Solid-state dye-sensitized solar cells measurements at different pressures and temperatures in a controlled vacuum chamber

Azhar Zia
Abstract

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Solid-state dye-sensitized solar cell devices based on dye LEG4 (4,4-dihexyl-4H-cyclopental[2,1-b:3,4-b’]dithiophene-CPDT) were investigated in systems containing different concentrations of LiTFSI. LiTFSI is an additive used to increase the conductivity of the different hole transport materials (HTMs). The ssDSSCs were photoelectrochemically characterized using a pressure and temperature controlled vacuum chamber setup. A new sample holder was also developed for performing photovoltaic measurements, specially incident photon to current conversion efficiency (IPCE) measurements. The performance of the new sample holder was found to be satisfactory in comparison to a standard IPCE measurements setup. Vacuum chamber setup IPCE measurements on ssDSSCs configurations with and without LiTFSI showed the importance of LiTFSI for the complete devices to function. IPCE measurements at different temperatures on ssDSSCs with P3HT and spiro-OMeTAD based systems were also tested. It was noticed that spiro-OMeTAD based cells performed better than P3HT based cells. IPCE at different temperatures varied and caused irreversible changes to the cells. At higher temperatures the IPCE decreased. Further increase in temperature can cause damages to the cells. The UV-Vis absorption responses of LEG4 at 2 micrometer (µm) TiO2 films and with different concentrations of LiTFSI were investigated. It was found that the HOMO-LUMO gap shrinks and becomes narrower with higher concentrations of LiTFSI. It was also observed that LiTFSI affects both the dye as well as the HTMs. Photoelectron spectroscopy (PES) was also used. The photovoltaic performances of ssDSSCs were found to be dependent on dye binding which showed differences in structure. It was observed that LiTFSI oxidized the LEG4 dye and caused internal modification in the structure, i.e. S2p and N1s PES spectra shifted towards the higher binding energies. It was also found that LEG4 coverage decreased when the concentrations of LiTFSI increased.
Summary

Nanotechnology opens a door to create a variety of nanostructures for use in photovoltaic (PV) materials. PV is rapidly growing renewable energy technology. The production of PV panels has exceeded 280 mega watt (MW) per year. The development of new materials and manufacturing methods over decades strongly assisted to the growth of the semiconductor industry regardless from their cost, i.e. the cost of solar cell has remained still high. The PV electricity is generally more expensive than the electricity produced by other resources. The need of the time is to reduce the cost of the solar cell which remains as driving force for the PV materials development.

In 1991, a new type of solar cell was developed which may be enabled production of low-cost solar cells in the future. The new type of solar cell is dye-sensitized solar cells (DSSCs). The DSSCs is a new type of PV device that can be produced to a tenth of the cost of crystalline silicon solar cell. DSSCs could be enable production of low-costs solar cells, easy fabrication, and relatively high efficiency. DSSCs normally consists of (i) the working electrode that can be deposited on fluorine coated tin oxide (FTO) or plastic substrate, (ii) the counter electrode, and (iii) the redox mediator usually a liquid electrolyte or solid (HTMs). The conversion of light energy into electric energy take place upon illumination that excites a dye electron to higher energy levels which can be transferred from the dye molecules to the conduction band (CB) of titanium dioxide (TiO2). Then the oxidized dye molecules are regenerated by getting electrons from the redox mediator. Finally the electrons are transported to the counter electrode (CE) and reduce the redox mediator to complete the cycle. Liquid-state DSSCs caused electrolyte leakage, corrosion, and evaporation problems. Thus recent research has been focused on ssDSSCs by replacing conventional liquid electrolytes with solid HTMs. The working principle of ssDSSCs is similar to liquid-state DSSCs, HTMs play the role as liquid redox electrolytes.

Generally, solid HTMs such as spiro-OMeTAD (2, 2′, 7, 7′-tetrakis (N,N-di-p-methoxyphenyl-amine)-9,9), P3HT (poly-3-hexylthiophene-2,5-diyi), and PEDOT:PSS poly (3,4-ethylenedioxythiophene) poly (styrenesulphonate) are applied on dye-sensitized TiO2 electrodes by spin-coating or through polymerization. However, it is not easy for HTMs to percolate into and intermingle with TiO2 pores. In order to increase the conductivity of HTMs the additive LiTFSI (Lithium bis (trifluoromethylsulfonyl) imide) is used. The purpose of this thesis is to investigate the role of LiTFSI in increasing efficiency to ssDSSCs. Three different methods are utilized to characterize the performance of ssDSSCs, i.e. photoelectrochemical measurements in a vacuum chamber setup, UV-Vis (Ultraviolet visible spectroscopy), and Photoelectron spectroscopy (PES). In order to perform vacuum chamber PV measurements, e.g. IPCE, a new sample holder was also designed.

In this thesis the organic dye LEG4 was used in the experiments. The dye LEG4 is considered to absorb more incoming light compared to its analogues. Different thicknesses of TiO2 layers with different concentrations of LiTFSI were used to optimize the solar cell devices. After a series of UV-Vis spectroscopy experiments it was found that absorbance spectra on thinner TiO2 surfaces were red shifted, i.e. towards the longer wavelengths. It is also observed from PES experiments that LiTFSI caused shift towards higher binding energies, i.e. from S2p and N1s spectra. Vacuum chamber setup measurements were also made to LEG4 based ssDSSCs with HTMs spiro-OMeTAD and P3HT in order to investigate the photovoltaic performances (IPCE) at different temperatures. In vacuum an initial increase in IPCE spectra were observed when higher concentrations of LiTFSI were used. It was found that temperature really affects the overall efficiency of ssDSSCs. The IPCE spectra of ssDSSCs varied at higher temperatures. It was assumed that temperature caused changes to the internal structure. The changes in IPCE spectra are irreversible. HTMs based DSSCs are a promising research
area and the vacuum technology for conducting temperature based measurements to ssDSSCs is an alternative way for future development.
Abbreviations

AM  air mass density
CIGS  copper indium gallium selenide
IPCE (λ)  incident-photon-to-current-conversion efficiency
LHE  light harvesting efficiency
WE  working electrode
LiTFSI  lithium bis (trifluoromethanesulfonyl) imide
H₂SO₄  sulphuric acid
TBAOH  tertbutylammonium hydroxide
eV  electron volt
FTO  fluorine doped tin oxide
HOMO  highest occupied molecular orbital
LUMO  lowest unoccupied molecular orbital
I₀  light intensity
L  length
MeCN  acetonitrile
tbP  4-tert-butylpyridine
ε (λ)  extinction coefficient
λ  wavelength in nanometer
c  speed of light
f  frequency
Eᶠ  fermi level
Eᵍ  band gap
ℏ  Plank’s constant
TiO₂  titanium dioxide
UHV  ultra high vacuum
UV  ultra-violet
CB  conduction band
VB  valence band
<table>
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<tr>
<td>DSSC</td>
<td>dye-sensitized solar cell</td>
</tr>
<tr>
<td>ssDSSC</td>
<td>solid-state dye-sensitized solar cell</td>
</tr>
<tr>
<td>Irradiance</td>
<td>light intensity (W/m²)</td>
</tr>
<tr>
<td>bpy</td>
<td>bipyridine</td>
</tr>
<tr>
<td>CE</td>
<td>counter electrode</td>
</tr>
<tr>
<td>D</td>
<td>dye</td>
</tr>
<tr>
<td>D*</td>
<td>excited dye</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>P3HT</td>
<td>poly-3-hexylthiophene-2, 5-diyl</td>
</tr>
<tr>
<td>Spiro-OMeTAD</td>
<td>2, 2', 7, 7'-tetrakis (N, N-di-p-methoxyphenyl-amine)-9, 9'-spirobifluorene (spiro-OMeTAD)</td>
</tr>
<tr>
<td>PEDOT-PSS</td>
<td>poly(3,4-ethylenedioxythiophene)-poly(4-tyrenesulphonate)</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width half maximum</td>
</tr>
<tr>
<td>TPA</td>
<td>triphenylamine</td>
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<tr>
<td>LEG4</td>
<td>linker unit modification of donor-linker-based organic dye</td>
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Bibliography
1. Introduction

1.1 Background

Energy production is an important part in our society. The worldwide energy consumption primarily originates from fossil fuels, e.g. 37% come from oil, 25% from coal, 23% from gas, and 2% from renewable energy sources as illustrated in Fig. 1.1 These energy sources like fossil fuels are finite and might be used over a few centuries more. Fossil fuels are mainly formed from hydrocarbons and their large scale of usage result in an increase of the concentration of greenhouse gases in atmosphere. The release of carbon dioxide (CO$_2$) by burning of fossil fuels can cause a greenhouse effect that affects the planet’s temperature.2 Climate change is certain fact.2 Nowadays, our planet is much hotter than at any time over the past two thousand years. But if the current situation continues then the temperature will increase to its highest value during the last two million years at the end of the century.3 Fossil fuels are non-renewable sources and they are the basis to run our planet.3 Reserves are used much faster than new ones are created. This makes the energy crisis more and more serious. In 1970s, the threat of the energy crisis was globally realized and it stimulates interest to put a demand on us to carry out research on renewable energy sources.

All renewable energy sources have many advantages but solar energy is the only in this competition which can meet the global demand by providing full spectral composition of sunlight with vast amount of clean energy. The earth atmosphere can absorb 3850000 exajoules (EJ=10$^{18}$) per year.4 The clouds and oceans absorb approximately 75%, while the remaining is reflected back to the space.4 It can be assumed that with an efficiency of 25%, a solar cell covered area of 367×367 km in Sahara desert can meet the global energy demand required till 2050.4 The global energy demand by the year 2050 is twice at its present level. The solar energy is reaching to the earth’s atmosphere in one year is twice than all storage of non-renewable resources in our planet.4 Therefore, the solar energy is the only which has potential to meet the global demand. The solar energy can be converted in different ways; (i) converting it to heat, (ii) converting it to fuel, and (iii) converting it to electricity.5 They will all help us to solve some of the urgent global problems which we are facing.

Solar energy is abundant, inexhaustible, and environmental friendly. Some of the countries around the world are much warmer and solar energy availability is much higher. Thus, warmer countries will contain most of the world population in the next coming decades. The population will be about 7 billion versus 2 billion in the cold countries like Russia, USA, some parts of China, and Scandinavian countries. So the solar energy is entering into new areas of competitiveness and is considered good competitive against oil-based electricity, especially in warmer countries where major source of production is based on oil that used for electricity.

![Fig. 1: World total energy supply. Cadet blue category represents the renewable energy supply including tidal, solar, and wind generation etc, source: IEA (2008).](image-url)
1.2 Solar Cells

In 1839, the French physicist Edmond Becquerel was observed the photovoltaic effect for the first time when illuminating an electrode of silver. Fifty years later, the American inventor Charles Fritts built a solar cell using selenium with ultra thin transparent layer of gold (Au) and its efficiency was around 1 %. A solar cell directly converts the incident light into electricity. A solar cell uses light to excite electrons from lower energy levels to higher energy levels. This is only possible when the energy of the incident photon matches with allowed energy transitions in the cell. After electron excitation a hole is left behind. After de-excitation of excited electrons energy is liberated. The photovoltaic device (solar cell) uses this excess amount of energy before it recombines, i.e. by separating the charges for some external use.

The first modern cell was based on silicon and was invented at Bell Telephone Laboratory in 1954. The first practical cell with efficiency of 6 % was performed by using p-n junction type solar cell. Today, silicon based solar cells are established with efficiency of 27 %. Silicon does not absorb sunlight well because it is an indirect semiconductor compared to the direct semiconductor gallium arsenide (GaAs). However, for good absorption of sunlight in the case of silicon based solar cells a thick layer of material is required in order to avoid the recombination losses. The material used for silicon based solar cell has to be of high quality and crystallinity to avoid recombination losses.

The second generation of solar cells is based on thin film materials that efficiently convert solar energy to electricity like amorphous silicon, copper, indium, gallium, and selenium (CIGS), cadmium and tellurium (CdTe), with a record efficiency of 25 % was reported in 1970. Thin film solar cells absorb sunlight more efficiently. The drawback for this type of solar cell is that highly toxic cadmiums used during the manufacturing.

The third generation solar cells are also based on p-n junctions and are known as tandem solar cells. The maximum theoretical efficiency of p-n junction based solar cells is not more than 30 % due to Shokley-Quisser limit. The tandem based solar cells can be considered to overcome this limit.

In 1991, Michael Grätzel and O’Regan first time introduced a promising type of new solar cell, the so called dye-sensitized solar cell (DSSC) that presents several advantages as low cost, a simple fabrication, and relatively high efficiency. The dye molecules are adsorbed to the surface of mesoporous TiO$_2$ film, which are excited upon visible light absorption. The excited state of the dye molecule is regenerated by the reduced form of a redox couple. An electron is collected by the oxidized form of the redox couple from the counter electrode.

1.3 Dye-Sensitized Solar Cells (DSSCs)

A DSSC is based on working electrode (WE), a counter electrode (CE), and a redox couple which can be a solid or liquid electrolyte. The WE consists of a mesoporous TiO$_2$ film which is attached to the conducting glass FTO substrate and the CE consists of FTO glass covered with an electocatalyst, e.g. platinum (Pt) or silver (Ag). Between the two electrodes is a redox mediator (liquid electrolyte or solid HTMs). Nowadays, the efficiency was recorded up to 15 %. A schematic drawing of the working principle of a liquid-state DSSC is shown in Fig. 2. The six major reactions involved in a typical DSSC can be summarized as follows:
I: dye + hν → dye* (photo excitation)

II: dye* → dye* + e−cb (TiO2) charge injection

III: dye* → dye (relaxation)

IV: dye*+I→ dye + I2+ (regeneration)

V: dye* + e−→ dye (recombination)

VI: dye* + e−→ dye (back reaction)

Dye on mesoporous TiO2 absorbs sunlight (reaction-I) which results in injection of electrons into the CB of TiO2 (reaction-II). The oxidized dye is then relaxed (reaction-III) by electron donation from the redox couple (reaction-IV). It can also possible that the injected electron recombines with the oxidized dye (reaction-V) or with the holes from redox mediator (reaction-VI). The regeneration of the dye from redox mediator can intercept the oxidized dye to recapture the electrons from the CB. Therefore, in order to prevent unwanted recombination losses of electrons from the FTO substrate with the oxidized redox mediator an additional blocking layer of TiO2 is applied with thickness of 70 to 100 nm.

Fig. 2: A schematic illustration of showing different electron transfer processes in the conversion of light to a power by liquid-state DSSC.

Fig. 2 shows dye excitation upon incident photon the excited electron is transferred to the CB of semiconductor (TiO2). After a while the electron is transported to the back contact (CE). Finally, the dye regeneration cycle is completed by redox mediator which itself is regenerated at the CE by passed electrons through the load.
1.4 Liquid-state dye-sensitized solar cells (liquid-state DSSCs)

The liquid based dye sensitized solar cells contains liquid electrolyte (I\(^{-}/I_3^{-}\)) or cobalt redox couple (Co\(^{II}/Co^{III}\)) as shown in Fig. 2. Efficiency of such conventional liquid electrolyte based DSSC has been reached up to 12.3 %\(^{56}\). Such electrolyte can easily intermingling to mesoporous TiO\(_2\) that is good for charge transport. The efficiency of such cells can be improved with mixed solvent, e.g. MeCN or THF.\(^{13}\) With this combination, the TiO\(_2\) network is fully filled with quasi solid-state electrolyte.\(^{13}\) The main advantage of using cobalt complexes over I\(^{-}/I_3^{-}\) is higher open circuit voltage (V\(_{oc}\)) to the solar cell.\(^{14}\) A cobalt redox couple has more positive redox potential than I\(^{-}/I_3^{-}\). But their performance dropped drastically under full sun illumination.\(^{14}\) The main disadvantage of using liquid electrolyte is high viscosity which caused low ion mobility. But still I\(^{-}/I_3^{-}\) is still the best electrolyte for DSSCs with efficiency of 12.3 %.\(^{56}\)

1.5 Solid-state dye-sensitized solar cells (ssDSSCs)

As liquid-state DSSCs have remarkable performances but several weaknesses can be reported, e.g. electrolyte leakage and electrode corrosion or dye desorption which prevents them to be produced in large scale for commercial purposes. They showed poor stability under high temperatures. Therefore, the research has focused on alternative materials that can sustain under varied temperatures. Alternative redox couples have been investigated in DSSCs in order to optimize the photovoltaic performances of the devices such as HTMs (Spiro-OMeTAD, P3HT, and PEDOT-PSS) and LiTFSI an additive. The dye LEG4 with different HTMs used in the thesis was presented in Fig. 3. Fig. 4 shows the device structure of a ssDSSCs where the device has a FTO glass, a compact blocking layer of TiO\(_2\), a mesoporous TiO\(_2\) layer with dye, a HTM layer, and a CE layer of Ag on top. The alternative redox couples include both organic and transition metal complexes.\(^{15}\) The working principle of ssDSSCs is the same as liquid-state DSSCs the only difference is that charge transfer occurs through hopping mechanism under the influence of electric field.\(^{16}\) The requirement to an alternative redox couple is fast electron transfer kinetics at the CE and slow interfacial electron recombination kinetics. However, ssDSSCs showed lower conversion efficiency as compared to liquid-state DSSCs. That could be due to poor pore filling problems, enhanced charge recombination, and limited charge mobility. These reduction losses of solid-state devices became the main challenges for further efficiency improvements but still to date the record certified efficiency of 7.2 %\(^{17}\) has been achieved.

However, ssDSSCs efficiency is lower as compared to liquid-state DSSCs.\(^{18}\) An ideal HTM should not absorb light but have a valence band edge with energy which is higher than the energy of the oxidized dye. The HTM should be photochemically stable and create a good electronic contact with the dye. In Fig. 4, the structure of an ssDSSC is described.\(^{19}\) In ssDSSCs, it is believed that solid HTMs with an additive can shift the CB of TiO\(_2\) negatively by displacing ions and protons.\(^{20}\)
The photovoltaic performances of DSSCs are critically dependent on the sensitizing dye. It absorbs light and also introduces an energetic barrier between the semiconductor and the HTMs. In this thesis LEG4 dye has been used as a photo absorber. LEG 4 belongs to the class of dyes called Donor-(π-Linker)-Acceptor (D-π-A). LEG4 offers excellent flexibility in the dye design as each fragment can be
modified independently. That can control and tune the electronic, spectroscopic, and structural properties of the sensitizers. The donor fragment was chosen because it retarded electron recombination. A demand on the dye is that its LUMO should be higher than the CB potential of the TiO$_2$. The dye binds to the TiO$_2$ via chemisorption or physisorption. The attachment group between titania and LEG4 is a carboxyl group COOH chemisorbing via bridging or chelation. For LEG4 the triphenylamine (TPA) is electron donor and cyanoacetic acid (CN) is electron acceptor as shown in Fig. 5.\textsuperscript{21}

![A](image1.png)

(A)

![B](image2.png)

(B)

Fig. 5: Schematic presentation of LEG4 (A) HOMO and (B) LUMO level.

The molar extinction coefficient is really important parameter of a dye. It is the measure of how strongly a dye absorbs light at a given wavelength with a thinner TiO$_2$ films particularly in ssDSSCs.\textsuperscript{21} LEG4 exhibits extremely high extinction coefficient of 3865 M$^{-1}$ cm$^{-1}$ at 464 nm\textsuperscript{21} which is most popular among the metal-free dye classes. A higher molar extinction coefficient dye can enhance the photocurrent. The stability of the dye is very important. However, the first attempt is made to thermal study of LEG4. The goal is to estimate how long the dye can survive for longer years.

1.7 LiTFSI- an additive to HTM

LiTFSI has been used as an additive to increase the conductivity in solid HTMs. It was observed in the earlier studies that LiTFSI is necessary for ssDSSCs devices and without LiTFSI the use of devices is
ordinary.\textsuperscript{20} LiTFSI has become an important part for absolute working conditions of ssDSSCs because it increases the charge mobility in organic HTMs. LiTFSI importance cannot be neglected during fabrication of ssDSSCs. It was tested experimentally and explained further in Section. 4. The influence of the increasing concentrations of LiTFSI in ssDSSCs is that it can increase short circuit current (\( J_{sc} \)) and decreasing (\( V_{oc} \)). It means that LiTFSI caused a band edge shift away from the vacuum level.\textsuperscript{20} It is also assumed that the use of LiTFSI as an additive reduces the recombination losses by restricting HTM reach to the TiO\(_2\), due to the shift of fermi level towards their HOMO level.\textsuperscript{22} Li\(^+\) ions were used to chemically p doped the HTM and is believed to participate in oxidation process that will impact to the devices for their long term stability. In this thesis different concentrations of LiTFSI have been tested in order to optimize the ssDSSCs efficiency. The reason is by increasing concentration of LiTFSI may cause changes to the density of states.\textsuperscript{23} Therefore, when increased the concentration of LiTFSI, it can increase the number of oxygen in LiTFSI. Oxygen has been appeared to be mostly related to the photo-oxidation which leads to good electronic coupling of HTMs.

### 1.8 Degradation of DSSCs

Degradation of DSSCs is a big issue that needs to be overcome by introducing different types of redox mediators, CE with different materials, and the new dyes. The degradation can be defined as the loss of performance in a cell with the passage of time. Degradation can be characterized in two different ways, e.g. irreversible and reversible. There are different possibilities that can influence the degradation; sometimes degradation originates from the chemical instabilities and sometimes stress factor such as temperature, humidity, and UV light intensity which affects the degradation. The long term stability of DSSCs is possible only with the right combination of materials at the right place.\textsuperscript{24}

The stability of DSSCs can be further divided into two different types, i.e. intrinsic and extrinsic. Both are important and one cannot neglect their importance while manufacturing DSSCs. The extrinsic stability describes the issues which are related to the sealing. The sealing should be mechanically and thermally stable, e.g. from external factor such as rain. The sealing should be flexible enough to stand any thermal expansion of the electrolyte. It is also important to look after the different manufacturing methods for instance thermally platinized shown better stability than to sputtered platinum at the CE on FTO glass.\textsuperscript{25} The intrinsic stability affects the degradation mechanism inside the DSSCs. Moreover, TiO\(_2\) films are also played an important role in stability of DSSCs.

### 1.9 The Commercialization of DSSCs

DSSCs are the next generation solar cells based on photosensitive and other substances which are able to convert energy from light to electricity. The overall manufacturing cost of the DSSCs is comparatively lower than conventional silicon based solar cells. The lightweight flexible DSSCs are attractive for different applications such as in room or outdoor light powered, e.g. portable electronic devices, solar power lamps, and IPod charger as shown in Fig. 6.\textsuperscript{26-27} DSSCs can be used as indoor colorful decorative elements. The commercialization of DSSCs modules are taking place on almost all continents especially Sony in Japan, IMRA-Aisin in Seiki/Tokyo, Dyesol in Australia, G24i in UK, and Solaronix in Switzerland.
1.10 Goal

The research efforts in this thesis have been focused on photovoltaic measurements of ssDSSCs based on LEG4 with different concentrations of LiTFSI. The aim was to combine different techniques to obtain a better understanding of working mechanism of ssDSSCs. LiTFSI is found to increase the efficiency of ssDSSCs but their effect is not fully studied. An attempt is made to understand the mechanism how LiTFSI can improve the efficiency. Furthermore, special attention of the thesis is given to design a new sample holder for the vacuum chamber. Then performs vacuum chamber photovoltaic measurements in order to studies clean surfaces within an oxygen and water free environment. To perform photovoltaic measurements with clean surfaces one need vacuum. This type of study on ssDSSCs in a vacuum chamber setup is one step forward to commercialization of this technology. Therefore, one focus of the thesis is to perform experimental investigation of photovoltaic measurements of ssDSSCs in vacuum chamber over a wide range of temperature span. This type of study is very important to test the thermal stability of newly sensitized dyes. Initially, there was a need to assemble the necessary parts for a vacuum chamber setup. The most important part was the “Sample Holder” for mounting purposes of ssDSSCs to a manipulator inside the vacuum chamber setup. The material used for new sample holder is stainless steel which is vacuum compatible and light weighted. The new sample holder design is capable of holding different types of DSSCs including liquid-state DSSCs along with standard mask with adjustable clips, e.g. to mount for different thicknesses. The mask protects the active area of other cells from incoming light source.
The questions studied are:

- The photovoltaic performances (IPCE) of ssDSSCs at low pressure
- Different temperature effect on IPCE of ssDSSCs
- Understand the effects from additives and temperature on the solar cell function at a molecular level

In this thesis the newly sensitized organic dye LEG4 obtained from KTH (Royal Institute of Technology) was used. There are four different parts. Firstly, a practically part is involving the assembly of a sample holder for vacuum chamber experiments. In order to meet the demands for the required assembly were brought in cooperation with the workshop staff at Ångström Laboratory. The method of trial and error was repetitively used concerning basic vacuum technology. Secondly, complete ssDSSCs IPCE were recorded on a computer controlled digital picoamperemeter (Keithley, Model 6487) by using a 100 W light source with higher photon flux by using a certified silicon simulator calibrated. The samples were mounted inside pressure/temperature controlled vacuum chamber with glass window allowing for light illumination, which has been performed at division of Molecular and Condensed Matter Physics Uppsala University. The thermal stability investigations were performed in order to observe how long ssDSSCs survives under different weather conditions. Thirdly, absorbance of different concentrations of LiTFSI with LEG4 pasted at TiO$_2$ nanostructure surfaces is examined. These experiments are performed by using UV-VIS spectroscopy at Ångström Chemistry Laboratory, to investigate how it affects and can improve the light harvesting efficiency with co-sensitization of LEG4. In the last part of the thesis, a comparison is made on LiTFSI contribution to LEG4 at TiO$_2$ surface with different atoms bonding relations from PES data which are performed at MAX-LAB facility Lund.

1.11 Thesis overview

The thesis consists of six Chapters. Ch.1 provides the historical background how solar cells overcome the global energy crisis problem. Then further in Ch.1 the advances which have been achieved after the invention of DSSCs are discussed. Still efficiency around 15% is not up to the required level for commercial utilization of DSSCs, work is therefore still ongoing. Ch.2 provides the information regarding vacuum technology, which is the main study of this thesis work. In Ch.3 a new sample holder design was discussed. The purpose of designing new sample holder is to use for mounting purposes in the vacuum chamber setup for testing photovoltaic measurements of ssDSSCs. The design is assembled in Pro-Engineer CAD program. In Ch.4 the experimental methods were discussed which have been performed during the entire thesis, e.g. in vacuum chamber setup measurements and UV-Vis spectroscopy measurements for the spectral response of the ssDSSCs. Then PES technique is also used to get detailed information about surface structures of the materials in photoactive interface bind to each other on a molecular level. Ch.5 provides the detail information about results and discussions part of the obtained data which was obtained from different techniques. In the beginning of Ch. 5 vacuum chamber setup IPCE measurements were discussed then looked into the absorbance spectra to understand the background phenomena by using LiTFSI. Finally PES results were discussed in order to get detail information about the performance of ssDSSCs in different working environments. In Ch.6 the conclusions are described. Ch.7 provides future suggestions were highlighted which are necessary to enhance the vacuum study for DSSCs.
1.12 Limitations

The change of components (sample holder) has constantly been made that complicate the comparison of photovoltaic measurements gathered at different times. The results should however be applicable to all types of ssDSSCs including liquid-state DSSCs as well as ssDSSCs. The higher temperature scale range is now possible to study. But there is still need to bake the vacuum chamber setup in order to achieve UHV because cooling cost condensation to the samples as shown in Fig. 7 can otherwise be a problem.

Fig. 7: Cooling caused condensation to the ssDSSCs.

Due to poor vacuum, complications can arise inside the vacuum chamber setup during different photovoltaic measurements at different temperatures. There is a need to keep a constant contact between the manipulator before pumping down the vacuum chamber in order to test temperature based measurements. The external current source should be in constant range, e.g. below 1 A for all high temperature measurements to safety use of the Peltier element, sample holder, and the solar cell. It is important to calibrate the monochromator again because there is still offset in wavelengths by a factor of 10 times. There is also a need of another bigger convex lens for smaller spot size that will reduce the access of light across the active area of cell. The most urgent need regarding vacuum chamber measurements is to mount light source and monochromator at rigid surface in order to avoid vibrational affects from the attached pumps as well as from the surroundings. It was observed during the measurements that spot size changes with time which caused variations in the results.
2 Vacuum experiments and technologies

Vacuum can be defined as space in which there is no matter or gas, in other word, a region with a gaseous pressure much lower than atmospheric pressure (1 atm = 101325 Pa). SSDSCs studied in this work may contain air sensitive compound (i.e. O₂ and/or H₂O sensitive) as Spiro-OMETAD or LiTFSI. Both are used to achieve higher efficiency but are rapidly oxidized in air. To avoid these side reactions, it is necessary to avoid air atmosphere and thus, ssDSSCs were performed in a vacuum chamber that was developed in this work. It was then possible to vary both temperature and pressure inside chamber allowing measurements at low or high temperature while condensation or oxidation affecting the sample might occur in air atmosphere in this extreme condition. Inside the vacuum chamber, individual gas particles are uniformly distributed and they are elastically colliding each other exerting pressure upon striking the walls (known as partial pressure P) which corresponds to their concentrations. The formula of pressure P is given mathematically in Equation. 1 and is schematically represented in Fig. 8.

\[ P = \frac{NkT}{V} \]  

where \( k \) is the Boltzmann constant \((1.38 \times 10^{-23} \text{ J.K}^{-1})\), \( V \) the volume \((\text{m}^3)\), \( T \) the temperature \((\text{K})\), and \( N \) the molecular number density of gas molecules \((1/\text{m}^3)\). Equation. 1 is only valid for ideal gases. The standard international (SI) unit of the pressure \( P \) is Pascal (Pa). 1 N/m² = 1 Pa, other units are also frequently used e.g. 1 mbar= 100 Pa, and 1 Torr= 133,322 Pa.²⁹

![Fig.8: Schematically representation of particles exerting pressure on the wall.](image)

The vacuum chamber setup shown in Fig. 9 is equipped with a turbo molecular pump connected to a baking pump (as shown in Fig. 10²⁹,³⁰) able to reach an ultra high vacuum with a pressure as low as 10⁻⁹ mbar.

![Fig. 9: Vacuum chamber setup for photovoltaic measurements of DSSCs.](image)
Liquid nitrogen was used to decrease the temperature inside the vacuum chamber below zero degree Celsius to perform IPCE measurements. Then heat is provided to the sample through a constant current via external voltage source to increase the temperature across the sample inside the vacuum chamber setup.

When using UHV chamber, leaks can be found and have different origins as trapped volume below screws, voids in the materials, trapped volume in the flanges, or incorrectly made welded joints for example.\textsuperscript{32} It is important to minimize leaks in order to get pressure as low as possible.\textsuperscript{33} Before starting the photovoltaic measurements leaks were detected using a “Mass Spectrometer” and then leaks were removed. Gases like oxygen and hydrogen usually dissolved on the surfaces via chemisorption and physisorption after exposure to the ambient atmosphere.\textsuperscript{34}

A change in thermal conductivity with pressure was measured using thermocouple gauges.\textsuperscript{16} It is done with heating a wire with constant current and then measured the temperature with thermocouple.\textsuperscript{16} Bayard-Alpert ionization gauge was used to measure very low pressures. A picocomparemeter was used to measure the photocurrent. A convex lens was also used to focus the light beam to the active area of the cell. The lens was placed between the output end of the monochromator and the glass window of the vacuum chamber setup as shown in Fig. 11.
3 Design of a sample holder for UHV systems

The design and implementation steps used for the new sample holder in the vacuum chamber setup experiments represent a substantial fraction of my thesis. The main idea of the sample holder was to allow the samples (ssDSSCs) to be mounted inside the vacuum chamber setup in order to perform experiments inside the chamber. Great care is needed during such an assembly, as finished sample holder should allow cooling and heating in a controlled vacuum environment. All parts of the sample holder were cleaned with ethanol in order to minimize the level of contamination. A deeper explanation of each individual piece of sample holder is given as following.

3.1 Sample holder design choice

The first step was to clearly define all the features of the desired system and it is not the easiest job as most of the equipment parameters are affected by system requirements. The sample holder design is a critical part of my thesis measurements. The more dedicated the sample holder is better the results of the experimental measurements should be. Sometimes results from measurement depend on the concept, design, and the material of the sample holder.

The new sample holder was designed in the Pro-engineer CAD software and fulfills several requirements, mounting of the samples should be fast, the new sample holder is able to fulfill both heating and cooling purposes. It was designed for vacuum measurements and is thermally and mechanically stable over the different temperature ranges of interest. The proposed design of new sample holder showed advantages compared with the former design, e.g. it does not induce any positional shift and it fixes sample orientation (ssDSSCs). New sample holder is held rigidly by the weight of the manipulator. A photo of the new design is shown in Fig. 12 and a 3D illustration is shown in Fig. 13.

Fig. 12: Assembled and mounted sample holder on manipulator.
Fig. 13: A 3D CAD drawing of the new sample holder.

3.2 Select the best material

The sample holder construction material used was stainless steel. Other materials, as aluminum, mild steel, titanium etc can be also used. However, stainless steel presents an excellent cost compromise shows high durability; in addition stainless steel doesn’t rapidly corrode with water.

3.3 Sample holder for any application

The sample holder configuration can easily be mounted on a translational rod with the help of two screws. Samples are held tightly to avoid noise in the measurements from poor mounting. The sample holder has a negligible resistivity all along its length. New sample holder has several advantages as a thermal heat shield, cooling connections, and six electrical contacts that can be used as follow:

- Two thermocouple contacts
- Two heating contacts
- Two contacts for the photocurrent measurements of the DSSCs

The sample holder dimensions are listed in Table. 1.

Table.1: Sample holder parameters.
Thermocouples are used to provide accurate temperature measurements out of the vacuum chamber. The contacts are durable and long lasting. The standard sample size is 5×4 mm but the new sample holder design allows larger samples which can be mounted and heated without any modifications of the sample holder. Sample holder can be tailored to the sample specifications, e.g. for solid and liquid-state samples.

3.4 Peltier element and PEEK

Higher temperature measurements in the vacuum chamber setup are made available by using a Peltier element. The Peltier element transfers heat as well as cooling to the sample holder by applying external voltage source. Top surface of the Peltier element is providing cooling to compensate the temperature around the sample holder. It will keep Peltier element safe from burning. Peltier element has certain limitations in temperature ranges. The Peltier element was mounted close to the sample to provide fast temperature. The main advantage of Peltier element is it small size, it can be controlled by changing current/voltage input, it can handle high voltage/current, and it presents a flexible shape. There are two connections for the Peltier element. The space between the clip and the holder has been filled with an insulator material: PEEK (polyether ether ketone) as shown in Fig. 14.

![Fig. 14: PEEK is used as insulation between clips and the rest of the holder.](image)

PEEK material is a thermal insulator used to resist to the thermal effects due to nearby current or heat. The thermal conductivity increases linearly versus temperature, but PEEK material is highly resistant to temperature, e.g. till 340°C. The whole sample holder is metallic so current can be easily influenced throughout the holder and caused dissipation to the measured photocurrent. PEEK is used to reduce the current conductivity throughout the sample holder which affects the output photocurrent measurements.

All connections were fastened with metal connectors vacuum compatible. A Kapton tape is used to avoid contacts between the metal connectors and the sample holder. At the lower part of the main sample holder a standard stainless steel mask (5×5 mm) was also attached and was used to avoid additional contribution from light illumination on device outside the active area during IPCE measurements.

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1 http://en.wikipedia.org/wiki/PEEK
3.5 Diagnostic test of the sample holder

Cooling and heating procedures were tested for the sample holder. The rate of increase and decrease in temperature is different accordingly to the temperature ranges. A lot of power is required to further increase in temperature, e.g. more than 100° C, however for safety reason of the sample holder, temperature ranges were kept in between room temperature till 75°C.

Liquid nitrogen was used for low temperature IPCE measurements. Liquid nitrogen was poured into the manipulator where the sample holder was mounted to maintain temperature below 0° C. The low temperature IPCE measurements were performed under pressure range 1.5×10^{-5} mbar and the temperature was maintained above -45° C. The temperature range was kept in order to secure not only the sample holder but also the ssDSSCs from the condensation. Material can also shrink upon variation of the temperature and can create serious issues.

In order to characterize the vacuum chamber setup two cells were tested a classical reference silicon solar cell and an ssDSSC. Comparison was made with a standard setup (IPCE measurement) at Ångström-Chemistry setup. It is important to note that the two setups have different light intensities. The vacuum chamber setup has a tungsten-halogen lamp with white light background (Spectral-Products ASBN-W-100) with intensity 400 W/m² and a slit size of 0.6 mm whereas in the standard setup, the light source is a Xenon lamp (Spectral Products ASB-XE-175) which is more intense than tungsten-halogen lamp, i.e. 680 W/m² with a potentiostat (EG&G PAR 273) and a slit size of 1.2 mm. Before measuring samples the system was calibrated with a certified silicon solar cell (Fraunhofer ISE) with an illuminated aperture area of 0.20 cm².

An IPCE measurement using the vacuum chamber setup was performed with a reference cell and the result was used to calibrate with measured power intensities. Light is illuminated at the active area of the cells after passing through the monochromator to the glass window. The obtained IPCE spectra of silicon cell from the standard device (Ångström-Chemistry setup) and from the vacuum setup are shown in Fig. 15.

![IPCE spectra](image)

Fig. 15: IPCE spectra obtained from vacuum chamber setup and the Ångström Chemistry setup of a silicon solar cell.
Fig. 15 shows that silicon cell response within visible wavelength range is similar in both setups. The peak shape is also similar. However, it is possible to observe differences between IPCE spectra due to two different setup measurements. The peak maximum is slightly different and is red shifted in Ångström-Chemistry setup. We can see a small peak at low wavelength in Ångström-Chemistry setup that is not observed on the spectrum from the vacuum chamber IPCE setup. This difference can be due to the use of two different gratings. The measured photocurrent is also different due to differences in intensities, e.g. vacuum chamber setup $I_{ph}$ is $5.3 \times 10^{-6}$ A compared to the Ångström-Chemistry setup $4.5 \times 10^{-3}$ A.

The quality of the vacuum chamber IPCE setup measurements have also been tested using ssDSSCs (see experimental section) and the response is shown in Fig. 16. The IPCE maximum position is similar and both spectra resembles although the efficiency with the vacuum chamber setup is lower than Ångström-Chemistry setup. The IPCE peaks are somehow partly different due to the difference in light source (more chromatic at Ångström Chemistry setup) in the two different working environments. But it can support reliable results when measuring on stable ssDSSCs in the vacuum chamber setup. The main advantage of vacuum chamber is to possibility to perform IPCE measurements within wide ranges of temperatures under controlled atmosphere.

![IPCE spectra comparison](image)

Fig. 16: IPCE spectra at vacuum setup and chemistry setup of ssDSSC at ambient air pressure.
4 Experimental Methods

In this chapter the main techniques used for experimental studies of the electronic structure are described. The electronic structure can provide information about what elements are present in the sample and their chemical state by letting well-known energy which ionizes the material. The kinetic energy (K.E) of the ejected electrons is measured as shown in Fig. 17. In 1887, Hertz first time reported the effect of light matter interaction. His experiments are on electric discharge in the presence of an ultraviolet radiation. In 1921, Albert Einstein was awarded by Nobel Prize for his explanation of photoelectric effect and explains emission of electrons from a material under illumination of incoming photons with certain energy above the threshold. In 1981, Kai Siegbahn was awarded the Nobel Prize for his contributions to the development of modern electron spectroscopy. The following chapter provides an introduction to the experimental techniques used in my thesis. The electron spectroscopy methods are used for experimentally study only on to electronic structure of solid samples, vacuum chamber measurements, and UV-Vis spectroscopy has been shortly described below.

4.1 Electron spectroscopic techniques

4.1.1 Photoelectron spectroscopy, PES

Photoelectron spectroscopy (PES) or often referred to as Core-level Photoelectron Spectroscopy is a versatile tool used for the surface characterization which gives information on occupied electronic energy levels in a system. PES is the powerful analytical tool for material development and surface testing of a wide range of samples, which is performed under high demands for vacuum around the sample. In vacuum the ejected electrons are free to fly a long distance without interacting with any other particles. That preserves the spectroscopic information about the probed samples. The spectrum provides information on what elements are present in the sample and their chemical states. The binding energy (E_b) with respect to Fermi level is given in Equation 2.

\[ E_b = h\nu - E_K - \Phi \]  

where \( h\nu \) is the energy of the incoming photon, \( E_b \) is the binding energy of the electron that corresponds to certain energy levels in the matter, \( \Phi \) is known as the spectrometer work function which is the energy difference between the fermi level and the vacuum level and \( E_K \) is the kinetic energy of so called photoelectrons as shown in Fig. 17.

![Fig. 17: PES process.](image-url)
In PES measurements the number of electrons have been recorded as a function of their K.Es. A PES spectrum can be divided into two regions; core level PES having high binding energies and valence level PES depends on the origin of the photoelectrons. During photoemission process only electrons emitted from the surface within a depth of 25 Å. The PES spectra were calibrated by the Ti2p substrate signal to 458.56 eV.

Core level electrons have their own characteristic energy level patterns and PES can thus be used to analyze the chemical composition of the sample. The energy positions of core level electrons are well separated out over a large range of energies. The core levels are not participating in the formation of chemical bonds and can be found in specific binding energy. Element specific information is obtained from core level spectra where the variation in binding energy provide information about differences in their chemical environment, so called chemical shift, was described by Hagström and Nordling in 1963. Core level lines are split up into two peaks; spin orbit split coupling (S2p is split into S2p\(_{1/2}\) and S2p\(_{3/2}\) one at higher binding energy and lower binger energy with separation distance of 1.18 eV).

Valence levels are loosely bound with lowest binding energy regions in the PES spectrum. The valence electrons are participated in the formation of chemical bonds and their analysis is gained by the comparison to theoretical calculations. There are several parameters responsible for the intensity of the peaks in a PES spectrum which are given in Equation. 3.

\[
I = I(\sigma, \rho, \Lambda, S)
\]

where \(\rho\) is the surface concentration of the material, \(\Lambda\) is the inelastic mean free path of the electrons, \(\sigma\) is the differential cross section for ejection of electrons from the corresponding orbits, and \(S\) is spectrometer function. The inelastic mean free path is the function of K.E of photoelectron and their dependency follows the so-called universal curve.

During the PES process when an electron leaves the core atom, the atom is left in a very unstable state. An electron fills the hole from a higher energy level. The energy liberated in this process is simultaneously transferred to another electron, i.e. some amount of energy is required to overcome the binding energy of that electron and remaining energy is retained by this emitted Auger electron as K.E.

### 4.1.2 Synchrotron Radiation (SR)

In this thesis work, PES measurements were performed at the Swedish National Laboratory MAX-IV in Lund at Beam Line (BL) I411 located around the storage ring MAX-II an overview of BL I411 is presented in Fig. 18. MAX-IV belongs to the third generation SR sources. The fourth generation SR facilities using hard X-ray free electron laser (FEL) are on-going and should be delivered in 2016.

SR was the first time observed at General Electric synchrotron accelerator in 1947. The working principle is based on high velocity charged particles emitting electromagnetic radiation. This emitted radiation: the SR can be used in the several beam lines located around the storage ring. SR comes in pulses that corresponds to electron bunches. The time difference between two pulses is 10 ns. The SR storage ring is kept under UHV in order to minimize particle collision, since collisions decrease the amount of electron in the storage ring. The most important part in a third generation synchrotron facility is the electron storage ring, where electrons are stored in a circular orbit at high speed. MAX II storage ring is operating at 1.5 GeV, has a circumference of 90 m, and maximum stored current of 280 mA.
Fig. 18: An overview of the experimental end station of BL I411 at MAX-Lab (a) horizontally focusing premirror, (b) plane grating inside SX-700 monochromator, (c) beam control exit slit, (d) toroidal refocusing mirror, (e) OM indicated 1 m section of beam line, and (f) end station containing Scienta R4000 WAL analyzer.

An intense electron beam is maintained in the straight sections of the storage ring by placing insertion devices, i.e. undulators or wigglers. It caused the electrons give higher brilliance (is photon flux and beam size combined) in order to bend out their orbitals.\textsuperscript{45} The intensity from SR is much higher that makes the measurements with improved statistics.

X-ray produced at a synchrotrons have different polarization, e.g. linearly and circular polarized.\textsuperscript{44} An essential part of the BL I411 is the monochromator that has been used to select discrete wavelengths.
of SR during measurements. At BL I411, the photon energy ranges between 50 to 1500 eV with a high flux (between \(10^{11}\) and \(10^{13}\) photons/sec) with linear polarization.\(^{40}\)

The end station (analysis chamber) is located at the end of the BL where the actual experiments are being performed under UHV. An electron spectrometer constitutes the end-station and it is made of two main parts; analysis chamber and preparation chamber. The electron analyzer is the section where the K.E of the emitted electron will be measured. This last section is made of electron lenses, the hemispherical analyzer, and the detector. The hemispherical analyzer consists of two hemispherical electrodes where the field is directed so that the electrons are accelerated towards the inner electrode. To achieve the pass energy of the electrons, a lens accelerates or retards the electrons before reaching to the hemispheres. Only electrons with corresponding energy range will hit the detector. BL I411 is equipped with a Scienta R4000 analyzer. The energy resolution of the analyzer depends on the pass energy (electrons are accelerated or retarded the electrons to this energy) on the radius of the two hemispheres and on the entrance slit width of the analyzer.

In this thesis, only solid samples have been used. Samples are transferred to the analysis chamber with the help of a manipulator. The required pressure is obtained by using different vacuum pumps, e.g. differential pumps and turbo molecular pumps.

### 4.1.3 UV-VIS spectroscopy

Ultraviolet–Visible spectroscopy (UV-Vis) is performed for qualitative and quantitative analysis of the dyes in UV-Vis region as shown in Fig. 19. The absorption of radiation in the UV-VIS region of the spectrum causes transitions amongst the electronic energy levels. Absorbance of different samples at specific wavelength is calculated by using Lambert-Beer’s law which is represented in Equation. 4.\(^{37}\) Lambert-Beer’s law is stated as when a beam of light passes through the transparent material (FTO), the reduction of light intensity is proportional to the extinction coefficient, the thickness of the absorbing material as well the concentration of the solution. Light from the Micropack DH 2000 BAL Deuterium-Halogen Lamp transmits through the optical fiber (I) which interacts with the sample. Another optical fiber is placed behind the sample and picks up the output intensity (I\(_0\)). Absorbance calculated by an Ocean Optics HR 2000 Spectrometer. UV-Vis spectra were recorded from OOBase32 software.

\[
A = \frac{1-I}{I_0} = 1 - 10^{\text{Abs}} = \varepsilon CL
\]  

(4)

Where \(\varepsilon\) is the extinction coefficient, \(l\) is the path length when beam of light travels through the sample and \(c\) is the concentration of the species in solution.

![Fig. 19: Experimental setup for UV-Vis spectroscopy.](image-url)
The background was subtracted with the help of a TiO$_2$ 2 µm thick film as a reference measurement. The absorbance spectra were recorded within the range of 300 to 1100 nm. UV-Vis spectroscopy is also used to determine the extinction coefficients and amount of the dyes at the surface compared to the solutions. A normal quartz cuvette (1 cm) was used for dye absorbance measurements.

4.2 I-V measurements of complete ssDSSCs

The IV measurements over the complete ssDSSCs are measured in a vacuum chamber. A General Electric 100 W source is used for IV measurements in this thesis. The spectrum from the lamp closely resembles to the AM 1.5 (air mass is the angle of radiations on sun’s elevation path through the sky) Global solar emission spectrum (100 mW$^{-2}$). The AM value is the ratio of the path length of the sunrays through the atmosphere when the sun is at angle $\theta$ to the zenith. Measurements are performed with a Keithley 6487 picoamperemeter connected to a laptop running LAB View 7.0. Mathematically expression of efficiency and FF are represented in Equations. 5$^{41}$ and 6$^{37}$, from that solar cell energy conversion efficiency can be determined.

$$\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = J_{\text{sc}} \cdot V_{\text{oc}} \cdot \text{FF} / P_{\text{in}}$$

(5)

$$\text{FF} = \frac{P_{\text{max}}}{J_{\text{sc}} \cdot V_{\text{oc}}}$$

(6)

$J_{\text{sc}}$ is short circuit current at zero applied potential of the cell, $V_{\text{oc}}$ is the open-circuit voltage when no current is passing through the external circuit. The conversion efficiency $\eta$ is defined as the ratio of the maximum power ($P_{\text{max}}$) of the solar cell divided to a known incident electromagnetic power ($P_{\text{in}}$). The maximum power is the product of the current, voltage, and the FF as indicated in Fig. 20.$^{42,20}$

![Fig. 20: The current-voltage characteristics.](image)

The obtained measurements are performed using a reference. The temperature should be 25 °C. The efficiency is proportional to the illuminated area. Therefore, the working area of the solar cell size was 0.25 cm$^2$. 

30
4.3 Incident Photon to Current Conversion efficiency (IPCE) measurements of ssDSSCs

IPCE is used to measure the spectral sensitivity of an ssDSSCs. IPCE spectra can provide very useful estimation of processes which may limit the performance of an ssDSSCs. The IPCE spectrum can give information how efficient the incident photons absorbed by the ssDSSCs can be converted to current at the specific wavelength. The measured IPCE at vacuum chamber setup is shown in Fig. 21. The IPCE spectrum of the ssDSSC should resemble the absorption spectrum of the employed sensitizer dye as shown in Fig. 21 with LEG4 and HTM spiro-OMeTAD with an additive LiTFSI. IPCE maximum is measured from vacuum chamber setup lies at 470 nm at same region as measured in Ångström Chemistry setup at room temperature. But there is a chance of rapid changes after exposing in air due to ssDSSCs sensitivity issue. IPCE in Fig. 21 is measured with low light intensity with 0.20 cm² area which affects the photocurrent. IPCE becomes zero after 650 nm, which indicates that mostly contribution to the photocurrent is from dye LEG4. Thus, the IPCE is the product of light harvesting; electron injection and electron collection efficiencies can be represented according to the following Equation. 7.41

\[ \text{IPCE} = 1240 \times J_{ph}/\lambda \times P \]  

Where \( J_{ph} \) is the photocurrent density converted by incident photons from monochromatic light, \( P \) is the light power density, and \( \lambda \) is the specific wavelength in nanometer. In this thesis, a halogen lamp, a monochromator (spectra product CM110), and a convex lens are used for the IPCE setup.

![IPCE Spectrum](image)

Fig. 21: IPCE spectrum of ssDSSC performed at vacuum chamber setup.

4.4 Preparation of working electrodes

4.4.1 Solar cell preparation

1) Substrates preparation
In this thesis work, to perform IPCE measurements ssDSSCs were prepared at Ångström Chemistry Laboratory according to the following procedure. Firstly, transparent conductive glass substrates with a FTO layers were used to cut into desired size for solar cells (25*15 mm) to prepare working electrodes. Then WEs was washed with water for 15 min in Ultrasonic bath. After that FTO glass pieces were washed with soap and acetone for 15 min in Ultrasonic bath. After a while glass pieces were rinsed with water about 10 min. Finally the FTO glass pieces were washed in ethanol for 15 min in Ultrasonic bath. Then WEs was washed with water for 15 min in Ultrasonic bath. After that FTO glass pieces were washed with soap and acetone for 15 min in Ultrasonic bath accordingly. After a while glass pieces were rinsed with water about 10 min. Finally, the FTO glass pieces were washed in ethanol for 15 min in Ultrasonic bath. Then they were dried under strong airflow. During the measurements, ssDSSCs sensitivity issue electrochemically deposition of P3HT on FTO glass were also prepared detail can be read in ref. 15. P3HT and PEDOT: PSS polymer based DSSCs are stable in air and do not oxidized when exposed in air as like spiro-OMeTAD. By using polymer based ssDSSCs the efficiency is not good enough as can be achieved by using spiro-OMeTAD.

2) Compact TiO₂ blocking layer

A compact blocking layer of TiO₂ with 100 nm thickness was deposited by using Spray Pyrolysis Deposition technique, by spraying the mixture solution of 0.2 M Ti-isopropoxide, 2 M acetylacetone (in isopropanol) on the pre-cleaned FTO glass that were heated at 450° C on a hot plate. Without blocking layer short circuit will occur.

3) Mesoporous TiO₂ layer

TiO₂ is used for Photovoltaic purposes. It is cheap, readily available, non-toxic, and stable that allows good attachment to dye. TiO₂ is a wide band gap semiconductor, i.e. 3.2 eV. It has three different mineral forms; anatase, brookite, and rutile. Anatase is the one that has been used in area of DSSCs. The main conduction mechanism in nanostructured titania isn’t pure band conduction as expected by semiconductor physics. Many suggested a model where a large amount of electrons are immobilized in so called trapped states beneath the CB. These electrons can participate in electric conduction unless they are thermally excited.

The mesoporous structure of the titania gives a surface area being up to 1000 times larger than the geometric area. It will increase the amount of dye possible to deposit drastically. The pore diameter should be chosen large enough so that good pore penetration by the HTM can be achieved.

The paste of nanocrystalline TiO₂ was deposited by spin coating method with a ration rate of 2500 rpm for 30s to obtain the working electrodes about 2 µm thick, as measured with a Dektak profilometer.

4) Dye bath

The obtained substrates were immersed into LEG4 dye solutions (0.2 mM) for 12 hours. Then the films were immersed into the solutions of spiro-OMeTAD as a HTM with an additive LiTFSI with different concentrations (5, 50, and 500 mM) for 10 minutes in order to penetrate into the films.

To complete a solar cell, a 100 nm thick silver (Ag) thin film which acts as CE was deposited onto HTM/LiTFSI-based dye-sensitized electrodes by thermal evaporation in vacuum (Leica EM MED020) under a pressure around 2.2x10⁻⁵ mbar.

4.5 Dye desorption measurements

The dye load on TiO₂ surfaces were estimated from dye desorption measurements. TiO₂ surfaces with one layer of Dyesol paste sensitized with LEG4 for 12 hours and post treatment of LiTFSI (with different concentrations) at a thickness of 2 µm, as measured with Dektak profilometer. After
sensitization with LEG4/LiTFSI the substrate was immersed in an alkaline solution containing 0.05 M TBAOH in Dichloromethane (DCM) for 2 hours to desorbs the dye. Sulphuric Acid was then added into the solution in order to re-protonate the dye desorption solutions. Finally UV-Vis measurements of the desorbed solutions were performed. Dye coverage was calculated by using Lambert-Beer’s law.
5 Results and Discussions

In this chapter, vacuum chamber IPCE measurements, absorbance spectra, and PES spectra will be shown and discussed. The aim of the experimental work was to investigate limitations in the ssDSSCs. The important characterization techniques were applied in order to highlight how LiTFSI affects and influences the efficiency of complete solar cells. Individual characterization of each component is crucial for the understanding and selection of the materials for building ssDSSCs.

5.1 IPCE measurements performed at low pressure and at different temperatures

IPCE measurements on LEG4 based ssDSSCs were obtained in high-vacuum range at $1.8 \times 10^{-5}$ mbar. At present UHV pressures were not tested. One reason is that temperature changes during cooling affects pressure inside the chamber and that makes it difficult to perform these kinds of studies. Therefore, IPCE measurements were kept between room temperature and 75°C. IPCE measurements were performed on two different HTMs, e.g. spiro-OMeTAD and P3HT. The purpose of the measurements is to observe the trends on systems with and without LiTFSI added to different HTMs (solid and polymer).

5.1.1 IPCE measurements on P3HT and Spiro-OMeTAD systems without the addition of LiTFSI

IPCE measurements of LEG4 based ssDSSCs without LiTFSI added to the HTMs, spiro-OMeTAD or P3HT were measured at ambient air pressure. The purpose of the measurements was to identify the important role that LiTFSI has in the HTMs.

Fig. 22: IPCE spectrum of ssDSSC of P3HT without LiTFSI additive at ambient air pressure.

Fig. 22 clearly shows that IPCE on cells without LiTFSI mixed into P3HT is very low, i.e. below 1% and cannot be useful in any applications. A low IPCE indicates that the solar cells have poor efficiency due to insufficient conversion of incoming photons to electrons. IPCE measurements were also performed on cells with the HTM spiro-OMeTAD (without the addition of LiTFSI) as shown in Fig. 23. Again the IPCE is low and thus similar behavior can be observed as for cells based on P3HT. The IPCE maximum occurs at lower wavelength for P3HT than for spiro-OMeTAD. It seems therefore that spiro-OMeTAD without LiTFSI provides better working efficiency than solar cells based on P3HT without LiTFSI.
Fig. 23: IPCE spectrum of ssDSSC of spiro-OMeTAD without LiTFSI additive at ambient air pressure.

5.1.2 IPCE measurements on P3HT and Spiro-OMeTAD systems with the addition of LiTFSI

Here we show IPCE measurements on LEG4 based ssDSSCs where LiTFSI have been added to the HTMs, P3HT and spiro-OMeTAD. The measured IPCE spectra are shown in Fig. 24 (a-b). It is clearly observed that by adding a small amount of LiTFSI to the devices IPCE increases substantially (compared to the measurements without LiTFSI, see Figs 22 and 23). It can therefore be concluded that LiTFSI is absolutely critical to obtain a high IPCE maximum. However, for P3HT the maximum IPCE is lower than for spiro-OMeTAD. A reason for this is that cells with P3HT suffers more from poor hole conductivity.22

Fig. 24: IPCE spectra measured at ambient air pressure of ssDSSCs including (a) P3HT with 50 mM LiTFSI and (b) spiro-OMeTAD with 20 mM LiTFSI.
Fig. 24 therefore provides information about the importance of LiTFSI for working efficiencies of ssDSSCs. A reason for the poor efficiency of solar cells including P3HT compared to spiro-OMeTAD can be due to that LiTFSI more easily can intermix with spiro-OMeTAD. Tertial butyl pyridine (tBP) is also added to the complete devices to help to solvate the Li salt. LiTFSI has shown to influenced the system as it can shift the fermi level of the HTM closer to HOMO level and by this increasing the hole conductivity.\textsuperscript{48,22} Li\textsuperscript{+} ions can interact strongly with oxygen atoms and can also cause changes to the morphology of the layers.\textsuperscript{52}

5.1.3 IPCE measurements on P3HT based ssDSSCs containing LiTFSI- the dependence on the pressure

The main idea of using two different HTMs is to test them in low vacuum pressure/temperature controlled chamber and to compare the solar cell efficiency. In the beginning LEG4-based ssDSSCs with the polymer P3HT were tested in vacuum. Before testing the temperature dependence, measurements were made in order to understand how the system is affected by vacuum. If the pressure is lowered, there are fewer molecules that the photons can be scattered against and also fewer molecules that can be physisorbed to the solar cells surface.

Fig. 25 (a-d) shows IPCE spectra taken before and after pumping down the chamber in order to investigate the light harvesting efficiency of ssDSSCs at different pressures. Generally, IPCE maximum increases in vacuum when sufficient LiTFSI is added. It shows that during light soaking in vacuum, the device (ssDSSCs) performance seems to be improved. The increase is dependent on LiTFSI concentrations, i.e. with higher LiTFSI concentration the IPCE maximum is also larger, possibly due to photo-oxidation.\textsuperscript{20} In Fig. 25 (a-d) spectra were compared relative to each other. Each spectrum in (Fig. 25) has an IPCE maximum at a wavelength around 480 nm.

IPCE maximum for all spectra in Fig. 25 (a-d) lies in same region except for Fig. 25 (a) where the IPCE maximum is slightly shifted towards lower wavelengths at low pressure. It was suggested that this shift was due to that pristine P3HT provide lower infiltration than doped (with LiTFSI). Fig 25 (a-d) also shows that the relative IPCE increases linearly with a higher concentration of LiTFSI due to altered conductivity of P3HT by doping LiTFSI\textsuperscript{53}. This is also the reason of a higher hole conductivity of polymer P3HT compared to spiro-OMeTAD.\textsuperscript{54} However, IPCE spectra of P3HT in vacuum are lower than for spiro-OMeTAD due to a small contribution of the photocurrent from the polymer.\textsuperscript{54} The spectra in Fig. 25 (a-d) shows not symmetric peaks and this might be due to that the resolution can be affected by instrument limitations.
Fig. 25: Relative IPCE spectra of ssDSSCs with LEG4+P3HT+tbp (a) without LiTFSI, (b) with LiTFSI 5 mM, (c) with LiTFSI 50 mM, and (d) with LiTFSI 500 mM LiTFSI measured at room temperature before/after pumping. Dotted line represents IPCE at normal air pressure and solid line represents IPCE in vacuum.

5.1.4 IPCE measurements on spiro-OMeTAD based ssDSSCs systems containing LiTFSI- the dependence on temperature

IPCE measurements with different temperatures in the vacuum setup were also performed on ssDSSCs containing spiro-OMeTAD as a HTM with 20 mM LiTFSI as shown in Fig. 26. The spectra are similar to the measurements at the Ångström-Chemistry setup with a knee at longer wavelength around 520 nm. When studying the IPCE during heating, it is possible to see some trends in the IPCE spectra with increasing temperature. Initially, IPCE increases when heating. At around 37° C a maximum is found and at higher temperatures the IPCE starts to decrease. It can be assumed that the solar cell is loosing efficiency at higher temperatures, e.g. the difference in IPCE between room temperature and 77° C is 20%. One can say that the stability of the ssDSSCs is poor which can be due to that heat has negative impact not only to the cells but also to the conductivity of the substrate, e.g. the FTO. The knee in the IPCE spectra of LEG4-based ssDSC started to decrease during heating. At higher temperatures the knee in IPCE spectrum has almost disappeared and this temperature also provides the lowest efficiency (as seen in Fig. 26).
Fig. 26: IPCE spectra of ssDSSC with 20 mM LiTFSI during heating. The arrow (solid line) in upward direction shows initially an increase. Then the IPCE decreases as represented with an arrow (dotted line) in downward direction.

Fig. 27: IPCE spectra of ssDSSC with 20 mM LiTFSI during cooling. The arrow (solid line) in upward direction shows initially an increase when cooling. Then the IPCE starts to decrease represented with an arrow (dotted line) in downward direction.

The purpose is now to follow the trend in IPCE maximum when first decreasing the temperature and then increasing it again to room temperature. All cooling IPCE spectra lack the knee at longer wavelength and also the IPCE maximum decreases when lowering the temperature.

Fig. 28: IPCE spectra of ssDSSC with 20 mM LiTFSI during heating from -43°C till room temperature. The arrow (solid line) represents the increase in IPCE with increasing temperature.
It seems that different temperature imposed irreversible changes to the cell. Fig. 28 shows IPCE spectra of ssDSSC at increasing temperature from -43°C. It is showed that IPCE maximum increased. However, it is not possible to reach the same state of IPCE as for the solar cells measured at room temperature. It is not following similar trend (without knee) as observed in cooling spectra (Fig. 27). It might be due to the different time that Li⁺ ions can migrate processes through the Spiro-OMeTAD.\(^\text{17}\) One reason could be due to moisture (H\(_2\)O contamination) on the surface that potentially leads to dye desorption if the encapsulation is insufficient.\(^\text{49}\) Li⁺ ions may also react with water and form lithium hydroxide (LiOH) as presented in Equation. \(^\text{8}\)

\[
\text{Li}^+ + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}^+ \quad \text{(8)}
\]

The formation of LiOH on the surface makes the devices less efficient at higher and lower temperatures. Fig. 29 (a-c) shows IPCE maximum efficiency versus different temperature performed during rising, cooling, and rising the temperature again from -43°C to room temperature. Fig. 29 (a) shows the efficiency decreases slowly with increasing temperature. Fig. 29 (b) shows same trend in decreasing efficiency. But the efficiency started to rapidly increases (Fig. 29 (c)) again with rising temperature from lowest temperature. Heating on sensitized electrodes in ambient air has also been tested and showed chemical changes to the dye that are incorporate in the cells.\(^\text{50}\)

Fig. 29: The effect of temperature (a) rising to higher degree on IPCE maximum spectrum, (b) cooling till lowest degree on IPCE maximum spectrum, and (c) rising from lower degree temperature till room temperature on IPCE maximum spectrum versus temperature.
5.1.5 IPCE measurements on P3HT based ssDSSCs systems containing LiTFSI- the dependence on temperature

IPCE measurements are also performed on ssDSSCs with the HTM P3HT with different concentrations of LiTFSI (5, 50 and 500 mM). Here different temperature based IPCE spectra are shown with concentration of 5 mM LiTFSI in Fig. 30. All other temperature based IPCE spectra of P3HT with different LiTFSI concentrations (50 and 500 mM) shows similar trend in IPCE maximum. Therefore, more focus is made on one P3HT based ssDSSC with 5 mM LiTFSI.

Spectra for P3HT based ssDSSC with 5 mM LiTFSI concentration obtained at different temperatures is shown in Fig. 30 (a-c). It is observed that IPCE decreases at low pressures but increases with increasing temperatures and the IPCE maximum also slightly shifts towards longer wavelength. During cooling (see Fig. 30 (b)) a decrease in IPCE and a shift towards lower wavelength can also be observed. It can be argued that cooling can cause permanent degradation of the cell for example through dye desorption. This type of temperature studies might help to determine the working efficiency or validity of solar cells with an organic based dye and a HTM during extreme weather conditions. This can be of interest for an up-scaled fabrication of this type of solar cells. From Fig. 30 (c) a slight decrease in relative IPCE towards lower wavelength is observed after rising temperature from the lowest temperature till room temperature. It can also be noticed from Fig. 30 (b-c) the higher relative IPCE at 32° C and -22° C.

Fig. 30: Relative IPCE spectra of ssDSSC with a LiTFSI concentration of 5 mM (a) during heating, (b) during cooling, and (c) during heating from -51° C till room temperature.
5.2 Optical measurements (UV-Vis spectroscopy)

The purpose of the UV-Vis spectroscopy measurements were to observed and followed the trends as seen earlier during the vacuum chamber setup IPCE measurements. It was observed from the vacuum chamber setup IPCE measurements that LiTFSI is crucial for better working performances of the devices. Thus, IPCE depends on LiTFSI contribution to the HTMs. It was also observed that LiTFSI may affect charge regeneration as well as charge transfer process differently to the different HTMs. Now it is need to identify the LiTFSI effect to the dye LEG4. The reason of these measurements was to verify that not only HTMs but also the dye can also be influenced with the addition of LiTFSI. Therefore, absorbance spectra of LEG4 with different concentrations of LiTFSI in solution and at TiO₂ films are presented in Fig. 31. The TiO₂ films were similar to the ones used for binding morphology measurements (PES) see section 5.3. The reason to perform absorbance measurements was to observe light soaking affects. It was assumed that LiTFSI altered the energy levels by providing driving force in terms of harvesting light. From Fig. 31 the absorbance spectra are taken from 5 µm thick dye sensitized TiO₂ films and compared with absorbance of LEG4 in solution. It is seen from Fig. 31 that the absorbance maxima in solution is red shifted compared to when the dye is adsorbed to TiO₂ films. It can be assumed that such red shift attributed to the changes in excited states of the dye molecules when adsorbed on TiO₂ films in the presence of Li⁺ ions. The absorbance is proportional to the thickness of the TiO₂ films. Therefore, TiO₂ films with thicknesses of 2 µm are also utilized in order to observe the trend in the absorbance as shown in Fig. 32. From Fig. 32, the main peaks (LEG4 in solution) are generally from HOMO to LUMO and HOMO-1 to LUMO respectively. An attempt is also made to calculate the band gap energies (Egs) in order to further investigate the LiTFSI support in the oxidation process. The result is presented in Fig. 33. For LEG4 HOMO is exclusively on the Triphenylamine nitrogen while HOMO-1 and LUMO orbitals are more spread out as shown in Fig. 5.

![Absorbance spectra of LEG4 with different concentrations of LiTFSI at TiO₂ films and in solution.](image)

From Fig. 32, broadening in peaks can be seen which is possibly due to the narrow HOMO-LUMO gap which raise the shift towards longer wavelengths. The HOMO-LUMO gap varies with increasing concentration of LiTFSI as can be seen in Fig. 33 and calculated Egs is presented in Table. 2. It shows that LiTFSI interact or induce a chemical reaction with LEG4 and affect the maximum absorption of incident light. It will be confirmed from PES data (section. 5.3) in the N1s spectra. From the absorbance spectra the light harvesting efficiency (LHE) of ssDSSCs can be determined, i.e. it is the fraction of incident photons which are converted to electrons as described in Equation. 9.

\[
LHE = 1 - 10^{-\text{Abs} (\lambda)}
\]  

(9)
Fig. 32: Absorbance spectra of LEG4 with different concentrations of LiTFSI at 2 µm TiO₂ films. Arrow shows broadening in absorbance when increasing the concentration of LiTFSI.

Using Equation. 9 the LHEs of LEG4 in solution of 2 ml (1 cm cuvette) and at 2 µm TiO₂ films are about 94 % and 98 % respectively. Absorbance beyond 2.5 cannot be measured accurately due to hardware limitation and because a lot of scattering is induced.

The approximation method was used for calculating E₉ as follow:

Firstly absorption was calculated from Beer-Lambert’s Law as described in Equation. 4. Then energy (E) was calculated in eV by using the wavelength by using Equation. 10:

\[ E = \frac{hc}{\lambda} \]  \hspace{1cm} (10)

where h is planks constant 6.63×10⁻³⁴ J/s, c is speed of light 3.0×10⁸ m/s, and λ is wavelength in nm. Then we plotted \( A² \) versus E by using the linear part (Fig. 33 (a)) in Equation. 11:

\[ A = k (E - E_g) \]  \hspace{1cm} (11)

where E₉ is band gap energy by considering this equation, when A=0, then E=E₉ data obtained is presented in Table. 2.

Fig. 33 (a-c): Graphical representations of (a) E versus \( A² \), (b) by using linear part, and (c) HOMO-LUMO level shifts due to different concentrations of LiTFSI, i.e. (-) without LiTFSI, (....) with LiTFSI 5 mM, ( .... .... ) with LiTFSI 50 mM, and ( .... .... ) with LiTFSI 500 mM.
Table. 2: Calculated $E_{gs}$ of LEG4 in solution and at 2 µm TiO$_2$ films with and without concentration of LiTFSI.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Band gap energy- eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEG4-solution</td>
<td>2.12</td>
</tr>
<tr>
<td>LEG4/5 mM LiTFSI</td>
<td>2.05</td>
</tr>
<tr>
<td>LEG4/50 mM LiTFSI</td>
<td>1.90</td>
</tr>
<tr>
<td>LEG4/500 mM LiTFSI</td>
<td>1.86</td>
</tr>
</tbody>
</table>

Dye load measurements have been also performed by using chemical processes for dye desorption as described in section. 2.1.4 result is presented in Fig. 34 (a). During dye load measurements, absorbance with different concentrations of LEG4 at 2 µm TiO$_2$ films was also performed. The purpose of the measurements was to calculate the extinction coefficients, i.e. 3865 M$^{-1}$cm$^{-2}$ as shown in Fig. 34 (b). From Fig. 34, the maximum absorbance is approximately at 515 nm. In dye desorption solutions a small amount of H$_2$SO$_4$ (about 6 µl) in 2 ml solution was added in order to protonate. Before the absorbance measurement, the background was subtracted with desorption solutions. The estimated amount of dye on TiO$_2$ films is presented in Table. 3.

![Fig. 34: (a) absorbance measurements of desorbed solutions of 2 ml with TBAOH from TiO$_2$ films and (b) absorbance measurements of different LEG4 concentrations at 2 µm TiO$_2$ films for extinction coefficient calculations.](image)

Table. 3: Dye coverage of at 2 µm TiO$_2$ films.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Dye coverage (Mol/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEG4</td>
<td>9.74×10$^{-8}$</td>
</tr>
<tr>
<td>LEG4/5</td>
<td>7.78×10$^{-7}$</td>
</tr>
<tr>
<td>LEG4/50</td>
<td>9.02×10$^{-7}$</td>
</tr>
<tr>
<td>LEG4/500</td>
<td>1.20×10$^{-6}$</td>
</tr>
</tbody>
</table>
5.3 PES surface characterization, the binding morphology of the dye with respect to the TiO$_2$ surface

PES is a powerful tool due to high surface sensitivity, element specific on electronic structure, and coverage on surface that is well suited for dye-sensitized surfaces investigation. The purpose of the PES study is specifically looking the answers regarding LiTFSI contributions as seen earlier during vacuum chamber setup measurements as well as UV-Vis spectroscopy. It was believed the oxidation affects can be explained from binding morphology through S2p and N1s core level spectra that were fitted using Voigt shape line profile with Lorentzian width set to 0.3 eV. Ti2p signal was used to estimate the thickness of the dye molecular layer as Ti2p remained unmodified. All spectra of S2p and N1s were intensity calibrated by dividing with the intensity of the corresponding Ti2p substrate signal. LEG4 has two sulphur atoms which are in similar chemical environment. While there are two nitrogen atoms one is at TPA and other lies at CN ligands.

5.3.1 Surface induced interaction with the sulphur atoms-the S2p spectra

S2p spectra are shown in Figs. 35 and 36 which built up by doublet peaks, i.e. spin orbit split coupling of 1.18 eV with intensity in ratios of 1:2$^{11}$ measured at two different photon energies, i.e. 758 and 454 eV. Two sets of spin orbit split peaks are needed for deconvolution. The doublets states are separated by approximately 0.6 eV. Spectra are covering a region between 155 and 175 eV.

![Fig. 35: S2p spectra of LEG 4 with different concentrations of LiTFSI at TiO$_2$ surfaces measured at photon energy 758 eV.](image)

![Fig. 36: S2p spectra of LEG 4 with different concentrations of LiTFSI at TiO$_2$ surfaces measured at photon energy 454 eV.](image)
Sulphur atoms are expected to be positioned close to the TiO$_2$ surface that makes them a suitable choice for comparing dye coverage. It is also noted that sulphur is not one of the possible impurities in the crystal. S2p core level spectra as shown in Fig. 35 and 36 are measured at 758 and 454 eV which splits with S2p3/2 at lower binding energy 163.7 eV and S2p1/2 at higher binding energy 164.9 eV. It can be seen from Figs. 35 and 36 that intensity signal from different concentrations of LiTFSI varied significantly, i.e. intensity decreases with increasing concentrations of LiTFSI (see Table.4). With a LiTFSI concentration of 500 mM the LEG4 concentration has decreased to about half the value of a film formed without the presence of LiTFSI. From Table. 4, it is observed that the percentage of sulphur from oxidized state is smaller at lower concentration but gets larger at higher concentration of LiTFSI. An extra oxidized S2p peak is observed which is at 758 eV (positioned at about 167.5 eV) and is growing when increasing concentration of LiTFSI (a comparison is presented in Appendix A). The extra contribution from LEG4 and due to the presence of LiTFSI on the surface can be also seen in peak fitted data as shown in Figs. 37 and 38. The relative intensity ratios are described in Table. 4. The presence of extra S2p signal can be explained due to sudden internal dye modification which facilitates both sulphur atoms in the dye to interact with TiO$_2$.

Fig. 37: S2p curve fit spectra of TiO$_2$ sensitized with (a) LEG4, (b) LEG4/5 mM LiTFSI, (c) LEG4/50 mM LiTFSI, and (d) LEG4/500 mM LiTFSI measured at photon energy 758 eV. Red curves originated from sulphur in LEG4 and black spectra originate from oxidized sulphur.
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Fig. 38: S2p curve fit spectra of TiO₂ sensitized with (a) LEG4, (b) LEG4/5 mM LiTFSI, (c) LEG4/50 mM LiTFSI, and (d) LEG4/500 mM LiTFSI measured at photon energy 454 eV.

According to the findings by Lei yang et al.¹⁷ Li⁺ ions are migrated inside the pores towards the titania. It correlates with obtained results (vacuum chamber setup and UV-Vis spectra) that LiTFSI somehow affects the chemical states of the LEG4 especially sulphur.

Table 4: Intensities ratios of S2p doublets for LEG4 and oxidized S2p with different concentrations of LiTFSI are measured at 758 eV.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Intensity of S₂ᵖ (oxidized)/Ti₂ᵖ</th>
<th>Intensity of S₂ᵖ (LEG4)/Ti₂ᵖ</th>
<th>Intensity of S₂ᵖ⁻ LEG4 (from different samples)/Intensity of S₂ᵖ (LEG4) %</th>
<th>Intensity of S₂ᵖ (oxidized)/tot intensity of S₂ᵖ (LEG4+TFSI) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEG4</td>
<td>0</td>
<td>1.96</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>LEG4/5 mM</td>
<td>0.03</td>
<td>1.35</td>
<td>84</td>
<td>2.73</td>
</tr>
<tr>
<td>LEG4/50 mM</td>
<td>0.04</td>
<td>1.34</td>
<td>85</td>
<td>3.35</td>
</tr>
<tr>
<td>LEG4/500 mM</td>
<td>0.2</td>
<td>2.35</td>
<td>54</td>
<td>8.64</td>
</tr>
</tbody>
</table>

It is also observed from Table 4, that intensity of S2p in (LEG4) on the surface with different concentrations of LiTFSI, i.e. 5, 50, and 500 mM compared to S2p in LEG4 decreases respectively. The binding energy difference between S2p reduced (LEG4) and S2p (LiTFSI) is 3.7 eV. The broadening of the peak indicates that a change in the sample condition or differential charging of the surface. It gives a multiple splitting of the core level signals.
5.3.2 Surface induced interaction with the nitrogen atoms-the N\textsubscript{1s} spectra

The N\textsubscript{1s} core level spectra of TiO\textsubscript{2} sensitized with LEG4 with different concentrations of LiTFSI are shown in Figs. 39 and 40 measured at two different photon energies 758 and 540 eV respectively. The N\textsubscript{1s} spectra (Figs. 39 and 40) are contained core level information about both donor and the anchor unit. The large peak at 399.36 eV is from TPA group and 398.21 eV belongs to CN moiety. The contribution from LiTFSI (in oxidized state) to the N\textsubscript{TPA} resulted in broadening of the peak towards the higher binding energies. It can be assumed that LiTFSI oxidized the TPA nitrogen as seen from Fig. 41. Binding energies and peak intensities are calibrated versus Ti2p. The relative intensity ratios for N\textsubscript{TPA}/Ti2p and N\textsubscript{1s} (oxidized)/Ti2p peaks are described in Table. 5. As seen from Table. 5, the percentage of the N1s-oxidized becomes smaller at higher concentration of LiTFSI, i.e. 500 mM compared to 5 and 50 mM when measured at 758 eV. The peak from oxidized nitrogen is also broader and is possibly influenced the total intensity of N1s. The general observations from Figs. 41 and 42 (curve fitted spectra) by comparing relative intensity of CN and TPA nitrogen in the spectra supports that all samples anchor unit is closest to the TiO\textsubscript{2} surface and the donor unit pointing out. As N\textsubscript{1s} spectra are measured at two different photon energies so their relative intensity ratios with different concentration of LiTFSI are presented in Table. 6. Comparing the relative intensity ratios (see in Table. 6) it is observed that ratios differ between the samples. The N\textsubscript{CN}/N\textsubscript{TPA} ratio for LEG4/50 mM is higher compared to LEG4/5 and LEG4/500 mM. By lowering the concentration of LiTFSI the TPA intensity is also affected. As seen in Table. 6, the percentage of N\textsubscript{CN} is smaller for 500 mM LiTFSI when measured at photon energies 540 and 758 eV. It indicates that TPA energy level relative to the TiO\textsubscript{2} substrate depends on the solvent. According to the theoretical calculations the HOMO is mainly localized around the donor and a shift of the TPA nitrogen energy level is expected to be strongly correlated with a shift in HOMO level relative to the TiO\textsubscript{2}.

Fig. 39: N\textsubscript{1s} spectra of TiO\textsubscript{2} sensitized with LEG4 with different concentrations of LiTFSI measured with photon energy of 758 eV.
Fig. 40: N1s spectra of TiO₂ sensitized with LEG4 with different concentrations of LiTFSI measured with photon energy of 540 eV.

Figs. 41 and 42, shows two signals from nitrogen atoms with a chemical shift of approximately 1.1 and 0.8 eV at photon energies 758 and 540 eV respectively. At higher photon energy the TPA nitrogen intensity increases. The lower ratios observations can be explained due to large attenuation of N<sub>CN</sub> compared to N<sub>TPA</sub> nitrogen from scattering. The rinsing can also affect the surface from removal of access amount of LiTFSI that influences the energy levels. Thus it can be assumed that the nitrogen from MeCN can contribute to the N1s signal. One reason cannot be neglected that PES only probes the outermost surface of the TiO₂ films (surface sensitivity changes at both energies) which implies only at the outer part of the molecule layer is affected by the solvent.

Table.5: The N1s intensity ratios of the reduced and oxidized form measured at 758 eV.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Intensity of N₁s (LEG4)/Ti₂p</th>
<th>Intensity of N₁s (oxidized)/Ti₂p</th>
<th>Intensity of oxidized-N₁s/(TPA+CN)-N₁s</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEG4</td>
<td>3.94</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LEG4/5 mM</td>
<td>1.19</td>
<td>0.45</td>
<td>0.37</td>
</tr>
<tr>
<td>LEG4/50 mM</td>
<td>0.95</td>
<td>0.42</td>
<td>0.44</td>
</tr>
<tr>
<td>LEG4/500 mM</td>
<td>2.00</td>
<td>0.18</td>
<td>0.09</td>
</tr>
</tbody>
</table>

TPA derivatives are used as HTMs in organic electrochemical devices. From Table. 6, we can see that CN signal at lower photon energy 540 eV closed to the surface.

Table.6: N1s intensity ratios (N<sub>CN</sub>/N<sub>TPA</sub>) for two different photon energies 758 and 540 eV.

<table>
<thead>
<tr>
<th>Samples</th>
<th>N&lt;sub&gt;CN&lt;/sub&gt;/N&lt;sub&gt;TPA&lt;/sub&gt; 758 eV</th>
<th>N&lt;sub&gt;CN&lt;/sub&gt;/N&lt;sub&gt;TPA&lt;/sub&gt; 540 eV</th>
<th>N&lt;sub&gt;CN&lt;/sub&gt;/N&lt;sub&gt;Int&lt;/sub&gt; 758 eV</th>
<th>N&lt;sub&gt;CN&lt;/sub&gt;/N&lt;sub&gt;Int&lt;/sub&gt; 540 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEG4</td>
<td>0.14</td>
<td>0.44</td>
<td>0.14</td>
<td>0.30</td>
</tr>
<tr>
<td>LEG4/5 mM</td>
<td>0.25</td>
<td>0.39</td>
<td>0.14</td>
<td>0.21</td>
</tr>
<tr>
<td>LEG4/50 mM</td>
<td>0.54</td>
<td>0.51</td>
<td>0.24</td>
<td>0.25</td>
</tr>
<tr>
<td>LEG4/500 mM</td>
<td>0.24</td>
<td>0.17</td>
<td>0.18</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Fig. 41: N1s curve fit spectra of TiO₂ sensitized with (a) LEG4, (b) LEG4/5 mM LiTFSI, (c) LEG4/50 mM LiTFSI, and (d) LEG4/500 mM LiTFSI measured at photon energy 758 eV. Red curves for nitrogen are from LEG4 (N1s) and black curve is from oxidized nitrogen (N1s).

Fig. 42: N1s curve fit spectra of TiO₂ sensitized with (a) LEG4, (b) LEG4/5 mM LiTFSI, (c) LEG4/50 mM LiTFSI, and (d) LEG4/500 mM LiTFSI measured at photon energy 540 eV. Red curves for nitrogen are from LEG4 (N1s) and black curve is from oxidized nitrogen (+N1s).
6 Conclusions

In this thesis, a vacuum chamber was reassembled for testing thermal stability of complete ssDSSCs under different temperatures. The vacuum chamber setup can be used to measure photovoltaic properties of the complete ssDSSCs. It is valuable to study thermal stability of ssDSSCs. A new sample holder was designed in order to investigate PV measurements of ssDSSCs sensitized with LEG4 and with different concentrations of LiTFSI. The new sample holder worked for PV measurements of ssDSSCs at satisfactory level. The task of the project was to highlight how LiTFSI affects HTMs or the dye with different concentrations. It was therefore interesting to compare results from three different techniques, e.g. vacuum chamber, PES, and UV-Vis spectroscopy. The use of LiTFSI in ssDSSCs has proven to proven to yield efficient devices.

The new design of the sample holder played an important role in testing IPCE measurements inside the vacuum chamber setup. It required an optimal light to current conversion efficiency measurement. Complete ssDSSCs showed an interesting behavior before and after the lowering the pressure inside the vacuum chamber. The errors include leakage from vacuum chamber, monochromator performance, and condensation to the sample surfaces caused impurities in the structure which are likely impact to ssDSSCs to perform in limited conditions. The task was to investigate and compare the performances of complete ssDSSCs with and without LiTFSI an additive to HTMs inside the vacuum chamber. Initial results of IPCE have proved that LiTFSI is critical for these kinds of devices. The result showed that with no LiTFSI the IPCE of spiro-OMeTAD and P3HT based ssDSSCs decreases a lot and cells did not work. But interestingly it was observed that with addition small amounts of LiTFSI, e.g. with 20 mM, IPCE increases drastically. These measurements were performed at ambient air pressure.

It is also noticed that with increasing concentration of LiTFSI IPCE at low pressure increases. Different temperatures IPCE measurements had showed very interesting concepts of thermal stabilities and performances of ssDSSCs. At higher temperatures IPCE maximum decreases alot as compared to the room temperature. It gives an idea that a rise in temperature affects negatively to the devices. This might starts degradation at higher temperature, e.g. at 40° C. It caused lower absorbing incoming photons at higher temperatures. It is not possible to retain the IPCE back at room temperature. During lowering the temperature from room temperature IPCE also drops. It showed that spiro-OMeTAD with LiTFSI based solar cells cannot perform well under extreme weather conditions.

One possibility regarding a decrease in IPCE may be the liquid nitrogen which caused changes to the internal structural due to moisture on the surface. Because Li+ ions can react with water in presence of moisture and form LiOH as well as Li2O. It can affect the overall performance of ssDSSCs. The difference in IPCE at vacuum by using two different HTMs is providing different freedom of diffusion to Li+ ions. It can be due to applying two different methods of adding LiTFSI on both devices, e.g. through spin-coating as co-sensitizer and pored after polymerization. Therefore, it can be the reason of having different light soaking effect from different HTMs based cells.

Absorbance measurements showed that the dye molecules in solutions absorb more compared to the dye desorbed at the TiO2 films. LiTFSI affects the absorption. An increase in light harvesting efficiency (LHE) was found when increasing the concentrations of LiTFSI, e.g. absorbance is red shifted and much broader. It showed that different concentrations of LiTFSI are altered the energy levels between the molecules. It gives us information of oxidizing the LEG4 towards longer wavelengths due to shrinking the HOMO-LUMO level. It was also found during absorbance experiments that the thicknesses of TiO2 surfaces are played an important role in terms of light
harvesting efficiency, i.e. thinner surfaces absorbs more light than the thicker ones. This leads us to an idea of incomplete filling of Li$^+$ ions with thicker films compared to thinner.

PES was used to quantify the surface concentrations from LEG4 and LiTFSI co-adsorbent specifically S2p and N1s were also used and experiments have been carried out at MAX LAB under controlled conditions. The PES surface study showed that increasing concentration of LiTFSI caused a shift towards higher binding energies. It is also observed that due to the presence of LiTFSI at surface, oxidized peaks of N1s and S2p at higher binding energies are slightly broader than dye sensitized TiO$_2$ film without LiTFSI. It indicates that somehow a modification in molecular surface structural of the dye when desorbed at TiO$_2$. The dye amounts on the surface decreases when increased the concentration of LiTFSI.

The purpose of this thesis work was to assemble and design a new sample holder for vacuum chamber setup. Then make a comparison to Ångström-Chemistry setup in results (IPCE). It was found that vacuum chamber setup can provide same results. Apart from the limitations of the setup because of lower light intensity and the working performance of the monochromator (calibration issue), it works satisfactory. Efforts were made to minimize the errors and finally measured the required data for the thesis. Due to time limitations IV measurements are not taking in account. The other issue regarding ssDSSCs is sensitivity. It was hard to prepare the solar cells with good efficiency due to very high humidity. The time was saved and spent on collecting data from vacuum chamber setup. The information gained in this thesis work will add one step ahead of commercializing the ssDSSCs and will open a new window towards implementation of employing other techniques in order to improve the efficiency under different weather conditions.
7 Future suggestions-vacuum based systems used for IPCE measurements

The main future work regarding vacuum chamber will be further improve the setup. It is needed to bake the chamber to minimize the impurities of air exposure. The restriction of changing the cell inside the vacuum chamber can be resolved by making small changes in the sample holder. It can be possible to create a movable sample holder substrate surface by connecting an external stepper motor. That will change the cells positions automatically without breaking the vacuum. An Isolated stand needs to be designed for placing the light source and monochromator. Because if the light spot changes then it affects the measurements. During pumping a tension is created that affects to the manipulator. Therefore, a new clip should be designed for external support of the manipulator. All inside connections for collecting data as well for peltier element should be tightly fastened. Because some lose connection inside chamber can affect the measurements. There is a need to purchase some new equipment for the setup to get an optimum data especially tri-axial cable.
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Appendix A:

Fig. 43: $S_{2p}$ originates from TFSI measured at 758 eV.