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Dye Sensitized Solar Cells as an Alternative Approach to the Conventional Photovoltaic Technology Based on Silicon - Recent Developments in the Field and Large Scale Applications

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1. Introduction

Utilization of renewable energies is of major importance because of the increase in fossil energy costs in combination with carbon dioxide reduction preventing global warming. The importance of the solar energy can be considered as the sustainable energy which may successfully satisfy a part of the energy demand of future generations. The $3 \times 10^{24}$ joule/year energy supply from sun to the earth is ten thousand times more than the global need. It means that the use of 10% efficiency photovoltaic cells could cover the present needs in electricity covering only the 0.1% of earth’s surface (Wu, et al. 2008). Handling this opportunity of solar energy utilization is a big bet for the future. Besides the development of new clean techniques to the electrical power generation is urgently important in order to protect global environment and assure economic growth of sustainable resources. Taking into account the present status in photovoltaic technology, some improvements have to be made which are summarized in three basic fields: (a) in costs, (b) in their applicability and (c) sustainability. Although the cost per peak watt of crystalline silicon solar cells has significantly dropped, it is still expensive compared to the conventional grid electricity resources. Silicon wafers made of pure semiconducting material to avoid limitations in energy conversion, are still expensive. For this reason developments on potentially cheaper solar cells based on thin-film technology have been made. According to this technology, thin films made of purely inorganic materials such as amorphous silicon, cadmium telluride, and copper indium diselenide successfully prepared on glass substrates. Almost two decades ago, dye sensitized solar cells (DSSCs) were proposed as low cost alternatives to the conventional amorphous silicon solar cells, owing to the simplicity of their fabrication procedures, practically under ambient conditions with mild chemical processes. DSSCs are placed in the category of third generation photovoltaics where new trends in the photovoltaic technology are applied. In the 1st generation PV cells, the electric interface is made between doped n-type and p-type bulk silicon. 1st generation PV cells provide the highest so far conversion efficiency. The 2nd generation PV cells are based on
thin film technology. These cells utilize less material and they thus drop the production cost, however, they are less efficient than the bulk cells. Both 1st and 2nd generation cells are based on opaque materials and necessitate front-face illumination and moving supports to follow sun’s position. Thus they may be either set up in PV parks or on building roofs. 3rd generation solar cells, are based on nanostructured (mesoscopic) materials and they are made of purely organic or a mixture of organic and inorganic components, thus allowing for a vast and inexhaustible choice of materials. Because of their mesoscopic character, it is possible to make transparent cells, which can be used as photovoltaic windows. Photovoltaic windows can be functioned by front-face light incidence but also by diffuse light and even by back face light incidence. Also because of their mesoscopic nature, 3rd generation solar cells are easy to make at ambient conditions, not necessitating severe measures of purity, thus dropping production cost. Among the different possibilities of 3rd generation solar cells, DSSC have the most promising prospect. The overall efficiency of ~12% (in laboratory and small size cells) placed DSSCs as potential inexpensive alternatives to solid state devices. Since the pioneer work of M. Grätzel and co-workers an intense interest to the development of such kind of solar cells has been recorded because of their low cost, simple preparation procedures and benign methods of construction compared with conventional methods applied in first and second generation photovoltaic technology (O’Regan & Grätzel, 1991). Although the solar to electrical energy conversion efficiencies recorded for DSSCs are lower than those measured for silicon based solar cells, a high potential for improvement in their efficiency, stability and commercialization has been announced till nowadays (Grätzel, 2006; Goldstein et al., 2010; Hinsch et al., 2009).

2. Principles of operation and cell structure

The working principle of a DSSC substantially differs from that of a conventional solar cell based on silicon. In silicon solar cell a \(p-n\) junction by joining semiconductors of different charge carriers’ concentration in a very close contact is necessary. In this case the processes of light absorption and charge transport are caused in the same material. In DSSCs, these
fundamental processes are occurred in different materials which avoid the premature recombination of electrons and holes. As these processes do not happen at the same material ultrapure materials are not required for a high performance DSSC. DSSCs are composed of four major components: a nanostructured n-type semiconductor, typically TiO$_2$, a dye-sensitizer to absorb visible light, an electrolyte, which creates the interface with the semiconductor and a counter electrode carrying an electrocatalyst, which facilitates transfer of electrons to the electrolyte. Figure 1a illustrates the basic principle of cell operation while Figure 1b the energy diagram of basic components of the DSSC.

Charge separation is occurred by the different electrochemical potentials between different species such as negative electrode (TiO$_2$/sensitizer) and electrolyte. Any electrostatic potential like in the case of silicon based solar cells is then ignored when a minimum concentration of 0.4M of mobile ions exist in the electrolyte (Grätzel & Durrant, 2008). The semiconductor must provide large active interface both for the attachment of the sensitizer and the contact with the electrolyte. Therefore, the semiconductor can be only conceived in nanostructured form. The sensitizer must have a large extinction coefficient and its energy states must match with those of the semiconductor so as to allow extensive light absorption and efficient excited–electron injection into the conduction band of the semiconductor. The electrolyte must have appropriate electrochemical potential so as to combine with the semiconductor and to efficiently provide charge mobility in a cyclic manner. The dye is regenerated by electrons donated from the electrolyte. The iodide is then regenerated by the reduction of triiodide at the positive electrode, and the circuit is completed by the electron migration through the external circuit. Finally, the counter electrode must efficiently catalyze the transfer of electrons from the external circuit to the liquid phase, i.e. the electrolyte. The open circuit voltage of the cell generated under illumination is attributed to the difference between the Fermi level of the nanostructured semiconductor and the electrochemical potential of the electrolyte. The photoelectrochemical processes occur in a DSSC can be expressed in equations 1-6 (Wu et al., 2008).

\[
\text{TiO}_2 | S + \text{hv} \rightarrow \text{TiO}_2 | S^* \text{ (dye excitation)} \tag{1}
\]

\[
\text{TiO}_2 | S^* \rightarrow \text{TiO}_2 | S^* + e_{(CB)} \text{ (electron injection in ps scale)} \tag{2}
\]

\[
\text{TiO}_2 | S^* + 3I^- \rightarrow \text{TiO}_2 | S + I_3^- \text{ (dye regeneration in } \mu\text{s scale)} \tag{3}
\]

\[
I_3^- + 2e_{(pt)} \rightarrow 3I^- \text{ (reduction)} \tag{4}
\]

While the dark reactions which may also happen are:

\[
I_3^- + 2e_{(CB)} \rightarrow 3I^- \text{ (recombination to electrolyte from ms to s scale)} \tag{5}
\]

\[
\text{TiO}_2 | S^* + e_{(CB)} \rightarrow \text{TiO}_2 | S \text{ (recombination from } \mu\text{s to ms scale)} \tag{6}
\]

From equations described above it is obvious that several issues have to be simultaneously satisfied in order to achieve an efficient solar cell based on nanostructured dye sensitized semiconductors. As a first issue we may refer that the dye has to be rapidly reduced to its ground state after it is oxidized while the electrons are injected into the conduction band of the TiO$_2$ otherwise the solar cell performance will be low. This means that the chemical potential of the iodide/triiodide redox electrolyte should be positioned in more negative values than the oxidised form of the dye. Furthermore the nanocrystalline TiO$_2$ film must be
able to permit fast diffusion of charge carriers to the conductive substrate and then to external circuit avoiding recombination losses, while good interfacial contact between electrolyte and semiconductor has to be ensured (Bisquert et al., 2004). Electrolyte long term stability (chemical, thermal, optical) which will guarantee solar cell high performance is under continuous consideration as in common DSSC structures the electrolyte is in the form of a volatile liquid bringing out the obvious problem of sealing (Zhang et al., 2011). Finally, the optimized concentration of redox couple for the cell efficiency has to satisfy one more parameter of the optical transparency in the visible region otherwise the absorbed light from the dye will be minimized and also triiodide can react with injected electrons increasing the dark current of the cell.

Although, the charge transport rate in DSSCs is relatively slow compared with conventional photovoltaics and the interface where the charge carrier could recombine is wide. Because of the mesoporous structure the charge collection quantum efficiency is surprisingly close to unity (Grätzel & Durrant, 2008). This is caused because of the slow rate constant for the interfacial charge recombination of injected electrons with the oxidised redox couple. The presence of a suitable catalyst (e.g. Pt) raises an activation barrier in one of the intermediate steps of redox reactions resulting in a slow overall rate constant for this reaction. This low rate constant for this recombination reaction on TiO₂ affects to an increased efficiency for DSSCs.

The kinetic competition between charge transport and recombination in DSSCs can be analyzed in terms of an effective carrier diffusion length \( L_n \) given by \( L_n = \left[ D_{\text{eff}} \tau \right]^{1/2} \) where \( D_{\text{eff}} \) is the effective electron diffusion length, and \( \tau \) the electron lifetime due to the charge-recombination reaction given by eq. 5 (Peter & Wijayantha, 2000). \( D_{\text{eff}} \) strongly depends on the position of the quasi Fermi level in the semiconductor and therefore on the light intensity. Typical values at 1 sun are \( 1.5 \times 10^{-5} \text{ cm}^2\text{s}^{-1} \). Since diffusion is the only driving force for electron transport, the diffusion length \( DL \) must be at least as long as the thickness of the TiO₂ electrode. \( D_{\text{eff}} \) generally increases with light intensity while \( \tau \) proportionally decreases. As a consequence the diffusion length is independent of the light intensity. Typical values for diffusion length are 5–20 μm. These limitations set the rules according to which the researchers are challenged to make a choice of materials that will lead to efficient cell functioning.

3. DSSCs’ basic components

The basic structure of a DSSC, as it is referred in previous section, is consisted of two glass electrodes in a sandwich configuration. For the first electrode (negative) a nanocrystalline n-type semiconductor, typically titanium dioxide film is deposited on a transparent conductive glass (TCO) (Fig.2) and then a dye-sensitizer is adsorbed and chemically anchored in order to sensitize the semiconductor in the visible. For this purpose, the dye sensitizer bears carboxylate or phosphonate groups, which interact with surface –OH groups on the titanium dioxide. Several efforts have been made to apply dyes of various structures; however, Ru-bipyridine complexes have established themselves as choice sensitizers (Xia & Yanagida, 2009). This is the negative electrode of the solar cell. A similar transparent conductive glass (positive electrode) covered with a thin layer of platinum is faced to the previous electrode. The space between the two electrodes is filled with an electrolyte. The most efficient electrolytes applied with DSSCs are liquid electrolytes with dissolved I⁻/I₃⁻ redox couple, which are obtained by co-dissolving an iodide salt with iodine (Hagfeldt & Grätzel, 2000). Since some crystallization problems have been encountered
with simple salts, like LiI or KI, recent research is concentrated on the employment of ionic liquids, principally, alkylimidazolium iodides (Papageorgiou et al., 1996).

Fig. 2. AFM (a) and HR-TEM (b) images of a nanocrystalline TiO$_2$ film.

3.1 Nanocrystalline semiconductor

In DSSC technology a variety of nanocrystalline mesoporous metal oxides have been used such as TiO$_2$, ZnO, SnO$_2$ and Nb$_2$O$_5$ (Sayama, et al., 1998, Jose, et al., 2009). Despite the fact that some of them exhibited promising results in cells’ performance only titanium dioxide has extensively used because of some advantages which are only present in this oxide. TiO$_2$ performs excellent thermal stability; it is impervious to chemicals and non-toxic and finally a cheap material. The common crystalline form in application to solar cells is the anatase although a mixture of anatase/rutile form is often used mainly by the formation of very active commercial Degussa-P25 powder. Rutile has proved to be less active as it is less chemical stable than anatase form. Combinations of metal oxides as negative electrodes have also been examined such as WO$_3$/TiO$_2$, TiO$_2$/ZrO$_2$ and SnO$_2$/ZnO or SnO$_2$/TiO$_2$ with moderate results (Tennakone, et al., 1999). In the case of mixed oxides, the core-shell nanostructure formation is mentioned as a new class of combinational system which is typically comprised of a core made of nanomaterials and a shell of coating layer covering on the surface of core nanomaterials (Zhang & Cao, 2011). The use of core-shell nanostructures is usually referred to lower the charge recombination in the TiO$_2$ nanoparticles and it is based on the hypothesis that a coating layer may build up an energy barrier at the semiconductor/electrolyte interface retarding the reaction between the photogenerated electrons and the redox species in electrolyte. Different systems that consisted of mesoporous TiO$_2$ films coated with oxides such as Nb$_2$O$_5$, ZnO, SrTiO$_3$, ZrO$_2$, Al$_2$O$_3$ and SnO$_2$ are also referred. The results revealed that, compared to photoelectrode made of bare TiO$_2$ nanoparticles, the use of e.g. Nb$_2$O$_5$ shell might increase both the open circuit voltage and the short circuit current of the cells.

The basic goal in films preparation is the high surface area of the inorganic semiconductor particles in order to achieve high amounts of dye adsorbed on it. Therefore, a much interest has been drawn to the preparation of highly crystalline mesoporous materials in the form of homogeneous films with an average thickness of 6-12 μm. Usually TiO$_2$ nanoparticles are fabricated by the aqueous hydrolysis of a titanium alkoxide precursor. It is then followed by autoclaving at temperatures up to 240°C to achieve the desired nanoparticle size and
crystallinity (anatase) (Barbe et al., 1997). The nanoparticles are deposited as a colloidal suspension by screen printing or by spreading with a doctor blade technique, followed by sintering at ~450°C to achieve good interparticle connections. The film porosity is maintained by the addition of surfactants or organic fillers; the organic content is removed after sintering of the films in order to obtain pure titanium dioxide (Stathatos et al., 2004). Figure 3 shows a SEM cross sectional image of a mesoporous TiO₂ film prepared by titanium dioxide powder formed with screen printing method. The average pore size is 15 nm and particle diameter 20-25 nm. Film morphology is a crucial parameter in DSSCs' performance mainly to the influence in electron recombination rate. As referred in literature this phenomenon usually happens in the contact between TiO₂ film and conductive substrate (Zhu, et al., 2002). Therefore, a condensed non-porous thin film of TiO₂ is formed between nanocrystalline thick film and TCO substrate and referred as “blocking layer”. The thickness of the compact film is around a few hundreds of nanometres. An alternative method to prepare highly porous nanocrystalline TiO₂ with even more smaller particles is the sol-gel. The sol-gel method for the synthesis of inorganic or nanocomposite organic/inorganic gels has become one of the most popular chemical procedures (Stathatos et al., 1997). This popularity stems from the fact that sol-gel synthesis is easy and it is carried out at ambient or slightly elevated temperatures so that it allows non-destructive organic doping (Brinker & Scherer, 1990).

![Fig. 3. Nanocrystalline TiO₂ film made of Degussa-P25 powder. A TiO₂ blocking layer is also present.](www.intechopen.com)

Indeed, the sol-gel method has led to the synthesis of a great variety of materials, the range of which is continuously expanding. Thus the simple incorporation of organic dopants as well as the formation of organic/inorganic nanocomposites offers the possibility of efficient dispersion of functional compounds in gels, it allows modification of the mechanical properties of the gels and provides materials with very interesting optical properties. A typical sol-gel route for making oxide matrices and thin films is followed by hydrolysis of alkoxides, for example, alkoxysilanes, alkoxytitanates, etc (Brinker & Scherer, 1990).
However, a review of the recent literature reveals an increasing interest in another sol-gel route based on organic acid solvolysis of alkoxides (Birnie & Bendzko, 1999; Wang et al., 2001). This second method seems to offer substantial advantages in several cases and it is becoming the method of choice in the synthesis of organic/inorganic nanocomposite gels. As it has been earlier found by Pope and Mackenzie (Pope & Mackenzie, 1986) and later verified by others, organic (for example, acetic or formic) acid solvolysis proceeds by a two step mechanism which involves intermediate ester formation (Ivanda et al., 1999).

Simplified reaction schemes showing gel formation either by hydrolysis or organic acid solvolysis are presented by the following reactions. (Note that in these reactions only one metal-bound ligand is taken into account, while acetic acid (AcOH) is chosen to represent organic acids in organic acid solvolysis):

\[
\begin{align*}
\text{Hydrolysis} & : \\
\text{Polycondensation} & : \\
\text{Acetic acid solvolysis} & : \\
\equiv M-OR + H_2O & \rightarrow \equiv M-OH + ROH \quad (7a) \\
\equiv M-(OH) & \rightarrow -M-O-M- + H_2O \quad (7b) \\
\equiv M-OR + AcOH & \rightarrow \equiv M-OAc + ROH \quad (8a) \\
ROH + AcOH & \rightarrow ROAc + H_2O \quad (8b) \\
\equiv M-OAc + ROH & \rightarrow ROAc + \equiv M-OH \quad (8c) \\
\equiv M-OR + \equiv M-OAc & \rightarrow ROAc + M-O-M \quad (8d)
\end{align*}
\]

where M is a metal (for example, Si or Ti) and R is a short alkyl chain (for example, ethyl, butyl, or isopropyl). Hydrolysis (7a) produces highly reactive hydroxide species M-OH, which, by inorganic polymerization, produce oxide, i.e. M-O-M, which is the end product of the sol-gel process. More complicated is acetic acid solvolysis (8) where several different possibilities may define different intermediate routes to obtain oxide. Reaction (8a) is a prerequisite of the remaining three reactions. Occurrence of reaction (8b) would mean that water may be formed which may lead to hydrolysis. Reaction (8c) would create reactive M-OH which would form oxide, while reaction (8d) directly leads to oxide formation. The above possibilities have been demonstrated by various researchers by spectroscopic techniques. However, there still exists a lot of uncertainty and there is no concrete model to describe a well established procedure leading to oxide formation by organic acid solvolysis. For this reason, more work needs to be carried out on these systems. Reactions (8) reveal one certain fact. The quantity of acetic acid in solution will be crucial in affecting intermediate routes. Thus reaction (8b) is possible only if an excess of acetic acid is present. Also the quantity of acetic acid will define whether the solvolysis steps will simultaneously affect all available alkoxide ligands or will leave some of them intact and subject to hydrolysis reactions. Figure 4 shows a SEM cross sectional image of a mesoporous TiO\(_2\) film prepared by sol-gel method with dip-coating. The average pore size is lower than 10 nm and particle diameter 10-12 nm. In this case, it is proved that no compact TiO\(_2\) layer acting as “blocking layer” is needed for high performance DSSCs.

From previous paragraphs is obvious that nanoparticulate films are the common choice in photoelectrode preparation for use in DSSCs. However, the nanoparticulate films are not thought to be ideal in structure with regard to electron transport. For this reason, recent developments in nanostructured electrodes are proposed such as nanowires, nanotubes, nanorods which belong to 1-Dimensional structures in contrast to 3-D structures referred to films consisted of nanoparticles.
Fig. 4. TiO$_2$ nanocrystalline film made of sol-gel procedure (a) cross sectional image and (b) higher magnification of the film.

One-dimensional nanostructures might provide direct pathways for electron transport in DSSCs and ~25 μm thick film consisting of ZnO nanowires in diameter of ~130nm was mentioned to be able to achieve a surface area up to one-fifth as large as a nanoparticle film used in the conventional DSSCs (Law et al., 2005).

Fig. 5. (a) Schematic diagram of a DSSC with titania nanotubes, (b) a SEM image of titania nanotubes taken from reference (Zhang & Cao, 2011).

Moreover, the low manufacturing cost by using roll-to roll coating process creates the need of replacing the glass substrate with light weighted flexible plastic electrodes, expanding this way the area of DSSCs’ applications. Flexible plastic electrodes like polyethylene terephthalate sheet coated with tin-doped indium oxide (PET-ITO) appear to possess many technological advantages (no size/shape limitations, low weight, high transmittance) as they present very low production cost in relation to F:SnO$_2$ (FTO) conductive glasses. The use of such plastic substrates requires that all processes needed for the fabrication of DSSC, including the formation of TiO$_2$ nanocrystalline films, to be designed at temperatures lower than 150°C. In the direction of replacing the glass substrates with flexible plastics, mesoporous TiO$_2$ films have to be prepared at low temperature and also with nanocrystalline dimensions for better efficiency to energy conversion. So far, the methods that obtain the most-efficient TiO$_2$ films for DSSCs have been based on high-temperature calcination. High-temperature annealing, usually at 450-500°C, is necessary to remove
organic material needed to suppress agglomeration of TiO$_2$ particles and reduce stress during calcination for making crack-free films with good adhesion on substrates. Besides, high-temperature treatment of films promotes crystallinity of TiO$_2$ particles and their chemical interconnection for better electrical connection. Low sintering temperature yields titania nanocrystalline films with high active surface area but relatively small nanocrystals with many defects and poor interconnection, thus lower conductivity. High sintering temperature for TiO$_2$ films is then the most efficient method for the preparation of high performance DSSCs but it is also a cost intensive process. In addition, high temperature treatment of TiO$_2$ films cannot be applied to flexible plastic electrodes which in recent years emerge as an important technological quest. Different approaches appear in the literature to avoid high temperature annealing of thick and porous TiO$_2$ films. Among a variety of methods used for the low-temperature treatment of TiO$_2$ films like hydrothermal crystallization (Huang et al., 2006), chemical vapor deposition of titanium alkoxides (Murakami et al., 2004), microwave irradiation (Uchida et al., 2004), ultraviolet light irradiation treatment (Lewis et al., 2006), and sol-gel method (Stathatos et al., 2007), the efficiency of DSSCs employing ITO-PET substrates was in the range of 2-3% at standard conditions of 100 mW/cm$^2$ light intensities at AM 1.5. A very simple and also benign method for the formation of pure TiO$_2$ nanoparticles surfactant-free films of nanocrystalline TiO$_2$ at room temperature with excellent mechanical stability is the mixture of a small amount of titanium isopropoxide with commercially available P25-TiO$_2$ (surface area of 55 m$^2$/g, mean average particle size of 25 nm and 30/70% rutile/anatase crystallinity) powder. The hydrolysis of the alkoxide after its addition helps to the chemical connection between titania particles and their stable adhesion on plastic or glass substrate without sacrificing the desired electrical and mechanical properties of the film. Promising results have obtained by the use of this method.

3.2 Sensitizers
The dye plays the important role of sensitizing the semiconductor in the visible and infrared region of solar light. For this reason several requirements have to be succoured at the same time such as, broad absorption spectrum, good stability, no toxicity, good matching of the HOMO, LUMO levels of the dye with semiconductor’s bottom edge of conduction band and chemical potential of redox system of the electrolyte. Besides, the chemical bonding between the dye and semiconductor’s surface is absolutely necessary for effective electron transfer. The ideal sensitizer for nanocrystalline TiO$_2$ particles has to absorb all the light below a threshold wavelength of about 900nm. Moreover it has to carry out carboxylate or phosphonate groups which are permanently grafted on oxide surface by chemical bonds so as after excitation to inject electrons into the semiconductor with a quantum yield close to unity. The stability of the sensitizer is ensured by 100 million turnover cycles which refer to approximate twenty years of light soaking (Grätzel & Durrant, 2008). The common sensitizers for DSSCs are ruthenium complexes with bipyridine ligands and they follow the structure ML$_2$(X)$_2$ where L is the organic ligand and M the metal ion (either Ru or Os) and X can be cyanide, thiocarbamate or thiocyanate groups. Electron transfer from sensitizer to semiconductor after optical excitation is based on metal to ligand charge transfer and then the transfer to the semiconductor via the chemical bond between them. The N3 dye ($\text{cis}$-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II)) was first reported as the most efficient sensitizer for DSSCs (Nazeeruddin et al., 1999). Then Black Dye [cis-
diisothiocyanato-bis(2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium(II) bis(tetrabutyl ammonium) was also introduced by Grätzel and co-workers as a most efficient sensitizer because it covers solar light in longer wavelengths than N3 (Nazeeruddin et al., 2001). Modified N3 with tetrabutyl ammonium groups (N719) tris(isothiocyanato-(2,2’:6’,6”-terpyridyl-4,4’,4”-tricarboxylato) ruthenium(II) tris(tetra-butyl ammonium) was finally found to be the most applicable dye in DSSCs’ technology as it enhances the open circuit voltage of the cells of at least 15%. Next generation of dyes is based on the formula of N3 while it contains different size groups on the ligands covering two basic demands: (a) chemical stability and good penetration of electrolyte because of suitable organic groups (b) absorbance in longer wavelengths. Recent years the combination of dye properties with organic p-type semiconducting side groups seems to attract much attention. Another case of sensitizers is pure organic dyes in replacement of costly ruthenium complexes. Metal free sensitizers for DSSCs are referred: hemicyanines, indoline dyes, phthalocyanines, coumarins, perylene derivatives etc. Promising results have been obtained where in the case of D149 indoline dye an efficiency of 9.5% was recorded while SQ2 (5-carboxy-2-[[3-[(2,3-

![Fig. 6. Incident Photon to current efficiency for N3 and Black dye (Grätzel, 2006).](image)

dihydro-1,1-dimethyl-3-ethyl-1H-benzo[e]indol-2-ylidene) methyl -2-hydroxy-4-oxo-2-cyclobuten-1-ylidene[methyl]-3,3-dimethyl-1-octyl-3H-indolium) an efficiency of 8% was also recorded (Goncalves et al., 2008). Finally the strengths and weaknesses of organic dyes in DSSCs are the followings:

The strengths are:
- They exhibit high absorption coefficient (abundant $\pi \rightarrow \pi^*$ within molecules)
- it is easy to design dyes with various structures and adjust absorption wavelength range
uses no metal and they have no limitation to resources
lower cost than organic metal dye and enables synthesis.

While the weaknesses of organic dyes are:

- still lower efficiency than organic metal dye
- short post-absorption excited state (π*) lifetime
- narrow absorption spectrum wavelength in visible ray field that it is difficult to absorb light from all visible range.

3.3 Electrolytes

The key composition elements for DSSC include fluorinated tin oxide (FTO) which is used for either electrode substrate, nanoparticulated oxide semiconductor layer like TiO\textsubscript{2} and ZnO, sensitizer, metallic catalysts like platinum which plays the role of the opposite electrode and the electrolyte which includes redox couple and it is positioned between the two electrodes. The composition and the form of the electrolyte have great affect on the total energy conversion efficiency. The majority of the proposed DSSCs is based on liquid electrolytes with a variety of solvents where an overall maximum efficiency of \(\sim 12\%\) was finally achieved. Nevertheless, there are still questions which own an answer about the stability and sealing in order to prevent the leakage of the solvent. Solid or quasi solid electrolytes could be an answer to the questions. In the case of solid electrolytes we may refer polymeric materials which incorporate the iodide/triiodide redox, organic hole transporting materials or inorganic p-type semiconductors. As quasi-solid electrolytes we can refer composite organic/inorganic materials which appear as a gel or highly viscous ionic liquids.

3.3.1 Liquid electrolytes

The electrolyte is generally composed with oxidation-reduction of I\textsuperscript{-}/I\textsubscript{3} where LiI, NaI, alkyl ammonium iodine or imidazolium iodine is used for materials of I\textsuperscript{-} ion. For instance, 0.1M LiI, 0.05M I\textsubscript{2}, and 0.5M tert-butyl pyridine (TBP) are mixed in acetonitrile solution or 3-methoxypropionitrile, propylene carbonate, \(\gamma\)-butyrolactone, N-methylpyrrolidone as alternative solvents. I\textsuperscript{-} ion is responsible for offering electrons for holes generated in dye molecule’s HOMO level, whereas the oxidized I\textsubscript{3}\textsuperscript{-} ion accepts electrons that reach counter electrode to be reduced (Snaith & Schmidt-Mende, 2007).

3.3.2 Solid electrolytes

When it is referred the use of solid electrolytes it is generally accepted that people mean the use of p-type semiconducting materials either organic or inorganic. In the case of organic materials the most popular is spiro-MeOTAD which initially proposed by Grätzel and co-workers (Kruger et al., 2002). The recorded efficiency was about 4\% while new organic semiconductors were appeared in the meanwhile. Polymer based solid electrolytes are usually referred as efficient alternatives to liquid based electrolytes but the efficiency is still poor. Polymer usually containing polyether units can be used as solid electrolytes in DSSCs. These types of electrolytes are solid ionic conductors prepared by the dissolution of salts in a suitable high molar mass polymer containing polyether units (de Freitas et al., 2009).

In the case of inorganic materials, CuSCN (O'Regan & Schwartz, 1998) and Cul (Tennakone et al. 1995) are the most popular, but the efficiency of the solar cells is lower than 2\% because of the poor contact between TiO\textsubscript{2} and p-type inorganic semiconductor. Optimized interface
between the two different types of semiconductors and instability problems of copper based p-type semiconductors have to be improved before the p-n junction between them to be more efficient.

3.3.3 Quasi-solid electrolytes

In some cases the very viscous ionic liquids but in most cases the composite organic/inorganic materials are referred as quasi-solid electrolytes. Nanocomposite organic/inorganic materials are constituted of two interpenetrating subphases which are mixed in nanoscale. The organic subphase is usually consisted of few surfactants or polyether chains and the inorganic subphase is made of an inorganic network which typically is silicon dioxide or titanium dioxide. Such nanocomposite gels can accommodate appropriate solvents within the organic subphase (that is within the pores left by the inorganic network) so that ionic conductivity can be raised to a satisfactory degree. The design and synthesis of such materials makes for fascinating research with numerous scientific and technological implications in iono-electronics, mechanics and optics. There are two prospects of making organic/inorganic blends which are depended on the specific interactions between the two subphases (scheme 1). Such blends which were obtained by simply mixing of the two components together, characterized as materials of Class I corresponding no covalent or iono-covalent bonds. In these materials the various components only exchange weak interactions such as hydrogen bonding Van Der Waals interactions or electrostatic forces. On the other hand, materials which are formed by chemically bonding between the two subphases are characterized as Class II (hybrid materials). Class II materials organic/inorganic components are linked through strong chemical bonds e.g. covalent, iono-covalent or Lewis acid-base bonds. Usually materials of Class II have better mechanical properties than Class I as they present rubbery behavior (Stathatos, 2005).

Sol-Gel chemistry allows the combination at the nanosize level of inorganic and organic since solubility of most organic substances, especially, hydrophobic ones, is limited in pure oxides (e.g. SiO₂) causing migration and aggregation with subsequent decrease of their functionality. Nanocomposite gels made of the two different subphases the oxide network, as the inorganic subphase and the polymer or surfactant as the organic subphase mixed in nanoscale providing in this way an access to an immense new area of materials science. In principal, in sol-gel chemistry a metal alkoxide (including silicon alkoxides) is hydrolyzed and the subsequent inorganic polymerization leads to the formation of the corresponding oxide with an oncoming condensation of the material. The whole process is carried out at ambient conditions. The process can be summarized to reactions 7 mentioned before. An alternative route to the oxide synthesis is the slow water release in the solution with no initial water addition into the solution. In this case the existence of an organic acid in the sol is indispensable, typically acetic or formic acid as initially referred in reactions 8. (In reactions 7a and b, as well as in the above reaction 8, only one of usually four reacting alkoxy groups is taken into account, for reasons of simplicity). Reactions 8 show that the end product of the sol-gel process is -M-O-M-, which can be obtained by successive chemical reactions. Metal ester (M-OAc) as a result of (2) can react with the metal alkoxide forming -M-O-M-, additionally; water released through esterification reaction 3 can yield oxide by the hydrolysis route. When ethanol is introduced in the sol, which is a common recipe in many works, even more water can be released by direct esterification reaction between the ethanol (EtOH) and the acetic acid (AcOH). Furthermore, intermediate M-OAc ester or -M-O-M-
oligomers may create entities which offer polymorphism to the sol-gel evolution. Thus the presence of a self-organizing agent, e.g. a surfactant, plays a crucial role in organizing the structure of the material and in creating well defined and reproducible nanophases. Slow water release, organic acid solvolysis and surfactant organization are then the key factors that dictate the structure and the quality of the nanocomposite organic/inorganic gel. A different approach to the gel process of quasi-solid electrolytes is the use of modified materials (Jovanovski et al., 2006) with silicon alkoxy-groups which may easily hydrolyzed and finally lead to a gel formation (e.g. scheme 2). The modified materials could be a series of additives usually employed in liquid electrolytes e.g. benzyl-imidazoles for open circuit voltage enhancement which are now bearing alkoxy-groups for jellifying process.

As a consequence, gel electrolytes are roughly distinguished into three categories: (1) One way to make a gel electrolyte is to add organic or inorganic (or both) thickeners. Such materials may be long-chain polymers like poly (ethylene oxide) or inorganic nanoparticles like titania or silica; (2) A second way is to introduce a polymerizable precursor into the electrolyte solution and polymerize the mixture in situ; (3) a third route is to produce a gel incorporating the I⁻/I₃⁺ redox couple through the sol-gel process by using a sol-gel precursor, like a titanium or silicium alkoxy. This precursor may be a functionalized derivative of one of the components of the electrolyte. This last method has been very successful since the sol-gel process leads to the formation of nanocomposite organic-
inorganic materials. Such materials are composed of an inorganic subphase, which binds and holds the two electrodes together and seals cell and an organic subphase, which assures dispersion of ionic species and supports ionic conductivity. The whole composition is compatible with titania nanocrystalline electrode and provides good electrical conduct and finally satisfactory ionic conductivity. Such cells are easy to make. After dye-adsorption on titania electrode, it suffices to place a small drop of the sol on the surface of the electrode and then press the counter electrode on the top by hand under ambient conditions. The two electrodes bind together while the fluid sol enters into titania nanoporous structure and achieves extensive electrical conduct.

Scheme 2. Example of a hybrid organic/inorganic material used as quasi-solid electrolyte. (Jovanovski et al., 2006)

3.4 Positive electrode (catalysts)
The counter electrode is one of the most important components in the dye-sensitized solar cell. The major role of the counter electrode in addition to the cell finalization is the reduction of the redox species used as a mediator in regenerating the sensitizer after electron injection, or collection of the holes from the hole conducting material in a solid-state DSSC. Counter electrodes of dye-sensitized solar cells can be prepared with different materials and methods. Platinum, graphite, activated carbon, carbon black, single-wall carbon nanotubes, poly(3,4-ethylenedioxythiophene) (PEDOT), polypyrrole, and polyaniline can be used as catalysts for the reduction of triiodide. Moreover, for the ultimate in low-cost counter electrodes, it is also referred in literature a carbon-black-loaded stainless steel electrode for use as a novel counter electrode (Murakami & Grätzel, 2008).

4. Manufacturing of Dye sensitized solar cells
While many research groups investigate the working principles of DSSCs and new developments have been achieved concerning their efficiency and large scale applications, new companies founded in the meanwhile try to carry DSSC technology in market place evaluating all process steps are needed for industrial production. Experimental results for small size solar cells cannot directly applied in large scale DSSCs as the efficiencies measured for small size solar cells cannot be repeated in large scale (Späth et al., 2003). This is caused by the high internal resistance of FTO substrates which eliminates their efficiency and it is found to be drastically decreased. Below are referred some of the main issues which have to be taken into account before DSSCs go to a production line:
- Large area deposition of TiO\(_2\) layers. The layers have to be homogeneous and uniform
- New methods for dye staining and electrolyte filling
- Electrical interconnection of individual cells. A major factor for limited efficiency of the DSSC is the ineffective contacts on FTO glass. The external connections of the individual cells are also a problem.
Sealing process for modules in case of liquid electrolytes
Long-term stability of at least 10 years for outdoor use.
Evaluation costs, which is believed to be approximately 10% of that needed for silicon solar cells

Moreover, for the durability of the cells, it was considered necessary to replace the liquid electrolyte with quasi-solid state, solid, polymer electrolytes or p-type inorganic semiconductors as the manufacturing cost and convenience of preparation is highly simplified. However, the low manufacturing cost by using the recently developed roll-to-roll coating process especially for DSSCs creates the need of replacing the glass substrate with light weighted flexible plastic electrodes, expanding this way the area of DSSCs’ applications. Three basic structures for large scale DSSCs are proposed either for high current (cells in parallel) or for high voltage (cells in series) collection:

4.1 Monolith module
The monolith modules have similar structure to amorphous silicon modules that are currently used in the market. Monolith modules use a single sheet of conductive glass (FTO) where successive layers of TiO₂ are formed on the substrate. Prior films deposition the glass is scribed by a laser in order to isolate one cell from the other. Direct wiring is not needed in this type of modules. It records relatively broad available area and high conversion efficiency, and enables simultaneous production of multiple cells (Wang et al., 2010). Usually, the TiO₂ stripes are formed according to screen printing method. It also entails shortcomings that it must secure even efficiency of each cell since it is in serial connection mode, it may by damaged due to relatively weak surface, and it rather has low transmittance. The figure 7 appears below, illustrates the manufacturing method of a monolith module:

4.2 Z-module
It concerns series connections of individual cells and consists of two opposing electrodes with inner-connections between neighbouring cells by a metal conductor. A sealing material is needed to protect the metal conductor from corrosion by iodide ions. It has wide available area to realize relatively high photovoltaic conversion efficiency and enables transparent and double sided cell production. The Z-module entails shortcomings that it is difficult to match the junction for large-area cell production, it needs to reduce each cell efficiency deviation due to the series connection, and it is greatly affected by inner-connector reliability and conduction property (Sastrawan et al., 2006). The advantage of Z-type module fabrication is the high voltage output. On the other hand, the disadvantage of this
connection is the low active area and overall efficiency because of the complicated structure and the resulting high series resistance. Figure 8b illustrates a possible Z-module manufacturing process.

4.3 W-module
It also concerns a series connection of the cells while inner-connections are avoided. Unlike the z-module and monolith module that are manufactured in the same direction to the adjacent cell, the W-module secures a structure that are in an opposite direction of the adjacent cell. Hence, it does not require direct wiring or bus electrode and realizes high reliability since the inner-cell contact occurs directly on the substrate. It also secures a structure to maximize the available area to record relatively high conversion efficiency. It is able to simultaneously manufacture multiple cells and can also manufacture cell and module at the same time. It entails shortcomings as well that it needs to adjust the output since the amount of light absorption is different in each serially connected cell and the colorants of adjacent cells are different. The main disadvantage of this structure is the differences referred for currents of single cells which are illuminated from back side and front size resulting different values of current because of the different light transmittance of the two cells.

4.4 Parallel-module
A simple fabrication procedure of making DSSC modules is parallel connection. According to this structure small cells in the form of long stripes are connected in parallel.

In this structure parallel grids utilizing conductive fingers to collect current are printed on the two electrodes of the cells. The printing method of current collectors is quite similar to that applied in conventional photovoltaics based on silicon. Common metals used as current collectors reducing the distance of electron transfer and internal resistance of FTO glass are: Ag, Cu, Ni, Ti. The solar cell efficiency is considerably reduced when it is converted to module despite the high unit cell efficiency. This is because of the increased possibility to lose electrons, which are created by light absorption, through either internal defect or recombination with hole at interface with other materials during the delivery when the electrode area to absorb light enlarges. Therefore, the efficiency radically decreases when DSSC active electrode width becomes greater than 1 cm (Wang et al., 2010).
Dye Sensitized Solar Cells as an Alternative Approach to the Conventional Photovoltaic Technology Based on Silicon - Recent Developments in the Field and Large Scale Applications

It is essential to design and manufacture effective packaging system along with designing photovoltaic absorption-use electrode and charge collection-use grid in order to allow the electron flow to collect without losses in large-areas like module. Mainly opposed cell module has been manufactured and researched since 1995 until now. The opposed cell module used ceramic fragment paste (glaze) or polymer in order to protect the conductive internal pattern from electrolytes. Such opposed cell R&D activities slowed down until 2001 and newly begun afterwards (Displaybank, 2010). The parallel type module records broad active area and high conversion efficiency. Large-area photoelectric chemical solar cell must use transparent electrode which has weaker electric conductivity than the metal wiring that it requires a grid to play a role of charge collection to realize smooth electron delivery. Therefore, the large-area solar cell exhibits different carrier generation and delivery from the unit cell.

Fig. 9. Parallel connection of DSSC in a module

Fig. 10. (a) artistic DSSC module by Sony (http://www.sony.net/SonyInfo/technology/technology/theme/solar_01.html) and (b - c) DSSC panels made of Fujikura (http://www.fujikura.co.jp/eng/rd/field/mt.html)
A general grid in DSSCs mainly uses metal material. This is connected to active area decrease and becomes the factor to increase the generation unit cost of cell. Therefore, it is essential to secure effective module design and manufacturing technology for commercialization.

The DSSC is manufactured by a process that is relatively simpler than the conventional solar cells made of silicon and compound semiconductor solar cells, but it entails a shortcoming to generate metal corrosion when using the metal with outstanding electric conductivity as grid due to iodine based electrolyte. Therefore, the DSSC is in need for electrolyte development with outstanding activity without corrosive property or metal development with outstanding electric conductivity without being separated or corroded from the electrolyte. The inverter development must progress to be appropriate for DSSC which secures electric property that is different from the conventional silicon based solar cell.

In order to accomplish this, a circuit must be composed to match arrangement and response properties of DSSC module. The inverter technology development maximizes the DSSC power generation efficiency. The system is matched to the solar cell’s generation property in order to effectively supply the power of electric condenser, which stores electricity generated during daytime, at desirable time. The commercialization of DSSC requires power system development together with unit cell efficiency enhancement technology development. The DSSC commercialization is delayed due to unprepared peripheral technologies despite the fact that its current power generation unit cost can realize commercialization (Displaybank, 2010). Right now, the ultra small high efficiency inverter technology is insufficient for module/system efficiency enhancement and manufacturing technology of module which can be installed in targets such as buildings.

5. Outlook
The quest and demand for clean and economical energy sources have increased interest in the development of solar applications. DSSCs have proved to be an alternative approach to the conventional silicon based solar cells. Research on DSSCs has grown rapidly in the recent years due to the several attractive figures of this interesting field: The international awareness of the necessity to develop new technologies in Renewable Energy Resources; The need of easy and inexpensive procedures for fabricating Solar cells; The fact that DSSCs can be transparent so that they can be integrated into mobile or immobile constructions as Photovoltaic Windows. All these features are carried by DSSCs and for this reason they are popular and they are expected to be even more popular in the near future. Till then some issues have to be overcome in order this technology considerably has commercial interest. The overall efficiency of ~12% for small size cells (~0.2cm²) which substantially gets lower (~5%) when modules of DSSCs are prepared is a reason for further improvement is many stages of cells preparation. Improvement of the cells is focused on (a) the enhancement of electron transport and electron lifetime in the mesoporous metal oxide (b) design of new high-extinction coefficient dyes which will effectively cover the whole range of visible light and near infra red and finally (c) new stable solid electrolytes which will have effective penetration into semiconductors pores and enhanced. Moreover, in large scale applications the effective collection of the current is also an issue as the internal resistance from conductive glass substrates and metal grids which are necessary for current collection and need to be covered from corrosive electrolyte, drastically eliminate the DSSCs efficiency if they are not seriously taken into account.
6. References


The second book of the four-volume edition of "Solar cells" is devoted to dye-sensitized solar cells (DSSCs), which are considered to be extremely promising because they are made of low-cost materials with simple inexpensive manufacturing procedures and can be engineered into flexible sheets. DSSCs are emerged as a truly new class of energy conversion devices, which are representatives of the third generation solar technology. Mechanism of conversion of solar energy into electricity in these devices is quite peculiar. The achieved energy conversion efficiency in DSSCs is low, however, it has improved quickly in the last years. It is believed that DSSCs are still at the start of their development stage and will take a worthy place in the large-scale production for the future.

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