DEVELOPMENT OF DYE SENSITIZED SOLAR CELLS: A LIFE CYCLE PERSPECTIVE FOR THE ENVIRONMENTAL AND MARKET POTENTIAL ASSESSMENT OF A RENEWABLE ENERGY TECHNOLOGY

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ABSTRACT

Thanks to the research and development for achieving a larger distribution, many photovoltaic technologies are available in the market presently. Those accepted as "conventional" are well along in the process of commercialization while those classified as "new generation" photovoltaics are at an early stage of industrialization as of yet. To the latter category belong the non-conventional technology of dye sensitized solar cells. Since their first assembling at the beginning of the 1990s, these devices have attracted much interest and have been extensively investigated, because of their ease for assembling of readily available materials and the employment of well-established processes. So far, many configurations have been developed, tested and reported in literature. Each of them is based on the improvement and/or replacement of one or more components of a single solar cell: the substrate, the semiconductor, the dye, the electrolyte and the counter electrode.

The efficiency of dye sensitized solar cells at lab scale is now comparable with amorphous silicon photovoltaics technology, but with much more potential than silicon for performance improvements and for becoming a cost-effective means for electricity production. In spite of these favourable aspects, dye sensitized solar cell prototypes for large scale production are not yet sufficiently efficient to be industrially competitive.

In this study, we present an environmental sustainability overview of the principal dye sensitized solar cell configurations proposed to select the proper set of materials suitable for improving their performances. This is done on the basis of data published in literature, pre-industrialization tests by several companies and lab data obtained through the Fotosensorg Project. The analysis will be integrated with considerations on the potential for a larger distribution and competition of dye sensitized solar cells with presently available solar electric technologies on the photovoltaic market.

1. ADVANCES IN DYE SENSITIZED SOLAR CELL TECHNOLOGY

The Photovoltaic market has experienced a rapid and wide development in recent years [1].

Research, development and industrialisation have led to a portfolio of available PV technology options at different levels of maturity. So far, the chief workhorse of solar energy technology has been the silicon-based solar cell, the first generation of solar PV technology. With an average electrical efficiency rate of around 20 %, this solar cell has been widely used for small and large scale applications. With an efficiency rate approaching the theoretical limit of solar cells (known as the Shockley–Queisser limit) using a p-n junction, and with manufacturing costs stubbornly high, research then focused on developing solar cells that could produce similar efficiency rates but at a fraction of the cost. These are the thin film solar cells, a group that collectively is referred to as the second generation of solar cells, providing the manufacturing gains required by industry at acceptable efficiency rates (currently, between 15 % and 17 %). The family of thin film solar cells can be divided into either silicon-based (amorphous and micromorph silicon technologies) or non-silicon based (cadmium-telluride, copper-indium-diselenide and copper-indium-gallium-diselenide technologies) [2].

In the last years, some rather different and innovative thin film solar cell technologies, commonly grouped together in the category of third generation solar cell technologies, have expanded the potential of the solar industry with promising applicability opportunities. These emerging technologies, based on newly advanced materials, alternative conversion concepts and processes, have entered the photovoltaic market by means of niche applications but are now moving toward a modelling phase for wider commercial exploitation.

The class of the dye-sensitized solar cells (DSSCs) is one of the major representatives of this new generation solar technologies.

DSSCs first gained attention more than thirty years ago. Based on the premise that an illuminated organic dye could generate electricity at the oxide electrode, DSSCs were investigated and further expanded to estabilish that photons could be converted into an electric current by employing dye molecules.

With an efficiency rate of roughly 1 %, the early chlorophyll sensitized zinc oxide electrode DSSC was inadequate and this was due to the structure of the cell. The dye molecule layer was only able to absorb about 1% of the light, severely hindering the practical exploitation and commercialization of this technology. Progress came in the form of a DSSC with an efficiency rating of 11 %, created in 1991 by Michael Grätzel and Brian O'Regan of the École Polytechnique Fédérale de Lausanne, Switzerland [3].

Their work allowed them to overcome the efficiency limiting issue by introducing a porous titanium dioxide nanoparticle layer. This oxide nanoparticle layer (which acts as the anode), covered with an organic molecular dye (photosensitive ruthenium-polypyridine dye) and immersed in an electrolyte solution, is placed next to a platinum catalyst (which acts as a cathode) in a schematic analogous to a modern alkaline battery (Fig 1).

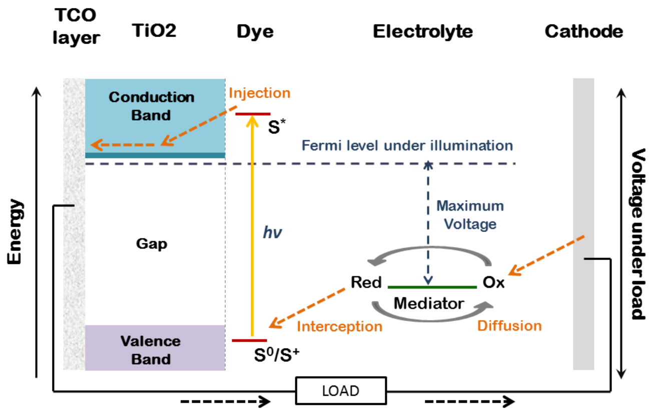


Figure 1 Structure of the dye solar cell: conducting substrates, semiconductor (TiO2), dye) electrolyte, cathode

When exposed to sunlight, the dye sensitizer is excited and an electron is injected into the conduction band of the mesoporous oxide film. These generated electrons diffuse to the anode and are utilized at the external load before being collected by the electrolite at cathode surface to complete the cycle.

While improving the efficiency rating is one goal of the progresses to a solar cell, the other aim is to lower the manufacturing costs. By using the DSSC created by Grätzel, the efficiency rating was improved dramatically from 1 % to 11 % but this result pales in comparison to the records for first-generation silicon solar cells. The expectation is that this efficiency rating will further rise through time thanks to the active and internationally spread research. This idea was featured in the European Union Photovoltaic Roadmap [4], indicating the role this pioneering technology has in contributing to the development of photovoltaics.

Compared to conventional photovoltaics, DSSCs has the following differentiation advantages:

-they show a low dependence on the angle of light
-they are characterized by a stable operating voltage in all light conditions
-they can be produced with various colourings
-they allow for transparency
-they lend for aesthetically pleasing integrations
-they can be manufactured as a building product
-they can provide additional functionality for energy efficiency and noise reduction

Notwithstanding, issues related with DSSCs handling have slowed their adoption. For example, the liquid electrolyte suffers from stability problems at low temperatures.

Another drawback is connected with the molecular dye and the range of electromagnetic spectrum wavelenghts they can absorb through. The cost of the organic molecular dye, the platinum catalyst, and the conducting glass are variables that need to be controlled to ensure DSSCs remain cost-effective solar cells. Given that these three components are not fixed, this could be viewed as a disadvantage.

Since 1991, research has produced numerous advancements to overcome these problems and work to make DSSCs suitable for widespread commercial utilization is in progress [5-7].

2. LIFE CYCLE ASSESSMENT

This work is based on the outcomes of the life cycle analysis (LCA) of the manufacturing process of a DSSC module in accordance to the relevant recommendations defined by ISO 14040 and 14044 standards [8,9].

The LCA methodology allows one to assess the potential environmental impacts associated with all the stages of a product, process or service during its whole life cycle, i.e. from raw material extraction through materials processing, manufacture, distribution, use, repair and maintenance, and disposal or recycling. The methodological framework characteristic of such an analysis consists of four main phases (goal and scope definition, life cycle inventory analysis, life cycle impact assessment and interpretation). These are sequentially developed and accomplished in order to determine the relative importance of each material and energy fluxes contributes to the overall environmental burden of the studied system.

The present case study is on the industrial production process of a photovoltaic module based on different configurations of DSSC that have been developed, tested and patented. The fabrication steps have been modeled according to information derived from existing scientific literature and web resources. Data for laboratory solar cells production were derived from the analysis developed in the Fotosensorg Project framework (POR FSE 2007-2013) “Design and Synthesis of new organic sensitizers for non conventional solar cells production”. This analysis was developed by our group at the University of Siena and the ICCOM-CNR of Firenze [10-12] and cross-checked with pre-industrial process data published by companies active in the sector [13-17]. Secondary data were selected from the the Ecoinvent v 2.2 database [18,19]. Module dimensions were set to 60×100 cm^2 [20] (encapsulation and framing are not considered in the analysis) and this device represents the functional unit to which all the fluxes are referred for the life cycle inventory building. The analysis is defined as cradle-to-gate because recycling and end-of-life scenarios are not considered due to the lack of data for these phases.

All calculations were performed with the SimaPro Software v. 7.3.3 [21]. Three impact assessment methods were used to assess the potential impacts of the input and output flows collected in the life cycle inventory. The Recipe 2008 method at the endpoint level and hierarchist perspective approach [22] was employed for the assessment of the relative contributes to some relevant environmental impact categories (climate change human health, agriculture land occupation, human toxicity, natural land transformation, particulate formation, fossil depletion, climate change ecotoxicity).

The global warming potential (GWP_{100}) was evaluated with the Intergovernmental Panel on Climate Change (IPCC) 2007 data for a timeframe of 100 years [23]. The Cumulative Energy Demand (CED) was calculated with the method described in Ecoinvent v 2.2 by summing all fossil, nuclear, hydro and renewable energy demand into one single CED value [24].

3. DSSC CONFIGURATIONS AND PRODUCTION PROCESSES OVERVIEW

Since their first assembling in the classical configuration [1], many DSSC variants have been studied and patented in recent years [5-7]. All of them rely on the principal components of Grätzel cell (see Table 1), but the specific materials used for different structural elements can vary depending on the designed configuration. In this work we have considered the DSSC typologies that have demonstrated better efficiencies for prototype modules functioning tests.

Table 1 Material life cycle inventory for dye sensitized solar cell module (6000 cm^2)

Input for DSSC module manufacturing	Range quantity
Substrate	168-12000 g
Titanium Dioxide	8-12 g
Dye	~0,06 g
Electrolyte	12-15 g
Metallization paste, silver	3,5-4,5 g
Isopropanol	700-900 g
Electricity	1,29-3,98 kWh

Table 2 DSSC Configurations analyzed in this study (substrate-electrolyte-counterelectrode-substrate)

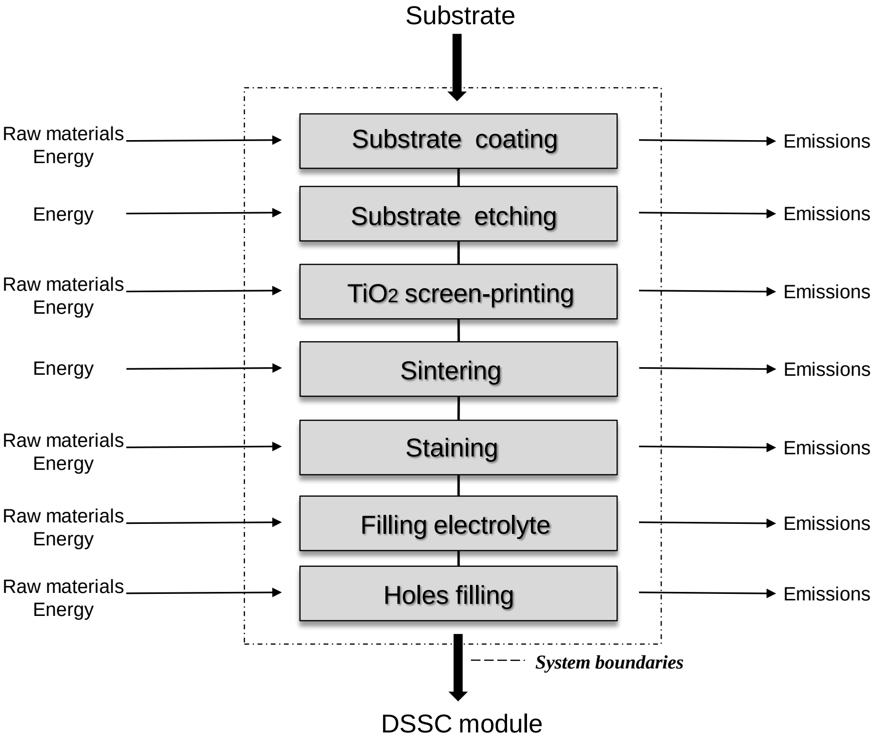
Configurations	Acronyms
Glass - Liquid Electrolyte - Carbon	Glass - Liq El - Carbon
Glass - Ionic Liquid 1 - Cobalt Sulfide PET	Glass - ILE1 - CoS PET
PET - Liquid Electrolyte - Platinum PET	PET - Liq El - Pt PET
PET - Liquid Electrolyte - Platinum Glass	PET - Liq El - Pt Glass
Steel - Liquid Electrolyte - Platinum PET	Steel - Liq El - Pt PET
Steel - Liquid Electrolyte - Platinum Glass	Steel - Liq El -Pt Glass
Glass - Ionic Liquid (type 7) - Platinum Glass	Glass - ILE7 - Pt Glass
Glass - Ionic Liquid (type 6) - Platinum Glass	Glass - ILE6 - Pt Glass
Glass - Ionic Liquid (type 3) - Platinum Glass	Glass - ILE3 - Pt Glass
Glass - Liquid Electrolyte - Platinum Glass	Glass - Liq El - Pt Glass

Specifications and acronyms for these variants are reported in Table 2.

Energy inputs for all the considered configurations are the same except for the high temperature processes (glass substrates fusion and sintering steps) that have been eliminated or modified in order to be reliable for PET or steel subtrates.

There are many other DSSC variants in the literature, however they have not been considered in this LCA study for several reasons, i.e. the low solar energy conversion efficiencies, limited data availability, small chance to be up-scaled in the near future, etc.

Silicon-based and inorganic thin film technologies rely on complex vacuum deposition techniques for cell active layer preparation, principally because of their high sensitivity to impurities and contaminates. The specific production line for these systems is large, complex and very expensive. In addition the raw materials (such as silicon) are costly and always less available. On the other hand, the cost of equipment and tool for modules manufacturing is favorable to DSSC because they require simpler estabilished processes (screen printing, doctor blading, roll-to-roll techniques, spray deposition, air ovens) and cheaper materials compared to conventional technologies. A general scheme for DSSC module fabrication is reported in Figure 2. It has been outlined for the classical glass-glass configuration but it can be related to other process variants. The process starts with the glass substrate entering the manufacturing chain. The principal steps considered are then the substrate coating and etching operations. The following steps are the screen-printing of the semiconductor on the substrate and the sintering of the photo-electrode. After this preparation, the sensitization of the semiconductor is carried out by immersing the as prepared TiO_2 electrode in a dyeing tank (staining phase). To facilitate the following electrolyte injection process, injection holes are predrilled before coupling the TiO_2 electrode with the Pt counter-electrode. Finally the injection holes are hot sealed by



4. RESULTS AND DISCUSSION

In Figure 3 the environmental impact assessment of the DSSC module production using the Recipe 2008 method is reported.

Material and energy inputs for DSSC module containing the N-719 dye have been taken as a reference for different configuration module production processes modelling.

The calculated environmental profiles show a large impact reduction related to the choice of substrate materials, as it can be seen from the reported diagram. The substitution of glass with PET gives a lower contributes for all impact categories, while the use of steel for the solar cell back contact produces a larger contribution principally to the fossil depletion and the climate change human health categories.

Similar behaviour can be observed for the other two environmental indicators used for the comparative analysis and reported in Figure 4. Liquid electrolite substitution with a ionic one does not determine a large change in the overall impact profiles. From a deeper inspection of the results, we can assess that the replacement of the platinum cathode with a cobalt sulfide one could determine a better environmental

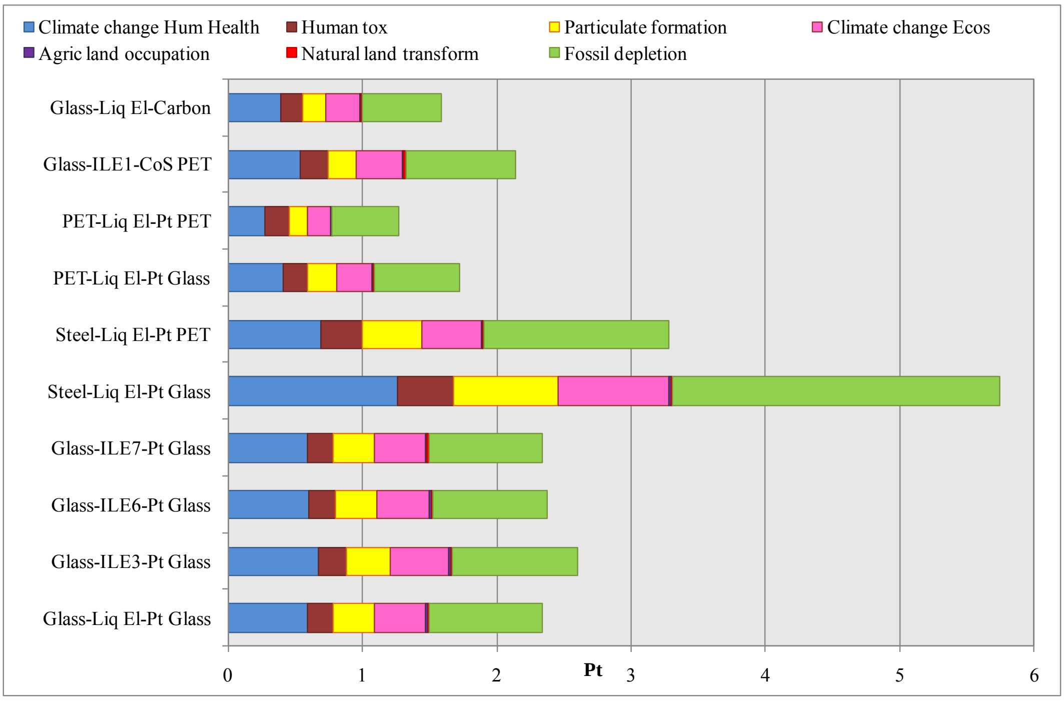


Figure 3 Environmental impact assessment of DSSC panel using the Recipe 2008 method

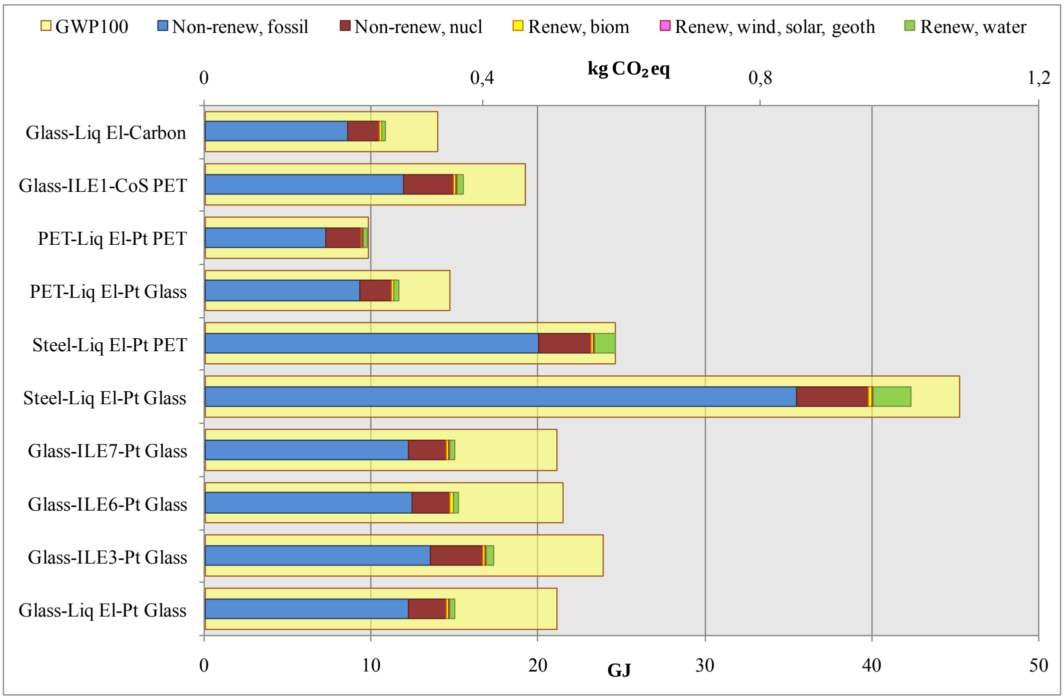


Figure 4 Environmental impact assessment of DSSC panel using the GWP and CED method

behaviour associated with a good stability and ease of laboratory and industrial manufacturing. Unfortunaltely, better performances for solar energy conversion for a DSSC containing such a counter-electrode have been reported only for a laboratory-scale device containing a Zn-porphirine sensitizer which is more energy-demanding for the dye synthesis step.

5. DSSC POTENTIAL IN THE PV MARKET AND PERSPECTIVES

The driving force for any emerging solar cell technology to estabilish in the PV market is the achievement of an installed cost-per-watt level that reaches grid parity compared with conventional fossil fuel technologies and also the possibility to compete favourably against current PV technologies. First generation silicon module costs have continued to reduce from € 3/W in 2008 to just € 1/W in 2011, with module efficiencies ranging from 15% to 20% and with lifetimes guaranteed to 25 years. It is realistic to expect that silicon photovoltaic modules could continue to reduce in manufacturing costs to around € 0.55/W, with module efficiencies rising to 18–22% for real applications.

Great strides have also been made in the commercialization of second generation thin-film technologies. CdTe has achieved module efficiencies of 10–12.5% at costs of about € 0.55/W and current roadmaps expect to achieve module efficiencies of 14% at costs of € 0.4/W. CIGS modules are now commercially available, with effciencies of 12–15% and module costs expected to be less than € 0.4/W.

In this context, DSSCs will compete in the future photovoltaic market if research efforts succed in increasing the power-conversion efficiencies and in modeling the development of ultralow-cost architectures that might be stable over 20 years. Moreover, DSSCs should compare favourably with other solar cells depending on market factors such as the overall photovoltaic demand and the scarcity of rare elements. An important aspect, in fact, is that DSSCs can be constructed from abundant non-toxic materials, which is a significant benefit over current thin-film technologies.

The evaluation of an innovative photovoltaic solar cell market potential is quite complex since it must take into account the commercialization volume and production plant capacity for that particular technology. Recently, researchers from the Fujikura Ltd Japan reported that the current material cost for a DSSC is as high as about € 70/W but with 100 MW annual production it could be lowered down to € 0.3/W [25]. The current high material costs can be explained by the fact some of the required materials are prepared in small quantities mainly for scientific research purposes.

In a larger capacity production scenario of 10% efficient modules, it is possible to estimate the possible cost savings (not including consideration for the 'balance-of-system'). For example, the glass substrate is the most expensive component of classical DSSC, thereby removing at least one glass laminate, a reduction of at least € 15/W can be obtained. Lower-cost DSSCs could be built from cheap metal foils (such as stainless steel and aluminium) and plastic sheets, given that stability issues for these solar cells would be addressed and mechanical robustness would be increased. Concomitant with these aspects, the optimizations of printing solutions could help to decrease the overall manufacturing process costs. Moreover, in addition to raw material costs, attention needs to be given also to the straightforward and low cost manufacturing of the pastes and inks that could produce further € 8/W savings. A significant proportion of the total cost is also allocated to the so-called inactive material, i.e. sealants, encapsulants, wirings for external connections and laminating materials. However such considerations are beyond the scope of this study that encompasses the production process of a DSSC module without taking into account the required operations for photovoltaic system installation mechanical set-up.

If a solar cell could be manufactured inexpensively yet still maintain a high degree of mechanical robustness, then its future could be quite succesfull. So far, as it has been demonstrated by prototype test and pilot-scale productions that DSSCs can envisage applications ranging from home and car rooftops to window glass panes and even intelligent home sensors.

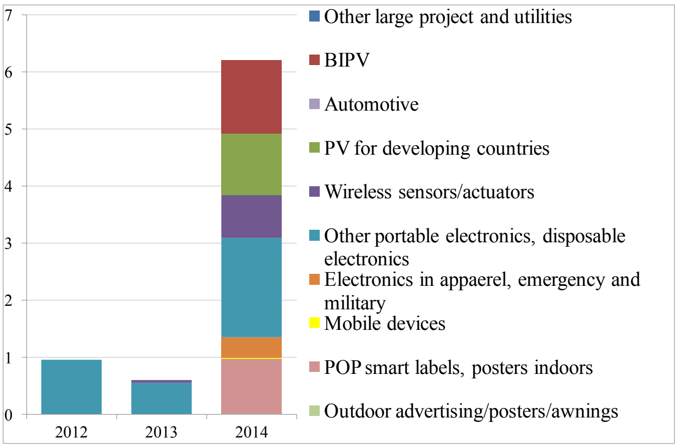


Figure 5 Forecasted growth of DSSC in different market segmentes (in $ milion) - Nanomarkets Report, 2012

As previously stated above, the main issues that DSSC technologies have to solve are related to performance limitations in lifetime and efficiency. There is a clear handicap in the best performance achieved by DSSCs when compared to technologies that have been under development for longer and that have achieved much better efficiency levels. On the other hand, it must be noted that, for example, the performance gap with amorphous silicon, one of the present day technologies, has closed dramatically in recent years, especially for indoor applications. This is a positive result that allows the assessment of DSSCs development to have a good chance for the near future. Moreover, it is important to identify the best fitting initial applications for DSSCs in order to achieve a faster commercialization.

6. CONCLUSIONS

In this study we present an environmental sustainability overview of the principal DSSC configurations that have been assembled in order to select the proper set of materials suitable for improving photovoltaic performances. The life cycle analysis has been developed on the basis of data published in the literature, pre-industrialization tests conducted by several company involved in DSSC development and lab data obtained through the Fotosensorg Project by our research group.

The calculated environmental profiles show a large dependency on the choice of the substrates and counter-electrode materials, while the substitution of the photosensitizer and electrolyte determines minor contributions on the overall impact. The same trend is observed for the assessment of the primary energy content (CED indicator). In our analysis, the best configuration turned out to be the one employing PET as substrate for both sides of the cell, a liquid electrolyte and a platinum counter-electrode.

In order to perform a wider and more realistic evaluation, the analysis has been integrated with considerations on the potential for a larger distribution and competition of DSSCs with present available solar electric technologies on the photovoltaic market. The results obtained, conveniently associated with efficiency and stability data for the specific DSSC configuration and integrated in the right application framework, would allow an overall evaluation of the opportunities for the exploitation these solar cells and would give a strong support in the choice of the more compatible technology for a given end-use.

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