Novel materials and New design for Dye Sensitized Solar Cells Technology

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Novel materials and new design for Dye sensitized solar Cells Technology Towards a better and ecologic world

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Economy's Uneologic
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Abstract: Novel Materials and new design for DSSC technology

This thesis work was devoted to the study of possible application of new materials for the development of Dye Sensitized Solar Cells (DSSC) with improved solar conversion efficiency and stability. A DSSC is a photoelectrochemical device allowing electric power generation from sunlight. The DSSC working principles are illustrated in figure 1. Sunlight is absorbed by the dye which is absorbed on a TiO$_2$-based electrode. Absorbed photon excites an electron from the HOMO to the LUMO of the dye. As a consequence, the excited electron is transferred into the titania electrode up to the external circuit. The dye is regenerated thanks to the presence of a redox couple (typically I$^-$/I$_3^-$) contained into the electrolyte (normally in a liquid phase). Up to now, the best efficiency of light conversion obtained by using DSSC technology is ca 12 % and is reached using Ruthenium complexes as sensitisers, liquid electrolyte (based on acetonitrile or methoxiproponitrile solvents), TiO$_2$ nanoparticles for the electrode preparation and Platinium-based counter electrode.

In this thesis work, particular attention was given to the use of novel nanostructured materials for the preparation of innovative and more stable non-liquid electrolytes and novel organic dyes as light absorbers. The thesis work was developed in the frame of the European project Innovasol concerning Innovative Materials for future generation excitonic solar cells that is devoted to the optimization of DSSC technology; thanks to the collaboration of six academic institutions (Cambridge, EPFL, Unito, Unipmn, TUD, Universidade de Campinas) and two industrial partners (Centro ricerca Fiat and Solaronix). One of the major problems of DSSC is their low stability, due to the high volatility of the liquid electrolyte together with the toxicity of some components (solvent used in the electrolyte and dyes). In this work non-liquid electrolytes were prepared by adding to methoxiproponitrile-based electrolyte 5wt% of inorganic or hybrid...
organic-inorganic nanoparticles prepared by researchers of University of Eastern Piedmont and Campinas University. Synthetic clays with different chemical composition (i.e. saponite and talcs) and TiO$_2$ aiming to prepare stable electrolytes. Saponites are phyllosilicates whose TOT structure is represented in figure 2. These materials have a negative charge layer, due to interstitial substitutions of Si(IV) with Al(III) atoms. This charge is normally balanced with cations located in the interlayer space. The nanoparticles size can be tuned by varying the amount of $H_2O/Si$ ratio used for the preparation of the synthesis gel. In this work, saponite materials prepared by using $H_2O/Si$ ratio of 20, 50, 110, 150 were tested (characterized by particles with dimensions ranging from 200 to 50 nm) were tested. The electrochemical measurements done on cells prepared by using non-liquid saponite-based electrolyte revealed a slight increase of efficiency for all cells. In addition, for all saponite-based devices (except for saponite prepared with $H_2O/Si$ ratio of 150 ratio) an increase of short circuit current ($J_{sc}$) suggesting a light scattering phenomenon, due to saponite nanoparticles, allowing to increase the overall cell efficiency. Beside saponite, synthetic talcs (that are magnesium silicates with neutral layers) were used as additive for non-liquid electrolyte preparation. In particular the surface of tested talcs were functionalized, by one-pot synthesis, with organic pendent groups ($CH_2CH_2CH_2NH_2$ or $CH_2CH_2CH_2NHCH_2CH_2NH_2$) into the interlayer space. I-V curves of talc-based devices revealed that the addition of talc has positive effect on the overall cell efficiency especially thanks to an increase in the open circuit voltage $V_{oc}$. This effect should be due to a possible positive influence of talc on avoiding recombination of electrons. The best performance obtained was an improvement of the relative efficiency of ca +12.5% for the cells with talc with respect to those prepared by using liquid electrolyte. After this preliminary work, quasi-solid electrolytes were prepared by adding 20%wt of saponite (both inorganic or hybrid organic-inorganic saponite prepared by introducing COOH and $NH_2$ groups on the surface) to ionic-liquid based electrolytes. Obtained results showed that the DSSC performances strongly depend on the nanoparticle size. An increase on the relative efficiency of ca +15% was obtained by using greater saponite particles. Beside layered solids, gel electrolytes were also prepared by adding to ionic liquids $TiO_2$ nanoparticles. Obtained results showed that the solar cells performance increase occurs only by using gel ele-
trolyte prepared by adding 15wt% or 20wt% obtaining an increase of relative efficiency of ca. +25.6% with respect to the ionic liquid electrolyte. These results suggested the occurring of a possible Grotthus-like mechanism which allows an increase in the redox couple $I^-/I_3^-$ diffusion. Novel sensitisers were in addition tested for DSSCs preparation. Two antisymmetric squaraine dyes (Fig. 3), with different length of carbon chain prepared by researcher of University of Turin were tested. The obtained results indicated that the VG10C8 (squaraine with longer chain) allowed to increase the performances of DSSC devices improving both efficiency and stability. It was pointed out that an increase in the carbon chain length allowed to obtain increased relative efficiency of 37% with respect to the dye with the short chain. An emitting dye, based on diphenylaniline group, the so-called D5 dye (fig. 3), was tested in DSSC prepared with a ionic-liquid-based gel electrolyte prepared by adding saponite nanoparticles. The so-prepared DSSC showed good performances with respect to cells prepared by using Ruthenium dyes and ionic liquid electrolyte overcoming the $RuL_2(NCS)_2$:2TBA(L=2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA = tetrabutylammonium), N719 in literature, in combination with an IL electrolyte, and the $RuLL'(NCS)_2$:2H_2O(L=2,2'-bipyridyl-4,4'-dicarboxylic acid; $L' = 4,4'$-dinonyl-2,2'-bipyridine), Z907 in literature, in combination with the gel electrolyte. As conclusion of this work, in order to solve the sealing problems encountered during the preparation of QuasiSolid-DSSCs two new cell designs were tested. The first method, called electrolyte bath, consists in soaking the titania electrode into the electrolyte solution before the sealing process. In this way, using gel electrolyte it should be possible to obtain more stable junction and it should be possible to solve the physical problem due to the sealing. Even if worse performances were obtained, the $V_{oc}$ enhances of +11% with respect to the reference acetonitrile-based electrolyte. The second method consists in the use of coloured $TiO_2$ nanoparticles. The coloured $TiO_2$ nanoparticles were obtained by soaking the untreated titania nanoparticles into a N719 dye solution for one night; then the mixture was filtered, by using a Buchner funnel, obtaining a coloured powder with the dye absorbed on the $TiO_2$ surface. The powder was injected into an ionic liquid electrolyte. The method was tested adding 5wt% or 10wt% of nanoparticles, coloured and untreated, demonstrating that the coloured particles into the electrolyte don’t affect the performance of the cells.
Introduction: Solar Energy market and new technologies

"There is something fundamentally wrong with treating the earth as if it were a business in liquidation"
Herman Daly

Crisis, from ancient Greek "Krisis", decision, choice, or, in the younger and newer meaning, any event that is an unstable and dangerous situation, is our actual situation. In the last twenty years all over the world, people, politicians, economist and governments have understood that our world is collapsing. The last two centuries of industrialization and of exploitation of all useful resources have brought us to a situation in which it is not possible to continue with the same lifestyle, with the same principles which lead economy for years. In particular it is not possible anymore to produce energy and electricity only exploiting fossil fuel and non-renewable resources. The effect of the Green House Gases was recognized ten years ago with the Kyoto Protocol and finally countries all over the world have started to fight the rampant pollution. Off course the control of GHG emissions is not enough if there are not efficient and ecologic way to produce energy and electricity. Here the crisis, or the Krisis, from the ancient greek meaning: decision. There are many possible routes to "save our planet" and many possible technologies to produce clean and green energy: from the wind or with the hydroelectric power plant, from the nuclear energy, if in future will be possible to use the cold fusion or from the sun power. In any case if, all us, we start to think with an ecologic-minded and we stop us to exploit and waste each possible resource, our world and next generation will thanks us.

Solar Energy

In a global view, as said, it is not possible anymore to think to produce energy only from fossil fuels. One of the best way to realize all EU limit about renewable energy and Green House Gas emissions, or in a more general idealist and ethic way to preserve our planet, is obviously the solar energy. Solar energy research was born in 1954 when Bell Labs announced the invention of the first modern silicon solar cell. The first cells have about 6% efficiency. Obviously it
was too early and too much expensive for a huge spread of this technology, nevertheless the future revolution in energy productions got its starting point. For many years researches continued in different directions without seeing a satisfied business market. From the primitive silicon solar cell built in the Bells laboratory, the solar devices have increased (figure 4) their efficiency conversion, in an incredible way, obtaining last conversion coefficient for aerospatial application of 42.8% at the University of Delaware [1].

I, II, III generation. Today’s solar energy technologies concern many different types. The different types of solar devices can be subdivided into three big categories evolving in time. I generation regards in major part today’s commercial module production and it is based on a well-certified technology (for all types a 20 years stability is the minimum guarantee); in other words it concerns all silicon based modules: from heating solar panels to monocrystalline modules and from amorphous Si-PV to polycristalline Si-Panels. II generation is the so-called thin film technology, concerning CdTe, GaAs, InGaP, CIGS/CIS, and other types which are conquering a big part of the solar energy world market. In particular, their principal attractive should be less materials used, and consequently lower costs, respect to the I generation devices. A very interesting innovation of the thin film solar cells is the possibility to make flexible cells on polymer sublayers, instead of glass layers; this characteristic allows to many commercial applications. III generation, instead, includes all new technologies which take advantage of different working principles. Particularly III generation devices[2] should can overcome the Schkley-Queisser limit (around 30 − 40% of efficiency) imposed for p-n junction solar converter. Specifically this III generation concerns devices as: Dye Sensitized Solar Cells(DSSCs), Organic
Polymeric Solar cells (OSCs), concentrated solar power and generic multilayer devices. In particular the most utilized, even if costs and LCA prediction states the contrary, is the silicon based PV. As shown in figure 5 the solar market in the year 2006 was completely dominated by silicon technology, over the 70% of the total production. In these years it is to consider that every prediction is very difficult to do, due to the fact that solar market is in constant growth as well as new solar technologies. In fact observing datas predicted in 2007 for the whole world (figure 5) and datas of 2009 only for EU countries (figure 6), it is clear that predictions strongly underestimate the solar market explosion. For instance, it is interesting to know an Italian law, the so called "conto energia", which should be help all investments in renewable energy, particularly the solar sector, that started to consider the thin film technology and the third generation only since the third "conto energia" of the 6/08/2010. Symbolic, to understand how much the politicians is not able to evaluate this economic phenomenon, is the white paper, where EU underestimated the solar market explosion which it was made in 1997 when the European Commision set a target for the 2010 of only 3000 MW. If the EU, ten years ago, didn't understand the phenomenon, the Italian politicians do not understand it yet very well. Quite funny, in fact, is the Italian environmental policy. With the third "conto energia", the Italian governement fixed public investments for solar energy only for 8000 MW up to the 2020. In the first two months of the 2011 the limit was overbounded!

Labour market. Apart from incentives, the development of photovoltaics requires the transfer of knowledge from academic institutes and research centres. In a world crisis period, especially for EU countries, the photovoltaic sector can give some real answer to the huge problem of the unemployment all around the Europe. In fact, a recent EU project, PVEmployment, has tried to predict the consequence of a green economy based on the explosion of the photovoltaic sector in next years, up to the year 2030. The conclusion is incredibly satisfying: in best simulations the new market can be overcame milions of new job places, as direct and indirect jobs, with an average growth of more than 150000 new worker each year. Particularly interesting is the changing in the job market...
mentality: from a vertical enterprise idea to a decentralised new way; in other words the photovoltaic sector with its decentralised structure leads to jobs in the less industrialised areas and decrease the disequality scissor of money and power holder and moreover it can be brought different countries on the way of the energy self-sufficiency.

Solar energy and DSSC production costs. A very early study [8] estimated the costs for a 20 x 30 cm$^2$ sized 3 Wp DSSC to be 4-5 dollars according to the following table (figure 7). These predicted costs were equivalent to the unthinkable price, in comparison with today’s price, of 28000 dollars for a 3KWp DSSC module; nevertheless the huge total price was less than the first monocrystalline silicon cells, which they were around 45000 US dollars for 3KWp.

This right prediction opened the doors to this young research field up to now, when today’s price are much more economical advantageous. For instance, the levelized electricity cost (LEC) of OSCs, assuming 5% efficiency and a durability of 5 year, should be around 0.85 dollars/KWh. Instead assuming 15% efficiency and a durability of 20 years (next step for DSSC reasearch) the LEC decrease until the order of 0.10-0.05 dollars/Kwh, a very competitive price[9].

Interesting is to observe as the great difference between the cost of a DSSC and a OSC is due principally to the ITO glass price. In fact all the other costs are almost equivalent or lower for DSSC (figure 7). Finally, here below, it’s showed the general comparison in cost among different solar technologies and among OSC and all different common types of energy (figure 8). The most incredible innovation for organic PV is the industrial production process, based on screen printing: it was demonstrated that it’s possible to produce 1000 100000 m$^2$ per day(an equivalent production of Silica solar cell takes 1 year)[10]. In the end the cost of the solar energy starts to be comparable and competitive, against other energy production methods, with all organic types, while for the more mature si-PV technologies it remains too much expensive for the world market.

As said just above, organic cells LEC varies between 0.07− 0.13 dollars/KWh (for $\eta = 15\%$ and durability 20 years) and 0.49−0.85 dollars/Kwh (for $\eta = 5\%$ and durability 5 years) . Obviously higher prices are completely out of suitable business investments.
Figure 7: (top) an early business study on DSSC (1996). (bottom) comparison cost (2009) between DSSC and organic solar cell (OSC)

<table>
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<tr>
<th>Material Type</th>
<th>DSSC</th>
<th>OSC</th>
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<tbody>
<tr>
<td>Active</td>
<td>4.25</td>
<td>0.84</td>
</tr>
<tr>
<td>Inactive</td>
<td>10.79</td>
<td>3.01</td>
</tr>
<tr>
<td>Total</td>
<td>15.04</td>
<td>3.85</td>
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<table>
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<tr>
<th>Process Costs</th>
<th>Overhead Costs</th>
<th>Module Material Costs</th>
<th>Module Costs</th>
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<tr>
<td>($/m²)</td>
<td>($/m²)</td>
<td>($/m²)</td>
<td>($/kWp)</td>
</tr>
<tr>
<td>OSC</td>
<td>9.20</td>
<td>11.76</td>
<td>20.96</td>
</tr>
<tr>
<td>DSSC</td>
<td>25.24</td>
<td>18.26</td>
<td>43.50</td>
</tr>
<tr>
<td>CGT</td>
<td>4.48</td>
<td>12.13</td>
<td>16.61</td>
</tr>
</tbody>
</table>

Figure 8: (top) Cost comparison between different solar technologies; (bottom) Comparison between OSC energy production and common resources.
Environmental costs: a LCA study. There are many LCA studies on DSSC but unfortunately, there no exist a precise prediction, as for the money costs. This aspect is a direct consequence of the fact that a well-defined industrial production process doesn’t exist yet and of the fact that DSSCs are still prototypes and suffer of many ”hand-build” processes. However a general, low accurate studies can be take into account to observe which parts of the process are more expensive in terms of energy and pollution.

A recent study of ECN Solar Energy in Netherlands \[11\] estimates very interesting values of Energy Payback time (EPBT) and of GWP for the DSSC production. In fact, in South Europe the EPBT was estimated around only 1 year, while the life-cycle greenhouse gas emissions can be as low as 20\text{gCO}_2\text{eq/KWh}, depending on the lifetime of the DSC systems. For this study was used a performance factor of 0.75, which takes into account all losses due to inverter, not-optimal orientation, temperature fluctuations and other factors. As said just above, many parts of the production process, unfortunately, are not taken into account in this result because of different technique of the different research centers. All results reported here refers on an hypothetical 1\text{m}^2 area module. Figure 9 shows all percentage impact of different parts of the device. It can be seen that large part of the environmental impact of DSSC derives from the TCO glass. This situation can be improved by using thin glass or other types of substrates, such as metal or polymer foil. The two final histograms (figure 10) the evaluation of the \text{gCO}_2\text{eq} emissions. The GWP strongly depends on the lifetime. It was estimated in a range of 20-120 \text{gCO}_2\text{eq/KWh}. Comparing this result with other renewable energy (figure 10) it’s possible to see that if 120 is still too big for a promising technology, the result of 20 \text{gCO}_2\text{eq/KWh} is a completely satisfactory value to compete and substitute (in future) the classical Si-PV modules. For the energy payback time the result is quite incredible. In fact in the South Europe hypothesis ( AM 1.5, irradiation of 1700 kWh/m2/yr), it is only of 0.8 years.

Figure 9: LCA of different parts of a DSSC \[12\]
Figure 10: (on the left) Green house gas emission depending on the life time (5, 10, 30 years) (on the right) Comparison among different energy production methods in terms of $gCO_2eq/KWh$ [13]
Chapter 1

DSSC: an overview

1.1 Working principles

DSSC, as all solar devices, in order to generate energy from the photons energy must be able to adsorb the light, generate excited and delocalized electrons and collect them into an external circuit. The great difference, from typical silica-based solar cells, is that the three different mechanisms were inspired by observations in nature. In fact leaves of every plants split this process into different parts: adsorption of photons, the transport and the collection. DSSCs, in fact are composed by different interacting parts. First dyes, organic or inorganic, act as a photons antenna and are able to adsorb the energy light. Second, the electrode, usually based on dioxide semiconductors, acts as charge carriers, in order to separate all excited electrons generated by the dye. The regenerative behaviour, necessary to obtain a useful device able to work for many years, is obtained by an electrolyte. It must regenerate the vacancy in the energy level of the dye, using its redox couple, usually the couple $I^-/3I^-$. The latter part of the cell consists of the counter electrode, as in every electrochemical cell, to complete the oxidoreduction process of the electrolyte. Figure 1.1 shows in a schematic way the basic working principles which can be resumed in few oxidoreduction reactions:

1. absorption of a photon of energy $h\nu > E_{gap}$ of the dye;
   - $Dye + h\nu \rightarrow Dye^*$

2. transport of the delocalized electron generated through the electrode of $TiO_2$ until the ITO;
   - $Dye^* + TiO_2 \rightarrow Dye^+ + TiO_2^-$
   - $TiO_2^- + ITO \rightarrow TiO_2 + ITO^-$

3. regenerative oxidoreduction process into the electrolyte;
   - regeneration of oxidized dye; $3I^- + 2Dye^+ \rightarrow I_3^- + 2Dye$
   - redox couple regeneration by the counter electrode $I_3^- + 2e^- \rightarrow 3I^-$
All these processes must have some requirements in order to obtain high performance for the photoelectrochemical cell. In fact it is necessary that all components interact perfectly with all the others, in particular it’s compulsory to analyze the energy levels among materials and the recombination kinetic to minimize all leakage current and losses of energy inside the device. The first point to take into account is the limit of available energy. The maximum f.e.m. corresponds to the difference of potential between the conduction band of the $TiO_2$ and the redox potential of the electrolyte.

![Dye sensitized solar cells cycle](image)

**Figure 1.1: Dye sensitized solar cells cycle**

### 1.1.1 Titanium electrode

Electrode materials must have some fundamental requirements. First of all, by the fact that the light is absorbed by the dye, the electrode must be transparent; for this purpose large band gap semiconductors ($E_{gap} \geq 3.0eV$) are the best choice. Second requirement is about the energy level, relatively to other components: in particular relative the LUMO of the dye, it must be less negative in order to create a rapid spontaneous flux. Third requirement is the high porosity and the high surface area. This is a consequence of some economic trade-off but also for some physics limit for the electrons transport; high-surface area means less materials needed because of the high quantity of dye on the electrode surface. Consequently it means cheaper material cost but it also means a reduction in recombination effect of electrons during the transport. Last fundamental characteristic for the electrode is obviously the high reactivity with the dye: the best materials reacting with carboxylic groups which lie in the dye, are the dioxide semiconductors. There exist many materials with suitable characteristics, like $ZnO$, $SnO$, $Nb_2O_5$, $In_2O_3$, $TiO_2$ or combination among them. For instance high performance was obtained with a mixture of $SnO_2/ZnO$.

However state of arts for the electrode in DSSCs technology is to use titanium dioxide $TiO_2$ in the anatase phase and best performances are obtained with it.
1.1.2 Dye

The dye has probably the most important aim in DSSCs. A good choice for a sensitizer must follow some basic rule. First it should absorb as much light as possible; in particular it must absorb light in the visible spectrum and it mustn’t generate only heat energy; in order to achieve this feature best dyes have different peaks into the visible range to minimize the waste of photons absorbed. In fact as described later in chapter 2 the best absorbing efficiency for SC and dye corresponds in the region close to the peak, while photons with energy too high are wasted. For this purpose a very useful measurement is the IPCE, incident photon to current efficiency, to well-understand the efficiency conversion. Second, dyes must be very reactive with the SC surface and must be attached easily and strongly. Usually dyes utilized carboxylate or phosphonate functional groups, to attach to dioxide semiconductors. Third characteristic, that a dye must have, is a good electron injection efficiency in the SC conductive band. In order to generate the electron flux from the excited state of the dye towards the SC the energy hopping must be spontaneous; thus the excited dye must have a more positive state respect of the CB of the semiconductor. Moreover the ground state of the dye must have the energy level just below the redox potential of the solution in order to ease and to speed the regeneration of the dye, in order to avoid recombination and back current effect. Finally, it should be stable enough to sustain about $10^8$ turnover cycles corresponding to about 20 years of exposure to natural light.

1.1.3 Electrolyte

The electrolyte in DSSCs, together with the semiconductor is the responsible of the positive energy generates by the solar cell. In fact the maximum power allowed by a DSSC is the difference of potential between the conduction band of the SC and the redox potential level of the electrolyte. A second fundamental feature, that a suitable electrolyte must have, is about the reduction of the photo oxidized dye: it must be as fast as possible. For this purpose the electrolyte must have its redox potential a little bit more positive than the ground state of the dye. Last task of the electrolyte is as charge carrier between the counter electrode up to the junction surface with the dye, in order to close the circuit cell. For this task a well-chosen electrolyte must have high diffusion coefficient and low viscosity in order to obtain a transport process as faster as possible. For quasi solid electrolyte, instead the key feature is only the diffusion coefficient, cause the high viscosity sought. The most used redox couple for DSSc is the iodine/triiodide couple. Even if it is the most suitable couple found up to now, it presents some no-negligible problems. In fact the iodine/tri iodine is high corrosive and consequently cell sealant must be resistant against iodine oxydation; moreover the triiodide is darkly colored and can absorb a portion of the visible light. This aspect, in fact is the last basic feature on which it is possible to easily "joke" with the electrolyte. In general a transparent electrolyte is the best choice, in order to do not absorb the light in a useless part of the cell for the electron collection but it is not the only choice available. In fact, in some cases it can be a good behaviour if the electrolyte interacts with the light and reflects it again towards the electrode.
1.1.4 FTO and surlyn

One of the last part of the complete cell, but not for importance, is the sealer tool. In fact, in order to obtain a good stability and durability of DSSCs, it is necessary an efficient way to attach the two glasses, electrode and counter electrode, together. Best sealants got are the surlyn gasket. Essential feature is that it has to be resistant to electrolyte oxidation to avoid leakage of the liquid; moreover it has to be very tiny, from $20\mu m$ up to $100\mu m$, and it must have the melting point at a temperature about $100^\circ C$ in order to bind the two glasses without damage the other parts of the cell. The utilized surlyns have thickness of $25\mu m$ or $60\mu m$.

Both glasses for the electrode and the counter electrode must have a conductive layer because electrons accumulated by the electrode must flow outside the cell towards the external metal contacts. Obviously glasses and conductive sublayers must be transparent, must have a good light transmittance (figure 1.2) and they must have a very low resistance. In general TCO (transparent conductive oxide) glasses are used with a layer of fluorine doped tin oxide (FTO) with conductive resistance of $7 \Omega/cm^2$ or less.

![Figure 1.2: FTO transmittance spectrum](image)

1.1.5 Counter electrode

The last part of a DSSC is the cathode of the photoelectrochemical cell. It works as catalyst for the reduction of the oxydized species of the electrolyte ($I_3^-$). The best catalyst for the redox couple iodine/tri-iodine, up to now, is the platinum elements and the best way to spread it on the glass it seems to be to use an alcoholic precursor of platinum and then burn it.

1.2 A bit of theory

Some few concepts are needed to understand the working mechanism of the DSSCs. First of all the Planck-Einstein relation which relates the energy of the photons to the frequency, or the wavelength of the light.

$$E = h \nu = \frac{hc}{\lambda} \quad (1.1)$$

where $h, c$ are the constant Planck and the constant speed of light and $\nu, \lambda$ are the frequency and the wavelength.
Noteworthy is the concept of AirMass (AM); in fact if it’s known that the solar constant, the maximum solar power on a perpendicular surface, is 1367 W/m² just outside the atmosphere, it’s quite much difficult to know perfectly the solar constant at the ground. The irradiance which arrives to the sea level depends on many factors: the latitude, the season, the hour during the day, etc.. The Air Mass, by definition, is the effective length of the path and the most quick path. After defining the Air Mass as $AM = 1/\sin\phi$ (fig. 1.3) it’s possible to compute the effective light path by $d = h/\sin\phi$:

- AM 0, solar constant outside the atmosphere (1367 W/m²);
- AM 1, perpendicular condition;
- AM 1.5 ($\phi = 42^\circ$C) this last one is Europe real condition. In fact AM 1.5 is one of the standard for all solar panel tests.

In order to measure the conversion efficiency of the power light incident it is necessary introduce two quantities: the open circuit voltage $V_{oc}$ is the maximum voltage generated by the solar device when it’s connected to an infinite resistance, thus when no current flows. On the contrary, when there is no resistance, the short circuit current $I_{sc}$ can be measured; the latter is an evaluation of how many photons, and of which energies, can be absorbed and used to generate usefull electric energy. Their product is the ideal power, in other words the maximum power, that can be generated by the photoelectrochemical cell.

The last terms must be introduced is the fill factor $FF$, defined as follow:

$$ FF = \frac{V_{max}I_{max}}{V_{oc}I_{sc}} $$

(1.2)

where $V_{max}, I_{max}$ are respectively the maximum voltage and current generated. The fill factor is a usefull parameter to quickly understand the well design of a cell tested; in fact, it is a measure of how much is filled the theoretical box representing the maximum power available in the I-V curve (figure 1.4 Using this three parameters, which depend on many intrinsic factors and on the design of the cell, it miss only the definition of the power efficiency conversion of the cell, which can be defined as:

$$ \eta = \frac{P_{max}}{P_{inc}} = \frac{V_{max}I_{max}}{P_{inc}} = \frac{FFI_{sc}V_{oc}}{P_{max}} $$

(1.3)
For the sake of completeness it must also be introduced the so-called **Incident photon to current efficiency** IPCE, or **quantum efficiency**, which is nothing else that the total conversion efficiency. 

\[
IPCE = \frac{J}{\phi_{\text{photons}}} = \eta_{\text{abs}}\eta_{\text{sep}}\eta_{\text{coll}} \tag{1.4}
\]

where \( J \) is the photocurrent generated, \( \phi_{\text{photons}} \) is the flux of photons incident and the three \( \eta \) are respectively the efficiency of absorption, of separation and of collection as described at the top of this chapter. In this way is possible to split and analyze the process of light conversion into the cell in the different parts; thus all factors introduced can be referred to intrinsic properties and to the kinetic of electrons movement. As said just above the excited states, the electron transfer and dye and electrolyte regeneration are in competition among them. In a very generic way the order of magnitude of this processes is shown in figure 1.5. For a more exhaustive and mathematical treatments let’s see next chapters.

### 1.3 Basic equivalent circuits

In order to well-understand all working principles involved in DSSCs, some simple equivalent circuits are noteworthy. A photoelectrochemical cell, in first approximation, works exactly as an ideal generator. The generated photocurrent, when the cell is illuminated, is directly proportional to the flux of photons incident and to the external quantum yield, a measure depending on the intrinsic chemical and physics properties of materials used, such as adsorption of light, transport and separation of charges. In a very generic way the short circuit
density photocurrent can be expressed as:

$$J_{SC} = q \int \phi_s (E) \cdot QE (E) \, dE \quad (1.5)$$

where $\phi(E)$ is the spectral density incident flux of photons and QE(E) is the external quantum efficiency.

Another terms necessary to modelize the cell is the dark current, which appears just closing the cell on an external resistance. This term has an exponential trend, is opposite in sign to $1.5$ and represents the so-called diode behaviour

$$J_{dark} (V) = J_0 \left( e^{\frac{qV}{k_BT}} - 1 \right) \quad (1.6)$$

where $J_0$ is a constant that depends on material intrinsic properties, which they are described in the following chapters, $k_B = 1.3806503 \times 10^{-23}$ m$^2$ kg s$^{-2}$ K$^{-1}$ is the Boltzmann constant and $T$ the absolute temperature. Thus, the ideal characteristic of a photoelectrochemical cell is obtained by adding $1.5$ and $1.6$

$$J(V) = J_{SC} - J_{dark}(V) = J_{SC} - J_0 \left( e^{\frac{qV}{k_BT}} - 1 \right) \quad (1.7)$$

$$J(V = V_{OC}) = 0 \Rightarrow V_{OC} = \frac{k_BT}{q} \ln \left( \frac{J_{SC}}{J_0} + 1 \right) \quad (1.8)$$

Analyzing these results, taking into account the power relationship $P = V \cdot I$, it’s clear that the ideal cell generated positive power only for $0 < V < V_{OC}$; otherwise the ideal device works as a photodetector and adsorbs potential energy (fig. 1.6).

Obviously this is an ideal behaviour. The first step to modelize a realistic device
Figure 1.6: (on the left) equivalent ideal circuit: the diode represents the voltage at junction, while the generator represents the current create by the light. (on the right) an ideal example of the J-V curve

is to introduce the resistance, $R_s$ and $R_{sh}$, respectively in series and in parallel. The first one takes into account many factors: in particular contact resistances among different materials, the external electric contacts, etc.. The second one, $R_{sh}$, instead considers leakage current, the recombination effect and the ions diffusion into the electrolyte. The latter it will be analyze in more details in the following chapters. In conclusion a more realistic equation can be written as follow, and it is represented by figure 1.7

$$J(V) = J_{sc} - J_0 \left( e^{\frac{eV}{nKT}} - 1 \right) - \frac{V + JAR_s}{R_{sh}}$$

Figure 1.7: first: equivalent circuit; second: effect of changing in $R_s$ and $R_{sh}$
Chapter 2

Photoelectrochemistry principles

One of the main differences between classical solar energy systems and photoelectrochemical cells, as said in the introduction chapter, is the way in which electrons are carried until external circuits in order to generate a potential energy. In fact, in typical silica-based solar cells, photons are harvested by the semiconductor, then, electrons generated are carried outside the cell by the semiconductor itself.

Instead, in photoelectrochemical cells, the process is split into different parts. Dyes, organic or metal-based, harvest photons, while carry mechanism is done by the semiconductor. In every semiconductor-based systems there is, instead, a huge difference with the photosynthesis natural process in particular in the part concerns the transport. In fact, in nature, carriers move through the system by a molecular hopping mechanism, while in SC systems carriers are highly delocalized and move following a simple diffusion process; consequently, they can quickly move for large distances avoiding surface recombination and other "dark current" mechanism.

Well-understanding of these mechanisms is possible only with a more deep point of view.

2.1 Electronic properties of semiconductors

2.1.1 Crystal structures

First deep look necessary to understand SC properties concerns lattice structures of these inorganic solids. There are many different available structures for SCs. It’s possible to subdivide the major part of SCs into two big classes:

- Adamantine solids, sharing common feature of having an average per atom of 4 valence electrons;
- Non adamantine solids.

The most basic structure is the so-called face-centered cubic (fcc) lattice (fig. a). Many covalent semiconductors, belonging to the adamantine class, are
based on fcc lattice with some variants. For example, Si and Ge, attempt to achieve maximum bonding between nearest neighbors; this implies that tetrahedral structure is maintained but atoms follow the same principles of NaCl crystals adopting a cubic diamond lattice (fig. b). Another typical structure is the zinc blende, taken by covalent, binary SCs, with atoms of similar electronegativities, as GaAs, InAs, InP and GaP (fig. c). Otherwise in SCs with atoms with different radii and electronegativities, in order to maintain a lattice with a 1:1 cation-anion stoichiometry, the lattice adopted is hexagonally close-packed with only one-half of the possible sites are occupied. This configuration, called wurtzite structure, adopted by ZnO and CdSe (fig d) is more open than the zinc blend and the bonding is more ionic.

**Non adamantine** solids include the general classes of metal oxides like Fe$_2$O$_3$, TiO$_2$ and SrTiO$_3$. In particular titanium dioxide occurs in two different structures: the rutile lattice, derived from a body-centered cubic (bcc) configuration and the anatase lattice, derived from a fcc. In both cases to maintain a 1:2 stoichiometry only on-half of sites are occupied by Ti atoms. Titanium dioxide is the most used SCs in DSSC technologies due properly to its properties (fig. e,f), specially the anatase phase. Last structure is denominated a *layer-type* and is based on van der Waals interactions between different layers (fig. g).

Figure 2.1: SC lattice; a)NaCl, b)Si, c) GaAs, d)ZnO, e)TiO$_2$ rutile, f) TiO$_2$ anatase, g)MoS$_2$. Black circles represent more electronegative elements, while white circles the less negative.
2.1.2 Band structure

The band structure for SCs could be explained in a very simple and fashionable way by analogy, using some concepts involving Molecular Orbitals (MO) treatments of organic chemistry. Anyway, as first step it should be interesting to see the physics approach to SCs.

**Fermi level in SCs and band model.** Consider a solid of N atoms, its frontier will have 2N energy eigenstates, each with two electrons of paired spin. Atoms with odd valence number (Al: 3s^23p^1) will have a partially occupied frontier band and consequently solids of this type have electrons delocalized. Instead, atoms with even valence number (Si: 3s^22p^2) will have a fully occupied frontier. Energy gap of SCs depends on many parameters as atoms energy levels, lattice structures, doping, ... Picture 2.2 shows a very simple representation of SC and insulator energy gap.

![Figure 2.2: Energy Gap for (a) SC (b) generic insulator](image)

In a statistics point of view for high density electron ensembles it’s necessary the introduction of the **Fermi level**. In a thermodynamic meaning, the Fermi level, is defined as the energy where the probability of finding an $e^-$ is one-half. Thus in solids, $E_F$ represents a sort of electrochemical potential (with reference at $T=0K$ and in vacuum) such that all electronic levels below $E < E_F$ (VB Valence Band) are occupied while for $E > E_F$ all levels are empty (CB conduction band). Correctly speaking, this is a *likely* behaviour. Electrons occupancy in SCs follow the Boltzmann distribution function:

$$n_e \approx N_C e^{-\frac{E_0 - E_F}{k_B T}}$$  \hspace{1cm} (2.1)
where $E_C$ is the conduction energy level, $N_C$ is the electron density at the conduction level and $K_B T$ controls the thermal excitation of electrons from VB to CB. This is a fundamental point of SCs; in fact for each electron excited in CB there exists a vacancy, a hole in VB working as a positive carrier. This vacancy occupancy in VB also follows the Boltzmann distribution:

$$n_p \approx N_V e^{-\frac{E_V - E_F}{k_B T}}$$

Let’s suppose $n_p = n_e$, in other words, for each excited electron exists a corresponding vacancy, equations 2.1 and 2.2 become:

$$n_i^2 \approx N_0 e^{-\frac{E_C - E_F}{k_B T}} \approx N_0 e^{-\frac{E_G}{k_B T}}$$

This explanation refers to the intrinsic SCs where the Fermi level is in the middle of the band gap. In the extrinsic SCs, instead the Fermi energy level lies closer to VB, in the p-type, or to CB, in the n-type(figure 2.3). This is due to a doping with donor or acceptor atoms, exactly as adding acids or bases into a solution that moves the Fermi level because the equality $n = p$ is no longer correct. For example, P atoms (group V) can act as donor for Si (group IV), while B or Al atoms (group III) act as acceptor. The doping technique is widely used for Si-based solar cells while is not used for DSSCs, except in rarely cases. Anyway, in this work, it will not be take into account even if could be an interesting field of research in order to improve SCs properties not only as charge carrier but also to harvest photons.

Figure 2.3: a) intrinsic type, b) n-doped, c) p-doped.

**Extended Huckel theory.** The model is based on Molecular Orbital treatment in organic chemistry (see chapter 3 about dyes). The band structure can be obtained like for the LUMO-HOMO gap by analogy defining as HOMO (the highest occupied molecular orbital) of the SC the set of valence band and as LUMO (lowest unoccupied molecular orbital) the set of conduction band. In this way the delocalization properties of electrons and holes were obtained simply by increasing lattice structures to infinity. In physics is also called *tight binding theory.*

Another usefull observation is that all energy levels are located with respect
to a reference level which, by definition, is the energy level of the electron in vacuum; in general more tight bound correspond to more negative energies (for instance the energy of 1s in H atom corresponds to -13.6 eV).

**Chemical and optical properties.** Most of SCs can be subdivided in covalent and ionic solids, as seen just above. This characteristic, of course, affects the charge transport behaviour. A covalent solid, such as Si, can be modeled, by analogy with polyene, as bonding and antibonding combinations of Si atomic orbitals. In an ionic crystal, instead, such as TiO$_2$ the valence band derived from the 2p orbitals of O$^{2-}$ while the conduction band derived from the empty 3d orbitals of Ti$^{4+}$. The different nature of VB and CB will obviously affects band structure. One first consequence is that ionic SCs generally are more stable towards corrosion and passivation than covalent solids. An explanation can be derived relating chemical reactivity to energy band gap. Thus, in covalent SCs, where $E_G$ derives from bonding and antibonding orbitals of the same atom type, the $E_G$ is relatively small and consequently the solid is highly reactive. On the other hands, in ionic solids, atoms are very different in energy, so the band gaps are usually very large. Consequence of great band gap is the poor chemical reactivity, such oxidation as corrosion. This property, of course, is an expected good behaviour for materials which must be stable for long time. Another important observation concerns valence and conduction band; as said valence band derives from orbitals of anions for metal oxides. In fact, since experiments results, an important behaviour of all metal oxides is to have all the same valence band ( from the 2p orbital of O$^{2-}$) while the band gap is widely different, deriving also from cations. This characteristic can be generalized to all SCs. The generalization, called common anion rule, states that the valence band is dominated by orbitals of the lattice anion, while conduction band is dominated by the lattice cation.

In order to analyze optical properties of semiconductors, the fundamental equation that must be defined is obviously the relation between the energy and the light wavelength:

$$E = h\nu = \frac{hc}{\lambda} \quad (2.4)$$

where $\nu$ is the frequency, $\lambda$ is the relative wavelength and $h = 6.62606957 \times 10^{-34}$ Js the Planck constant. This relation with the Spectral irradiance (fig. 2.4) gives a very clear idea of which are the best semiconductors able to adsorb photons. In fact, even if SCs with small ($E_G \approx 1eV$) can adsorb almost all the sun spectra, it is also true that the major part of energy, such that $E > E_G$ is wasted. On the contrary, SCs with large band gap, such that TiO$_2$ ($E_G \approx 3.2eV$), are not very able to adsorb lot of the sun spectra, but they don’t waste any energy due to Joule effect, recombination or simply excitation of electrons. This is one of the reasons that brought to utilize TiO$_2$ in the DSSCs with an appropriate dye able to harvest missing wavelengths.
2.2 Reference potentials

2.2.1 Nernst equation

First of all, it’s necessary to describe the Nernst equation for a electrolyte solution that contain electroactive acceptors $A$ and donors $A^-$. The equation can be written as follows:

$$E\left(\frac{A}{A^-}\right) = E^0\left(\frac{A}{A^-}\right) + \frac{kT}{n}\ln\left(\frac{[A]}{[A^-]}\right)$$ (2.5)

where $[A],[A^-]$ are the concentration of respectively donors and acceptors ions, $E$ is the actual electrochemical potential, while $E^0$ is the formal, or reference, potential for the redox couple.

2.2.2 Fermi Level

In order to describe the exchange of charges in the SC/electrolyte interface the most important intrinsic value of a semiconductor is the Fermi level, which was already defined in 2.3; in fact, it determines the tendency of the semiconductor to transfer electrons, or in general charges, to other phases and materials. For intrinsic SCs, as already defined, Fermi level lies at mid point between VB and CB; for n-doped SCs it lies closer to electron vacuum reference level, so it has more negative potential, while for p-doped, it increases its potential.

By analogy, and remembering these assumptions, the Fermi level can be written as:

$$E_F = E_{Fi} - kT\ln\left(\frac{n}{n_i}\right)$$ (2.6)

$$E_F = E_{Fi} + kT\ln\left(\frac{p}{p_i}\right)$$ (2.7)

where $E_{Fi}$ is the Fermi level for the intrinsic SCs. If we want to shift the reference levels to more suitable values, $E_F$ can be trasformed into:

$$E_F = E_{CB} - kT\ln\left(\frac{n}{N_C}\right)$$ (2.8)

$$E_F = E_{VB} + kT\ln\left(\frac{p}{N_v}\right)$$ (2.9)
2.3 Equilibrium state at SC/electrolyte junction

The fundamental aspect to be understood in this junction is the presence of an electric field at the interface due to difference in two electrochemical potentials. The strength can be of the order of $10^5 \text{V cm}^{-1}$ and it develops spontaneously. Because the high delocalization of charges, the electrical field accelerates particles until velocities of the order of $10^7 \text{cms}^{-1}$ and separates charges for distances greater than 1 µ in less than 10 ps [17]. The charge transfer between the semiconductor and the electrolyte is governed simply by the difference into the density charge between them up to equilibrium is reached.

Depletion layer. For instance, to describe the junction let’s suppose a n-type SC. Obviously for this type of semiconductor before equilibrium is reached, the potential, thus the Fermi level $E_F$ of the SC is more negative. The solution potential, instead, can be related to the redox potential by $E_{\text{redox}} = qE(A/A^-)$. The initial difference of potential allows a flow of negative charges between the junction which disrupts the neutrality of the two parts separated. In other words, the SC charges itself positively, while solution negatively: in total a capacitor-like is charged. The depth over which charges can move is a well-defined zone in SC and it is called depletion layer $W$. Knowing $N_d$ of the semiconductor and the charges transferred per unit area $Q$, there exists a very simple definition $W = Q/N_d$. Thus, more doped (greater $N_d$) is the SC, thinner the depletion layer is and viceversa for a given redox potential for the solution. Of course the depletion layer can be control varying the redox potential level and it relative position against the Fermi level of the SC.

To well-understand all microscopic parameters, let’s suppose a test negative charge moves from the bulk of the SC, a quasi-neutral region, towards the junction up to the solution. Starting from the bulk, the testing charge is not influenced by the presence of any electric field. As the test charge goes closer to the surface and enters in the depletion layer it starts to react with the electric field due to the negative charges, which is directly proportional to the density of charge of the doped SC and the distance $x$ from the separation between the depletion layer and the quasi neutral region, exactly as in all Gauss problems.

Thus the electric field increases, for $0 \leq x \leq W$, as the distance $x$:

$$E(x) = \left(\frac{qN_d}{\epsilon_s}\right) x$$

(2.10)

where $\epsilon_s$ is the static dielectric constant. By the last equation, it is trivial, that the maximum of the electric field will be in $x=W$:

$$E_{\text{max}} = \left(\frac{qN_d}{\epsilon_s}\right) W$$

Thus, the maximum electric field in a SC/electrolyte junction is at the interface. Immediate it is the expression of the potential in function of the distance $x$ that it will be:

$$V(x) = -\left(\frac{qN_d}{2\epsilon_s}\right) x^2$$

(2.11)

that shows that the potential at the surface is more negative than in the bulk. Equation 2.10 and 2.11 can be schematically represented in fig. 2.5; the behaviour of the potential tipically is called band bending and it is the work need
to bring a test charge from the bulk up to the surface. It could be also interpreted as an activation potential for a determined process. One more definition

Figure 2.5: (a,b,c) respectively charge density, electric field and electric potential (d,e) band bending effect on CB and VB potentials

is necessary to do. Let’s define the *built-in voltage* \( V_{bi} \) as the maximum potential value, in absolute value, in the depletion layer. As shown in figure 2.5 it corresponds to \( x = W \):

\[
V_{bi} = \left( \frac{qN_d}{2\varepsilon_s} \right) W^2 \tag{2.12}
\]

\[
W = \sqrt{\frac{2\varepsilon_s V_{bi}}{qN_d}} \tag{2.13}
\]

This is the fundamental point, in fact, the built-in potential is a direct result of the initial potential difference between SC and solution.

\[
V_{bi} = \frac{|E_F - E(A/A^-)|}{q} \tag{2.14}
\]

The last quantity, that must be defined, is the *barrier height energy* \( \Phi_b \), introduced in the figure 2.5

\[
\Phi_b = V_n + V_{bi} \tag{2.15}
\]

\[
V_n = \frac{E_F - E_{cb}}{q} \tag{2.16}
\]

because recalling eq. 2.14 the barrier height energy depends only on the conduction band energy \( E_{cb} \) and the redox potential \( E(A/A^-) \) and consequently it is independent on the SC doping:

\[
\Phi_b = \frac{|E(A/A^-) - E_{cb}|}{q} \tag{2.17}
\]
The last concept, that must be understood to be able to calculate the most suitable junction, is the reference potential for the redox couple and for the Fermi level. Typically the Fermi level used as reference is the electron energy in vacuum, while for the redox potential usually it is assumed the normal hydrogen electrode (NHE). The NHE is more negative respect to the vacuum level of few electronvolt and precisely it may be defined, with a common reference as:

$$E_{F,\text{redox}} = -4.5\text{eV} - e_0E(A/A^-)$$

where $E(A/A^-)$ refers to the NHE and now $E_{F,\text{redox}}$ refers to the vacuum level. With this knowledge it is quite easy to calculate and graph some common potentials as shown in figure 2.6. A final useful consideration on charge density

![Figure 2.6: Energy level of several semiconductor and redox couples with vacuum level reference](image)

must be done: simply remembering the Boltzmann equation in SC it is possible to write a relation between bulk charge concentration $n_b = N_d$ and surface charge concentration.

$$n(x) = n_b\exp\left[\frac{qV(x)}{kT}\right] \quad (2.18)$$

$$n_s = n_b\exp\left[\frac{-qV_{bi}}{kT}\right] \quad (2.19)$$

where eq. 2.18 is the density in the depletion layer, while eq. 2.19 is the charge density on the interface. As shown, last equation the density reaches a minimum on the surface.

**Accumulation layer.** Different behaviour there appears when the redox potential of the solution is more negative than the Fermi level. In fact, in this situation charge flow is in the opposite direction and electrons move from the solution directly into the conduction band of the SC, a set much more similar
to the excited dye in DSSC. Injected electrons into the CB are delocalized and can move through all lattice and they are not limited to the doped sites. On the contrary the free zone in the SC, the so-called accumulation region is much thinner than the depletion layer. In fact, typically a depletion layer is approximately up to some micrometers, while the accumulation width is about 100 Armstrong.

**Fermi level Pinning.** The whole discussion is an ideal description. In fact during the equilibration process may occur that there is no direct correspondence between the amount of charge exchange and the changing in Fermi level. This behaviour is due principally to surface states which trap electrons during the process. This effect is called Fermi level pinning and can affect the theoretical prediction on the junction. In fact ideally, changing the concentration of redox couple, and consequently the potential level of the solution should correspond a modification in the \( V_{bi} \). When this doesn’t occur, it can cause by the surface states. It is possible to plot the degree of ideality of a junction only plotting \( V_{bi} \) or \( \Phi_b \) as a function of \( E(A/A^-) \). When the slope is 1 the ideal behaviour is obtained, instead, when is equal to 0 the complete Fermi level pinning effect. Anyway much more deep studies are needed to explain the surface states, which in this thesis work, are not treated.

### 2.4 Charge transfer

The difference of electrochemical potentials at a junction and the spontaneous developed field are necessary but not sufficient to create a constant flow of energy. To convert solar energy there should exist a non equilibrium flow of charges. Simplifying all the charge transfers could be shown as:

\[
e^{-}_{sc} + A_{solution} \rightleftharpoons p_{sc} + A^-_{solution}
\] (2.20)

Of course, at equilibrium the charges flow must be proportional to the concentration of electrons in SC near the surface and to the concentration of acceptors \( A^- \) in the solution, and vice versa. In a very generic way, the rate of injection into the solution can be written as:

\[
k_{direct} = k_{et} n_s [A]_s
\]

where \( k_{et} \) is the rate for electron transfer and \([A]_s \) is the concentration of acceptors. On the contrary the rate from the solution can be written:

\[
k_{reverse} = k_{et}^{-1} [A^-]_s
\]

At equilibrium, obviously they will be equal:

\[
K_{et} n_s [A]_s = k_{et}^{-1} [A^-]_s \tag{2.21}
\]

Away from equilibrium the dynamics should be explained by the difference of two opposite flow in the following way:

\[
-\frac{dn}{dt} = k_{et} [A]_s n_s - k_{et}^{-1} [A^-]_s
\]

and using (2.21):

\[
-\frac{dn}{dt} = k_{et} [A]_s (n_s - n_{so}) \tag{2.22}
\]
2.4.1 The Dark Current-Voltage

At this point a trivial step is the expression of the interfacial current. It’s enough to multiply for the charge and the area of the electrode A:

\[ I = -qA \left( -\frac{dn}{dt} \right) = -C(n_s - n_{so}) = -Cn_{so} \left( \frac{n_s}{n_{so}} - 1 \right) C = qAK_{ct}[A]_s \]  \hfill (2.23)

In these equations it still misses the explicit dependence from the voltage that can be obtained remembering:

\[ n_s = n_{so} \exp \left( -\frac{q(V_{bi} + V)}{kT} \right) \]

where \( n_s = n_{so} \) when \( V = 0 \). In this way the voltage dependence of the fraction \( \frac{n_s}{n_{so}} \) could be explicit and the dark current relationship becomes:

\[ I = Cn_{so} \left[ \exp \left( -\frac{qV}{kT} \right) - 1 \right] \]  \hfill (2.24)

2.4.2 Properties of the interface: from microscopic to macroscopic

By analyzing the last equation, now it’s possible to extract some general properties of the junction. First of all, from the exponential behaviour, it’s clear that for \( V < 0 \) the current generated is dependent on \( V \), while for \( V >> 0 \) it’s completely independent. This can be understood (fig: 2.7) by the effect of an external voltage which changes the charges density on the surface.

Figure 2.7: Voltage dependence: a) \( V > 0 \), b) \( V < 0 \)

This behaviour can be interpreted by the Le Chatelier’s principles in chemistry, which states “If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established”; thus, for reverse bias (\( V > 0 \)) the change of charge density doesn’t involve any change in current because it’s negligible, while for forward bias (\( V < 0 \)) the surface reactants increase exponentially.
Another typical way to write the I-V curve is:

\[ I = -I_0 \left[ \exp \left( -\frac{qV}{kT} \right) - 1 \right] \]  
\[ I_0 = Cn_{so} \]  

where \( I_0 \) is called exchange current. Obviously the same consideration also works if there is a ions concentration changing in the solution. Physically an increase in positive ions will produce a larger \( V_{bi} \), thus a larger \( n_{so} \) and in conclusion a smaller exchange current, due to the minus sign, and a highly rectifying diode behavior (curve 1). Vice versa more negative ions produce a poorly rectifying diode behaviour (curve 2 figure 2.8). This is a fundamental point to design a well-working photoelectrochemical cell; in fact, to generate high current under illumination, an high rectifying behaviour is needed.

As last observation it’s interesting to note that the exchange current, in a more deep view, also depends on the electron-transfer rate constant \( k_{et} \); the latter constant is a fundamental one to understand the working principles in kinetic models that describes this type of junction but for the moment it’s better to avoid these considerations.

### 2.4.3 I-V curve under illumination

The effect of photons in a SC/electrolyte junction now is quite simple to describe. First, the current flow must be split into two contributions: one for minority carriers and one for the majority carriers. At this point it was observed that the contribution on the majority carriers is negligible, while the only contribution takes into account is on the flux of minority carriers. Considering this experimental observation the total current can be written (with photocurrent generated with opposite sign of spontaneous current) as:

\[ I = I_{ph} - I_0 \left[ \exp \left( -\frac{qV}{kT} \right) - 1 \right] \approx I_{ph} - I_0 \exp \left( -\frac{qV}{kT} \right) \]  

(2.26)
where in the last passage \( I_0 \) is considered to be neglected respect to \( I_{ph} \). Considering this curve is very simple to see the effect of the illumination on a SC/solution junction (figure 2.9).

2.4.4 Fundamental characteristic of a photoelectrochemical cell

At this point understand the three quantities defined in the chapter 1 is very simple. In fact the Open circuit Voltage \( V_{OC} \) is obtained by computing \( V(I = 0) \) neglecting the constant contribute of \( I_0 \) if \( I_{ph} > I_0 \):

\[
V_{OC} = \frac{kT}{q} \ln \left( \frac{I_{ph}}{I_0} \right)
\]  

(2.27)

Thus, \( V_{OC} \) is logarithmically dependent on the two currents. Consequently smaller values of \( I_0 \) imply slower equilibrium rate and higher \( V_{OC} \) values; in other words, higher maximum free energy available.

Second fundamental quantity is the short circuit current density:

\[
J_{SC} = \frac{I_{SC}}{A} \rightarrow \overrightarrow{V} = 0 \rightarrow \frac{I_{ph}}{A}
\]  

(2.28)

The short circuit current provides a measure of the collection photogenerated carriers. Many factors can affect \( J_{SC} \); in fact, the light can be adsorbed by the SC surface, or by the bulk, by the electrolyte or any other elements into the cell. Off course, best performances are obtained if photons are adsorbed by the SC surface. This is one of the reason brings to DSSC technology, to take advantage to maximum power conversion. Moreover, short circuit current can be subdivided into two different terms:

- internal quantum yield measures the yield of collected charges considering the number of photons adsorbed: \( \frac{J_{SC}}{\text{photons adsorbed}} \);
- instead the external quantum yield is \( \frac{J_{SC}}{\text{total photons incident}} \).

Thus the internal yield depends only on intrinsic properties of the junction, while the external yield also depends on the particular design of the cell.
The last two quantities are the efficiency and the fill factor. The fill factor \( FF \), as already defined, is nothing else that:

\[
FF = \frac{I_{\text{max}} V_{\text{max}}}{I_{SC} V_{OC}} \tag{2.29}
\]

while the efficiency can be written:

\[
\eta = \frac{I_{\text{max}} V_{\text{max}}}{P_{in}} * 100 = \frac{FF * I_{SC} V_{OC}}{P_{in}} * 100 \tag{2.30}
\]

In conclusion, some last observations must be done. In order to improve \( \eta \) it’s necessary to maximize the three factors. 

\( I_{SC} \) can be maximized by reducing recombination losses such using some additive, like CDCA, to control recombination at the surface. 

The \( V_{OC} \) instead can be maximized by reducing the exchange current \( I_0 \); in other terms increasing \( V_{bi} \) or reducing \( k_{et} \). 

Fill factor, instead, depends principally on the cell design and all the cell resistance between different parts. Taking into account all these considerations is possible to start to maximize the total conversion efficiency of a photoelectrochemical cell.
Chapter 3

Dye

3.1 Ruthenium Dye

Ruthenium was discovered by the Russian scientist Karl Ernst Claus in 1844 who named it after Ruthenia, the Latin word for Russia. Up to now best efficiencies and performances for DSSC were obtained with dyes derived by Ruthenium Complex. It is a rare transition metal belonging to the VIII group (the same of the platinum), with coordination number of 6 and the property of create strong bonding with imine group (-C=N-). In general the ruthenium complexes bind to the TiO$_2$ through the carboxylic group (-COOH ) which is anchored to two 2-2' bipyridine (figure 3.1). In the opposite side there are two isothiocyanate groups. When the dye is photoexcited electrons flow from the diimmine group to the titanium substrate through the carboxylic group; the injection into titanium dioxide is very fast, in the order of femto(pico) seconds. The positive charge density remaining in the dye move towards the Ru atom and the isothiocyanate groups due to electrostatic repulsion; in this scheme the recombination with electrons excited is retarded by electrostatic forces.

Three most used ruthenium dyes are the so-called N3, N719 and the black dyes. These three dyes show good adsorbance spectra, but low extinction coefficients in comparison with other dyes as Z907 or the K19.

3.1.1 N3 dye

It is also called Ruthenium 535 [18]; it has the structure as described just above (see picture 3.2). It has absorption maxima at 518 and 380 nm and extinction...
coefficients in the order of $1.3 \times 10^4 M^{-1}/cm$. The ground state of this dye differs about 0.7eV from the redox potential of the electrolyte (respectively 0.85V vs 0.15V with reference the SCE). In general a difference of 0.2-0.3eV should be sufficient to ensure a fast recombination rate. The absorbance spectrum (figure 3.3) shows a good absorbance in the visible range.

Figure 3.3: N3 (Ru 535) absorbance Spectrum

### 3.1.2 N719 dye

It is also called Ruthenium 535 BisTBA: it is perfectly the same of the N3 but with the di-tetrabutylammonium salt bound in the dicarboxylic anchoring group\[19\], as shown in the chemical structure in figure 3.2 that should help to attach to titanium dioxide and to slow the recombination effect during the injection process. The spectrum of N719 is perfectly in agreement with the N3 spectrum (figure 3.4). As shown in figure 3.5 N3 (and also N719, has a good incident-photocurrent-efficiency (IPCE) for at least all wavelengths near the absorbance peaks, that exceeds 80\%, and even at 700 nm, where there are not any absorbance peaks the IPCE still is about 50\%. Best performance of N719 respect to N3 can be explained with less percentage of protons near the
TiO₂ surface due to the tetrabutylammonium: in fact experiments demonstrate that positive charges near the semiconductor surface decrease the $V_{CB}$ of the titanium, decreasing the $V_{oc}$[20].

Figure 3.4: N719 (Ru 535 BisTBA) absorbance Spectrum

3.1.3 Black Dye

Discovered in 2001 [21], is the tri(cyanato)-2,2,2-terpyridyl-4,4,4-tricarboxylate) Ru(II) and allow to achieve a record in efficiency of 10.4% with AM 1.5[22]. This record was overcome by N3 only with the adding of the additive GuNcs. The absorbance spectrum and the IPCE graphs show that the response of the black dye extends 100 nm further into the IR than that of N3, allowing the better performances obtained.

Figure 3.5: (on the left) Black dye absorbance Spectrum (on the right) IPCE response of N3 and black dye
3.1.4 Dyes for ionic liquid and gel electrolyte.

Another promising dye for DSSC is the so-called Z907, with chemical name cis-Bis(isothiocyanato)(2,2'-bipyridyl 4,4'-dicarboxylato)(4,4-di-nonyl-2-bipyridyl)titanium(II), is shown in figure 3.6. In an acetonitrile-based electrolyte, Z907 gave a conversion efficiency of 9.5% under AM 1.5G full sunlight [23], still lower than N719 or black dye performances. With ionic liquids, instead, the hydrophobic sensitizer Z907 overcomes the N719 dye; the latter showed lower total conversion efficiencies due to faster back transfer of electrons from the conduction band of the TiO2 film to triiodide, which lowers the Voc. Apparently the back reaction is retarded by the long hydrocarbon chains of the Z907 dye (figure 3.6), which form an insulating layer, thereby increasing the distance between triiodide and electrons trapped on the TiO2 surface. The main reason for this difference is that the ILs requires much higher concentrations of triiodide to avoid the mass transfer limitations of the Jsc. This increases the dark current, reducing the $V_{oc}$, FF and overall conversion efficiency. Looking for the way to substitute the liquid electrolyte with a gel, or a quasi solid electrolyte, it’s useful find some new dyes which have higher extinction coefficients in order to decrease the TiO2 layer due to the higher viscosity of the electrolyte and the lower mobility of the redox couple. An example with very good result with quasi solid electrolytes is the so-called K19 dye [24] (figure 3.6) which with its long carbon chain should have an higher extinction coefficient as well as lower the recombination effect, as said just above. The result is an increase of the extinction coefficient from 12200 cm$^{-1}$M$^{-1}$ and 14000 cm$^{-1}$M$^{-1}$ respectively of Z907 and N719 up to 18200 cm$^{-1}$M$^{-1}$ for the K19 at the wavelength of $\lambda = 543$ nm [25].

![Figure 3.6: Z907 and K19 chemical structures. Their long carbon chains reduce recombination effect and the dark current](image)

3.2 Organic Dyes

Actual results in terms of efficiency and IPCE for organic dye are not equivalent to the Ru-based dyes; nevertheless organic dyes (OD) have some interesting characteristics with which it should be possible to increase future performances and costs for DSSCs. In particular organic dyes have:

- high molar extinction coefficients, of the order of 100 cm$^{-1}$M$^{-1}$, at least one order greater than Ruthenium dye;
• simpler synthesis processes;
• lower costs for materials and synthesis.

Up to now one of the best efficiency obtained is over 9%\textsuperscript{[26]}. In general in DSSCs with organic dyes the \( V_{oc} \) characteristic is lower than using Ruthenium dyes while \( J_{sc} \) is generally higher. Another interesting characteristic of ODs is the low concentration of the dye for the solution which in the electrode is soaked. In fact if for ruthenium dye is necessary a concentration, in general, of \( 10^{-3} \) for the organic dye it is enough \( 2 - 3 \times 10^{-4} \), at least one order higher; consequently it is necessary to use less materials. However some particular problems must be solved; the major defect for the organic dyes is about the absorbance spectrum: in fact almost all ODs have a very narrow absorbance band and consequently can absorb just a part of the sun irradiance. Main precursor molecules for ODs are: triphenylamine\textsuperscript{[27]}, indoline\textsuperscript{[26]}, coumarine\textsuperscript{[28]}, squaraine\textsuperscript{[29]}, cyanine\textsuperscript{[30]}, perylene\textsuperscript{[31]}. Some of the basic structure of the precursor molecules are shown in figure 3.7.

![Image](image_url)

Figure 3.7: Some precursor of organic dyes

### 3.2.1 The system \( D - \pi - A \).

In general organic dyes have a structure subdivided into different parts: an \textit{Electron Donor} \( D \) and an \textit{Electron Acceptor} \( A \) linked by a bridge-like \( \pi \) part. At the end of the Acceptor group, in the case of DSSCs obviously there is the anchoring group bound to the \( TiO_2 \). The nature of the attraction in a charge-transfer complex is not a stable chemical bond, and is much weaker than covalent forces. The attraction is created by an electronic transition into an excited electronic state, and is best characterized as a weak electron resonance\textsuperscript{(figure 3.8)}. This type of system for organic compounds is called \textit{Charge-transfer complex}. The bridge between \( A \) and \( D \), in general is a carbon chains, which can be quite simply modified. Longer chains are desirable because greater molecules block recombination between the redox couple and the \( TiO_2 \), but it is known that longer chains reduce the band gap between HOMO and LUMO.

The band structure in linear conjugated polyenes and the Huckel model. Starting from the description of the band gap for the ethylene, then
is immediate to understand the band gap for a general straight-chain polyene just as iteration. The Huckel molecular orbital description states:

1. it is limited to conjugated hydrocarbons;
2. Only electrons in $2p$ orbital are included, while electrons in $\sigma$ orbital are ignored. It is justified by the orthogonality of $\sigma$ and $2p$ in planar molecules. In fact the model is limited to planar systems;
3. The method predicts how many energy levels exist for a given molecule, which levels are degenerate and it expresses the MO energies as the sum of two terms:
   - $\alpha$, the energy of an electron in a $2p$-orbital;
   - $\beta$, an interaction energy between two p orbitals which are still unknown but importantly have become independent of the molecule.

For linear and cyclic systems, with $n$ atoms, general solution exists:

- for linear chains:
  \[ E_k = \alpha + 2\beta \cos \frac{k\pi}{(n+1)} \]
- for cyclic chains:
  \[ E_k = \alpha + 2\beta \cos \frac{2k\pi}{n} \]

and then the HOMO-LUMO band gap, in terms of $\beta$, for linear chains, is:

\[ \delta E = -4\beta \sin \frac{\pi}{2(n+1)} \]  

where $\beta$ is of the order of $-250 \div -290 KJ/mol$ and it correlates directly with the respective molecular electronic transitions observed in UV/VIS spectroscopy.

In order to explain the model in a deeper simple way, it must be taken as example...
the ethylene molecule: the carbon atoms are $sp^2$ hybridized into a $\sigma$ orbital. The remaining carbon $p$ orbitals interact to yield two orbitals of $\pi$ symmetry, one is bonding and one is antibonding with C-C interaction. In figure 3.9 the bonding $\pi$ (the ground state for ethylene, HOMO in general) is occupied by two electrons, while the $\pi$ antibonding is unoccupied (LUMO). Increasing the ethylene chains, the $\pi$ bonding will become more delocalized and more levels are allowed. In general the energy band gap obeys to the equation 3.1 and graphically can be represent as in the figure 3.9 and each ethylene added to the chain decreases the band gap. This process can continue until infinite but HOMO and LUMO never overlap; on the contrary there is a well-defined energy band gap, which cannot be overcome even if the carbon chain increase up to infinite [33].

![Figure 3.9: HOMO LUMO representations for carbon chains. For ethylene the HOMO corresponds to $\pi$ bonding orbital while the LUMO corresponds to $\pi$ antibonding. Increasing the carbon chain length, HOMO-LUMO band gap tends to a well-defined limit.](image)

3.2.2 Fluorescence of donor group in organic dyes

Basic donor groups, in the major part of organic dyes utilized in the DSSC, are fluorescence groups. Generic ground state $S_1$ of molecules is in the singlet state with antiparallel spins. During the excitation, due for incident light or for any other reason, the new states can be in both singlet $S_2$ or triplet state $T_1$, less likely. When excited electrons return to the ground state, in general they have many step and pass through different excited states before to reach again the ground state. All relaxations without any emission are in general called internal conversions and they only produce heat, while if the excited electrons change their spin state from singlet to triplet, the process is called intersystem crossing (see figure 3.10). At the end, for fluorescence or phosphorescence material, the last relaxation emits a photon with higher wavelength respect to the incident photon, and consequently lower energy. The difference between fluorescence and phosphorescence is about the excited state. In fact fluorescence is much more likely and it is a transition between a singlet excited state and fundamental state (singlet too). On the contrary phosphorescence is due a transition between

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a triplet state and the singlet ground level, less likely and consequently much more less common. For this reason fluorescence transitions are in the order of ns, while phosphorescence occurs in the order of ms or s. In general fluorescence

\[ S_0 + h\nu_{\text{phot}} \rightarrow S_1 \] (3.2)
\[ S_1 \rightarrow S_0 + h\nu_{\text{emitted}} + \text{heat} \] (3.3)

where eq. 3.2 represents the excitation process and eq. 3.3 represent the emission transition.

### 3.2.3 An OD examples: squaraine

**Squaraine.** Squaraine dyes are organic dyes showing intense fluorescence, typically in the red and near IR region with absorption maxima between 630 and 670 nm and emission peaks between 650,700 nm. Basic structure is characterized by the squaric acid (fig. 3.7), which is an aromatic cycle with four \( sp^2 \) hybridized carbon atoms. There exist many types, but they can be subdivided into two big groups: symmetric or antisymmetric; the LUMO and the HOMO can be respectively resumed with the structure \( D - A - D \) for the symmetric or the \( D - \pi - A \) for the antisymmetric (figure 3.11).

For instance, Graetzel, Nazeeruddin & al \[34\], synthetized an antisymmetric squaraine in order to solve some particular problems. Specifically a strong conjugation across the chromophore and anchoring groups is required for a good electronic coupling between the LUMO and the \( TiO_2 \) conduction band. In order to satisfy thiss essential requirement, the carboxylic acid group is directly attached to the chromophore (see synthesis process 3.12). The dye tested presents an absorption maximum at 636 nm and a very high extinction coefficient (\( \epsilon = 158.5 \text{cm}^{-1} \text{M}^{-1} \)); in fact exhibits a very high short circuit photocurrent even in presence of few \( \mu \text{m} \) of \( TiO_2 \) (with 2.5\( \mu \text{m} \) of thickness \( J_{sc} = 8.20 \text{mA/cm}^2 \)). Overall performances are still bad in comparison with other dyes: \( V_{oc} = 603 \text{mV} \).
**Figure 3.11:** (a) symmetric squaraine (b) antisymmetric squaraine

\[ FF = 0.71, \, J_{sc} = 10.50 mA/cm^2 \text{ and } \eta = 4.5\% \] nevertheless, this example is a good starting point for the engineering of squaraine organic dye.

**Figure 3.12:** Main step in a generic squaraine synthesis

3.3 Additives

During the phase of dye absorption on the TiO₂ surface, it could be occur that some molecules of dye aggregate to themself. This fact affects the final performance of the whole cell due to the fact that there will be some dye molecules which absorb the light but they can’t inject photoexcited electrons directly into the conductive band of the titanium. This negative effect occur particularly for organic dyes because of their planar geometry. There exist fundamentally two types of aggregates:

- **J aggregates** where the electron transition dipole is parallel to the molecular plane. In this case there is a red shift in absorbance, which can improve cell performance;

- **H aggregates**, where the dipole is perpendicular to the molecule plane. In this case there is a blue shift which affects the performance.

In general aggregates, avoid shifts in light absorbance, decrease the electron injection, because as said, only molecules linked to the titanium surface can easily inject electrons without recombination effects.

In order to block this effect there are some additive must be added to the dye
solution. First of all there is the *Chenodeoxycholic acid* (CDCA, figure 3.13) which link itself directly to the dye molecules, or to the titania surface and block the creation of aggregates. In particular the CDCA act as spacer among dye molecules and it also act as electron recombination slower between dye and electrolyte. In fact the CDCA is hydrophobic and can push away the $I_3^-$ from the surface [35]. Similar effects occur with other two additives: the tert butylpiridine (TBP) and the Guanidium Thyocianate (GUNCS). The GUNCS (fig. 3.13 in general is added to electrolyte solutions and it should be able to help to create the monolayer of dye [36]. The TBP, instead, linking to the electrode surface should increase the conductive band potential and consequently increase the $V_{oc}$ and it should protect the SCN group to corrosion [37].

![Chemical structures of principal additives](image)

Figure 3.13: chemical structure of principal additives
Chapter 4

Electrolyte

4.1 A Bit of Theory: Fundamental equations

First of all, it’s necessary to clarify and explain some of the fundamental equations used during the electrolyte studies. Many studies on electrolytes, liquids and quasi solid, involve different instruments and techniques: Electrochemical impedance spectroscopy (EIS) in order to study resistances of the electrolyte and of contacts between electrolyte and electrodes, conductivity thermal stability, viscosity and ions diffusion test. Without enter into specifically technique problems, all of them should be explain, in a empirical way, by considering some equations. Let’s see that in order to study ionic liquids and gel electrolytes, only few fundamental equations are enough but it’s necessary to consider some modification from the theoretical formulas.

4.1.1 Einstein-Stokes diffusion coefficient

One of the most important results of Einstein, is properly the equation of diffusion for Brownian motion. It explains as a particle moves in a fluid due to random hits with all other particles in absence of any external forces. The more general form is:

\[ D = \mu k_B T \]

where \( D \) is the diffusion coefficient, \( \mu \) is the mobility of the particle and \( k_B \) and \( T \) are respectively the Boltzmann constant and the absolute temperature. The equation assumes different expression according to the physical set described. For instance in the case of spherical particles moving through a liquid it becomes the famous **Einstein-Stokes Relation:**

\[ D = \frac{k_B T}{6\pi \eta r} \]  \hspace{1cm} (4.1)

where \( \eta \) and \( r \) are respectively the viscosity of the fluid and the radius of the particle.

The diffusion coefficient is strictly related with the diffusive flux to the concentration by the **Fick’s first law**, which postulates that the flux goes from
high concentration regions to regions of low concentration proportionally to the concentration gradient:

\[ J = -D \frac{\partial \phi}{\partial x} \]  

(4.2)

where \( J \) is the "diffusion flux" (mol/m^2s) and \( \phi \) is the concentration of particles (mol/m^3).

In chemical systems the potential is given by the chemical potential \( \mu_i \) and the Flick’s law becomes:

\[ J_i = -\frac{D c_i}{RT} \frac{\partial \mu_i}{\partial x} \]

where \( c_i \) is the concentration of the i-th molecules.

### 4.1.2 Walden’s Rule

Walden’s Rule is an empirical law, that simply states that for any electrolytes, the Molar conductivity \( \Lambda \) and the viscosity \( \eta \) are inversely proportional. In other words, the Walden’s Rule is:

\[ \Lambda \eta = const \]  

(4.3)

The proof derives from some simple mechanical observations. In an electrolyte, all ions move themselves, due to two forces:

- an electrical force, \( z e E \)
- a frictional force, from the Stokes formula \( 6\pi \eta rv \); where \( \eta \) is the viscosity, \( r \) is the radius of the ion, \( v \) the velocity.

The two forces act in opposite directions, and ions reach quickly a constant speed \( v \).

\[ z e E = 6\pi \eta rv \]

Taking into account that \( \Lambda \propto \frac{1}{\eta^\alpha} \) it’s demonstrated the rule.

In a more general way the Walden’s Rule could be expressed as:

\[ \Lambda \eta^\alpha = const \]  

(4.4)

where the coefficient \( \alpha \) is determined empirically and take into account all possible contributions, physical and chemical effects, as the Grotthus exchange.

### 4.1.3 Grotthus Exchange

Studies on the Grotthus exchange [28] started at the beginning of the XX century to explain the proton mobility in water which is abnormally high. For instance, a room temperature its limiting ionic conductance is about seven times that of a \( Na^- \) ion, or five times that of \( K^+ \) ion. The classical explanation is a sequence of proton-transfer reactions, proton hops, between \( H_2O \) molecules, that strongly increase the protons diffusion. Even if, a suitable general theory doesn’t exist yet, a very familiar picture (it could be find in all physical chemistry textbooks) but wrong can show the proton hops mechanism in a very simple way (see figure 4.1).

This mechanism can be generalized to explain the behaviour of many different ions, from ionic liquids electrolytes to latest mixed gel electrolytes. Thus well-understanding Grotthus-like mechanism is a open research field that could be very interesting and useful results to maximize the effect.
4.1.4 Dahms-Ruff Equation

The Dahms-Ruff equation is simply a revisited Einstein-Stokes classical equation considering not only the physical diffusion but also the Grotthus-exchange contribution. It could be stated as follows:

\[ D = D_{\text{phys}} + D_{\text{ex}} = D_{\text{phys}} + \frac{1}{6} (k_{\text{ex}} \delta^2 c) \]

where \( D_{\text{phys}} \) is the physical diffusion, \( D_{\text{ex}} \) is properly the exchange diffusion, \( k_{\text{ex}} \) is the rate constant of the iodide/triodide bond exchange, \( c \) is the iodide concentration and \( \delta \) is the average distance between the center of iodide and triiodide. Thus, the contribution due to the Grotthus Effect is due simply by \( D_{\text{ex}} \).

4.2 Ionic Liquid electrolytes: brief history and types

4.2.1 IL: an overview

Currently one of the most interesting field of research over electrolytes is in ionic liquids. Ionic liquid is simply a salt in the liquid state. ILs are object of a lot of studies due to their stability properties as: negligible vapour pressure, thermal stability, non-flammability, high ionic conductivity and wide electrochemical stability window. Salts with melting point below 370K are particularly studied, the so-called room temperature ionic liquids. Most common RTILs (resumed in the figure 4.2) are formed by organic salts: cations such as imidazolium, pyridinium or quaternary alkylammonium ions and anions from the halide or pseudo halide family and noncoordinating ions such as \( BF_4 \) and \( PF_6 \).[41]

4.2.2 Multicomponent Imidazolium: Eutectic melt

A very exhaustive and interesting experiment was done by Graetzel & al [41] in order to achieve the maximum ions conductivity, and consequently the maximum efficiency conversion, for RTILs. Studying diffusivity and viscosity characteristics of some solvent free electrolytes it was possible to create a new eutectic melt between many imidazolium-based reagents. In the experimental set studied PMII has the lowest viscosity at room temperature, while DMII, EMII and AMII has higher conductivity but they has melting point above room temperature, thus they are solid in standard conditions (see figure...
In order to take advantage of all characteristics of all materials, some eutectic melts were studied in the following way: melt I, PMII/I\textsubscript{2} (24:1); melt II, DMII/EMII/AMII/I\textsubscript{2} (8:8:8:1); melt III, PMII/1-ethyl-3-methylimidazolium tetracyanoborate(EMITCB)/I\textsubscript{2} (24:16:1.67); melt IV, DMII/EMII/EMITCB/I\textsubscript{2} (12:12:16:1.67). Interesting to observe is the alkyl chain length: in fact as it increases as well as the electrostatic attraction between cations and iodide decreases and the Van Der Waals interaction between the imidazolium cations increases.

In the right graph, instead, are shown diffusion coefficients. As it is trivial to observe tested melts don’t obey anymore to Einstein-Stokes diffusion equation and to fit well experimental datas it’s necessary to recall the Dahms-Ruff equation. The Melt V is an electrolyte with a low iodide concentration and it was used as reference within the Grotthus-like exchange is negligible.

Taking advantage of these considerations Graetzel & al tested two eutectic-based melts with another two routine additives for DSSCs: device A, DMII/EMII/AMII/I\textsubscript{2}/NBB/GNCS (8:8:1:2:0:4) and device B, DMII/EMII/EMITCB/I\textsubscript{2}/NBB/GNCS (12:12:16: 1.67:3.33:0.67). In conclusion an efficiency of 8.2 % was achieved under an irradiance of AM 1.5G sunlight, an amazing result for an ionic liquid.
4.3 Gel electrolytes

A gel is defined as a solid 3-D cross-linked network, derived from a sol-gel processing in which the liquid phase is removed. Some classical types of gel are: Hydrogels, organogels, aero or xerogels. In elettrochemistry however, there is a new gel-type much more interesting for its conductivity properties, derived from the ionic liquids. This new material was called ionogel. In particular electrochemical studies, based on EIS method, reveal that in many cases the total conductivity through the ionic electrolyte remains unchanged during gelation process, or in some cases even increase. This behaviour that is in strongly disagreement with the Walden’s Rule could be explained in many curious ways: from ions preferential channels to ambipolar diffuson\cite{42}, from the Grotthus effect\cite{43} \cite{44} to inhomogeneous density of charge. It’s noteworthy that ionogels maintain the same thermal stability as the IL and that, in general, are quite stable in non polar organic solvents, whereas in polar solvents ions can be extracted. These generic characteristics of ionogels, together to some other properties of ionic liquid as thermal stability, low volatility are strongly recommended for application such as dye sensitized solar cells. Many types of ionogels can be made: from silica nanoparticles, with silicon alkoxides as precursors, to metal alkoxides as $TiO_2$, from polymeric materials to mixed compositions.\cite{45}

Before discussing some results for dssc let’s notice two big classifications for ionogels, and in general for any gels, used particularly in (photo)electrochemistry, due to their useful properties:

1. • Active gelators: gel based on some precursors, nanoparticles which adsorb or react with the light. In this case, they must be choose some gel reagents suitable for the devices studied.

• passive Gelators;

2. • gelation precursor (room temperature gel) such that precipitation occurs swiftly at room temperature when all reagents are mixed;

• latent gelation precursor: gels composed with materials of this type, have the property such that gelation occurs only after heating. For dssc application L-gel-pre are very interesting in orer to solve sealing problems due to gel electrolytes.

4.3.1 Polymeric gel

First and obvious type of gel, which must be study, are polymeric based, due to intrinsic properties of these materials. L. Wang, B. Ma & al\cite{42} analyzed the electrically conductive behaviour of an high-molecular weight polymer, PEO, ($M_W = 2 \times 10^6 \frac{\text{g}}{\text{mol}}$) injected into an electrolyte composed by: 0.1 M LiI, 0.1 M I$_2$, 0.6 M DMPII, 0.45 M NMBI with MePN solvent, with different weight percentage (from 2% to 15%). The interesting result is the enhance of total conductivity in the cell increasing weight percentage even if a viscosity increase of almost 500 times. In fact if the total conductivity is written as:

$$\sigma = \Sigma_i \frac{|Z_i|^2 F_{ci} D_i}{K_B T}$$
where $Z_i, c_i, D_i$ are charge, concentration and diffusion coefficient for each ion, $F, K_B$ and $T$ are Faraday and Boltzmann constant and the absolute temperature it is simple to notice that particular behaviour could derive from different ions. For instance, ions $I^-/I_3^-$ decrease their conductivity constantly, while total conductivity, first increase and then decrease; this could be explained by $Li^+$ diffusivity into the gel electrolyte enhances by PEO. This effect could be explained by the **Ambipolar diffusion coefficient** written in the following way:

$$D_{amb} = \frac{n + p}{D_n + D_p}$$

where $n, p$ are the densities of electrons and cations (in this case $Li^+$, and $D_n, D_p$ are the diffusion coefficients. This effect works for both electrolyte and porous $TiO_2$; in fact was demonstrated by Yanagida & al [46] that the diffusivity of electrons in the titania is enhanced by the presence of lithium cations.

### 4.3.2 Physically cross-linked gel: Nanoparticles as gelator

In Material Technology laboratory of the University of Tokyo, Usui & Al. [47] tested different types of nanoparticles into a ionic liquid electrolyte with a base of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm-TFSI)( figure 4.4) and a 0.8 wt% of deionized water, and: 1.5 M of EMIm-I, 0.1 M of LiI, 0.15 M of $I_2$, 0.5 M of TBP.

![Figure 4.4: EMIm-TFSI](image)

In their experiment, they injected 1 %wt of:

- multi-walled carbon nanotubes (MWCNTs);
- carbon black;
- $TiO_2$ nanoparticles;
- single-walled carbon nanotubes;
- carbon fibers and graphite.

into the ionic electrolyte, in order to obtain the gel electrolyte.

Interesting results were obtained, in particular with $TiO_2$ nanoparticles; some of them need a comment: in particular the fact that $TiO_2$ increases the performance more than nanotubes or other conductor even if his behaviour is a
Figure 4.5: SEM of a) MWCNTs; b) CB; c) TiO$_2$; d) SWCNTs; e) CFs; f) graphite
semiconductor; this effect could be explained by the Grotthus Effect that enhances ions exchange on the TiO$_2$ surface.

In a very similar way, Katakabe, Kawano and Watanabe [48] studied another EMIm-TFSI based IL electrolyte with SiO$_2$ nanoparticles, increasing their %wt from 0.05 (gelation point) to 0.2 (dry powders). As shown in figure 4.6 addition of nanoparticles doesn’t affect the ionic conductivity; this fact brings to attribute the increase in the limiting current only to the exchange-reaction diffusion of the redox couple.

![Figure 4.6: Ionic conductivity at 25Â°C in a EMIm-TFSI electrolyte with SiO$_2$ nanoparticles](image)

In fact, if we analyze the limiting current (also denoted as steady state current $I_{ss}$) formula:

$$I_{lim} = 4nFD_{app}rc = 4nF(D_{phys} + D_{ex})rc$$

where the three diffusion coefficient are respectively, apparent, physical and exchange-reaction, $n$ is the number of transferred electron, $F$ is the Faraday constant, $r$ is the electrode radius, $c$ is the concentration of the redox couple. Recalling the equation of Dahms-Ruff [4,5] and assuming $D_{phys}$ to be constant, due to no change in the ionic conductivity, the only diffusion term is $D_{ex}$. The addition of the SiO$_2$ enhances the local concentration of the redox couple: in fact the presence of surface SiO$^-$ groups, which adsorb EMIm cations, creates iodide/triiodide rich regions whiches create a continuous path into the electrolyte. In conclusion the total performance is not much better than the pure IL but it’s interesting the effect on the limiting current.

Park, Kim and Moon[49] studied a gel electrolyte composed by nanoparticles of laponite in a solution based on acetonitrile and valeronitrile 85:15 (0.6 M butylmethylimidazolium iodide, 0.03 M I$_2$, 0.1 M guanidinium thiocyanate and 0.5 M TBP), in order to take advantage of the so-called active gelators; in other words, as introduced just above, utilizing materials able to reflect, or in general
interact with the light in the visible wave length, it’s possible to increase the optical path of the light and consequently the photocurrent produced. Gelation occurs by adding 17% of laponite into the electrolyte. With 20% wt of laponite was obtained a total efficiency of 7.1% with an increase about 20%. In conclusion, because the nanoclay alone cannot produce a photocurrent, it can be concluded that the higher current in the DSSC with the nanoclay is primarily due to light scattered, as it’s schematized in figure 4.7.

Figure 4.7: An example of active gelators: nanoclay reflection

4.3.3 Latent Gel Precursor

A new fashionable way to obtain gel electrolyte for DSSCs is the so called Latent Gel Precursor. In a very simply way, it’s possible to use thermal properties of polymeric materials to look for some eutectic materials such that the gelation process occurs at a well-defined temperature above the room temperature; such materials could allow to inject the electrolyte, in the liquid state at room temperature, and then, heating the seal cell, to obtain the desired gel. This method is strongly suggested also to improve the performance of DSSCs because the delayed gelation occurs only inside the sealed cell, and only when the electrolyte is perfectly mixed with the porous TiO₂. This fact enhances contacts between the TiO₂ surface and the quasi solid electrolyte.[50][51]

For instance, Kato, Okazaki and Hayase[52] studied a latent gel precursor with dicarboxylic acids and different nanoparticles. The electrolytes studied were composed as shown in figure 4.8 while the process is shown, in a very generic way, for polymeric materials with nanoparticles as cross-linked gelators, it’s schematized in figure 4.9. Thermal studies show that for the C6, with a short alkyl chain, gelation immediately occurs when it’s mixed with Silica nanoparticles. Instead for C12 and C16, with longer alkyl chain, gelation at room temperature doesn’t occur for many days. In these cases gelation immediately occurs only after heating (∼ 80°C) and the process is not reversible; the process could be associated with a thermal phase transition of the dicarboxylic acid into IL electrolytes. The liquid phase is obtained only above 110°C.
Moreover, it’s interesting to report that the TiO$_2$ surface reacts with COOH group and decreases interfacial resistances, increasing the photo-energy conversion efficiencies.[53]

Kato et al. [54] also studied thermal properties of latent gel precursor in another set of experiments using an IL electrolyte composed by: 5 %wt H$_2$O, I$_2$, LiI and MePrImI (Methylpropylimidazolium iodide) with PVP and dicarboxylic acid with different alkyl chain length, as gelator (see figure 4.10).

A total efficiency of 5.5 % was obtained, but the interesting of this study is about latent thermal properties and the corresponding with the endothermic and exothermic peak of the electrolyte. In fact, stated that endothermic peaks on heating correspond to phase-transition from ordered to disordered states (melting point) and that exothermic peaks on cooling correspond to the op-
posite phase-transition (crystalization), Kato&al observed as the dicarboxylic acids, with shorter chain (C6 and C9), have no peaks, while C12 and C16 have, and it could be suppose that acids with longer chain, have two peaks below 100°C, always with $T_{\text{exothermic}} < T_{\text{endothermic}}$. 
Chapter 5

Testing of new materials for DSSC application

5.1 Innovasol project

The Innovasol project is an EU project which involves many partners from Europe and Brasil aiming to improve third generation photovoltaic devices. The project is indeed focused on the improvement of Dye sensitized solar cells technologies and their industrial applications. Both academic and industrial partners are involved in the project (figure 5.1): six high degree partners, expertise in solid-state physics and chemistry, nanoscience and nanotechnology such as the University of Cambridge, Instituto de Quimica de la Universidade de Campinas, Ecole polytechnique Federale de Lausanne, University of Turin, University of Eastern Piedmont, Technische Universitat Dresden, and high level industrial research teams from Italy and Switzerland (Centro Ricerche Fiat and Solaronix) are partners of the Innovasol project.

Figure 5.1: Innovasol partners institutions
5.2 Optimization of the cell design and reagents description

In this section the materials used to prepare DSSC cells and the methodology adopted to their assembly are described. Each result is an average over five identical cells and the photoactive area of each cell is of 0.36\(cm^2\).

**Titania layers and procedure.** Two types of titania paste have been used for the preparation of the cells:

- Solaronix Ti nanoxide T/SP with 20nm size particles; this \(TiO_2\) is quasi transparent up to UV wavelengt;

- Solaronix Ti nanoxide R/SP with 100 nm size particles; this paste was used in order to render reflective the layer between the other \(TiO_2\) layer and the electrolyte.

The reflective layer was used to increase the optical path of light into the electrode without increasing the thickness of the electrode. A SEM image showing the cross section of the \(TiO_2\) electrode, after the heating process, is reported in figure 5.2. Several techniques can be used to create a thin \(TiO_2\) layer: doctor-

![Figure 5.2: SEM image of TiO\(_2\) electrode cross section. Electrode with 4 T/SP (transparent Solaronix paste) layers and 1 R/SP (Reflective Solaronix paste) layer. Each layer has about 3 – 4\(\mu m\) thickness.](image)

blade, screen-printing, spin-coating, dipping, inkjet or electrospray. In this work all electrodes were made with the screen printing method. With this method each layer is about 3 – 4\(\mu m\); each layer is printed and then burned at 90\(^\circ\) – 100\(^\circ\)C for 10 minutes. At the end, the electrode is dried at 475\(^\circ\)C for 2 hours, reaching the maximum temperature in the first hour.
Titanium tetrachloride treatment  O Regan & al \[61\] demonstrated that TiCl₄ treatment allows a reduction in the recombination electron rate constant in the TiO₂ surface and decrease of almost 80mV the conduction band of the titanium. In particular the decreasing in recombination allow to reach a major concentration of electron in the conduction band and then a bigger short circuit density current.

In this work, before and after the screenprinting, the electrodes have been treated in a chemical vapour bath for 30 minutes at 60°C using a solution of 0,9 ml of TiCl₄ into 200 ml of distilled water. The effect of the treatment, is shown in figure 5.3. The TiCl₄ treatment is a kind of glue between the titanium nanoparticles; this can also increase the probability of an efficient percolation process for the electron diffusion.

![Figure 5.3: SEM images of (on the left) hierarchically structured (HS) TiO₂ nanoparticles electrosprayed. (on the right) HS-nanoparticles post TiCl₄ treatment \[62\]. The nanoparticles size in the photo is not the same of this work thesis](image)

Counter electrode and glasses.  TCO (transparent conductive oxide) glasses were used; the transparent conductive films consist in a layer of fluorine doped tin oxide (FTO) with a resistance of 7 Ω/sq.

The counter electrode consists in Platisol T (Solaronix) paintbrushed on a glass and then burned at 475°C for 30 minutes (heating rate of 30°C/min for 15 minutes and 15 minutes at constant T).

Reference dye solutions.  Two reference dyes were used for cell preparation: the N719 and the Z907. The N719 was used mainly for all liquid electrolytes, while the Z907 (for the reason explained in Chapter 3) was used with gel electrolytes. The two mixture are composed as follows:

1. **N719**
   - 28.75 mg of Ru 535-BisTBA
   - 97.5 mg of CDCA
   into 50ml of solvent (MetOH or EtOH)

2. **Z907**
- 16 mg of Ru 520-DN
- 117 mg of CDCA

into a solution of Acetonitrile:Terbutanol 1:1 (15mL:15mL)

The titania electrode is dipped, just after the calcination at 475°C, into the dye solution and leave overnight into it.

In order to optimize the performance of the cells a preliminary study with N719 dye was done, testing different TiO$_2$ thickness and different solvent. Cells with 2 layers of titania (7-8µm of electrode thickness) or with 3 layers (11-12 µm of electrode thickness) were tested with two N719 dye solution with ethanol or methanol solvent. Results (figure 5.4) show that best performances were obtained with 3 layers of titania, with a total electrode thickness of 11-12µm, and with Ethanol as solvent. In all next test cells Ethanol was choosen for N719 dye solution and 11-12 µm TiO$_2$ thickness as optimized cell design for liquid electrolytes.

**Electrolytes.** Four different electrolytes were used: two acetonitrile based electrolyte for the high efficiency test cells, Solaronix Iodolyte AN-50 and the JH163. Tipically electrolytes with acetonitrile present very high performances but low durability, due to its low boiling point of 80°C. The AN-50 is based on the iodide/tri-iodide redox couple, with ionic liquid, lithium salt, pyridine derivative as additives. The JH163, is always based on the iodide/tri-iodide couple but has TBP (Tertbutylpirydine), GUNCs (Guanidine Thiocyanate) and ionic liquid (IL) as additives into a mixture of acetonitrile:valeronitrile (AN:VN).

For all cells with 5%wt of nanoparticles, instead, Solaronix iodolyte Z-50 was uti-
lized. It is intended for high performance and temperature stable cells, thanks to its boiling point of 160°C. It is based on iodide/tri-iodide redox couple with ionic liquid, alkylbenzimidazole, guanidine thiocyanate additives into 3-methoxypropionitrile.
For the gel electrolyte the solvent free ionic liquid electrolyte Z952 was used. The composition, described in the multicomponent Eutectic electrolyte part in Chapter 4, is based on ionic liquid into 1-ethyl-3-methylimidazolium tetra-cyanoborate.

**TiO$_2$ and surlyn thickness optimization.** A brief preliminary test (fig. 5.5) was made to choose different thickness combinations, especially for liquid electrolyte with ruthenium complexes as dye. Different thickness of TiO$_2$, 3 or 4 T/SP layers, were tested with surlyn of 25 or 60 $\mu$m. The best performances were obtained with 3 layers of T/SP titania paste and with surlyn thickness of 60$\mu$m.

### 5.3 Towards gel electrolyte: 5 % wt nanoparticles

In this section, different electrolytes were tested using nanoparticles as additive. In particular electrolytes were made by adding into the Solaronix Z946-50 solution 5% in weight of different nanoparticles and then mixed overnight with a magnetic stirrer. These preliminary studies were done in order to examine the effect of adding external nanoparticles, neutral or positively/negatively charged. In general adding nanoparticles viscosity increases, thus a decreasing in electrolyte diffusion coefficient occurs; if the efficiency, and cell performances in general, remains almost the same or increase, the nanoparticles added can be considered as a suitable gelator for the electrolyte solution, as described in Chapter 4. The performance can remain the same, or increase, as consequence of different effect: some scattering effect of the light, a Grotthu-like mechanism, an ambipolar diffusion effect, and other mechanisms. The test cell design used for all nanomaterials tested at 5% wt is the one obtained during the optimization; thus 3 T/SP titanium nanoxide screenprinted layers for a total of 10-12 $\mu$m of TiO$_2$, 60 $\mu$m surlyn thickness, Ruthenium 535 Bis-Tba dye (in literature

<table>
<thead>
<tr>
<th>Type</th>
<th>Thickness</th>
<th>Anthocyanin</th>
<th>$\Delta\phi$</th>
<th>$\eta$</th>
<th>$\xi$</th>
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</thead>
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<td>Std</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>3 T/SP - surlyn 25$\mu$m</td>
<td>Avg</td>
<td>120.00</td>
<td>120.00</td>
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<td></td>
<td>Std</td>
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<td>0.00</td>
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</tr>
<tr>
<td>4 T/SP - surlyn 60$\mu$m</td>
<td>Avg</td>
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<td>120.00</td>
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<td>Std</td>
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<td>0.00</td>
<td>0.00</td>
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</tr>
</tbody>
</table>

Figure 5.5: Experimental details: (dye) N719 in Methanol (electrolyte) AN50 (surlyn) 60 or 25 $\mu$m (TiO$_2$ 3 (or 4) T/SP + 1 R/SP + TiCl$_4$ post treatment
N719) in an EtOH solution, Platisol T (Solaronix) precursor as counterelectrode and a TCO glass, with a sublayer of FTO (fluorine tin oxide) with a resistance of 7 Ω/sq were used. The active test area for each test cell is of 0.36cm².

5.3.1 Silica

Some interesting precursor studies with 12 nm fumed silica nanoparticles size, from Degussa, were performed by Graetzel & al. [56] in a MPII:3-methoxypropionitrile (13:7) based ionic liquid electrolyte with 0.5 M iodine (I₂) and 0.45 M N-methylbenzimidazole (NMBI) obtaining a 7.0% efficiency with stable performance relative to liquid electrolyte without nanoparticles. Starting from the good result obtained in this work, amorphous silica was tested as additive for DSSC electrolyte. Commercial silica F5 (from Degussa) and two functionalized silica with NH₂ group and NH⁺₃, synthetized by the University of Oriental Piedmont, were tested. The first functionalized silica derives from the using of an aminopropylsilane during the synthesis (figure 5.6), while the second functionalized silica was obtained by protonation of the amine group. An average performance

![Aminopropylsilane structure used to functionalize the amorphous silica F5 during the synthesis process.](image)

Figure 5.6: Aminopropylsilane structure used to functionalize the amorphous silica F5 during the synthesis process.

obtained in this work, amorphous silica was tested as additive for DSSC electrolyte. Commercial silica F5 (from Degussa) and two functionalized silica with NH₂ group and NH⁺₃, synthetized by the University of Oriental Piedmont, were tested. The first functionalized silica derives from the using of an aminopropylsilane during the synthesis (figure 5.6), while the second functionalized silica was obtained by protonation of the amine group. An average performance

![Test on electrolyte Z946-50 with 5%wt of amorphous silica nanoparticles, NH₂ and NH⁺₃ functionalized silica nanoparticles (chemical structure described in the text). (top) Relative and (bottom) absolute results calculated using Solaronix Z946-50 iodolyte as reference.](image)

Figure 5.7: Test on electrolyte Z946-50 with 5%wt of amorphous silica nanoparticles, NH₂ and NH⁺₃ functionalized silica nanoparticles (chemical structure described in the text). (top) Relative and (bottom) absolute results calculated using Solaronix Z946-50 iodolyte as reference.

of \( I_{sc} = 4.29\,mA,\; V_{oc} = 0.719\,V,\; FF = 0.64\,mA/cm²,\; J_{sc} = 11.92\,mA/cm² \)
and an efficiency of $\eta = 5.47\%$ was obtained for reference electrolyte in perfect agreement with other mixtures as shown in figure 5.7. It can be observed that the amorphous silice F5 increase the $J_{sc}$ of 15mA/cm$^2$ but decrease the $V_{oc}$ of 0.1mV, with no change in efficiency with respect to the reference electrolyte. On the contrary the $NH_2$ functionalized silica increase the $V_{oc}$ of the cells tested while it doesn’t affect the $J_{sc}$ characteristic. The $NH_3^+$ functionalized silica is in perfect agreement with the performance of the reference cells (apparently there is no change in any characteristic, except a decrease of 0.07 mV in the $V_{oc}$). Even if no observable changing in efficiency were obtained, the results reported mean that silica, functionalized or not, are suitable as gelators. This consideration derives from the fact that consequence of the addition of nanoparticles into the electrolyte is an increase in viscosity (which bring to a decrease in the diffusion) and if the performances are not affected, it means that there exist some behaviour which increase the chemical diffusion, as described in Chapter 3.

5.3.2 Talcs

Talcs are lamellar materials belonging to the pyrophyllite species with a structure TOT (tetrahedral-octahedral-tetrahedral) (figure 5.8). The chemical formula of a generic talc is $Si_4Mg_3O_{10}(OH)_2$. In this work four different types of functionalized talcs were tested. The synthesis process allows to obtain hybrid materials by attaching to the Si atoms in the interstitial space a defined amount of organic groups. In this way it’s possible to change in a controlled way the amount of organic chain and consequently to control the surfacial properties.

Figure 5.8: (left) General 3D structure of layered talc. (right) Talcs structure of the type of TA 021/31, TA029B, TA 035/41 (1st picture) and TA027B (2nd picture).

Chemical composition of the used talcs is the following:

1. **TA021/31**: $Mg_3Si_4O_{10}(OH)_2(CH_2CH_2CH_2NH_2)_{2.96}$
2. **TA 029B**: $Mg_3Si_4O_{10}(OH)_2(CH_2CH_2CH_2NH_2)_{1.43}$
3. **TA 035/41**: $Mg_3Si_4O_{10}(OH)_2(CH_2CH_2CH_2NH_2)_{1.40}$
4. **TA 027B**: $Mg_3Si_4O_{10}(OH)_2(CH_2CH_2CH_2NHCH_2CH_2NH_2)_{0.33}$
Figure 5.8 shows the functionalized talcs; in particular TA021/31, TA029B, TA 035/41 are of the type in the left side, while TA027B is of the type in the right side. Figure 5.9 shows the TEM of the two different types of talc tested: TA 021/31 and TA 027. The TEM analysis reveals aggregates of 500 nm with a lamellar structure of size around 20-50 nm for TA 027 and aggregates of 300 nm with no identified substructure for TA 021/31. Cells tested were made as described at the begin of this section: in particular the electrolyte was obtained by adding 5 %wt of nanoparticles of talc into the Solaronix Z946-50 iodolyte, stirred overnight. The stirring of the electrolyte solution was stopped 20 minutes before using the mixture for the cell preparation, according to the DLS (dynamic light scattering) for the Ta027 and for the Ta021/31 into 3-methoxypropionitrile. The DLS analysis was done for the two sample in the same condition of the electrolyte used in the cells: a solution of 3-methoxypropionitrile with Ta027 and Ta021/31 nanoparticles (figure 5.10). The analysis shows that the initial size of $\sim 4.5\mu m$ for Ta027 immediately falls down to $\sim 0.4\mu m$ (in the first 15 minutes), while for the Ta021/31 the size slight decreases up to a size of 50nm. Best efficiency and performance results were obtained for TA021/31 and for TA035/41, with a relative increase of 112% for the second one, with values respectively: $I_{sc} = 4.5\text{mA}$, $V_{oc} = 0.744\text{V}$.
Figure 5.10: Dynamics light scattering (DLS) analysis of two talcs sample (Ta027 and Ta021/31), at 5%wt into 3-methoxypropionitrile solution with waiting time from 15 minutes up to 6 hours and 30 minutes.

\[ FF = 0.67 mA/cm^2, \quad J_{sc} = 12.61 mA/cm^2, \quad \eta = 6.27\% \quad \text{and} \quad I_{sc} = 4.24 mA, \]
\[ V_{oc} = 0.791 V, \quad FF = 0.70 mA/cm^2, \quad J_{sc} = 11.77 mA/cm^2, \quad \eta = 6.47\% . \]

Figure 5.11 shows the obtained results revealing that the increase in efficiency is due to an increase in the \( V_{oc} \), while the short circuit current remains almost the same or decrease in the cases of TA035/41 and TA029B. Some basic considerations can be done only by observing the chemical composition of used talcs; the worst result of Ta027B may be due to the low amount of chains or to an effect of the longer chains. Some more studies need to be done. Instead observing Ta 21/31 and Ta 35/41 should be almost clear that the increasing of the amount of the carbon chain beyond 1.40 doesn’t affect anymore the performances. Moreover it’s interesting to observe the great difference between Ta 29B and Ta 35/41; in fact the two talcs have apparently the same stoichiometric number. The first one was synthetized at room temperature, while the second one was synthetized at the temperature of 100°C. The difference can be explained by residual water and organic parts of the built up process.

5.3.3 Saponite

Structure and properties  Saponites are a trioctahedral phyllosilicate belonging to the smectite group. They are principally composed of allumium, silicium, Magnesium and oxygen; the general chemical formula is:

\[
M_{x/n}^{+\,+}[Mg]_6(\text{OH})_4[Si_{8-x}Al_x]_2O_{20}mH_2O
\]

where M is the exchange cation with charge n lying between the lamellars, x is the fraction of Al atoms and m is the number of water molecules [57]. Saponite is a Si:Al 2:1 phyllosilicate type and it has a TOT structure (figure: 5.12). T-sheets contains Si atoms, while O-sheets contain Mg atoms. The negative charge of the structure is due to interstitial substitutions \( \text{Al}^{III} \rightarrow \text{Si}^{IV} \); this negative charge is balanced with cations \((\text{Na}^+, \text{K}^+, \text{Ca}^{2+}) \) between different layers. Interlamellars space is between 0.1 nm and 10 nm and different sheets are bonded with weak ionic bonds with the exchange cations up to 100 nm lamellar packets.
Figure 5.11: Test on electrolyte Z946-50 with 5%wt of talcs nanoparticles (chemical structure described in the text). (top) I-V curve representation (refers only to best cells); (bottom) Absolute results calculated using Solaronix Z946-50 iodolyte as reference.

The general macrostructure of saponite is in the so-called turbostratic stacking: in other words there is no order in the lamellars packet and they link among them in an open house of cards[58].

<table>
<thead>
<tr>
<th>Type</th>
<th>Average</th>
<th>$I_m$</th>
<th>$V_m$</th>
<th>$FF$</th>
<th>$A$</th>
<th>$b$</th>
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<tbody>
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<td>8.39</td>
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<td>8.39</td>
<td>0.99</td>
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</tr>
<tr>
<td>NaSap 200</td>
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<td>1.88</td>
<td>0.86</td>
<td>8.39</td>
<td>0.99</td>
<td></td>
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<tr>
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<td>0.86</td>
<td>8.39</td>
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<td>0.86</td>
<td>8.39</td>
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<tr>
<td>NaSap 750</td>
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<td>0.86</td>
<td>8.39</td>
<td>0.99</td>
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</tr>
<tr>
<td>NaSap 1000</td>
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<td>1.86</td>
<td>0.86</td>
<td>8.39</td>
<td>0.99</td>
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</table>

Figure 5.12: (on the left) Representation of the structure of the Saponite; in this example a saponite which contains sodium cations and (on the right) the open house of cards structure.

The four type of tested saponite are NaSap20 (50, 110, 150). The prefix represents the exchange cations in the interlayers space, while the suffix number corresponds to the amount of water used during the synthesis process; in particular it refers to the relation $H_2O/Si$. For instance a sample of NaSap 50 means that during the synthesis the relation $H_2O/Si = 50$ was used for the preparation of the gel, while the Na prefix means that the exchange cations in the interlayer space is $Na^+$. In order to test and understand the behaviour of the different
type of saponite, in this section TGA, TEM and DLS analysis are presented. Saponites are stable up to 550°C as shown in figure 5.13. Up to 550°C there are only two losses of weight. The first one, between 30 and 150°C corresponds to the H$_2$O adsorbed to the surface, while the second one, between 150°C and 550°C, is due to the interlayers water. Beyond 550°C the lamellar structure starts to collapse.

Figure 5.14 shows the TEM of the different samples (with different amount of water) and the nanoparticle size. The analysis reveals that the sample NaSap20 presents an ordered lamellar structure, while increasing the amount of water the disorder of the structure increases and the open house of cards structure appears. The size of nanoparticles, depends on the amount of water used during the synthesis (represented by the suffix in the name) as the fraction of H$_2$O/Si: it has values of: 200nm for the NaSap20, 70nm for the NaSap 50 [59] and about 40nm for the NaSap 110-150. Figure 5.13 also shows the DLS analysis (dynamic light scattering) of the saponite nanoparticles into a solution of 3-methoxypropionitrile (5%wt of nanoparticles, the percentage tested in the preliminary studies into the test cells). It is interesting to observe the size of the lamellars in time; in fact, NaSap20 (50 and 110) maintains the same size in time (between 3 and 5 µm), while the NaSap150 has a completely different behaviour. It starts with nanoparticles size of 1 µm and only after 15 minutes the size decrease up to 0.5µm and remains constant.

**Obtained results.** The test cell design used for saponite was exactly then the previous. Experimental datas are reported below.

In figure 5.15 efficiency for all different saponites increases respect to the reference electrolyte (except for the NaSap150, which shows the same results of Z946-50 electrolyte). This good performance is due principally to an increase in the short circuit current. It is interesting to observe that best performances, on average, are obtained for NaSap 110, while best absolute performance are quite similar for NaSap50 and NaSap110 with respectively: $I_{sc} = 5.01 mA$, $V_{oc} = 0.741 V$, $...$
Figure 5.14: TEM images of (a) NaSap20 (b) NaSap50 (c) NaSap110 (d) NaSap150. Increasing the amount of water the nanoparticles size and the order of the structure decrease
Figure 5.15: Test on electrolyte Z946-50 with 5%wt of saponite nanoparticles (chemical structure described in the text). (top) Absolute results and (bottom) relative results calculated using Solaronix Z946-50 iodolyte as reference.

\[ FF = 0.68 \text{mA/cm}^2, \quad J_{sc} = 13.93 \text{mA/cm}^2, \quad \eta = 7.02\% \quad \text{and} \quad I_{sc} = 5.05 \text{mA}, \]

\[ V_{oc} = 0.746 \text{V}, \quad FF = 0.67 \text{mA/cm}^2, \quad J_{sc} = 14.02 \text{mA/cm}^2, \quad \eta = 7.03\% \quad \text{after 4 days of aging into the light soaker}. \]

It is interesting to note that NaSap150 is the only saponite which presents worse performance than reference, in aging and absolute results. This should be explained observing the DLS analysis (figure 5.13): in fact as shown by the size particles analysis the NaSap150 is the only one which differs from the other particles. Thus the worse performance could be explained by the smaller particles into a 3-methylpropionitrile solution (as Z946-50 electrolyte). However, figure 5.16 shows the stability graphs (for the efficiency and the \( V_{oc} \)) over a week of light soaking and all materials exhibit a perfect stability.

Figure 5.16: Stability results over 7 days of light soaking for electrolyte Z946-50 with saponite at 5 %wt
5.3.4 Electron carrier materials: TiO$_2$ nanoparticles

As described in Chapter 4, Usui & Al. [47], injected different nanoparticles into a ionic liquid electrolyte based on EMim-TFSI, obtaining best performances for titanium dioxide nanoparticles. In that experiment, 1%wt of TiO$_2$ was injected into the IL electrolyte and then the solution was centrifugated in order to obtain a kind of gel paste. The same experimental design was used with some modifications; in particular Emin-TCB IL was used, instead of Emin-TFSI, which showed better performances, the electrolyte wasn’t centrifugate in order to investigate the relation between the percentage of TiO$_2$ injected into the electrolyte and the performance of DSSCs. Different amounts of nanoparticles were tested: 1%, 2% and 5%. For all cells tested the following design was adopted: 3 T/SP plus 1R/SP layers of titania, 60$\mu$m thickness surlyn, N719 EtOH dye and no special treatment. The electrolyte was composed of:

- 1.5 M Emim-I,
- 0.1 M LiI,
• 0.15 M $I_2$,
• 0.5 M TBP

into Emim-TCB solution. Titania nanoparticles were added in different percentage and the electrolyte was stirred for at least 1 hour and sonicated for 30 minutes. The following results were obtained (figure 5.17) which demonstrates that TiO$_2$ nanoparticles are a good gelators. The low efficiency is due principally to bad design of dye and additives. In fact, as demonstrated by Graetzel & al [23], Z907 is a better dye for high viscous ionic liquid with consequently change in performance. The additives percentage has to be changed too. This preliminary study only shows another type of gelator without trying to optimize the cell design. Moreover, stability measurements were done over more than 800 hours of light soaking (more than 20 days). As shown in figure 5.18 all tested cells with different titania percentage exhibit a good durability in time except the cell with the electrolyte with 1% wt of nanoparticles. Probably this behaviour is only due to a bad sealing process.

Figure 5.18: Efficiency, $J_{sc}$ and $V_{oc}$ stability measurements over 20 days of light soaking for Emim-TCB IL with 1%, 2% and 5% wt of titania nanoparticles

5.4 Gel electrolyte

In order to maximize performances of QuasiSolidDSSCs (QSDSSCs) another set design was used. Following data in literature and other preliminary studies, better performances were obtained with the so-called Z907 dye. This is due to faster back transfer of electrons from the conduction band of the TiO2 film to triiodide, which lowers the Voc, and consequently the efficiency of the cell with N-719 dye. Instead Z907, with its long hydrocarbon chains, slows the back reaction[60].
The gel electrolytes studied in this work are based on the Z952 ionic liquids mixture, the surlyn thickness is of 25 µm, lower than in the other test cells; it was chosen thinner because of the lower mobility of ions into the quasi solid electrolytes. 20% of different types of nanoparticles were added to Z952 in order to take advantage of some behaviour as electron conduction increase, hole transport diffusion or more simply the reflection of some wavelength, as described for the active gelators.

The titania electrode was made with three layers of T/SP, with 20 nm size nanoparticles, and a final reflective layer of 1 R/SP with 100 nm size nanoparticles. Moreover the electrode were TiCl$_4$ treated, in order to improve chemical bonding between the first TiO$_2$ layer and the FTO sublayer on electrode glasses (Pre-treatment) and to improve the diffusion process in the electrode (Post-treatment).

5.4.1 Gel electrolytes based on silica nanoparticles

The following cells were prepared using the design set described just above and adding 20% wt of nanoparticles of commercial F5 silica to the IL Z952. Performance and stability measurements are reported. Unfortunately due to the high standard deviation obtained from datas collected, it is impossible to say something about repeatability of experiment and about relative results. In fact, even if Silica gel apparently shows better result it is impossible to derive some conclusion. These tests were affected by reproducibility problems probably due to the sealing process of the cells. Instead observing stability graphs is clear that the decreasing efficiency is principally due to a short circuit current decreasing (figure 5.19 and 5.20).

These results can be due for many reasons: principally the high inefficient stability is for problems during the sealing process. In fact gel electrolytes were spread on the titanium electrode by hand or by doctor blade and then the cell is fixed with a quasi instantaneous glue. This low precision method allows to air bubble to lie into the close cell. Moreover the surlyn thickness is affected by a big error. Another consideration must be take into account: all gel electrolyte tested suffer a drying process in the first days. In fact if just stopped to stir the solution is quite liquid, after few minutes it starts to solidify. This drying process, added to little air bubbles inside the cells, creates big cracks.

5.4.2 Saponite

The same cell design was used for the Saponite gel. According to the general description, 20 % wt of saponite nanoparticles was added into the ionic electrolyte in order to obtain a gel electrolyte. Saponite 20, 50, 110 and 150 was added.
Figure 5.20: Efficiency, $J_{sc}$ and $V_{oc}$ stability measurements over 120 hours of light soaking for Z952 ionic liquid electrolyte with 20%wt of commercial silica F5 nanoparticles

Performance and stability results are shown in figure 5.21 and in figure 5.22. In comparison with electrolyte Z952 all gels show equal or better performance, while observing the stability graphs it is possible to see a good stability up to 150 hours of light soaking; then all saponite gel start to lose both short circuit current and open circuit voltage. All materials exhibit a little loss after the first days of light soaking probably due to a stabilizing process into the solar cells. Completely different is the behaviour of the NaSap110 that shows a constant increase of open circuit voltage and a good stability for the short circuit current. Particular attention is necessary to derive some conclusion for the stability because of the constant increasing of the cells based on the reference electrolyte Z952.

5.4.3 Functionalized Saponite

In order to obtain materials with higher diffusivity and in agreement with other materials into the DSSCs, at the University of Oriental Piedmont, some modifications to the saponite surface were made. In particular the structure of the NaSap110 (described in the previous section) were modified with some organic groups attached to the saponite surface by covalent binds. The synthesis process of the saponite was modified by one-pot synthesis methods by introducing 1-aminopropyltriethoxysilane in order to attach $NH_2$ groups or by introducing 3-methoxypropionitrile silane in order to attach the COOH groups to the saponite surface. The schematized structure is shown, like for functionalized talcs, in figure ??, using COOH and ammine groups.

The test cell design was the same described in the introduction of this section. 20 %wt of $NH_2$-NaSap110 and of the COOH-NaSap110 nanoparticles
Figure 5.21: Test on Z952 electrolyte ionic liquid (composition described in the text) with 20%wt of Saponite nanoparticles (Saponite with relation $H_2O/Si = 20, 50, 110, 150$ during the synthesis process and with sodium ions as exchange cations into the interlayers space; structure and properties are described in previous section). (top) Absolute results and (bottom) relative results calculated using IL electrolyte as reference.

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Figure 5.22: Efficiency, $J_{sc}$ and $V_{oc}$ stability measurements over more than 200 hours of light soaking for Z952 ionic liquid electrolyte with 20%wt of NaSaponite nanoparticles (NaSap20,50,110,150)
were added into the Z952 ionic liquid electrolyte. Good performances (figure 5.23) were achieved for both cells with the two functionalized saponite gel, particularly for COOH Saponite. Characteristic of best cells (showed in I-V curve) are respectively for COOH and NH$_2$ saponite: $I_{sc} = 2.66mA$, $V_{oc} = 0.714V$, $FF = 0.7mA/cm^2$, $J_{sc} = 7.4mA/cm^2$, $\eta = 3.67\%$ and $I_{sc} = 2.3mA$, $V_{oc} = 0.683$, $FF = 0.74mA/cm^2$, $J_{sc} = 6.39mA/cm^2$, $\eta = 3.22\%$. These results can be compared with the reference Z952 ionic liquid electrolyte ($I_{sc} = 2.27mA$, $V_{oc} = 0.679$, $FF = 0.69mA/cm^2$, $J_{sc} = 6.306mA/cm^2$, $\eta = 2.965\%$) and it reveals a good result for both nanoparticles. Stability graphs (figure 5.24) reveal that cells with COOH saponite, which have the best results in performance, unfortunately dies quickly. The $V_{oc}$ characteristic remains almost constant while the short circuit current decrease constantly. On the contrary cells with NH$_2$ saponite have a good durability in time; they remain constant up to 70 hours (3 days), and start to lose short circuit current, and consequently efficiency, since the third day of light soaking. The $V_{oc}$, instead, shows a good stability up to 120 hours 5 days.

Figure 5.23: Test on Z952 electrolyte ionic liquid (composition described in the text) with 20%wt of functionalized NaSap110 nanoparticles (with NH$_2$ or COOH groups on interlayers surface). (top) I-V curve of best cells obtained. (middle) Absolute results and (bottom) relative results calculated using Z952 IL electrolyte as reference.
5.4.4 Titania nanoparticles as gelators

In this section the same electrolyte based on Emim-TCB (described in previous section) was used to test the electrolyte made with respectively 10%, 15% and 20%wt of titania nanoparticles. In the case of 15% the solution is still liquid but consequence of too high viscosity, it was not possible to use anymore the vacuum chamber to fill the cells; the gelation point occurs between 15% and 20% of TiO₂. Results obtained are shown in figure 5.25 revealing a relative increase in efficiency of 120% and of 125% respectively for 15% and the 20% wt gel; the results show that the increase in efficiency is due to an increase in all characteristics. Cells with only 10%wt of TiO₂ nanoparticles into the electrolyte show a worse behaviour than the reference cells with only the ionic liquid electrolyte. This could be to the fact that the benefit by adding TiO₂ nanoparticles occur only near the gelation point of the electrolyte.

5.5 Novel Organic Dyes for DSSC application

5.5.1 Squaraine

Some novel organic dyes were tested for the DSSC preparation. In particular, two squaraine dyes were used to study the effect of changing the carbon chain in the structure (R in figure 5.26): indeed, as described in the Chapter 3 a longer carbon chain can have some benefit on the cell performance, especially to block the formation of aggregates, to create some void space between the TiO₂ surface and the dye, which should be able to decrease the electron recombination, thus improving the charge transfer mechanism. The squaraine molecules studied in this work is shown in figure 5.26, where the R is an eight carbon chain (VG10C8) or an ethyl group (VG10C2). The absorbance spectra and IPCE characteristic
Figure 5.25: Test on electrolyte based on Emim-TCB ionic liquid (composition described in the previous section) with 10%, 15% and 20%wt of TiO$_2$ nanoparticles. (top) I-V curve representation (refers only to best cells); (middle) Absolute results and (bottom) relative results calculated using IL electrolyte as reference.
The tested cells had 3 T/SP layers plus 1 R/SP reflective layer of TiO$_2$ and pre and post TiCl$_4$ treatment (explained in the introduction), 25 µm surlyn thickness, N719 dye in an EtOH solution as reference, Platisol T as counter electrode and a TCO glass, with a sublayer of FTO. The electrolyte was the JH163 described in the optimization part. The dye solution was prepared with 0.1mM of squaraine, 10mM of CDCA in EtOH. Collected data (figure 5.28) show that the use of this squaraine dyes does not allow to reach the typical efficiency of Ruthenium complexes. The two squaraines have lower $V_{oc}$ respect to N719 dye. VG10C8 shows an higher $J_{sc}$ with respect to the VG10C2, but still lower than N719. As explained in the chapter above, organic dyes decrease the $V_{oc}$ because of they lower the conduction band of the titania, but in general they have very high short circuit photocurrent, due to high absorption coefficient. A low photocurrent can be explained by:

- dye aggregates on the surface of TiO$_2$;
- high degradation of the dye during the sealing process, due to the low photostability of squaraine;
- a TiO$_2$ thickness design problem.

Squaraine, as many organic dyes, have a very high molar extinction coefficient; usually they present an high photocurrent still with few µm of titania despite
of the ruthenium complexes which need at least 10 \( \mu m \). If for Ruthenium dye the optimized thickness is around 10 \( \mu m \), it is not always the best for organic dyes. Figure 5.20 shows the stability graph over 320 hours (almost two weeks) of light soaking. The VG10C2 dye has the worst stability: after the second day, it starts to lose both \( V_{oc} \) and \( J_{sc} \). On the contrary the VG10C8 dye shows a good stability during two weeks. In fact it loses less than 1mA in \( J_{sc} \) in two weeks while the \( V_{oc} \) remains stable, completely due to a loss in the fill factor (from 0.69 to 0.63). It is interesting to note that cells with VG10C2 after some days became completely white. VG10C8 was tested with two different electrolytes in order to study the stability of cells prepared with different electrolytes. The first electrolyte tested was Solaronix Z150 and the second was JH163 (the composition is described into the optimization section). Best performances for JH163 and Z150 were respectively: 

- For JH163: 
  - \( I_{sc} = 4.094mA \), \( V_{oc} = 0.532V \), \( FF = 0.675mA/cm^2 \), \( J_{sc} = 11.373mA/cm^2 \) and \( \eta = 4.083\% \), and 
  - \( I_{sc} = 3.068mA \), \( V_{oc} = 0.549V \), \( FF = 0.683mA/cm^2 \), \( J_{sc} = 8.522mA/cm^2 \) and \( \eta = 3.195\% \). 

Obiously the acetonitrile based electrolyte shows better performance. Tested cells stayed were left for more than 1 month under light soaking at 1
5.5.2 D5

A promising dye for QSDSSCs was studied by Hagberg & al [63], the so-called D5. The D5 is an organic dye based on diphenylaniline (figure 3.7) as electron donor. D5 dye should be very interesting due to its simple and cheap synthesis process and, as all organic dyes, to its high extinction coefficient. In dye tested the diphenylaniline acts as electron donor while the cyanoacetic part
acts as electron acceptor and anchoring groups (figure 5.31). The three step synthesis of the dye involve well known reactions. The thiophene moiety was coupled to 4-(diphenylamino)benzaldehyde accordingly to the Wittig reaction, followed by formylation of the thiophene functionality. Finally condensation of the aldehyde with cyanoacetic acid by the Knoevenagel reaction in the presence of piperidine: an acetonitrile (MeCN) solution of 5-(2-(4-diphenylamino-phenyl)-vinyl)-thio-phene-2-carbaldehyde and cyanoacetic acid was refluxed in the presence of piperidine for 4 h. Solvent removal by rotary evaporator yielded a dark purple solid. UV-vis and fluorescence spectra of the dye in acetonitrile show two absorption bands with absorption maxima at 476 nm and 300 nm and the extinction coefficient determined is $37,600 \text{ M}^{-1}\text{cm}^{-1}$ at the absorption maximum 476 nm in acetonitrile (figure 5.32). Instead when the dye is attached to TiO2, a blue shift of the absorption maximum from 476 nm to 444 nm was found. In this work, D5 dye was first tested into cells with ionic liquid electrolyte; in particular N719 was used as reference dye, in combination with ionic liquid Z952 electrolyte, 25 $\mu$m thickness surlyn, 3 transparent (T/SP) layers of TiO2 more 1 reflective (R/SP) layers of TiO2 and pre-post TiCl4 treatment (described in the introduction section). The following results were obtained (figure 5.33). Due to good comparison to the N719 dye, D5 was also tested into cells with gel electrolyte based on ionic liquid Z952 plus 20%wt of NaSap150 nanoparticles. In this case only 2T/SP layers of titania were printed and the reference dye was the Z907. New results are shown in figure 5.34. Best performance for cells prepared with D5 dye was: $I_{sc} = 3.7\text{mA}$, $V_{oc} = 0.64\text{V}$, $FF = 0.63\text{mA/cm}^2$, $J_{sc} = 10.27\text{mA/cm}^2$ and $\eta = 4.12%$; while for Z907 was $I_{sc} = 3.24\text{mA}$, $V_{oc} = 0.693\text{V}$, $FF = 0.63\text{mA/cm}^2$, $J_{sc} = 8.99\text{mA/cm}^2$ and $\eta = 3.93%$. 

Figure 5.31: (top) D5 chemical structure (middle) HOMO representation (bottom) LUMO representation
Figure 5.32: D5 dye absorption (— line) and emission (continuous line) of the D5 dye in acetonitrile compared with the absorption spectrum of the dye attached to TiO2 (...). The excitation wavelength for emission was 460 nm. The absorption and emission maxima in acetonitrile are 476 nm and 625 nm. The absorption maximum of the dye attached to the TiO2 nanoparticles is blue shifted to 444 nm.

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<td>0.60</td>
<td>10.46</td>
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</table>

Figure 5.33: (right) relative results (left) absolute results. All values refers to an average over 5 cells.

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Figure 5.34: D5 dye with gel electrolyte based on Z952 and NaSap150 (right) relative results (left) absolute results. All values refers to an average over 5 cells.

It is clear that the D5 decrease the $V_{oc}$ and increase the $J_{sc}$, as almost all organic dye. Interesting is to observe the stability graphs (figure 5.35); in fact the total efficiency decrease during time, due to high instability of gel electrolyte, but the $J_{sc}$ and the $I_{sc}$ for D5 dye increase of some mA.

5.6 New approaches for DSSC preparation

In this section two new approaches for DSSCs are presented. The reported results are not complete but can be considered as a possible starting point for future experiments on DSSCs.

5.6.1 Electrolyte bath

One of the major difficulty for QSDSSCs and for gel electrolytes is the sealing process. In fact, even if some nanogelators were found in order to improve efficiency, open circuit voltage and short circuit current, an effective and useful way to seal Graetzel cells with gel electrolytes is not yet found. In fact, cell performances in the first day of aging are very competitive with respect to cells with other liquid electrolytes but the same cannot be said with their stability. The physical problems, due to the presence of air inside cells, due to electrolyte drying and surlyn contamination with the electrolyte during the melt phase can not be solved using doctor blade technique or using other handmade approaches. One solution may be to spread the electrolyte layer over the titania electrode before the sealing process, waiting some hours, or days (it depends on the material and the concentration of gelators), in order to allow to dry the electrolyte and better adhesion with the titania layer. Two type of bath were tested: for the first group two bath were used; first night the usual dye bath and the second night the cells were dipped directly into the electrolyte. For the second group only one bath with a mixture of half dye solution and half electrolyte was used for one night. Cell design was: 3 layers of T/SP more
1 reflective layer, pre-post TiCl$_4$ treatment, 25µm thickness surlyn, N719 dye solution and JH163 electrolyte.

Obtained results (figure 5.36) show that performances are not comparable with classical cell design, but it demonstrates that total performances are not too much affected by this treatment and this design way can be useful to well-spreading gel electrolyte. Even if average values obtained are not comparable, best cells for each type of bath are perfectly in agreement and after an optimization process results should be the same or better. The classical design with the electrode soaked by the dye solution overnight, the second design with the two days bath (TiO$_2$ soaked into the dye for 1 night and the second night it is soaked directly into the electrolyte) and the third design (TiO$_2$ soaked for 1 night into a mixture of 50% of dye solution and 50% of electrolyte solution) best results are respectively: $I_{sc} = 5.91mA$, $V_{oc} = 0.699V$, $FF = 0.68mA/cm^2$, $J_{sc} = 16.42mA/cm^2$ and $η = 7.76\%$, $I_{sc} = 4.79mA$, $V_{oc} = 0.779V$, $FF = 0.7mA/cm^2$, $J_{sc} = 13.31mA/cm^2$ and $η = 7.31\%$, and $I_{sc} = 5.2mA$, $V_{oc} = 0.737V$, $FF = 0.71mA/cm^2$, $J_{sc} = 14.44mA/cm^2$ and $η = 7.55\%$.

### 5.6.2 Coloured Titania nanoparticles

Another possible approach can be to colour nanoparticles added inside the electrolyte. The idea is to build an heterojunction cell with titania and electrolyte, also solid, perfectly mixed and to take advantage from the nanoparticles, not only for the transport properties but also increasing the light harvesting efficiency. The cell design was: 3 T/SP layers more 1 R/SP titania layer, 60µm thickness surlyn, N719 dye solution. The four electrolytes tested was based on the Emim-TCB ionic liquid electrolyte, described in the section of TiO$_2$
Figure 5.36: The TiO$_2$ were soaked into two type of bath: for the first group (1st bath) of cells two bath were used; first night the usual dye solution bath and the second night the cells were dipped directly into the electrolyte. For the second group (2nd bath) of cells only one bath with a mixture of half dye solution and half electrolyte was used for one night. The reference was the typical design with the dye bath overnight. (left) Relative and (right) absolute results.

nanoparticles, by adding 5, or 10, % of TiO$_2$, pure or coloured, and then strongly stirred for half hour. The coloured titania was obtained by using the same N719 dye solution adding the untreated TiO$_2$ powder inside and left overnight into the dye. Then, mixture was filtered in order to obtain the coloured powder. Results show a low increase in efficiency for the 5% solution while worse characteristics for the 10% solution were obtained.

Figure 5.37: Test on electrolyte based on Emim-TCB ionic liquid (composition described in the previous section) with 5% or 10% of TiO$_2$ (Degussa) nanoparticles, normal and coloured. (left) Relative results and (bottom) absolute results calculated using IL electrolyte based on Emim-TCB (described in previous section on TiO$_2$ gelator) as reference.

In conclusion this design and the electrolyte bath are two ways to solve the gel spreading into DSSC only if well-thought. These two experiments are just some preliminary study in order to open some new routes. In fact the external drying process, described in the electrolyte bath can solve effectively the sealing process, while TiO$_2$, coloured or not, can bring research on a new eterojunction design for DSSC; much better results, probably, can be obtained, for titania gel, by using dye with a greater band gap such as squarine or organic dyes. Linking the two methods should be also possible to decrease the titania layer, due to
light absorbing properties of the electrolyte, and to allow the screenprinting for
the electrolyte, or for a mixture between $TiO_2$ and electrolyte, method which
is showing quite interesting results.
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