

Adding a monolayer of N3 dye to the TiO₂ surfaces within the porous photo-electrode is accomplished by soaking the photoelectrode in a dilute alcohol solution of the dye, followed by drying at 100°C. Ethanol and isopropyl alcohol are likely solvents. Some of the research groups reported various preparation and purification steps for the dye, so it is not clear if additional processing will be required in an industrial setting. More information needs to be obtained in this area.

Exposure limits (PELs, RELs) have not been determined for the dye. Since it contains a metal and organic ligands, it is likely that it is poisonous, but toxicological data is not available. The application of the dye in an alcohol solution suggests that the usual precautions for handling flammable liquids will need to be followed. The potential for fugitive emissions exists. Collection and recycling of solvents can be expected, since this is a common industrial practice. In addition, because ruthenium is a rare metal, the cost of it and the dye will be of concern to any manufacturer. Optimization of use will almost certainly be directed toward minimizing loss of material during manufacturing operations and as a result of accidental spills.

Environmental impacts in the event that the dye is spilled may be a concern. However, the fate of the dye, specifically its stability in aqueous environments is not known. It is likely that the dye will undergo degradation through ligand replacement reactions in natural surface water or groundwater. The bipyridine ligands, if displaced from the ruthenium in the dye molecule, may present a separate hazard, depending on their toxicity and environmental mobility. Both may need to be evaluated eventually.

However, it is worth remembering that very small quantities are used in manufacturing, and this in itself may mitigate the hazard to some extent.

One approach for a preliminary evaluation is through consideration of the toxicity and environmental behavior of pyridine, which is a likely byproduct of the bipyridine ligands' degradation. Pyridine released on land biodegrades after leaching into the soil [9]. Release to the atmosphere will result in dispersal, and degradation will occur by reaction with hydroxyl radicals produced photochemically. Rain will reduce pyridine concentrations in the air through washout. The biodegradability of pyridine in surface waters has not been quantified. However, it will eventually evaporate from surface waters to be degraded in the atmosphere or washed into soil where biodegradation will occur. [9].

Step 3 – Preparation of the Counter-electrode

The counter-electrode consists of the conducting glass, $\text{SnO}_2:\text{F}$, covered on one side with a catalytic quantity of platinum metal. A likely route for production is through the electrodeposition of a hexachloroplatinate salt. This is accomplished by passing an electric current through an aqueous solution of the salt for a specified time and current, with the $\text{SnO}_2:\text{F}$ serving as one of the electrodes. Hexachloroplatinate is toxic, but aqueous solutions of it are not likely to be ingested by workers. If the aqueous solutions are prepared at the factory, some precautions may be required for handling powders. (Note the low REL of $0.002 \text{ mg}/\text{m}^3$ in Table 3.) The process is similar to electro-plating, but much smaller metal quantities are deposited on the surface.

Another possible route is the use of screen printing, which is being used at a commercial facility. This process uses hexachloroplatinic acid, but details have not been identified because they were considered proprietary. Other additives may be necessary to precipitate the acid, or to reduce the platinum in the acid to metal. For example, at the National Renewable Energy Laboratory (NREL), researchers use polymer surfactants, which totally vaporize when the cells are heated subsequent to screen printing. If heating is in a vented oven, then worker exposures need not be a concern. The surfactants, when vaporized can be expected to result in carbon dioxide or other carbonaceous emissions. These emissions would be of low volume, assuming that the screen print residue is about 20μ thick initially, and 50 wt% water. For a very conservative estimate of carbon dioxide emissions, assume that the remaining mass is 100% carbon (graphite) materials with a density of $3.5 \text{ g}/\text{cm}^3$ (and that platinum mass is negligible at about 0.01 wt%). Conversion of this solid carbon volume to carbon dioxide corresponds to 7.72 grams CO_2 per square meter of production. A nominal $100,000 \text{ m}^2$ per year production plant would thus produce 772 kg carbon dioxide per year. Note that this is a very conservative estimate. Actual emissions would be far smaller, by a factor of at least 10 and probably 100.

Because of the high cost of platinum, it may be expected, as with the N3 dye, that manufacturing processes will be optimized to use the smallest quantities possible, and that special attention will be given to preventing spills. Hexachloroplatinic acid, in

addition to being corrosive, is a strong oxidizing agent that yields finely divided platinum metal after most reactions. The platinum metal is toxic but will not disperse readily in the environment unless it is released as a suspension directly to surface waters. If releases to soils occur, the soils can be expected to absorb the metal particles, minimizing potential groundwater contamination. Because of the small quantities of platinum projected for use in a plant producing 100,000 m² per year, it is likely that any spills would be confined to the interior of the plant, without release to the environment.

Step 4 – Assembly of cell and electrical leads

Cell assembly is accomplished by placing the photoelectrode and counter-electrode together. Electrical leads for power connections would be attached at this time to the electrodes. A conductive adhesive may be used, or possibly soldering, if solder can be used on the SnO₂:F glass. If organic adhesives are used, worker exposure to fumes may need to be considered. More specific information is needed in this area.

Step 5 – Sealing the cell

Sealing the cell is crucial for long-term performance, since it prevents loss of electrolyte and the intrusion of water. Thermoplastics, waterglass (a syrupy sodium silicate solution), and melted glass frit have been tried in research studies. Thermoplastics require heating, and may give off vapors, depending on the specific one used. One of the better performing thermoplastics mentioned [10] is Surlyn 1702, a product from DuPont. In the assembly scenario considered here, ports for introduction of electrolyte have to be included, and sealed after the electrolyte has been added. Surlyn (like many thermoplastics) may give off vapors when heated, and the manufacturer recommends adequate ventilation. However, considering the small quantities used (much less than 1 gram per square meter), vapors from sealing operations are not expected to be a significant hazard.

In this analysis, the quantities of thermoplastic used are based on the use of a 25 μm thick strip 0.5 mm wide, to seal square cell modules that are 10 cm by 10 cm. However, it is a reasonable assumption that any material used will present relatively low worker exposure hazards and minor environmental impacts, because the final material needs to be inert and resistant to the electrolyte and redox couple solution.

Step 6 – Addition of electrolyte to porous TiO₂ photoelectrode

Preparation of the electrolyte/redox mixture will likely be carried out at the solar cell production plant. The electrolytes that have been used (acetonitrile, propionitrile, and methoxy-propionitrile) are fairly common solvents that are flammable, volatile, and toxic. Their toxicity is of concern in terms of worker exposure, and it is worth noting that the human body metabolizes the nitrile solvents and produces hydrogen cyanide in the process.

Mixing in iodide salts and iodine may seem relatively straightforward, but the mixture is extremely corrosive, and the mixing equipment must be made of resistant materials. Elemental iodine itself is toxic (REL=1 mg/m³), and sublimates readily. The potential for worker exposures to iodine and electrolyte solvents is high unless enclosed systems for addition of solids to the electrolyte are used.

In the process of adding the electrolyte to the solar cell, it is necessary to assure that water is excluded, or the dye monolayer will be degraded. The electrolyte is added through the ports installed with the seal. Capillary action may be sufficient to draw the electrolyte mixture in. The process would be accelerated if vacuum is applied. In either case, these methods of introducing the electrolyte provide some means of controlling worker exposures because the electrolyte would be contained and added through the ports by a tube or similar contrivance. At the commercial facility in Australia, vacuum systems are used to control the addition of the electrolyte/redox couple mixture to the cell. This part of the assembly operation was designed to minimize materials losses as well as worker exposures.

Research is being done on using a polymer instead of a liquid electrolyte so that the risk of leaking electrolyte from a damaged cell is eliminated. However, this development appears likely to remain in the research arena for some time [1].

The environmental impacts associated with the electrolyte/redox mixture revolve primarily around the mode of release. The electrolytes used (acetonitrile, propionitrile, or methoxy-propionitrile) are volatile and completely soluble in water. If an accidental spill occurs, evaporation of the solvent will follow, and photochemically produced hydroxyl radicals would cause degradation, most rapidly with acetonitrile. The iodide salt of the redox couple would not evaporate, but some elemental iodine could. Elemental iodine would react with surfaces, becoming reduced to iodide ion most often. In either case, atmospheric releases would be washed out of the atmosphere in rain [9].

For example, a spill of a one-month inventory (based on the projections in Table 1) of propionitrile containing 0.05 moles/L lithium iodide and 0.5 moles/L iodine would amount to 322 kg, or about 300 L (assume density of electrolyte/redox mixture \cong 0.9 g/mL). Of this mixture, 260 kg is solvent, and 40 kg is the weight of the redox couple components. If it is assumed that 100% of the solvent evaporates, then several processes would reduce the initial concentration of the propionitrile. These are dispersal/dilution, reaction with hydroxyl radicals, dissolution in surface waters, and absorption onto solid surfaces and soil. Concentration reduction by the hydroxyl reaction is slow, and proceeds with a half-life of 83 days [9]. Rain washout would be extremely rapid, and would reduce the air levels to background, because of the high solubility of propionitrile in water.

Accidental release of the electrolyte/redox mixture to the land or to surface waters as a mixture from a spill would have more serious immediate consequences, because of its corrosivity. However, the components would degrade relatively rapidly in soil, and be diluted quickly in surface waters. Elemental iodine would be converted quickly to

iodide, the common form of iodine in nature. Iodide ion may be dispersed by water because some of its salts are soluble. However, it is likely that clays and minerals in soil and sediments will absorb a large portion of iodide, slowing its dispersal. Acetonitrile and propionitrile both biodegrade readily in soil but rates are variable. Acetonitrile biodegradation in water occurs at varying rates, depending on whether acclimatization has taken place [9]. Propionitrile biodegradation has not been verified in surface waters.

3. EH&S CONSIDERATIONS ASSOCIATED WITH PRODUCT USE

The analysis above has been directed at the EH&S impacts in manufacture. The potential impacts of the solar cells in use are associated primarily with whether they are broken during service, and the breakage mechanism.

The degradation of a seal and subsequent loss of electrolyte is one impact to consider. However, the release of electrolyte to outside air, which can be expected from exterior roof and wall panels, is not expected to affect people nearby. This is because the volume of electrolyte is small (50 mL/m²) and the slow rate of release to outside air will result in dissipation well before permissible exposure limits can be approached. Catastrophic breakage followed by rapid evaporation of electrolyte could result in PEL concentrations very close to the break for a short time before diffusion reduced the concentrations. For instance, if acetonitrile were used, and a one-meter square cell was broken, the 39.5 grams vaporized would need to diffuse into 564 cubic meters of air before reaching the OSHA PEL of 70 mg/m³. For this scenario, it is worth noting that the commercial facility in Australia is producing panels much smaller than one square meter.

Another scenario to consider for a broken solar cell is the rinsing of dye from the cell by rainwater or water from fire hoses. As noted earlier however, the environmental fate of the dye needs to be investigated before this issue can be addressed. The environmental effects of the electrolyte/redox mixture were described in the previous section.

4. CONCLUSIONS

Since this is a very new technology, the material alternatives described in this report cannot be taken as an exhaustive list. However, although research continues, commercial production of cells using other materials appears to be at least 3 to 5 years away [1]. Steps in manufacturing DSC's, similar to those likely in use at one commercial production facility, have been described, and worker safety and exposure issues have been discussed. These are summarized in Table 4.

This preliminary EH&S evaluation of dye-sensitized nanocrystalline titanium dioxide solar cells indicates that some precautions will be necessary to mitigate hazards that could result in worker exposure. Metal alkoxides, which are sold commercially as alcohol solutions, require certain precautions in storage and handling, if titanium dioxide is fabricated on-site at the manufacturing plant. The electrolytes currently used (acetonitrile, propionitrile, and methoxy-propionitrile) are fairly common solvents that are flammable, volatile, and toxic. Toxicological information about the ruthenium-based

dye is not available, but dye is used in very small quantities and occupational exposures should not be an issue. Such information needs to be developed, however, to assess the potential environmental impact of dye leaking out of these cells when disposed at the end of their useful life.

A significant health concern is potential occupational exposures to respirable particles of TiO_2 , if this powder is produced and/or handled on site. Currently, the only pilot plant in the world purchases and uses TiO_2 in the form of a colloidal solution that prevents this hazard.

Additional information is needed in the following areas for a more complete assessment.

1. What is the toxicology and environmental fate of the N3 dye? Is the dye used as-received, or are there additional preparations steps? What are these steps?
2. What types of electrical leads are used, and how are they installed?
3. How is the electrolyte/redox mixture prepared?

Table 4 - Summary of EH&S Issues in DSC Manufacturing

Manufacturing Step, Activity	EH&S Issue
Titania photoelectrode preparation 1. Use TiO ₂ slurry/colloidal suspension, or Use of dry TiO ₂ powders, or Fabricate TiO ₂ powders on site. 2. Apply TiO ₂ by screen-printing 3. Heat-treat TiO ₂	None, or Inhaled powders, or Exposure to toxic/corrosive metal alkoxides None Hot surfaces
Dye application to TiO ₂ surfaces 1. Prepare dye solution 2. Apply dye (dip in bath) 3. Heat treat	Flammable carrier solvents for dye Dye toxicology not known Dye fate in environment not known
Counter-electrode preparation 1. Prepare hexachlorplatinate solution (aqueous) 2. Deposit by screen-printing 3. Heat treat	Exposure to platinum
Assembly of Cell 1. Install electrical leads and electrolyte ports	More information needed
Sealing cell 1. Place adhesive strips along cell edge 2. Apply pressure and heat	None Vapors from adhesive
Addition of electrolyte/redox mixture 1. Prepare mixture 2. Fill cell through ports 3. Seal ports	Exposure to solvent and iodine None, sealed system Vapors from adhesive

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