

## 2 Dye sensitized solar cells (DSSC)

This chapter aims to review the DSSC-device. For more than 16 years, dye sensitized solar cells (DSSC) have been under extensive research. Since the color of the device can be easily varied by choosing different dyes and cells on flexible substrates have been already demonstrated, DSSCs are especially attractive for Building Integrated Photovoltaics (BIPV). The cell concept is believed to reduce the production costs and energy payback time significantly compared to standard silicon cells or other thin film cells. The conversion efficiency varies between 6 -10 % depending on the module size and the technology is currently on the pilot plant scale.

In chapter 2.1 the operation principle of the cell is outlined, starting with a brief abstract of the device's history. Chapter 2.2 discusses current efforts to optimize the cell. First the main impediments for large-scale production are presented and then different approaches to improve the hole conduction in the electrolyte and the light harvesting of the dye are introduced. Chapter 2.2.2 reviews the standard iodine-based electrolyte, which gives the highest efficiency at the moment. But since iodine corrodes most metals and makes the upscaling of the device difficult, a lot of research is done of alternative hole conductors. Some examples are discussed in chapter 2.2.3. In chapter 2.2.4, it is tried to give an overview on the large variety of different dyes that are capable to inject electrons into wide band gap semiconductors like titanium dioxide.

The chapter closes with a preliminary feasibility study of DSSC production on the 1 MW scale. The price per  $W_p$  for each cell component is estimated and the availability of ruthenium as an integral part of the sensitizer is critically discussed.

## 2.1 DSSC - Operation principle

The history of dye sensitized solar cells (DSSC) started in 1972 with a chlorophyll sensitized zinc oxide (ZnO) electrode. For the first time, photons were converted into an electric current by charge injection of excited dye molecules into a wide bandgap semiconductor [5]. In the following years a lot of fundamental research was done on ZnO-single crystals [8], but the efficiency of these devices was poor. The main problem was that a monolayer of dye molecules on a flat surface can only absorb up to 1 % of the incident light. Introduction of nanoporous  $\text{TiO}_2$  electrodes with a roughness factor of ca. 1000 dramatically increased the light harvesting efficiency and in 1991 solar cells of 7 % efficiency were introduced [6]. This triggered a boom in research activities and today cells of 11.2 % [9] are state of the art.

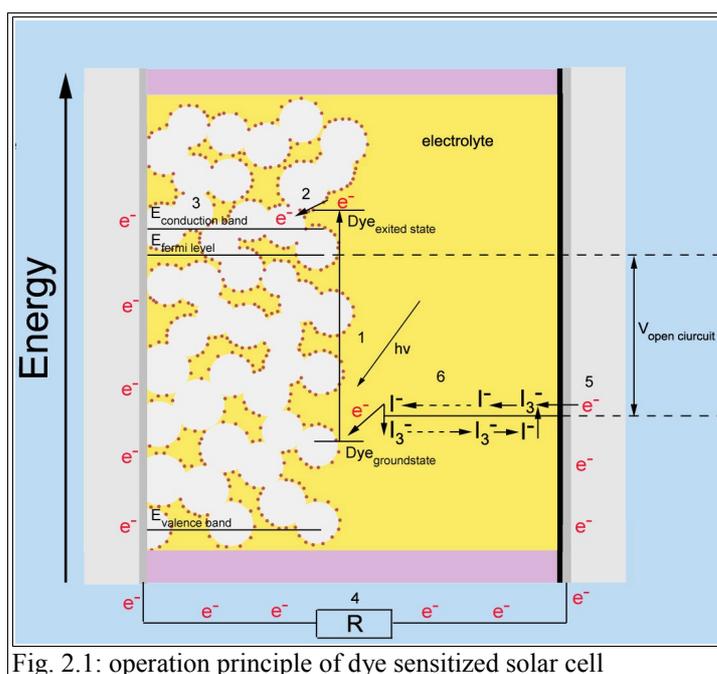


Fig. 2.1: operation principle of dye sensitized solar cell

Fig. 2.1 depicts the operation principle of a DSSC. In the following, an electron is traced passing through a complete cycle of excitation, injection into the  $\text{TiO}_2$ , diffusion in the  $\text{TiO}_2$ , iodine reduction at the counter electrode, diffusion in the electrolyte and regeneration of the oxidized dye.

**step 1**

The dye, which is typically a metallorganic Ru-complex, is excited by absorption of a photon. The onset of the absorption is in the range of 720 nm (Fig. 2.2) for most dyes, which corresponds to a photon energy of 1.72 eV. The formal potential of the dye redox couple ( $D^+/D^*$ ) is between -0.7 and -0.8 V vs. NHE [10]. The lifetime of the excited state is in the nanosecond range. At high iodine concentration reductive quenching might deactivate the excited state representing a loss channel [11].

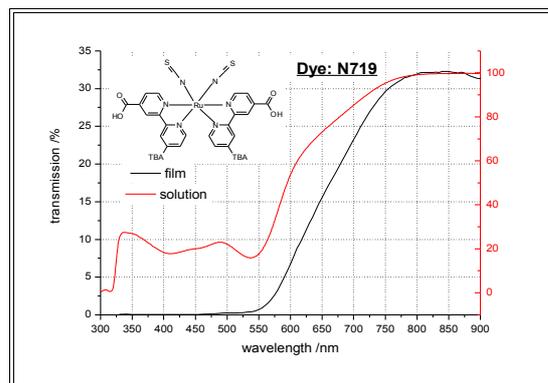


Fig. 2.2: absorption spectra of N719 in solution and absorbed on a  $TiO_2$  surface

**step 2**

The dye injects an electron into the conduction band of the  $TiO_2$ . About 60 % of the electrons are injected from the singlet state and about 40 % from the triplet state. The corresponding injection rate constants are in the femtosecond range (singlet state) and about one order of magnitude slower for the triplet state [12]. Since the energy level of the triplet state is only slightly above the conduction band edge of  $TiO_2$ , both the driving force for electron injection and the electron transfer probability is lower, which is believed to be the reason for the relatively slow injection rate. For efficient charge injection the energy level of the dye has to be between 0.2 V and 0.3 V above the  $TiO_2$  conduction band edge, which corresponds to -0.5 V vs. NHE on the electrochemical energy scale.

The back reaction, the reduction of oxidized sensitizer molecules by conduction band electrons occurs in the  $\mu s$  - ms range (chapter 6.3.3) and is thus several orders of magnitude slower. This huge difference is the main reason for the efficient charge separation in the device.

**step 3**

The nanoporous  $TiO_2$  layer contains spherical anatase particles with a diameter between 20 - 30 nm and a band gap of about 3.2 eV. The material is weakly n-doped due to oxygen vacancies in the lattice (charge carrier concentration  $10^{16} \text{ cm}^{-3}$  [13]). The thermodynamic most stable lattice plane is (101), which is also the predominant facet exposed. The size of the particles is between 20-30 nm and the thickness of the layer in the range of 10  $\mu m$ . With

$$\boxed{V_{particle} = \frac{4}{3} \pi r^3 = 654 \text{ nm}^3}, \quad \boxed{n_{particle} = \frac{V_{particle}}{V_{layer}} * p_{layer}} \quad (2.1)$$

$V_{particle}$  = volume of  $\text{TiO}_2$  particle / $\text{m}^3$ ;  $r$  = radius /m (25 nm in the example);  $n_{particle}$  = number of  $\text{TiO}_2$  particles in layer;  $V_{layer}$  = volume of layer / $\text{m}^3$ ;  $p_{layer}$  = porosity of the layer (0.5 in the example)

one finds that the electrode contains about  $10^{15}$  particles.

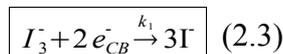
This huge number of more or less spherical particles has a surface area that is about 1000 times larger than the projected area. The properties of the layer (conductivity, flat band potential) are mainly governed by the surface and the sinter necks. Since the  $\text{TiO}_2$ -particles are too small for a macroscopic electric field to build up, the main transport mechanism for electrons in the  $\text{TiO}_2$  layer is diffusion.

A density of trap states that increases exponentially towards the conduction band edge is found in these nanoporous electrodes [14] and the transport can be best described with a trapping/detrapping model [15]. Depending on the depth of the trap state the electron remains a characteristic waiting time  $\tau$  in the trap before it is thermally activated to the  $\text{TiO}_2$  conduction band and hops to a neighboring trap site. If the density of trap sites is high enough and statistically distributed one can introduce an effective diffusion coefficient  $D_{eff}$  and describe the electron transport by Fick's law of diffusion.

$$\boxed{\frac{\delta n}{\delta t \delta A} = -D_{eff} \frac{\delta c}{\delta x}} \quad (2.2)$$

$n$  = number of electrons /;  $t$  = time /s;  $A$  = surface / $\text{cm}^2$ ;  $D_{eff}$  = effective diffusion constant / $\text{cm}^2\text{s}^{-1}$ ;  $c$  = electron concentration / $\text{cm}^{-3}$ ;

$D_{eff}$  strongly depends on the position of the quasi Fermi level and therefore on the light intensity. Typical values at 1 sun are  $1.5 * 10^{-5} \text{ cm}^2\text{s}^{-1}$  [16]. Since diffusion is the only driving force for electron transport, the diffusion length  $D_L$  must be at least as long as the thickness of the  $\text{TiO}_2$  electrode. The most important recombination reaction is the reduction of triiodide by conduction band electrons. The corresponding electron lifetime is  $\tau_{el}$ .



With

$$D_L = \sqrt{D_{eff} * \tau_{el}} \quad (2.4)$$

$D_L$  = diffusion length /cm;  $D_{eff}$  = effective diffusion coefficient /cm<sup>2</sup>\*s<sup>-1</sup>;  $\tau_{el}$  = electron lifetime /s

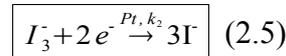
it turns out that for an efficient charge extraction an electron lifetime  $\tau_{el} > 20 \mu\text{s}$  is mandatory for a 10  $\mu\text{m}$  thick electrode, which is given for most electrolyte compositions

#### step 4

The electron flows through the outer electrical circuit and performs work. The external load is adjusted to the maximum power point (MPP) of the DSSC.

#### step 5

At the counter electrode the electron is transferred to a hole conducting medium (HTM). In most DSSC an iodide/iodine redox couple is employed. The reduction is catalyzed by a thin layer (ca. 3  $\mu\text{g} * \text{cm}^{-2}$  [17]) of platinum.



The efficiency of a DSSC is based on different rate constants for iodine reduction at the front- and counter electrode. The iodine reduction at the counter electrode ( $k_2$  in reaction 2.5) has to be orders of magnitudes faster than the recombination at the  $\text{TiO}_2$ /electrolyte interface ( $k_1$  in reaction 2.3). The exchange current density  $J_0$  for the iodine reduction (2.5) at the counter electrode can be calculated by the Butler-Volmer equation [18].

$$J = J_a - J_k = J_0 \left( e^{\frac{\alpha z q \eta_g}{kT}} - e^{-\frac{(1-\alpha)z q \eta_g}{kT}} \right) \quad (2.6)$$

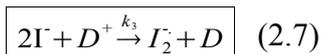
$J_a$  = anodic current /mAcm<sup>-2</sup>;  $J_k$  = cathodic current /mAcm<sup>-2</sup>;  $J_0$  = exchange current /mAcm<sup>-2</sup>;  $\alpha$  = transfer coefficient /;  $\eta_g$  = overpotential /V

For a standard electrolyte with 0.5 M LiI/0.05 M I<sub>2</sub> in acetonitrile one obtains an exchange current density of up to 250 mAcm<sup>-2</sup>. The corresponding charge transfer resistance is < 0.05  $\Omega\text{cm}$ . That means the potential drop for a photocurrent of 20 mAcm<sup>-2</sup> is only about

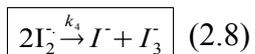
1 mV.

### step 6

The regeneration of the oxidized dye occurs in the nanosecond range [19], which is typically 100 times faster than any recombination reaction and about  $10^8$  times faster than the intrinsic lifetime of the oxidized dye. It is a two step electron transfer with a large driving force (ca. 0.6 V) [19].



$I_2^-$  then disproportionates



The loss of about 600 mV due to the energy mismatch between the dye and the redox couple is the main limitation for the low open circuit potential of DSSCs.

## 2.2 Optimization of dye sensitized solar cells

### 2.2.1 Key problems

Dye sensitized solar cells (DSSC) were introduced already 16 years ago but the learning curve up to this point is modest compared to other types of solar cells [20]. In 1993, the “Institut für angewandte Photovoltaik” was founded to upscale the device and it was estimated by that time that 1 m<sup>2</sup> modules with an efficiency of around 10 % should be available in 1995. Nine years later the institute was closed due to tremendous technical problems. Today the introduction of DSSC on the market is hard to predict. Though much progress was achieved in terms of intrinsic cell stability and upscaling, investors are reluctant due to the promises that were never fulfilled after the introduction in 1991. In the following the key problems of DSSC - low efficiency, low stability and low scalability – are discussed briefly.

#### **low efficiency**

The highest efficiency for a DSSC is 10.4 % at the moment [21], which is only about half as good as the best polycrystalline Si-cell (20.3 % [22]) and comparable to an amorphous Si-cell (9.5 % [22]).

The parameters of the record DSSC cell are  $I_{sc} = 20.5 \text{ mAcm}^{-2}$ ,  $V_{oc} = 0.72 \text{ V}$  and  $FF = 0.70$  for a dye with an absorption onset at 1.4 eV [21]. Using an AM1.5 spectrum, it turns out that this record cell has an average incident photon to current conversion efficiency (IPCE) of 62 % for a wavelength  $\lambda < 900 \text{ nm}$  and the potential of these electrons is 51 % compared to the excited state of the dye. Assuming the transmission of the FTO glass to be 0.8 in the visible region the internal IPCE is 78 %. A higher IPCE will be hard to accomplish since the injection near the absorption onset is low for all dyes. Thus a higher short circuit current can only be achieved if the absorption of the dye is extended in the near infrared (NIR). So far no dye has been found that injects in the whole visible and the NIR with the same efficiency but the development of new organic dyes raise hope that such a dye might be synthesized one day.

A more feasible way to improve the conversion efficiency is to enhance the open circuit potential. Almost half of the initial photon energy is lost within cell.

An efficient charge injection requires a driving force of about 100-200 meV. The energy level of the excited dye molecule in present DSSCs is well adjusted to meet this requirement and little improvement can be expected at that point. However, about 650 meV are lost during the regeneration of the oxidized dye due to an energy mismatch between the electrolyte (redox potential ca. 150 mV vs. SCE [23]) and the oxidized dye (potential ca. 790 mV vs. SCE [24]). Partly this large driving force is needed because the two-electron-transfer involves high energy intermediates ( $I_2^-$ ) and the electrostatic repulsion between the negatively charged triiodide and the conduction band electrons has to be compensated. Still the development of new electrolytes with a higher oxidation potential seems to be a promising way to increase the cell potential. For example by employing a  $Co^{II}/Co^{III}$ -redox couple, a  $V_{oc}$  of 840 mV was demonstrated recently [25], which was attributed to the higher oxidation potential (0.36 V vs. SCE) of the electrolyte. With organic hole conductors already 900 mV were achieved [26].

### **low scalability**

Due to the chemically aggressive electrolyte, it is not possible to use silver fingers for current collection in DSSCs. This makes it difficult to upscale the device as the sheet resistance of the FTO-glass is about  $10 \Omega/\square$  and the series resistance of the FTO becomes a limiting factor for an active cell area  $> 1 \text{ cm}^2$ . Furthermore it is very difficult to maintain a constant spacing between the front and counter electrode without short circuiting the cell. For this reason, the distance between the electrodes is typically increased from  $25 \mu\text{m}$  to  $50 \mu\text{m}$  [27] in small modules, which increases the series resistance of the electrolyte.

As a consequence the conversion efficiency, which is 10.4 % for a  $1 \text{ cm}^2$ -cell [22], drops to 6.3 % for a  $26.5 \text{ cm}^2$  [22] submodule. Currently, two approaches are investigated for upscaling. On the one hand it is tried to employ silver fingers for current collection and protect them by a hotmelt foil. These modules consist of small stripes (1 cm) of active cell area with adjacent silver lines [27][28]. However, this layout is very susceptible for leakage and the total active cell area is reduced by 32 % [27].

The second, more promising approach is to enhance the conductivity of the transparent conducting oxide (TCO). By combination of indium tin oxide (ITO), which is highly conductive but has a low chemical stability, and a cover layer of FTO (less conductive, more stable), it was possible to reduce the sheet resistance of the TCO-glass to  $1.3 \Omega/\square$  [29]. A  $21 \text{ cm}^2$  submodule with a conversion efficiency of 7.2 % (not certified) was demonstrated with this technique [29]. If the production

costs of these TCO-layers can be reduced, the current collection for large area modules would be greatly simplified.

### **low stability**

Introduction of DSSCs on the market requires stable performance comparable to standard silicon cells. Most manufacturers give a warranty of 80 - 90 % of the initial performance after 20 years of cell operation. To meet this requirement, the cell must be intrinsically and extrinsically stable under elevated temperature, cyclic changing temperatures, exposure to humidity and prolonged illumination.

#### *extrinsic stability:*

little effort has been undertaken so far to investigate the stability of the sealant in DSSCs systematically. Most commonly hotmelt foils like Surlyn<sup>®</sup> and Bynel<sup>®</sup> are employed [28][29] to seal the cells. It is known that the sealing capability of these hotmelt foils decrease drastically if pressure builds up within the cell [30]. In preliminary studies it was found that the sealant is especially vulnerable if exposed to cyclic temperature changes [31]. On the other hand, hotmelt foils are very easy to process and cheap. The adhesion of the foil to the glass substrate can be improved by pretreatment of the glass with metal oxide particles. Still, at this point it is very questionable if this sealing system will be stable for 20 years of outdoor application. Alternative sealants based on low melting glass frits [32] are more stable than hotmelt foils but not suitable for large area module production.

#### *intrinsic stability:*

The intrinsic stability of a DSSC is usually tested with an accelerated aging experiment lasting for 1000 hours, which is based on the standard test condition required for thin film and crystalline silicon modules (IEC 1646:1996 and IEC 1215:1993). This test elucidates the thermal stability of the sensitizer, the electrolyte and the Pt-coated counter electrode at 80 °C. In recent publications it was demonstrated that small test cells can retain 90 % of the initial efficiency under elevated temperatures. The initial efficiency was 7.6 % [33] and 8 % [34] respectively. The devices were also stable for 1000 hours under AM1.5 and a moderate temperature between 55 - 60 °C. However, when combining both stress factors, 80 °C and light soaking, rapid degradation was found in another study [31]. Since a temperature of 80 °C can be easily reached on a sunny day, the intrinsic stability is not sufficient at the moment and has to be further improved.

### 2.2.2 Iodine based electrolytes

Iodine based electrolytes can be optimized in terms of efficiency and stability.

An increased efficiency is usually achieved by varying the solvent, adding coadsorbents or changing the counterions of iodide. The optimization process is unique for each dye/electrolyte combination and only some general trends are described in this chapter.

A better stability can be obtained by modifying the TiO<sub>2</sub>-dye interface or reducing the vapor pressure of the electrolyte's solvent. The latter is especially important for outdoor applications where cyclic temperature changes require a very robust sealing. Low-viscous solvents can induce a leakage of the cell. Solidified electrolytes can be achieved by in situ polymerization of a precursor solution containing the monomer/oligomer and the iodide/iodine redox couple. Like this the TiO<sub>2</sub>-network is completely filled with the quasi solid state electrolyte and the vapor pressure is negligible. An initial efficiency of up to 8.1 % has been already demonstrated [35] with this approach. However, it is questionable whether the polymer matrix does not degrade under prolonged (UV) irradiation.

Another approach employs nanosized SiO<sub>2</sub>-particles, which are added to the solvent for solidification [36]. Efficiencies of over > 5 % have been achieved so far and since this technique uses only inorganic material no degradation of the solidifying agent is expected.

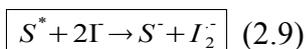
The by far most significant advances towards electrolytes with negligible vapor pressure were achieved with ionic liquids, which are introduced in the following section. The chapter concludes with a brief summary of the most important additives currently applied in DSSC.

#### **ionic liquids**

Ionic liquids (IL) exhibit a negligible vapor pressure and a high electric conductivity at room temperature. Combined with the low-flammability and a wide electrochemical window, ILs are a promising candidate to replace the organic solvent. At the moment derivatives of imidazolium salts are exclusively applied in DSSC.

Initially it was tried to simply replace the organic solvent by an IL. In 1996 a cell employing 1-methyl-3-ethyl-imidazolium iodide (MEII) demonstrated that ionic liquids can in principle be applied in DSSC [37]. But since the viscosity of MEII is 3000 times higher compared to acetonitrile (ca. 1000 mPa\*s and 0.32 mPa\*s respectively), the short circuit current was limited by the iodine mass transport already at low light intensities. In the following years it was tried to find ILs with a

lower viscosity and to increase the iodine concentration in order to overcome the transport problem. In 2003 a 6 %-cell was introduced, containing 1-methyl-3-propylimidazolium iodide as the ionic liquid and an iodine concentration of 0.5 M. Although the viscosity of this electrolyte was still 2000 times higher (680 mPa\*s compared to 0.32 mPa\*s), the apparent diffusion coefficient of iodine differed only by a factor of 58 compared to the acetonitrile equivalent ( $1.88 \cdot 10^{-7} \text{cm}^2 \text{s}^{-1}$  compared to  $1.1 \cdot 10^{-5} \text{cm}^2 \text{s}^{-1}$ ), which is explained in terms of a Grotthuss type transport mechanism [38]. In 2004 laser transient measurements revealed that the high iodide concentration present in the pure ionic liquid leads to a reductive quenching of the excited dye molecule [11].



Thus part of the iodide was replaced by another counterion (e.g. thiocyanate). The resulting mixture is called binary ionic liquid. It was observed that the  $I_{SC}$  for a binary ionic liquid was higher compared to a pure ionic liquid with the same viscosity.

Since then it was tried to find chemically stable, binary ionic liquids of low viscosity. The IL of choice should have a large counterion where the negative charge is delocalized as much as possible. For example 1-ethyl-3-methylimidazolium dicyanamide has a viscosity of only 21 mPa\*s [39]. In combination with 1-propyl-3-methylimidazolium iodide (PMII, volume ratio 1:1) an efficiency of 7.4 % was obtained. Though the initial efficiency was very good some degradation after prolonged illumination was observed. Recently a stable 7.0 % cell, that retained at least 90 % of its initial efficiency after 1000 h at 80 °C in darkness and 1000 h at 60 °C and AM1.5 was introduced, which employed a binary ionic liquid of 1-ethyl-3-methylimidazolium tetracyanoborate in combination with PMII [40].

### electrolyte additives

Soon after the development of efficient DSSCs in 1991 [6], it was found that the open circuit potential of the cell can be dramatically increased by the addition of 4-*tert*-butylpyridine to the electrolyte ([41], from 0.38 V to 0.72 V). Since then a number of coadsorbents have been identified that increase the  $V_{OC}$ , the long term stability of the cell and/or suppress dye aggregation on the  $\text{TiO}_2$ -surface. The research is mostly done by trial and error and no general accepted correlation between the molecule structure of the coadsorbent and its effect on the cell could be identified so far.

A positive effect of the coadsorbent on the cell performance is typically claimed if the cell has a higher efficiency compared to the corresponding reference without coadsorbent. However, in many cases an increased efficiency is observed on a 5 % level, but when going to an already optimized cell of 10 % conversion efficiency, the difference is not seen anymore. For this reason, only additives that have shown improvements in highly efficient cells (> 7 %), are introduced here.

There are two mechanisms by which the coadsorbent can alter the photovoltage of the DSSC. Firstly it may change the recombination rate between the TiO<sub>2</sub>-conduction band and the electrolyte. Secondly the coadsorbent may alter the band edge position of the TiO<sub>2</sub>-conduction band.

### *pyridine derivatives*

Most electrolytes in DSSCs contain a pyridine derivative in a concentration of about 0.5 M. Introduced in 1993, 4-tert-butylpyridine (TBP) was almost exclusively used for a decade [41], although previously 2-propylpyridine was found to give slightly higher photovoltages [42]. Detailed intensity modulated photovoltage spectroscopy studies (IMVS) revealed that the positive effect of pyridine on the  $V_{oc}$  is due to a positive band edge movement and that charge recombination is only slightly effected [43]. Thus upon adsorption on the TiO<sub>2</sub>-surface the pyridine ring induces electron density into the TiO<sub>2</sub> creating a surface dipole. The band edge movement reduces the driving force for electron injection and thus the  $I_{sc}$  is a little bit lower than in untreated cells [42]. Recently N-methylbenzimidazole (NMBI) replaced TBP as the standard additive because it was found to be more stable in long term stability tests under elevated temperature [33].

### *alkyl phosphonic/carboxylic acids*

Decylphosphonic acid (DPA) [33] and hexadecylmalonic acid (HDMA) [44] have been successfully applied as coadsorbents in DSSCs. The long alkyl chains are believed to self-assemble on the TiO<sub>2</sub> surface to form a densely packed, hydrophobic monolayer. Though the dye uptake is reduced by the coadsorption, the loss of short circuit current is overcompensated by the increase of  $V_{oc}$ . The long alkyl chain is believed to repel iodide from the TiO<sub>2</sub>-surface and thus reduce the recombination rate. Furthermore both additives have proven to increase the long term stability of the cell by repelling water and other contaminants from the surface.

### *guanidinium-derivatives*

Guanidinium thiocyanate has been found to suppress the recombination rate by a factor of 20, which causes an increase of the  $V_{oc}$  by ca. 120 mV. However, at the same time the conduction band edge is shifted downwards by ca. 100 mV [45]. The difference, 20 mV is gained for the open circuit

potential.

Guanidinium derivatives are especially interesting because if the electron affinity of the molecule was manipulated in such a way, that the TiO<sub>2</sub> conduction band was not shifted downward, a substantial improvement for the overall conversion efficiency could be expected. No other coadsorbent can suppress the recombination rate as effectively as guanidinium derivatives. So even in the present stage, guanidinium-derivatives are frequently used as coadsorbents in DSSCs [46].

### 2.2.3 Hole conducting materials

Iodine/Iodide based electrolytes have the disadvantage that they are chemically very aggressive. No silver fingers might be used to collect the current at the front/counter electrode and since iodine has its own photochemistry the impact on stability in a purely organic surrounding is yet not clear [47]. Thus, hole conducting materials (HTM) have been developed and tested in DSSCs. Most HTMs are inorganic solids, organic polymers or p-conducting molecules. Though most HTMs are chemically less aggressive, a number of other problems are encountered, which is the reason why the iodine/iodide-redox couple is still unmatched in terms of efficiency.

- 1) Since most HTMs are solids, one of the main problems is the pore filling within the nanoporous TiO<sub>2</sub>-layer. Poor pore penetration leads to an incomplete dye regeneration. Thus the photocurrent is lower and the stability of the cell is poor.
- 2) For organic hole conducting molecules, the hole mobility is significantly lower than in a liquid electrolyte, which increases the series resistance of the cell.
- 3) The recombination rate of conduction band electrons with the HTM is typically higher compared to an iodine based electrolyte. As a consequence the open circuit potential is lower.

The ideal HTM should have a valence band with an energy that is slightly above the energy of the oxidized dye. It should not absorb light, must be photochemically stable and has to make a good electronic contact to the dye.

In the following some approaches are discussed, including inorganic Cu<sup>I</sup>-salts, the hole conducting molecule spiro-OMeTAD and some examples of hole conducting polymers:

### inorganic Cu<sup>I</sup>-salts

Cu<sup>I</sup>-halogens and pseudohalogens have been successfully applied as hole conducting materials (HTMs) in DSSCs.

Within the halogens, CuBr gives the highest efficiency of 1.53 % (with thioether as an additive) [48]. The device is fairly stable upon prolonged irradiation (200 hours at room temperature), which was the first stability study in that field.

A higher conversion efficiency is achieved with pseudohalogens, CuSCN being the most intensively studied compound. A very simple preparation method developed by O'Regan *et al.* gives an efficiency of ca. 2 % [49], whereas Tennakone *et al.* have achieved 2.4 % with doped CuSCN [50]. The modest efficiency is due to a low short circuit current (maximum 9 mAcm<sup>-2</sup>) [50] and a low fillfactor, which is typically around 0.5 for the best devices. It is difficult to establish a good electronic contact between the dye and the CuSCN and even if the wetting of the surface is good, an insufficient pore filling leads to a high series resistance. Furthermore the charge carrier mobility in the CuSCN is too low to support a higher current. One could increase the p-doping and thus the conductivity by adding more SCN, however, at high concentration SCN tends to polymerize.

Another problem is the high recombination rate between conduction band electrons and CuSCN. At V<sub>OC</sub> operation it is about 10 times higher and at I<sub>SC</sub> operation about 100 times higher than in a liquid electrolyte [51]. Additional blocking layers of insulating materials like SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> were coated around the TiO<sub>2</sub>-particle to suppress the recombination reaction and enhance the open circuit potential. This was found to increase the V<sub>OC</sub> by up to 200 mV [52].

### holeconducting molecules

The most established hole conducting molecule so far is spiro-OMeTAD (Fig. 2.3), though some other triphenylamin-derivatives have also given notable efficiencies [53].

spiro-OMeTAD was introduced in 1998. An incident photon to current conversion efficiency (IPCE) of 33 % was demonstrated yielding an overall efficiency of 0.74 % [54]. The main advantage of this material is its

high glass transition temperature of ca. 120 °C. It forms amorphous layers, which is a prerequisite

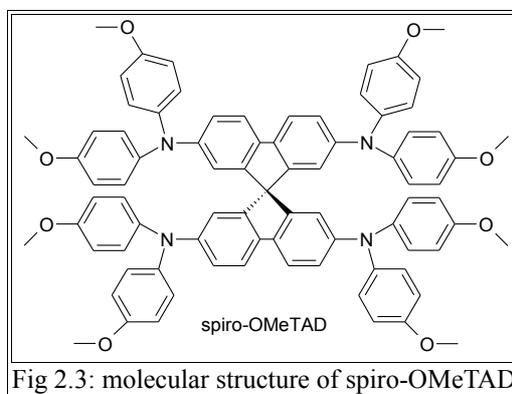


Fig 2.3: molecular structure of spiro-OMeTAD

for complete pore filling. In the following years the device was optimized continuously and the current state of the art is at 4 % efficiency with an ambiphilic sensitizer Z907 [55]. It is questionable that further improvement can be obtained since the charge carrier mobility for spiro-OMeTAD is rather low (ca.  $10^4$  cm<sup>2</sup>/Vs [53]). That limits the thickness of the nanoporous TiO<sub>2</sub>-layer to about 2 μm, which is not sufficient for complete light harvesting with the sensitizers currently available. The second bottleneck is the high recombination rate at the TiO<sub>2</sub> and FTO interface. The FTO-interface can be shielded with a compact TiO<sub>2</sub>-layer to avoid short-circuiting of the cell, but the recombination with conduction band electrons is inherent and is difficult to suppress.

### **hole conducting polymers**

Hole conducting polymers are most commonly applied in purely organic solar cells with C<sub>60</sub>/polythiophene-derivatives. The best conversion efficiency is currently about 3.5 % [56]. Only few groups are trying to take advantage of p-conducting polymers for DSSCs and thus the field develops rather slowly. The main reason is that the deposition of the polymer cannot be accomplished by standard methods (e.g. CBD) because the solid polymer cannot penetrate the nanoporous TiO<sub>2</sub>-network.

The most promising technique today is *in situ* photoelectrochemical polymerization (PEP), in which an organic precursor (e.g. pyrrole, thiophene) is polymerized by applying a positive potential [57][58]. This technique ensures a complete wetting of the TiO<sub>2</sub>/dye surface and suppresses the formation of voids within the nanoporous network. The conductivity of the film strongly depends on the applied potential and the duration of the polymerization [57]. The best efficiency achieved with polypyrrole is ~0.1 % [57][58]. Somewhat higher efficiencies were obtained with electrochemically polymerized PEDOT (0.53 % [59]). Though the proof of principle was given, it is doubtful whether PEP-deposited polymers will ever be employed in highly efficient DSSC since the deposition technique is limited to a few precursors and the charge carrier mobility is too low.

One way to overcome the deposition problem is to use p-conducting polymers, which can also sensitize the TiO<sub>2</sub>. In this case the TiO<sub>2</sub>-layer may be much thinner (~100 nm) and the polymer can be deposited by a simple dip coating technique. Using a fluorene-thiophene copolymer a monochromatic efficiency of 1.4 % (at 440 nm) was demonstrated recently [60].

## 2.2.4 Developments in dye synthesis

This chapter aims to give an introduction in recent developments of dye synthesis. Table 2.1 summarizes the current state of the art for different dye groups currently employed in DSSCs. The by far most important group are Ru-complexes, which are unmatched in terms of efficiency and stability. However, when looking at the learning curve, organic dyes like some indole derivatives, show the most rapid progress in the last few years and the efficiency today is almost the same as for Ru-complexes.

Other important dyes are porphyrin derivatives. This research is inspired by the porphyrin derivative chlorophyll, which absorbs light and transfers its energy to neighboring proteins in green leaves. Because of this analogy, the conversion of light to electric energy in DSSCs is sometimes called artificial photosynthesis.

Besides the artificial synthesis of sensitizers, some groups have focused on the extraction of various natural dyes. However, the efficiency of natural dyes in DSSCs is usually low, why they are mainly employed in model systems and for educational purposes. The best efficiencies are achieved with phthalocyanines and perylene derivatives.

The different dye groups are introduced in more detail at the end of this chapter.

Dyes employed in highly efficient DSSC have to meet several requirements, among these are the absorption spectrum on the nanoporous  $\text{TiO}_2$  layer, the energy level of the ground/exited state, the rate constant of charge injection/recombination and the stability.

### 1) absorption spectrum

The concentration of the dye within the nanoporous  $\text{TiO}_2$  electrode and the absorption coefficient determine the fraction of light that is absorbed in a layer with the thickness  $d$ . Therefore the dye should have a high absorption coefficient in the visible region and a high affinity to the  $\text{TiO}_2$  to ensure a dense coverage of the surface. With increasing absorbance of the  $\text{TiO}_2$ -electrode, the layer thickness can be decreased, which is advantageous for two reasons:

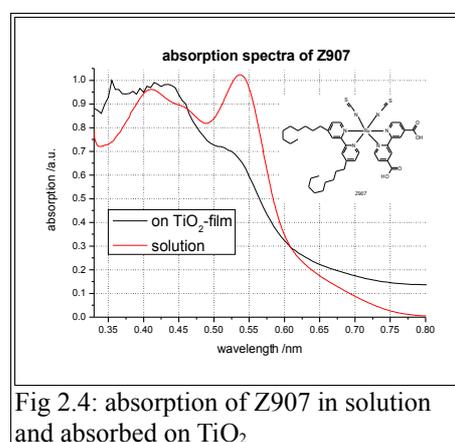


Fig 2.4: absorption of Z907 in solution and absorbed on  $\text{TiO}_2$

- The recombination probability decreases with decreasing electrode thickness.
- more viscous electrolytes with low vapor pressure can be applied.

Fig. 2.4 shows the absorption spectrum of a standard Ru-complex in solution and absorbed on TiO<sub>2</sub>. It can be seen that the absorption peak at 540 nm is broadened on TiO<sub>2</sub> compared to the solution, indicating a strong electronic coupling between the dye and the TiO<sub>2</sub>. Going to longer wavelengths, the absorption decreases significantly, thus a substantial fraction of the solar spectrum is lost. As a first approximation the absorption of the dye can be described with Lambert's Beers Law

$$\frac{I(x)}{I_0} = 10^{-\alpha(\lambda) * x * c_{\text{dye}}} \quad (2.10)$$

$I(x)$  = light intensity at the point  $x$  /Wm<sup>-2</sup>;  $I_0$  = initial light intensity /Wm<sup>-2</sup>;  $\alpha$  = absorption coefficient /M<sup>-1</sup>cm<sup>-1</sup>;  $\lambda$  = wavelength /nm;  $c_{\text{dye}}$  = dye concentration /M;  $x$ =distance /cm

Taken  $\alpha \approx 2 * 10^4$  M<sup>-1</sup>cm<sup>-1</sup> (s. table 2.1) and  $c_{\text{dye}} \approx 10^{-1}$  M, it turns out that the thickness of the electrode needs to be 5  $\mu\text{m}$  for an absorption of 90 % of the incident light.

If it was possible to synthesize novel dyes with an absorption that extends into the near infrared (NIR), the short circuit current could be significantly improved. As outlined in chapter 6.1, the maximum conversion efficiency can be achieved with absorbers having a bandgap between 1.1 and 1.4 eV, which corresponds to a wavelength between 900 nm and 1100 nm. None of the dyes presently employed in DSSCs absorb in this spectral region, which is one reason for the rather low efficiency compared to silicon solar cells.

## 2) energy level

The energy level of the excited dye molecule should be about 0.2 - 0.3 eV above the conduction band of the TiO<sub>2</sub> to ensure efficient charge injection [23]. In this case the activation energy for the back reaction – the reduction of the oxidized sensitizer by a conduction band electron – is high and the corresponding rate constant too slow to compete with the dye regeneration by the electrolyte. The formal oxidation potential of the excited state  $\Phi_{\text{D}^+/\text{D}^*}^0$  can be approximated by the formal oxidation state of the ground state  $\Phi_{\text{D}^+/\text{D}}^0$  and the excitation energy  $E_{0-0}$  according to equation 2.11.

$$\Phi_{D^+/D^*}^0 = \Phi_{D^+/D}^0 - E_{0-0}/F \quad (2.11)$$

$\Phi_{D^+/D^*}^0$  = formal oxidation potential of excited state /V;  $\Phi_{D^+/D}^0$  = formal oxidation potential of ground state /V;  
 $E_{0-0}$  = excitation energy /J; F = Faraday constant = 96485 Q\* $\text{mol}^{-1}$

The formal oxidation potential of the ground state is accessible by square wave voltammetry of the anchored dye and the excitation energy can be estimated by analyzing the emission spectrum of the dye in the NIR [24].

The energy level of the dye can be shifted if it agglomerates on the  $\text{TiO}_2$ -surface, which happens especially at high dye coverage. The formation of dimers or higher aggregates are in particular a problem for hydrocarbons, phthalocyanines and porphyrins. This may result in different electronic properties of the ground state and/or the excited state, which can affect the charge injection efficiency. Typically, one can monitor the formation of agglomerates by a redshift of the absorption maximum [61]. One way to overcome this problem is to introduce rigid bridges between the anchoring group and the chromophore of the dye molecule (review article: [62]) or to coadsorb spacer molecules like cholic acid [61] or phosphonic acid derivatives [33].

### 3) charge injection and charge recombination

Charge injection occurs from the  $\pi^*$ -orbitals of the anchoring group (carboxylic or phosphonic acid) to the titanium 3d-orbitals. A good overlap of these orbitals is mandatory for efficient charge injection.

Injection of electrons from the dye into the  $\text{TiO}_2$  typically happens on a femto- to picosecond time scale whereas charge recombination in the micro to millisecond time scale [63][64][12][10]. Laser transient absorption spectroscopy is usually utilized to measure the ultrafast time constants. Typically the dye is excited in the visible and the absorption of conduction band electrons (mid-IR) or the oxidized dye (NIR) is monitored with a probe pulse. For the standard Ru-dyes, a difficulty arises since all species involved – the dye in its ground-, excited and oxidized state – have a significant overlap in their absorption spectra, which makes the analysis of the data complicated [12].

A prerequisite for an efficient charge injection is that the back reaction of a conduction band electron to the oxidized dye is much slower than the reduction of the oxidized dye by the electrolyte. For example for the dye K19, one finds a recombination rate of  $k_{\text{rec}} = 1.4 \cdot 10^3 \text{ s}^{-1}$  and a

regeneration rate of  $k_{\text{reg}} = 1.1 \cdot 10^5 \text{ s}^{-1}$ . Thus the regeneration is a hundred times faster, which ensures an injection yield of 99 % [65].

Charge injection can occur either from the singlet or the triplet state. The rate constant for injection from the singlet is on a time scale  $< 100 \text{ fs}$  [64]. The rate is comparable to the rate of intramolecular energy redistribution, so a fraction of the electrons is not thermalized when being injected, which is referred to as a nonergodic process. After intersystem crossing (ISC) the injection occurs from a thermalized triplet state with rate constants on a picosecond time scale [64]. The fraction of singlet and triplet injection is according to [12] ca. 60 % : 40 %.

#### 4) stability

Any sensitizer in a DSSC has to sustain at least twenty years of operation without significant degradation. Considering a standard DSSC with 6 % conversion efficiency ( $V_{\text{oc}} = 0.7 \text{ V}$ ,  $I_{\text{sc}} = 12.2 \text{ mA cm}^{-2}$ ,  $\text{FF} = 0.7$ ), a total charge  $Q_t$  of ca. 878000 C is injected into the  $\text{TiO}_2$  if one assumes a solar irradiation of  $1000 \text{ W m}^{-2}$  for 1000 h per year.

$$Q_t = I_{\text{sc}} \cdot t_{\text{sun}} \cdot \text{lifetime} \quad (2.12)$$

$Q_t$  = charge /  $\text{C cm}^{-2}$ ;  $I_{\text{sc}}$  = short circuit current (example:  $1.22 \cdot 10^{-2} \text{ A cm}^{-2}$ );  $t_{\text{sun}}$  = time of AM1.5 irradiation per year (example: 1000 hours/year); lifetime = expected lifetime of DSSC /years;

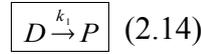
In a typical DSSC the dye coverage of the  $\text{TiO}_2$ -surface is  $\Gamma \approx 1 \cdot 10^{-7} \text{ mol cm}^{-2}$ . With equation 2.12 the number of redox cycle per dye molecule  $n_{\text{redox}}$  can be calculated by

$$n_{\text{redox}} = \frac{Q_t}{e \cdot N_A \cdot \Gamma} \quad (2.13)$$

$n_{\text{redox}}$  = number of redox cycles /;  $Q_t$  = charge (example:  $878000 \text{ C cm}^{-2}$ );  $e = 1.6022 \cdot 10^{-19} \text{ C}$ ;  $N_A$  = Avogadro constant ( $6.023 \cdot 10^{23} \text{ mol}^{-1}$ );  $\Gamma$  = surface concentration of sensitizer (example:  $10^{-7} \text{ mol cm}^{-2}$ )

With the values given, it turns out that each dye molecule undergoes 91 million redox cycles in twenty years lifetime. Ideally, the electron injection and regeneration is completely reversibly. However, in any real device, some degradation of the dye occurs. In the following, a rough estimation of the maximum rate constant for degradation in the dark and under illumination is given if 90 % are retained after twenty years of operation.

The degradation in darkness is assumed to be a decomposition of the dye in the ground state following first order kinetics:



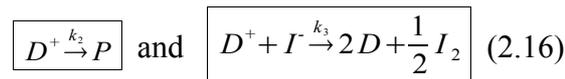
The decomposition rate constant  $k_1$  can be expressed as

$$k_1 = -\ln \frac{c_{dye, lifetime}}{c_{dye, 0}} * lifetime \quad (2.15)$$

$k_1$  = rate constant for degradation from the ground state /s<sup>-1</sup>;  $c_{dye,0}$  = initial dye concentration /M;  $c_{dye, lifetime}$  = dye concentration at some time t /M; (example:  $c_{dye,0} / c_{dye, lifetime} = 0.9$ ); lifetime = lifetime of the cell (example: 20 years  $\approx 6.3 * 10^8$  s)

With the values given it turns out, that the maximum rate constant for the decomposition is  $1.7 * 10^{-10}$  s<sup>-1</sup>. At this point it is not clear if the Ru-complexes currently employed can fulfill this requirement especially under elevated temperature.

Under illumination degradation might occur from the excited state  $D^*$  or from the oxidized state  $D^+$ . Since the injection from the excited state is ultrafast it is believed that light induced degradation mainly occurs from the oxidized state  $D^+$ . The irreversible degradation of the oxidized dye molecule with a rate constant  $k_2$  competes with the regeneration by the electrolyte with a rate constant  $k_3$ .



Following the argumentation of [66], one can calculate the branching ratio of  $k_3 * I^-$  and  $k_2$  to be

$$\frac{k_3 * I^-}{k_2} = \frac{-Q_t}{F * \Gamma * \ln \frac{c_{dye, lifetime}}{c_{dye, 0}}} \quad (2.17)$$

$k_3$  = regeneration rate constant /M<sup>-1</sup>s<sup>-1</sup> (example:  $10^{10}$  M<sup>-1</sup>s<sup>-1</sup>); iodide concentration /M (example: 1 mol/l);  $k_2$  = rate constant of irreversible degradation /s<sup>-1</sup>;  $Q_t$  = charge passing through the cell within 20 years /Qcm<sup>-2</sup> (example: 878000 Ccm<sup>-2</sup>); F = Faraday constant = 96485 C/mol;  $\Gamma$  = surface concentration of sensitizer /mol\*cm<sup>-2</sup> (example:  $10^{-7}$  mol\*cm<sup>-2</sup>);

For the values given, the branching ratio turns out to be  $8.6 * 10^8$ , which means, that the regeneration

reaction has to be almost nine orders of magnitude faster than the light induced degradation.

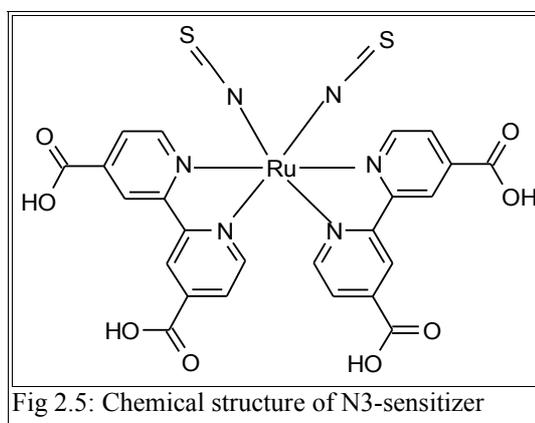
The regeneration reaction is typically measured by transient absorption spectroscopy and is very sensitive to the applied voltage and the precise electrolyte composition. The values for  $k_3$  found in literature vary significantly between  $1.6 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$  [67],  $2.3 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [68] and  $3.6 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [69]. Only one detailed study was done on the light induced degradation reaction, which found  $k_2$  to be  $4 \cdot 10^{-2} \text{ s}^{-1}$  [70].

Taken the fastest regeneration rate given in [69], the branching ration would be  $9 \cdot 10^8$  which is sufficient for 20 years cell operation. However, with the slowest rate from [67], equation 2.17 predicts a lifetime of only a few months.

The standard accelerating aging test lasts typically for 1000 hours, which corresponds to one year of outdoor application. Little or no data is available on real outdoor tests for several years. One has to keep in mind that photoinduced degradation might not affect I/V-parameters for a long time even if one assumes a linear degradation rate because there is a large access of dye molecules present on the electrode. If this buffer is consumed the cell efficiency might decrease rapidly. Therefore it is questionable if stability data based on 1000 hour aging tests [31][33][34] can be taken to predict the degradation patterns for 20 years of outdoor application.

## Ru-complexes

Polypyridinium Ru<sup>II</sup>-complexes show intense metal to ligand charge transfer (MLCT) bands in the visible region, a prerequisite for efficient charge injection into wide bandgap semiconductors like TiO<sub>2</sub>. The history of these complexes goes back to the seventies, when tris(2,2'-bipyridyl)Ru(II) was intensively investigated as a redox sensitizer, because it has a very long-lived excited state [71]. The closely related bis(2,2'-bipyridyl)LL'Ru(II)-complexes (bpyLL-Ru), which are today almost exclusively employed in DSSCs, were not investigated to a larger extent for a long time, because the excited state is usually too short-lived to allow homogeneous bimolecular electron-transfer reactions [41]. However, in heterogeneous systems, like in sensitized wide bandgap semiconductors, an ultrafast electron injection (in the femtosecond range) can successfully compete with deactivation of the excited state and consequently the research interest focused on these dye in the late eighties [72]. The bpyLL-Ru-complexes are less susceptible to photoinduced ligand loss and have a broader absorption in the visible compared to the previously employed tris(2,2'-bipyridyl)Ru(II)-complexes.



In 1993, the introduction of the so called N3-sensitizer (Fig. 2.5), where LL' are two thiocyanate ligands and which has additional carboxylate groups as anchoring sites, set a benchmark for all following dyes [41]. Today it is still widely employed as a reference. It is named after the chemist Md. Khaja Nazeeruddin working in the group of Prof. Grätzel who numbers his dyes in ascending order. The efficiency of 10 % reported for a N3-sensitized DSSC [41] could only be slightly improved since then.

Using the N3-dye as a reference, many research groups have started to tune the electronic and optical properties by exchanging one or more of the ligands. Five different approaches are discussed in the following, which all employ Ru<sup>II</sup>-complexes with two bipyridil ligands.

Only one noticeable exception from this basic matrix was reported so far, which is a terpyridil-Ru<sup>II</sup>-complex introduced in 2001. Its extended absorption in the near infrared significantly enhances the overall incident photon to current conversion efficiency. Thus, DSSCs sensitized with this so-called “black dye”, have a higher short circuit current. The conversion efficiency of 10.4 % (1 cm<sup>2</sup> [21]) and 11.1 % (0.26 cm<sup>2</sup> [73]), are the highest certified efficiencies so far. However, the stability of the

dye has not been proven yet.

1. substituting the chromophore of the dye

One approach was to substitute the thiocyanate ligand, which is the chromophore of the dye. The idea was to employ ligands with an extended absorption into the red and near infrared region. Though a better absorption has been demonstrated for a number of sensitizers, the overall cell efficiency could not be improved. Besides halogen ligands [41], a number of organic ligands were tested. The most successful was acetylacetonate (6 % [74]), followed by a pteridinedione-complex (3.8 % [75]) and a diimine dithiolate-complex (3.7 % [76]).

2. different protonation level of N3

When the sensitizer is chemically bound to the  $\text{TiO}_2$  in an esterification, the protons of the anchoring group (carboxylic acid, phosphonic acid) are partly transferred to the surface of  $\text{TiO}_2$ . In a comparative study [9][77], the photovoltaic performance was correlated with the number of protons on the N3-sensitizer, ranging from zero protons (N712) to four protons (N3). The protons were exchanged by a bulky tetra-n-butylammonium (TBA) group.

With increasing number of protons the  $\text{TiO}_2$ -surface is positively charged and the Fermi-level of the  $\text{TiO}_2$  is shifted down. The electric field associated with this surface dipole enhances the dye absorption and leads to a higher dye coverage. Another consequence is a higher driving force for charge injection, which increases the short circuit current (N3:  $19 \text{ mAcm}^{-2}$ ; N712:  $13 \text{ mAcm}^{-2}$  [77]). At the same time, the energy gap between the quasi-Fermi-level of the  $\text{TiO}_2$  and the redox electrolyte, which determines the open circuit potential, decreases (N3: 600 mV; N712: 900 mV [77]). The maximum conversion efficiency was found for the monoprotonated sensitizer  $\text{N3}[\text{TBA}]_3$  (9.3 %), closely followed by the diprotonated  $\text{N3}[\text{TBA}]_2$  (N719, 8.4 %) [77].

In general, the ideal protonation level differs from dye to dye and has to be optimized individually. Recently the use of density functional theory calculations have been employed to predict the ideal protonation level [9][78][79].

### 3. extending the $\pi$ -system

Compared to a number of organic dyes, the standard Ru-complexes have significantly lower absorption coefficients. Therefore relatively thick  $\text{TiO}_2$  layers are needed to harvest most of the incident light, which enhances the probability for electron recombination.

The absorption can be enhanced by exchanging two carboxylic anchoring groups of the N3-sensitizer (Fig. 2.5) with ligands, that have conjugated  $\pi$ -systems. The idea is to create dyes with a high molar extinction coefficients, to tune the LUMO of the dye to get directionality in the excited state and to introduce hydrophobic side chains that repel water and triiodide from the  $\text{TiO}_2$ -surface. The best results are achieved with styryl-ligands attached to the bipyridil ring (detailed structures given in table 2.1). The molar extinction coefficients are  $1.69 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  (Z910 [24]),  $1.82 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  (K19 [80]) and  $1.89 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  (N945 [81]), which is at least 16 % more compared to the standard dye N3.

The performance of these novel sensitizers on thick electrodes and with volatile electrolytes is about the same as for the N3-reference (e.g. Z910 10.2 % [24] and N945 10.8 % [82]), but applied on thin electrodes and with non-volatile electrolytes, the conversion efficiency is significantly higher (e.g. K73 with 3-methoxypropionitrile 9.0 %). At the same time a remarkable stability at 80 °C in darkness and at 60 °C under AM1.5 is observed [82]. The excited state of these dyes is between -0.71 V and -0.79 V vs. NHE [24][80][81][65], which is sufficiently more negative than the conduction band of  $\text{TiO}_2$  (ca. -0.1 V vs. NHE) to ensure complete charge injection.

Another class of ligands, which were successfully applied, are substituted thiophene derivatives with a conversion efficiency of up to 9.5 % (HRS-1 [83]).

### 4. amphiphilic dyes with alkyl chains

The ester linkage of the dye to the  $\text{TiO}_2$  is susceptible to hydrolyze if water adsorbs on the  $\text{TiO}_2$ -surface [84]. For this reason, N3-based Ru-complexes were developed where two of the four carboxylic groups were replaced by long alkyl chains (detailed structures given in table 2.1).

In these sensitizers the conjugated  $\pi$ -system of the bipyridil-ligand is smaller and thus, the absorption coefficient is typically lower. Yet, the initial conversion efficiencies is still reasonable good, ranging from 7.3 % for Z907 (with 9 carbon atoms) [33] to 9.6 % for N621 (with 13 carbon atoms) [9]. The main advantage of these dyes is their extraordinary stability. For example, Z907

sensitized DSSCs passed 1000 h at 80 °C in darkness and at 55 °C under illumination without any degradation [85]. By coadsorption of decyl-phosphonic acid on the TiO<sub>2</sub> nanoparticles, the hydrophobicity of the surface could be even enhanced and stable cells have been demonstrated on a 7 % level [33].

#### 5. different anchoring groups

Most of the dyes employed in DSSCs have carboxylic acid groups to anchor on the TiO<sub>2</sub>-surface. The binding is reversible with high binding equilibrium constants ( $K \approx 10^5 \text{ M}^{-1}$ ). At a pH > 9 the equilibrium is typically shifted to the reactant side and the dye molecules desorb. This somewhat fragile linkage triggered the development of dyes with different anchoring groups. In general the binding strength to a metal oxide surface decreases in the order phosphonic acid > carboxylic acid > ester > acid chloride > carboxylate salts > amides [62], so most of the research focused on phosphonic acids. Besides the stronger adsorption on the TiO<sub>2</sub>-surface, phosphonic acids differ in the following points from carboxylic acids:

- each group carries one more proton. Thus the flat band potential of TiO<sub>2</sub> is shifted electrochemically more positive, which has a positive effect on the short circuit current and a negative effect on the open circuit potential.
- the phosphorous atom is sp<sup>3</sup>-hybridized in contrast to the sp<sup>2</sup>-hybridized carbon atom. That means, that the  $\pi$ -system of the bipyridil-ring does not extend into the anchoring group, which results in a blueshift of the absorption spectrum. The blueshift of the absorption spectrum leads to a lower short circuit current  $I_{\text{SC}}$  if all the other ligands are the same. For example, the analog to the N3, RuL<sub>2</sub>(SCN)<sub>2</sub> with L = 2,2'-bipyridine-5,5'-bisphosphonic acid, exhibit a ca. 45 % lower  $I_{\text{SC}}$  [86].

Recently, a Ru-complex with a phosphonic acid anchoring group (Z955) was introduced (detailed structures given in table 2.1), that gives a conversion efficiency of 8 % under AM1.5 accompanied by a good stability under prolonged light soaking (1000 h at AM1.5 and 55°C) [87]. This is the highest efficiency for a phosphonic anchoring so far.

In other comparative studies, the phosphonic acid anchoring group outperformed the carboxylic analog [88], however the highest efficiency obtained was only 3 %.

Beside the phosphonic acids, charge injection of Ru-complexes could be demonstrated with other anchoring groups like triethoxysilane [89] and boronic acid (IPCE<sub>max</sub> 22 %) [90], but no solar cells

with significant efficiency could be made with these dyes up to now.

Probably the most remarkably feature about the Ru-dyes is their extraordinary stability when being adsorbed on the  $\text{TiO}_2$ -surface. For example, the widely employed complex N3 sustains only 200 excitation cycles in solution, but between  $10^7$ - $10^8$  cycles on a metal oxide surface. The difference between the dye in solution and on the  $\text{TiO}_2$ -surface is an ester bond in the periphery of the molecule. Obviously the electronic state of the Ru-complex is significantly altered by the adsorption. The dye is probably not simply attached by physisorption or chemisorption, but creates a charge transfer complex (CTC) with  $\text{Ti}^{3+}$ -surface states, which are partly present in the semiconductor or are created upon charge injection. The CTC might induce a  $\pi$ -backbonding, which allows the local export of entropy and thus the stabilizes the Ru-complex [91].

### organic dyes

The efficiency of DSSCs with organic dyes has increased significantly in the last years and the current state of the art (9 %, [92]) is comparable to the conventional Ru-complexes. Especially promising is the fast learning curve, which raises hope for further improvement in the near future. Since organic dyes are not based on rare noble metal, the production costs mainly depend on the number of synthesis steps. Thus they are potentially very cheap. The absorption coefficients are typically one order of magnitude higher compared to Ru-complexes making very thin  $\text{TiO}_2$ -layers feasible. However, at this point none of the organic dyes have proven stability under elevated temperature and/or prolonged illumination. The following examples are the most promising dye classes at the moment:

### coumarin-dyes

Coumarin (figure 2.6) is a natural compound found in many plants. In a higher concentration, it occurs in tonka bean, woodruff and bison grass. Scientifically this dye class has been successfully employed in dye lasers. The first transient studies on a coumarin dye in DSSCs was performed in 1996, when Grätzel *et al.* found injection rates of 200 fs from C343

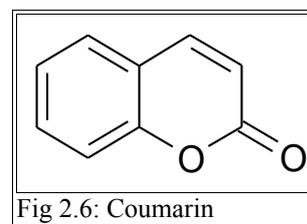


Fig 2.6: Coumarin

(table 2.1) into the conduction band of  $\text{TiO}_2$  [93]. Since C343 has a narrow absorption spectrum, the conversion efficiency of this specific compound was low. By introduction of a methine unit, the  $\pi$ -system could be expanded and in 2001 a respectable efficiency of 5.6 % was obtained with

NKX-2311 [94]. Adding more methine units (up to three) and introducing bulky substituents to prevent dye-aggregation could push the efficiency to 6.7 % in 2005 (NKX-2753) [95]. Currently other building blocks like thiophene are tested, which are believed to give a higher stability. First results of 7.4 % for NKX-2677 are encouraging [96].

### indole-dyes

Indole occurs naturally as a building block in the amino acid tryptophan, in dyes and many alkaloids. Substituted with an electron withdrawing anchoring group on the benzene ring and an electron donating group on the nitrogen atom, these dyes have a great potential as sensitizers. A remarkable efficiency of 6.1 % with D102 was published in 2003 which triggered a number of subsequent studies. By Optimizing the substituents, an efficiency of 8 % was achieved with D149 ([97]) This value was even exceeded recently by optimizing the TiO<sub>2</sub>-layer properties (9 % [92]).

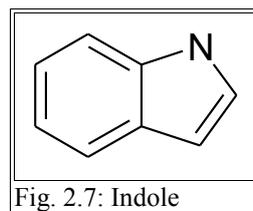


Fig. 2.7: Indole

Besides comarin- and indole derivatives, other organic dyes have been employed in DSSCs including perylenes [98] and xanthenes [99]. However, the conversion efficiency and/or the stability of these devices is poor.

### porphyrins

After the first publication on efficient sensitization of TiO<sub>2</sub> with porphyrins [100], there was an enormous effort to synthesize novel porphyrin derivatives with the underlying idea to mimick nature's photosystem I and II. The idea is to exploit the large molar extinction coefficient of the Soret and Q-bands. Soret bands have an extinction coefficient of  $10^5 \text{ M}^{-1}\text{cm}^{-1}$  in the range between 400 - 500 nm and Q-bands typically one order of magnitude less in the range between 600 - 800 nm. Porphyrins typically have a long lived excited singlet state ( $> 1 \text{ ns}$ ) and an electron injection rate in the femtosecond range [101]. The electron recombination occurs in the millisecond time range [102]. Studies revealed [103] that the nature of the anchoring group (carboxylic acid or phosphonic acid) has surprisingly little effect on the cell performance whereas the position of the anchoring group is very crucial for the electronic communication with the TiO<sub>2</sub>. The latter feature might explain, why many of the porphyrin dyes fail to give a high incident photon to current conversion efficiency (IPCE) despite the strong absorption.

Porphyrins tend to agglomerate on the TiO<sub>2</sub>-surface so that coadsorbents like cholic acid or

alkylphosphonic acids have to be added to the dye solution, which decreases the surface coverage. So far no stability tests under elevated temperatures were published for porphyrin-sensitized DSSCs.

The best initial efficiencies were achieved with differently substituted Zn-tetraphenylporphyrins (ZnTTP). In 2004, a sytryl substituted ZnTTP gave an efficiency of 4.2 % (ZnTPPSCA; detailed structures given in table 2.1) [104] and shortly after it turned out, that by exchanging the phenyl ligands by xylyl ligands (Zn2) the efficiency could be even slightly improved (4.8 % [105]). The highest conversion efficiency of 5.6 % [102] was achieved by introducing an electron withdrawing cyanid-group next to the anchoring group (Zn3).

Very recently, another Zn-porphyrin dye was introduced, that gives the unprecedented conversion efficiency of 7.1 % (07/2007) [106].

### **natural dyes**

Natural dyes are exclusively used for educational purposes representing a low-cost and environmentally friendly alternative to conventional Ru-complexes. Extracted dyes might also be a good starting point to evaluate, which dye classes are potentially interesting for sensitization. The screening at this point is mostly done by trial-and-error but already some interesting dyes have been found. Among the best results so far are the anthocyanins extracted from Jaboticaba and Calafate yielding  $I_{SC} = 9 \text{ mAcm}^{-2}$ ,  $V_{OC} = 0.59 \text{ V}$  and  $6 \text{ mAcm}^{-2}$ ,  $0.47 \text{ V}$  respectively [107]. Other antocyanins extracted from blackberries gave a conversion efficiency of 0.56 % [108]. Another interesting class of natural dyes are tannins because of their photochemical stability. DSSCs using tannins and other polyphenols extracted from Ceylon black tea gave photocurrents of up to  $8 \text{ mAcm}^{-2}$  [109].

### **organic complexes of other metals**

Other metal complexes have been scrutinized for their application in DSSC, among them Os- [110], Pt- [111], and Fe-complexes [112]. The reasoning to utilize Os-complexes although they are extremely toxic is to make use of the spin-forbidden singlet-triplet MLCT transition in the NIR where the complex has a quite intense absorption ( $\alpha_{811 \text{ nm}} = 1.5 \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ). Higher IPCE values are obtained in this spectral region, however the overall conversion efficiency is only 50 % of a standard Ru-dye [110]. Pt-complexes give modest efficiencies of ca. 0.7 % [111] and iron-complexes, which are very interesting due to the vast abundance of the metal and its nontoxicity are at a very low efficiency level at the moment (0.3 % [112]).

dye	year	absorption coefficient $/10^3 \text{ M}^{-1} \text{ cm}^{-1}$	efficiency	remarks	literature
<b>Ru-complexes</b>					
N3	1993	14.2 <sub>534 nm</sub> (ethanol)	10.0	$R_1 = R_2 = R_3 = R_4 = \text{H}$ data was never reproduced	[41]
N712	2003		8.2	different protonation level investigated $R_1 = R_2 = R_3 = R_4 = \text{TBA}$	[77]
N719	2005		11.2	$R_1 = R_2 = \text{TBA}; R_3 = R_4 = \text{H}$	[9]
Z910	2004	16.9 <sub>543 nm</sub> (acetonitrile)	10.2	$R_1=R_2=$	[24]
K19	2005	18.2 <sub>543 nm</sub> (acetonitrile: <i>t</i> -butylalcohol 1:1)	7.0	$R_1 = R_2 =$ low volatile electrolyte	[80]
N945	2006	18.9 <sub>550 nm</sub> (acetonitrile: <i>t</i> -butylalcohol 1:1)	9.6	$R_1 = R_2 =$	[81]
K73	2006	18.0 <sub>545 nm</sub>	9.0	$R_1=R_2=$	[10]
N621	2005		9.6	$R_1=R_2=$	[9]
Z907	2003	11.1 <sub>525 nm</sub> [84]	7.3	$R_1 = R_2 =$ solvent of the electrolyte: MPN	[33]
Z955	2004	ca. 8 <sub>519 nm</sub>	8.0		[87]
HRS-1	2006	18.7 <sub>542 nm</sub> (ethanol)	9.5	$R_1 = R_2 =$	[83]
black dye	2006	~610 nm (ethanol)	10.8	introduced 2001 by Grätzel [21]	[73]
<b>Coumarin-derivatives</b>					
C343	1996			first transient measurements	[93]
NKX-2311			5.6 %	introducing methine chains	[94]
NKX-2753	2005	50.3 <sub>492nm</sub> (ethanol)	6.7 %	bulky substituents to prevent agglomeration	[95]
NKX-2677	2005	64.3 <sub>511nm</sub> (ethanol)	7.4 %	thiophene units to extend $\pi$ -system	[96]
<b>indole-derivatives</b>					
D102	2003	55.8 <sub>491 nm</sub>	6.1%		[113]
D149	2004	68.7 <sub>526 nm</sub>	9 %	highest efficiency for organic dyes	[92]
<b>porphyrin-dyes</b>					
ZnTPPSCA	2004		4.2		[104]
Zn2	2004	225 <sub>439nm</sub> (THF)	4.8		[105]
Zn3	2005	153 <sub>455nm</sub> (THF)	5.6	highest efficiency for porphyrins	[102]

Table 2.1: state of the art for sensitizers employed in DSSC

## 2.3 Entry of the market

Most research on dye sensitized solar cells (DSSC) is still done on small cells ( $< 1 \text{ cm}^2$ ) and despite an increasing research activity in the last few years little is known about the upscaling of the device. The question arises what are the main impediments for commercialization. In this chapter a preliminary feasibility study of DSSC-production on the 1 MW-scale in the next ten years is presented with the underlying assumption that the price per  $W_p$  has to be in the range of about 1 € for the technology to be implemented. A close look at each of the cell components is made. The contribution to the total price of the cell is estimated and a general assessment, which might be the bottleneck of the device, is given as a conclusion.

Considering the learning curve of DSSCs in the past 16 years [20] and the current state of the art in the module-production [28], it can be deduced that the efficiency of the first DSSC-modules will be in the range of 5 - 6 %. In this chapter only DSSCs with a liquid electrolyte, which are based on a glass substrate, are reviewed because DSSCs with flexible substrates and/or solid hole conductors are currently not stable and/or efficient enough for large area application.

### dye:

As presented in chapter 2.2.4, Ru<sup>II</sup>-complexes are by far the most efficient and stable sensitizers for DSSCs. All the groups working on the upscaling of DSSCs [114][115][27][29] employ one of the Ru<sup>II</sup>-complexes, so they will most likely be applied in the first commercially available DSSC-modules. What are the implications?

A standard DSSC has a dye uptake  $\Gamma$  of ca.  $10^{-7} \text{ mol} \cdot \text{cm}^{-2}$  (layer thickness  $d = 10 \text{ }\mu\text{m}$ ), which corresponds to ca. 1 g of dye per  $\text{m}^2$ . The price for the dye varies between 600 €\*g<sup>-1</sup> (DYESOL [116]) and 1000 €\*g<sup>-1</sup> (SOLARONIX [117]). The price of the dye per  $W_p$  can be calculated by:

$$P_{total} = \frac{\Gamma * M_{dye} * P_{mass}}{I_{AM1.5} * \eta} \quad (2.18)$$

$P_{total}$  = price per  $W_p$  /€\*W<sup>-1</sup>;  $\Gamma$  = surface coverage /mol\*cm<sup>-2</sup>;  $M_{dye}$  = molecular mass of dye /g\*mol<sup>-1</sup> (e.g. N719: 1187.7 g\*mol<sup>-1</sup>);  $P_{mass}$  = price per mass /€\*g<sup>-1</sup>;  $I_{AM1.5}$  = light intensity of AM1.5 /W\*m<sup>-2</sup>;  $\eta$  = efficiency of DSSC /%

It is about 20 €/W<sub>p</sub> at the moment.

So significantly effort has to be undertaken to reduce the production cost of dye synthesis, which is mostly determined by the labor-intensive synthesis. The most expensive raw material of the dye, which is RuCl<sub>3</sub>, costs about 20 €/g. Neglecting all other materials and expenditure for labor force, it turns out that the limit for the total price is about 8 cents/W<sub>p</sub>.

Dai *et al.* calculate about 20 cents/W<sub>p</sub> at a production scale of 20 kg using their own production facilities [118]. That means that when aiming at a total price of 1 €/W<sub>p</sub>, already 20 % of the costs are due to the dye itself.

Looking at the problem from a more global perspective, the availability of ruthenium might be a bottleneck for large-scale DSSC-production. At the moment the total annual extraction of ruthenium is about 30 tons [119] worldwide, which is mostly used as a catalyst and as an additive in Pd- and Pt alloys. As a first approximation about 5 % of this amount is available for DSSCs on a short term, which correspond to 750 MW. Although this might be an impressive figure at a first glance, it will be not enough to compete with standard Si-cells. However, the total amount of ruthenium available is estimated to be 9\*10<sup>9</sup> tons [119] worldwide, which would certainly be enough to produce DSSC on the GW-scale. The question is how expensive the metal will be if the Ru-mines are exploited at a level of 100 - 1000 tons annually.

It can be concluded that Ru-complexes might be helpful to get the DSSC-production started. The availability of ruthenium would be sufficient for large-scale production, but the price is assumed to be too high in the long run.

#### **Transparent conducting oxide glass (TCO-glass):**

It is estimated that about 50 % of the total price for a DSSC-module will be made up by the TCO-glass [120]. At the moment fluorine doped tin oxide (F:SnO<sub>2</sub>) is exclusively used as a TCO to collect the current at the front and counter electrode. Other conducting oxides (e.g. ITO), which are widely used in the field of LED-displays, cannot be employed because they are chemically not stable enough. Only two companies (PILKINGTON, USA and ASAHI, Japan) produce F:SnO<sub>2</sub> coated glass at the moment. The price largely depends on the total area that is produced. Thus there is a high uncertainty of the price per m<sup>2</sup> and it will depend on the engagement of the two companies to scale up their production. Today, it is asserted that the price might be in the range of 10 \$/m<sup>2</sup>, which would correspond to 20 cents/W<sub>p</sub> [118].

### **electrolyte:**

It is assumed that an iodine/iodide based electrolyte is used for the first commercially available DSSC-modules. Though this system has some inherent disadvantages (chemically very aggressive, corrodes silver fingers, significant absorption in the visible) no substitute with comparable conversion efficiency has been found so far. From the technical point of view, the electrolyte imposes the following problems:

#### 1) complex current collection

Since the ohmic resistance of the TCO is too high (typically  $10 \Omega/\square$ ) additional current collectors like silver fingers have to be applied in modules. These have to be shielded from the electrolyte by some sealant. This complicated cell layout drastically reduces the active cell area. It is only about 68 % of the total area [27] for larger modules.

#### 2) viscosity of the solvent

For the cell assembly, the viscosity of the solvent should be preferably low in order to fill large modules bubble-free by capillary forces. From the stability point of view, the electrolyte should be as viscous as possible to reduce the risk of cell leakage.

Today, nitriles are commonly used as a solvent in DSSC-modules, acetonitrile [27], propionitrile [32], 3-methoxypropionitrile [121] or a mixture of them [28] being the most important ones. Long-term stability has been demonstrated for these solvents at 80 °C in darkness for 1000 h [33]. However, the exposure to day/night cycles with changing temperature constitute a major stress factor for the sealant and it has not been proven that the sealing is stable for years of outdoor application. Furthermore it can be questioned that people will accept irritant (3-methoxypropionitrile) or toxic (acetonitrile, propionitrile) liquids with considerable vapor pressure (ranging from 9 hPa [3-methoxypropionitrile] to 97 hPa [acetonitrile]).

Thus, both from a scientific and from a technological perspective, the standard iodine/iodide-electrolyte is only a temporary solution and needs to be replaced in the medium term.

From an economic point of view, the cost for the electrolyte will basically comprise the cost for the iodide salt. Currently, the most commonly applied compounds are imidazole iodide salts. For example, the standard salt 1-methyl-3-propylimidazolium iodide (PMII) costs  $2.6 \text{ €g}^{-1}$  (IOLITEC [122]). Using standard values from the literature, the price per  $W_p$  can be calculated by

$$P_{total} = \frac{c_{electrolyte} * d * M_{electrolyte} * P_{mass}}{I_{AM1.5} * \eta} \quad (2.19)$$

$P_{total}$  = price per  $W_p$  /€\* $W_p^{-1}$ ;  $c_{electrolyte}$  = concentration of PMII /M (example: 0.6 M);  $d$  = thickness of electrolyte layer /cm (example:  $5 * 10^{-3}$  cm)  $M_{electrolyte}$  = molecular mass of PMII /g\*mol<sup>-1</sup> (example: 252 g/mol);  $P_{mass}$  = price per mass /€\*g<sup>-1</sup> (example: 2.6 €g<sup>-1</sup>);  $I_{AM1.5}$  = light intensity of AM1.5 /W\*m<sup>-2</sup>;  $\eta$  = efficiency of DSSC /% (example: 5 %)

It is 0.39 € $W_p^{-1}$  at the moment neglecting the costs for iodine, the solvent, coadsorbents and labor costs. Unless the production costs cannot be significantly reduced, these imidazolium salts are not applicable for DSSC-production.

It can be concluded that the iodine/iodide based electrolyte in a liquid solvent is unmatched in terms of efficiency, but it imposes severe problems for the intrinsic stability, the durability of the module, the environmental compability and the total price of the module.

#### sealing:

The sealing of a dye sensitized solar cell is either made by a hotmelt polymer foil (Surlyn<sup>®</sup>, Byne1<sup>®</sup>) [121][27][28] or a glass frits [32]. The material costs for both sealing methods are negligible, however the employment of glass frits requires a temperature treatment of at least 650 °C, which would increase the energy consumption for the cell manufacture significantly. The polymer foil, on the other hand, has the disadvantage that the adhesion to the glass substrate is very sensitive to impurities and electrode spacing. This becomes especially critical for larger area devices (> 100 cm<sup>2</sup>), when the distance between front and counter electrode typically differs by a few micrometer. That is why thicker foils (> 50  $\mu$ m) are usually applied, which increases the internal resistance of the electrolyte and reduces the fill factor. Still it is expected that polymer foils will be the choice of any commercial application of DSSC.

It can be concluded, that currently available DSSC-technology is not applicable for a large-scale implementation. Even the costs for selected cell compounds add to ca. 0.8 €/ $W_p$ . Cheaper cell components (organic dyes, other iodide source), which give high conversion efficiencies and a good long term stability, need to be developed before the price for a DSSC can compete with other thin film solar cells.