

Hierarchical porous TiO2 and ionic liquid-like polysiloxane electrolyte for solid state-Dye-Sensitized Solar Cells

Anil Bharwal

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and

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Presented by

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Hierarchical porous TiO₂ and ionic liquid-like polysiloxane electrolyte for solid state-Dye-Sensitized Solar Cells

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Cellules solaires à colorant tout solide composées d'une électrode de TiO₂ à porosité hiérarchisée et d'un électrolyte polyliquide ionique à matrice polysiloxane

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Dedicated to my family

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Summary

DSSC is a 3rd generation photovoltaic technology with potential to economically harvest and efficiently convert photons to electricity. Full solid state-DSSC based on solid polymer electrolyte prevents the solvent leaking and evaporation during cell fabrication and operation, which will effectively prolong the cell life time. However, it suffers from low ionic conductivity and poor pore infiltration.

The present thesis is dedicated to the concomitant development of polysiloxane-based polymer electrolytes on one side, and TiO_2 photoanodes with tuned porosity on the other side, and their incorporation in solid-state dye-sensitised solar cell (ss-DSSCs), with the aim to improve their photovoltaic efficiency and the long term stability. To best of our knowledge, DSSCs comprising bimodal TiO_2 layers and polysiloxane electrolytes have never been reported.

The ionic conductivity and tri-iodide diffusion coefficient of the polysiloxane-based poly(ionic) liquids (PILs) were largely improved by adding of ionic liquids (ILs) or ethylene carbonate (EC), achieving ionic conductivities of $10^{-4} - 10^{-3}$ S cm⁻¹. The DSSCs fabricated with the optimized electrolytes showed efficiencies up to 6%, with long term stability for 250 days.

Bimodal TiO_2 films with dual porosity (meso- and macro-porosity) were fabricated by spincoating, by using soft and hard templating. The dual templated films benefit from increased pore size while maintaining high surface area for dye adsorption. Bimodal films were shown to be more efficient when tested with polymer electrolytes, having comparable efficiencies with liquid electrolyte when in DSSCs, despite lower dye uptake.

This thesis brings a significant contribution to the field of DSSCs as efficient and stable solar cells were prepared from newly synthesized polymer electrolytes and bimodal films.

Résumé

Les cellules solaires à colorant (DSSCs) sont une technologie photovoltaïque de 3^{eme} génération avec un fort potentiel économique et une efficacité dans la conversion des photons en électricité élevée. Les DSSCs tout solide comprenant un électrolyte polymère prévient de la perte et de l'évaporation du solvant pendant la fabrication et le fonctionnement des cellules, ce qui prolonge efficacement la durée de vie de celles-ci. Cependant, les électrolytes polymères présentent de faibles conductivités ioniques et leur infiltration dans les pores de l'électrode de TiO₂ est faible.

La présente thèse est dédiée au développement concomitant d'électrolytes polymères à base de polysiloxane et de photoanodes TiO_2 à porosité contrôlée et à leur incorporation dans des cellules solaires à l'état solide (ss-DSSC), dans le but d'améliorer leur efficacité photovoltaïque et leur stabilité à long terme. À notre connaissance, les études de DSSCs comprenant des couches de TiO₂ bimodales et des électrolytes de type polysiloxane n'ont jamais été rapportés.

La conductivité ionique des poly(ioniques) (PILs) à base de polysiloxane ont été largement améliorée par addition de liquides ioniques (ILs) ou de carbonate d'éthylène (EC), conduisant à des conductivités ioniques de l'ordre de 10^{-4} -10^{-3} S cm⁻¹. Les DSSCs fabriqués avec les électrolytes optimisés ont montré des rendements jusqu'à 6%, avec une stabilité à long terme pendant 250 jours.

Des films de TiO_2 bimodaux à double porosité (méso et macroporosité) ont été fabriqués spin coating, en utilisant des différents templates. Le caractère bimodal des films permet d'accroitre la taille des pores tout en maintenant une surface spécifique élevée pour l'adsorption du colorant. Les films bimodaux se sont révélés très efficaces lorsqu'ils ont été testés avec des électrolytes polymères, avec des efficacités comparables à celles obtenues avec un électrolyte liquide malgré une absorption plus faible de colorant.

Cette thèse apporte une contribution significative dans le domaine des DSSCs en tant que cellules solaires efficaces et stables utilisant un électrolyte polymère et des films bimodaux de TiO_2 .

List of Acronyms and Abbreviations

1-D	One-dimension
3-D	Three-dimension
x	Refractive index
ε	Dielectric constant
σ	Conductivity
μ	Viscosity
η	Photo Conversion Efficiency
Λ_{m}	Molar conductivity
$ au_{ m e}$	Electron lifetime
f_{\max}	Maximum frequency peak intensity of Bode
Н	Overall power conversion efficiency
k	Boltzmann constant

A

AM	Air mass
ACN	Acetonitrile
APPG230/400	Oligomers of poly(propylene oxide)
AFM	Atomic force microscopy
AcAc	Acetyl Acetone
ATR/FTIR	Attenuated total reflectance /Fourier transform Infrared

В

BIPV	Building-integrated photovoltaics
BL	Blocking layer
Brij 56	Polyoxyethylene (10) cetylether
Brij 58	Polyoxyethylene (20) cetylether
BMICl	1-butyl-3-methylimidazolium chloride
Br-PDMSX	Bromo-pentylpolydimethylsiloxane polymer
BET	Brunauer-Emmett-Teller
BMII	1-butyl-3-methylimidazolium iodide

С

Cadmium sulfide
Cadmium telluride
Copper, indium, selenide/sulfide
Copper, indium, gallium selenide/sulphide
Copper zinc tin selenide/sulfide

СВ	Conduction band
CE	Counter electrode
CuI	Copper(I) iodide
CuSCN	Copper(I) thiocyanate
CA	Cooperative Self-Assembly
CTAB	Cetyltrimethylammonium bromide
CPE	Composite polymer electrolytes
C2mimTCM	1-alkyl-3-methylimidazolium tricyanomethanide
[C1C1Im]I	1-alkyl-3-methyl-imidazolium iodide

D

DSSC	Dye sensitized solar cell
DMPII	1,2-dimethyl-3-propylimidazolium iodide,
DMII	1,3-dimethylimidazolium iodide
DSC	Differential Scanning Calorimeter
$D(I_3)$	diffusion coefficient of tri-iodide

E

Eg	Band gap
eV	Electron volt
EISA	Evaporation-induced self-assembly
ED-600	Block oligomer of poly(ethylene oxide)/poly(propylene oxide)
EIS	Electrochemical Impedance Spectroscopy
EMITf	1-ethyl-3-methylimidazolium triflate
EMITFSI	1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide
EMII	1-ethyl-3-methyl imidazoliumiodide
EMISCN	1-ethyl-3-methylimidazolium thiocyanate
EMIDCN	1-ethyl-3-methylimidazolium dicyanamide
EMIB(CN) ₄	1-ethyl-3-methylimidazolium tetracyanoborate
EMIBF ₄	1-ethyl-3-methylimidazolium tetrafluroborate
EC	Ethylene Carbonate
Ea	Activation energy
EDX	Energy-dispersive X-ray spectroscopy
EMIDCA	1-ethyl-3-methyl-imidazolim dicyanamide

F

FF	Fill factor
F127	Pluronic surfactant, PEO ₁₀₆ PPO ₇₀ PEO ₁₀₆
FTO	Fluorine doped Tin Oxide

G	GW GBL GuSCN (GNCS) GO	Gigawatt γ-butyrolactone Guanidine thiocyanate Graphene oxide
Η	HOMO HMII H-PDMSX	Highest occupied molecular orbital 1-hexyl-3-methylimidazolium iodide Poly(methylhydrosiloxane) co methylhydrosiloxane copolymer precursors with different Si-H functionality, (X=1, 2, 3 for respectively Si-H functionality 6% to 7%, 15% to 18% and 30% in mol%)
	Hex₄N ⁺ I⁻ HPC	Tetrahexyl ammonium iodide Hydroxypropyl cellulose
Ι	m	
	IR T	Infra red
		Triiodide
		Ionic liquids
	IP-PDMS	Poly[(3- N -methylimidazoliumpropyl)methylsiloxane-co- dimethylsiloxane] iodide
	IPCE	Incident Photon-to-electron Conversion Efficiency
	Im-PDMSX	Imidazolium-pentylpolydimethylsiloxane polymer
J	J _{sc}	Short-circuit current
K	kWh	KiloWatt hours
	KLE	Poly(o-hydroxypoly(ethylene-co-butylene)-co-poly(ethylene oxide) block copolymer
L	LCOE	Lovalised Cost of Electricity
		Levensed Cost of Electricity
		Lowest occupied molecular orbital
		Liquid Crystal Template
	LII I ITECI	Liunum Ioulue Dis(trifluoromethene)sulfonimide lithium selt
	LIIFSI	Dis(unituoromethane)sunominide intinum sait

M		
TAT	MW	Megawatt
	MMA	Methyl-methacrylate
	MPII	1- methyl-3-propylimidazolium iodide
	MPITFSI	1-methyl-3-propylimidazolium bis (trifluoromethanesulfonyl)
		imide
	MPN	3-methoxypropionitrile
	MgO	Magnesium oxide
	MgI_2	Magnesium iodide
	MeOx	3-methyl-2-oxazolidinone
Ν		
	Nb_2O_5	Niobium pentoxide
	N-3	Cis-Bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylate ruthenium(II)
	N-719	Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-
		4,4'-dicarboxylate)ruthenium(II)
	NMP	N-methylpyrrolidone
	NREL	National Renewable Energy Laboratory
	NMR	Nuclear magnetic resonance spectroscopy
	NBB	N-butylbenzoimidazole
0	OPV	Organic solar cells
	01 V	Organic solar cens
Ρ	PV	Photovoltaic
	P _{in}	Intensity of the incident light
	P _{max}	Maximum power
	Pt	Platinum
	P123	Pluronic surfactant, PEO ₂₀ PPO ₇₀ PEO ₂₀
	РЗНТ	Poly(3-hexylthiophene)
	PCE	Photo conversion efficiency
	PVC	Poly(vinylchloride)
	PAA-PEG	Poly(acrylic acid)-(ethylene glycol)
	PEO	Poly(ethyleneoxide)
	PAN-VA	Poly(acrylonitrile-co-vinyl acetate)
	PC	Propylene carbonate
	PVP	Poly(vinylpyrrolidinone)

PS	Polystyrene
PVE	Poly(vinylidene ester)
PVDF	Poly(vinylidenefluoride)
PMMA	Poly(methylmethacrylate)
PVDF-HFP	Poly(vinylidenefluoride-co-hexafluoropropylene)
PVP-co-VAc	Poly[1-vinylpyrrolidone-co-vinyl acetate]
PMII	1-propyl-3-methylimidazolium iodide
Poly[BVIm][HIm][T	Poly(1-butyl-3-(1-vinylimidazolium-3-hexyl)-imidazolium
FSI]	bis(trifluoromethanesulfonyl)imide)
POEI-II	Poly(oxyethylene)-imide-imidazole complex coupled with iodide anions
PDMS1Im ⁺ I ⁻	Poly(methylhydrosiloxane) co methylhydrosiloxane copolymer
	(H-PDMSX) precursors with different Si-H functionality, (6% to
	7% in mol% Si-H functionality)
PDMS2Im ⁺ I ⁻	Poly(methylhydrosiloxane) co methylhydrosiloxane copolymer
	(H-PDMSX) precursors with different Si-H functionality, (15% to
	18% in mol% Si-H functionality)
PDMS3Im ⁺ I ⁻	Poly(methylhydrosiloxane) co methylhydrosiloxane copolymer
	(H-PDMSX) precursors with different Si-H functionality, (30% in
	mot% St-H functionality)
	Poly(1-methyl 3-(2-acryloyloxypropyl) imidazonum iodide
Poly(VIPIDII)	Pory(1-vinyi-5-propynnidazonum lodide
QSSE	Quasi-solid-state electrolytes
Ru	Ruthenium
RBS	Rutherford back scattering spectrometry
RPM	Revolutions per minute
R _s	Ohmic resistance
K _{ct1}	Charge transfer resistance at the photoelectrode/electrolyte
K _{ct2}	Charge transfer resistance at the counter electrode/electrolyte
K _{diff}	Resistance at diffusion
K _{rms}	Root-mean-square roughness

S

Q

R

Silicon
Tin dioxide
Strontium titanate

Sb_2S_3	Antimony trisulfide
Spiro-OmeTAD	2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-
	spirobifluorene
SiO ₂	Silicon dioxide
SPE	Thermosetting polymer electrolyte
SiDII1	bis(1-methyl-3-methylene imidazoliumiodide)
	tetramethyldisiloxane
SiDII2	bis(1,5-dipropyl-3-methylimidazolium iodide)-1,1,3,3,5,5-
	hexamethyltrisiloxane
SiDII3	bis(1-methyl-3-propyl imidazolium iodide) terminated
	poly(dimethylsiloxane)
SiDPI1	1,3-Bis((1-methylpyridinium iodide)-3- methyl)tetramethyl-
	disiloxane
SiDPI2	(1,1,3,3,5,5-Hexamethyltrisiloxane)-1,5-dipropyl-3-
	methylpyridinium iodide
SiDPI3	1-Methyl-3-propyl Pyridinium Iodide Terminated
	Poly(dimethylsiloxane
SEM	Scanning electron microscope
SN	Succinonitrile

Т

TiO ₂	Titanium dioxide
TiCl ₄	Titanium tetra chloride
TCO	Transparent conducting oxide
TiOSO ₄	Titanium(IV) oxysulfate
TBP	4-tert-butlpyridine
TPE	Thermo plastic Polymer electrolytes
TBAI	Tetrabutyl ammonium iodide
TMP-TDI	Trimethylolpropane-Toluene diisocyanate Crosslinker
T _g	Glass transition temperature
TEM	Transmission electron miscroscopy
Ti(OBu) ₄	Titanium butoxide
TTIP	Titanium isopropoxide
THAI	Tetra-n-butylammonium iodide

U

USD	United States Dollars
UV	Ultraviolet

V	V _{oc}	Open-circuit photovoltage
Χ	XPS XRD	X-ray photoelectron spectroscopy X-ray diffraction
Ζ	ZnO Zn ₂ SnO ₄ Z-907	Zinc oxide Zinc stannate cis-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di- nonyl-2'-bipyridyl)ruthenium(II)

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CHAPTER-I

Introduction: Literature Survey and aims of the work

Abstract

This introduction part describes the context of the present work. First, an overview of the major photovoltaic technologies is discussed, followed by a focus on dye-sensitized solar cells. The chapter will focus on the TiO_2 photoanodes prepared by soft and hard templating routes. The chapter will also give an overview of the main progress in the field of poly(ionic)liquid's development as electrolyte in DSSC applications. In light to this the scope and objectives are defined and the thesis outline is finally summarized.

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1. Worldwide energy demand

In the modern world of technological advancements, energy has become one of the basic needs for life. With the increase in world population, so is rising the energy demand. The worldwide power consumption is expected to double in the next 3 decades, and the limited supply of fossil fuels is hardly expected to cope with this. It has been estimated that the world net electricity generation will increase 69% by 2040, from 21.6 trillion kiloWatt hours (kW h) in 2012 to 25.8 trillion kW h in 2020 and 36.5 trillion kW h in 2040.¹ Although, nuclear power is capable of providing large scale power generation but is being proven to be accountable in safety and waste management issues. Hence, eventually we need to turn to renewable energy sources, and the most feasible candidate of them is solar energy. Among all other abundant and renewable energy sources (wind, water and geothermal heat) in our planet, solar energy is expected to play a key role as a future energy source. The light from the sun is most readily available source of energy; one simple reason is that the Earth receives 3×10^{24} Joule of energy per year from the Sun which is nearly 10,000 times more than the world's energy consumption.² Apart from the abundance of potentially exploitable solar energy, photovoltaic cells have also other competitive advantages such as little need for maintenance, off-grid operation and silence, which are ideal for usage in remote sites or mobile applications. According to Greenpeace International, solar photovoltaic would provide 14% of total electricity generation by 2030, and would employ 10.3 million people.³ Therefore, photovoltaic technologies are really promising solutions to the present energy challenge.⁴

2. Photovoltaic

2.1. Photovoltaic market

After the development of the first silicon cell in 1954, photovoltaic devices were used primarily in space applications.^{5,6} It is only in the second half of the last decade that grid connected photovoltaic (PV) systems entered in the terrestrial market with significant contribution.⁷ Over the last decade, PV technology has shown the potential to become a major source of power generation for the world. That growth is expected to last in the years ahead as worldwide awareness of the advantages of PV increases. Global market of PV has grown over 25% year over year to more than 50 GW in 2015.⁸ PV is now, after hydro and wind power, the third most

important renewable energy source in terms of globally installed capacity. Europe became the first region surpassing an impressive 100 GW mark and expected to reach to 170 GW by the end of 2020.⁸



Figure 1- Evolution of the global annual solar PV installed capacity.⁸

Additionally, Solar PV also has experienced significant cost reductions. Between 2010 and 2015, the global weighted average Levelised Cost of Electricity (LCOE) of utility-scale (>1 MW) solar PV fell by almost 60%, driven primarily by reductions in module costs of around three-quarters during this period. In 2015, the most competitive utility-scale solar PV projects were regularly delivering electricity for just USD 0.08/kW h, without financial support, compared to a range of USD 0.045/kW h to USD 0.14/kW h for new fossil fuel power (excluding health and carbon emission costs).⁹ Therefore reduced PV system while increasing their conversion efficiency leads to the decrease of PV cost. However, efficiency improvement is not the only factor taken into account by the PV industry. One of the primary goal of the PV sector is to introduce more environmentally friendly materials to replace harmful materials.^{8,9}

2.2. The solar radiation

The sun emits light with a range of wavelengths from the ultraviolet and visible to the infrared. The efficiency of a solar cell is sensitive to variations of the intensity and the energy distribution of the incident light. Solar radiation reaching the Earth's surface strictly depends on the location, atmospheric conditions, time of the day, Earth-to-Sun distance and solar rotation and activity. Since the solar spectrum depends on so many variables, it is fundamental to define a standard spectrum and power density, thus allowing an accurate comparison among different solar devices. The Sun emission wavelength range covers the ultraviolet (UV), visible and infrared (IR) regions of electromagnetic spectrum, with a maximum peak at around 500 nm. Its spectrum is similar to that of a blackbody at 5670 K and it is influenced by the absorption of some molecules present in the atmosphere, such as O₃, CO₂, and, H₂O. When skies are clear, the maximum radiation strikes the earth's surface when the sun is directly above, having the shortest path length though the atmosphere. The pass length is called the air mass (AM) and can be approximately by the equation 1.

$$AM = \frac{1}{\cos\varphi} \tag{1}$$

Where, φ is the angle of elevation of the sun. The standard solar spectrum used for the efficiency measurement of solar cells is AM 1.5 G (global), giving that $\varphi = 42^{\circ}$. This spectrum is normalized so that the integrated irradiance is 1000 W m⁻² (known as 1 sun illumination). The AM 1.5 G solar radiation spectrum can be found from different sources.¹⁰ Figure 2 shows the spectrum as the irradiance of the sun as a function of wavelength. The solar spectrum changes throughout the day and with location. Standard reference spectra are defined to allow the performance comparison of photovoltaic devices from different manufacturers and research laboratories. The standard spectrum for space applications is referred to as AM 0. It has an integrated power of 1366.1 W m⁻². The spectrum is defined for solar concentrator work. It includes the direct beam from the sun plus the circumsolar component in a disk 2.5 degree around the sun. The direct plus circumsolar spectrum has an integrated power density of 900 W m⁻².



Figure 2- Reference solar spectrum Irrandiance.¹¹

2.3. Solar cell technologies

Currently the photovoltaic market for terrestrial applications is dominated by mono and polycrystalline bulk silicon which offer the best compromise between costs and performances. These devices are the main exponents of a group named as the first generation of photovoltaic cells and they comprise more than 80% of the solar cell market. This is the most mature PV technology with terrestrial cells efficiencies between 12 and 25%.¹² The advantage of silicon solar cells is the abundance of silicon. The disadvantage is the energy consumption for producing pure silicon. There are two types of crystalline silicon solar cells: mono-crystalline silicon produced by slicing wafers from a high-purity single crystal lingot and multi-crystalline silicon, made by sawing a cast block of silicon first into bars and then into wafers.¹³

Thin film technology devices include amorphous Si, CdS, CdTe, CuInSe₂ (CIS), CuInGaSe₂ (CIGS) and Cu₂ZnSnS₄ (CZTS).^{14,15} These devices are generally called second generation solar cells. Thin film technologies solar cells work with the same principle as the crystalline silicon photovoltaic: semiconductors are brought together and an electric field is established at the junction between the p-type and the n-type inorganic semiconductors. Thin-film technology has always been cheaper but less efficient than conventional c-Si technology. However, it has

significantly improved over the years. Terrestrial cells efficiencies between 7 and 21% have been established for thin film technologies.^{12,14} However, these technologies use toxic materials too.

Perovskite solar cells are a relatively new technology of photovoltaics.¹⁶ Terrestrial cells efficiencies of 19.7 % have been recorded.¹² Perovskites encompass a broad class of crystalline minerals. A disadvantage of the perovskite solar cells is that the record-breaking ones contain lead and that perovskites, being salt-like minerals, readily dissolve in water or even humid air.¹⁷

Since more than 20 years of research, a new generation of organic solar cells (OPV) and dye sensitized solar cell (DSSC) are emerging on PV market.¹⁸ DSSC presents terrestrial cell efficiencies between 9 and 12% and organic solar cell efficiency is 9.7% for mini module.¹² Unfortunately, these technologies are not so stable for long time. However, DSSC technologies are characterized by low fabrication costs and present some peculiar features like the transparency and the possibility of being fabricated in different colours, thus being interesting for building-integrated photovoltaics (BIPV) applications.^{19,20}

3. Dye sensitized solar cell

3.1. History

Although the electricity generation capability of organic dyes has been known since late 1960s, the first attempt to generate electricity form dye sensitized semiconductor film was from ZnO sensitized with Chlorophylls²¹ and that's why they are sometimes referred as 'Artificial Photosynthesis'. The first incarnation of modern day Dye-sensitized Solar Cell (DSSCs) dates back to late 1980s.²² However, not until the fundamental work of Grätzel and O'Regan in 1991²³, it was proven that DSSCs can be a feasible alternative energy source. The highest reported efficiency for DSSCs with conventional Ru-based dyes is around 11.5%.^{24,25} Recently, a Zn-based dye and Co-based electrolyte pair have been developed and their efficiency has exceeded 12%.²⁶

3.2. Advantages of DSSC

Although the power conversion efficiency of DSSC is not as good as compared to other inorganic 1st and 2nd generation solar cells, it has an advantage over them at some points. In the

normal operating temperature range of 20 - 70 °C, DSSC efficiency is nearly temperatureindependent. For the same range, the efficiency of Si solar cells declines by 20%.²⁷

- 1. Low light performance DSSC works in a wide array of lighting conditions that makes it suitable for a diverse range of shaded and diffuse light locations, without suffering from angular dependence of sunlight or light.
- 2. Low energy manufacturing process- DSSC is manufactured using low-energy consumption. The DSSCs are made of low-cost materials and cheaper to manufacture. Due to reduced manufacturing costs, DSSCs are less expensive when compared to other types of solar cells.
- **3. Ecologically friendly-** Materials used in DSSCs are eco-friendly nano-materials without concern about shortage of resources.
- **4.** Variety of substrates- DSSC is produced on a thin film, flexible, robust, plastic substrate, metal, and glass substrates.
- **5. Operates under lower temperature** Due in part to their mechanical robustness, the DSSCs have higher efficiencies at lower temperatures than traditional solar cells. DSSCs are able to radiate heat away much more efficiently than traditional silicon cells and operate at lower internal temperatures.

3.3. Principle Overview

DSSC is a photoelectrochemical device where several electron transfer processes run in parallel and in competition. In contrast to the semiconductor p-n junction solar cells, where light absorption and charge transport occur in the same material, the DSSC separates these functions: photons are absorbed by the dye molecules and transport of charges is carried out in the TiO_2 electrode and in the electrolyte. In DSSCs, the photoanode is a mesoporous oxide layer composed of nanometer-sized particles which have been sintered together to allow the electronic conduction. Attached to the surface of the oxide is a monolayer of dye molecules, which upon light absorption are promoted into an excited state. As a result, electrons are injected into the conduction band (CB) of the semiconductor, giving rise to the formation of excitons and to the subsequent charge separation.



Figure 3- Schematic overview of a dye-sensitized solar cell.¹⁰

The free electrons in the conduction band diffuse across the semiconductor towards the external circuit, performing electrical work. Once the electrons reach the counter electrode (CE), they react with the electrolyte that fills the space between the two electrodes. The original state of the oxidized dye is subsequently restored by electron donation from the electrolyte, which is itself regenerated at the platinum counter electrode by reduction of triiodide.^{10,28–30} The redox electrolyte therefore allows the transport of electrical charge between the two electrodes of the DSSC, closing the cycle.

The efficiency of a DSSC is strongly related to the electronic energy levels of the excited state (LUMO) and the ground state (HOMO) of the dye, by the electron Fermi level of the semiconductor and by the redox potential of the electrolyte. In particular, the dye LUMO must have an energy higher than the oxide CB and the HOMO should be lower with respect to the redox potential: for the above reasons the sensitizers have to be designed and synthesized in the appropriate way, to match the energy requirements of semiconductor and redox couple. The cell itself is able to produce a voltage drop between the two electrodes on the external load.



Figure 4- Operating principles and energy-level diagram of a dye-sensitized solar cell. S, S^+ , and S^* represent the sensitizer in the ground, oxidized, and excited state, respectively; R/R^- represents a redox mediator; CB denotes the conduction band.¹⁶

Reactions occurring during the cell operation

 The photosensitizer, adsorbed on the surface of the semiconductor, absorbs the incident sunlight and becomes excited from the ground state (S) to the excited state (S*)

 $S + hv \longrightarrow S^*$

 The excited electrons are injected into the conduction band of the semiconductor, resulting in the oxidation of the sensitizer (S⁺)

$$S \longrightarrow S^+ + e^-$$

3) The oxidized sensitizer (S^+) is regenerated by accepting electrons from the iodide ion

$$S^+ + 3/2 I^- \longrightarrow 1/2 I_3^- + S$$

4) The triiodide redox mediator diffuses towards the counter electrode and is reduced to iodide.

$$I_3 + 2e_{CE} \longrightarrow 3I$$

Additionally to the forward electron transfer and ionic transport processes, several competing electron loss pathways should be considered.

5) Decay of the dye excited state to the ground state.

 $S^* \longrightarrow S$

6) Recombination of the injected electrons with the dye cations.

 $S^+ + e_{CB} \longrightarrow S$

7) Recombination of the injected electrons with the triiodide redox mediator.

 $I_3 + 2e_{CB} \longrightarrow 3I$

4. Photovoltaic Parameters

4.1. I-V curve

A photovoltaic cell is a device able to convert the incident sunlight to electrical energy, exploiting the photoelectric effect. To determine the performance of a photovoltaic cell, a voltage ramp is applied in between the electrodes and the photocurrent delivered is measured, leading to *I-V* curve specific of the cell properties. Standard tests are realized at 25 °C under 1 Sun illumination ($P_{inc} = 1000 \text{ W m}^{-2}$) and air mass 1.5 (AM 1.5) corresponds to the sunlight spectrum modification when light coming from the sun passes through atmosphere with an incidence angle of 42°. For a resistive load, the load characteristic is a straight line with scope *I/V* = 1/*R*. It should be pointed out that the power delivered to the load depends on the value of the resistance only. However, if the load *R* is small, the cell operates in the region *M-N* of the curve (figure 5), where the cell behave as a constant current source, almost equal to the short circuit current. On the other hand, if the load *R* is large, the cell operates on the regions *P-S* of the curve, the cell behaves more as a constant voltage source, almost equal to the open-circuit voltage.



Figure 5- Typical I-V curve of PV cell.³¹

The **open circuit voltage**, V_{oc} (V) is the maximum voltage generated by the solar device when it is connected to an infinite resistance (i.e. when no current flows) and it is defined as the difference between the potential of the conduction band of the TiO₂ and the redox potential of the electrolyte. The experimental V_{oc} values are generally smaller due to the competition between electron injection processes and charges recombination.

The **short circuit current**, $J_{sc}(A)$ represents the maximum current when the electrodes are short circuited. The current flowing in the device is dependent on the area illuminated by the sun radiation, so it is preferable to refer to the short circuit current density, J_{sc} . This factor is mostly affected by the light-harvesting efficiency of the dye and also depends on the overall electron transfers involved in the cell operation.

The **maximum power**, P_{max} (W or W cm⁻²), is the operating point A (V_{max} , I_{max}) in Figure 5, at which the power dissipated in the resistive load is maximum:

$$P_{max} = V_{max} I_{max} \tag{2}$$

The **Fill Factor**, FF (%), which is a measure of the cell quality and is defined as the ratio between the theoretical maximum power obtainable $(J_{max}.V_{max})$ and the measured power $(J_{sc}.V_{oc})$. FF can vary from 0% to 100% and represents the deviation between the cell power output and its theoretical value. Normally, FF is affected by ohmic and overvoltage losses occurring during operation in DSSC.

$$FF = \frac{J_{max} V_{max}}{J_{sc} V_{oc}} \tag{3}$$

The **Photo Conversion Efficiency**, η (%), defined as the ratio between the maximum power developed, P_{max} by the cell and the power density of the incoming solar radiation in the cell P_{inc} .

$$\eta = \frac{P_{max}}{P_{inc}} = \frac{I_{sc} FF V_{oc}}{P_{inc}}$$
(4)

Cell efficiency is highly improved with maximizing the factors, I_{sc} , V_{oc} , and FF.

4.2. Incident Photon-to-electron Conversion Efficiency

Incident Photon-to-electron Conversion Efficiency (IPCE) is a powerful technique generally adopted to estimate the electrical response of a cell at different incident wavelengths. One of the advantages that this characterization technique offers is the possibility to investigate the wavelength range in which a particular dye molecule is able to absorb the light and efficiently inject electrons into the conduction band of nanostructured TiO₂ film. Generally, the set-up utilized to perform this kind of measurement on common silicon-based solar devices is constituted by two different lamps. The output beam provided by the first one passes through a chopper, then it is sent to a monochromator, and finally reaches the cell under test; the second lamp, instead, illuminates the device with a constant output, thus keeping it under normal working conditions. The short circuit current density produced by the cell in response to the sum of monochromatic and constant illumination is acquired through a lock-in amplifier which selects only the AC component related to the monochromatic beam $J_{sc}(\lambda)$. If the incident light power density at each wavelength $\phi(\lambda)$ is known, the IPCE value at a given wavelength can be calculated by using the formula.³²

$$IPCE(\lambda) = \frac{J_{sc}(\lambda)}{\lambda\phi(\lambda)} = \eta_{lh}(\lambda)\eta_{inj}(\lambda)\eta_{coll}(\lambda)$$
(5)

Where J_{sc} is measured in mA cm⁻², ϕ in mW cm⁻², λ in nm, and η_{lh} , η_{inj} and η_{coll} are the light harvesting efficiency, the charge injection efficiency and the charge collection efficiency, respectively.

4.3. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is one of the most important tools to elucidate the charge transfer and transport processes in various electrochemical systems including dyesensitized solar cells (DSSCs).³³ In EIS, the potential applied to a system is perturbed by a small sine wave modulation and the resulting sinusoidal current response (amplitude and phase shift) is measured as a function of modulation frequency. The impedance is termed as the frequency domain ratio of the voltage to the current and is a complex number. For a resistor (R), the impedance is a real value, independent of modulation frequency, while capacitors (C) and inductors (L) yield an imaginary impedance, whose value changes with frequency. The measured impedance in a wide range of frequencies can be explained in terms of an equivalent circuit consisting of series and parallel connected elements R, C, L, and W, which is the Warburg element that describes diffusion processes.

The EIS spectra can be interpreted and modelled using equivalent circuits, with each component reported in various literatures.^{33–36} After fitting the data with respective circuit, following parameters can be obtained: series resistance, charge transfer resistance of the counter electrode, diffusion resistance of the electrolyte, the resistance of electron transport and recombination in the TiO₂, and the chemical capacitance of the porous TiO₂ electrode.

When an EIS measurement is executed under dark condition, there is no photoexcitation and therefore only electrons and therefore only electrons from the external bias voltage determine the measured EIS characteristics. In those conditions, only electron injection and extraction take place across the electrode interface depending on the applied voltage. When an EIS measurement is performed under light illumination, the electrons created by photoexcitation will also contribute to the measured EIS.

4.4. Stability

Long term stability is very important for outdoor applications of DSSCs. The overall stability of this cell is controlled by two factors, namely physical and chemical stability. Physical stability is related to the possible evaporation of the liquid electrolyte at elevated temperatures. This is a technological problem, for which solutions can be found by using suitable sealing materials and techniques.^{37,38} The intrinsic chemical stability is related to irreversible (photo)electrochemical and thermal degradation of the dye or electrolyte components, which might occur during operation of the cell. However, as TiO₂ is known as a good photocatalyst, UV exposure has been proved to be detrimental for DSSCs.³⁹ Carnie et al. as well as Hinsch et al. reported the irreversible consumption of iodine leading to the bleaching of the electrolyte solution under prolonged UV irradiation of DSSCs.^{40,41} However, this stability issue was easily solved by the use of a UV filter. To ensure the long term stability electrolytes with low volatile solvent or solvent-free electrolytes have been developed.^{42,43} Numerous studies have been performed on the long term stability of liquid-state-DSSCs.^{44,45} Efforts have focused on using solid-state organic or p-type conducting polymer hole-transport materials, but their conversion efficiency remains modest due to poor filling of the nanoporous layer.^{46,47} One of the methods to solve these problems is using quasi solid-state electrolytes.⁴⁸ Regarding stability of DSSC device, the conditions for accelerated testing have not yet been standardized. Until now, 1000 h lightsoaking and 1000 h high temperature storage were implemented to show feasibility of the technology. Recently, Zhinpeng et al. demonstrated that quasi solid state DSSC based on supermolecular electrolyte exhibited excellent stability as compared to DSSC based on liquid electrolyte when tested under successive sun light soaking with UV cut-off filter at 50 °C for 1000 h.⁴⁹ Although the efficiencies of the DSSCs with quasi-solid-state-electrolytes are often lower than those of the DSSCs with liquid electrolytes, the quasi-solid electrolytes may become feasible alternatives to the liquid electrolytes owing to improved and better sealing ability.^{50–52} Recently, Marcelo et al demonstrated portable, parallel, grid-type DSSC modules containing polymer gel electrolyte and a standard liquid electrolyte to improve the long term stability.⁵³

4.5. Commercial Perspectives

The present challenges are to improve DSSCs performances and their stability (hole-transporting material or solid state electrolytes). During recent years, industrial interest in the DSSC has grown and the first commercial products have appeared. A number of industrial corporations, such as RWE in Germany, Solaronix in Switzerland, Konarka in the U.S.A., Dyesol in Australia, Samsung in Korea, Aisin Seiki in Japan, G24i in United Kingdom, are actively pursuing the development of new products.^{54–57} Particularly interesting are applications in building integrated photovoltaic elements such as electric power producing glass tiles.

5. DSSC Components

DSSC converts visible light into electricity based on the sensitization of wide band gap semiconductors and is primarily consisted of photoelectrode, redox electrolyte and counter electrode. Other materials include transparent conducting oxide and sealing agents. DSSC components have gone under various developments over the years in order to enhance the efficiency of the cell.

5.1. Photoelectrodes

Photoelectrodes are generally composed of conducting glass substrate coated with a wide gap semiconductor material. Glass is largely used in DSSCs because of its high transparency and its high temperature stability. The semiconductor structure deposited on conductive glass, typically 10-15 µm thick with a porosity of 50%, has a surface area available for dye chemisorption over a

thousand times than that of a flat, unstructured electrode of the same size. If the dye is chemisorbed as a monomolecular layer, enough can be retained on a given area of electrode to provide absorption of essentially all the incident light. Mesoporous oxide films are made up of arrays of tiny crystals measuring a few nanometres across.

Semiconductor materials such as metal chalcogenides and metal oxides based photoelectrode have been under extensive investigation due to their wide application in energy storage and environmental remediation.^{58,59} The metal oxide semiconductors like TiO₂, ZnO, SnO₂ and Nb₂O₅ gained a lot of attentions due to their wide bandgap.^{60–64} Besides these simple oxides, ternary oxides, such as SrTiO₃ and Zn₂SnO₄, have also been investigated.^{65,66} Since the discovery of DSSC in 1991 by O'Regan and Gratzel, mesoporous TiO₂ made up of arrays of nanoparticles photoelectrode has the highest efficiencies in DSSC so far.^{67,68} It has been found that TiO₂ is a stable photoelectrode in photo-electrochemical systems even under extreme operating conditions.

It is cheap, readily available and non-toxic and is normally used as dye in white paint and toothpastes. The TiO₂ photoelectrodes nanoparticles offers some unique properties making it a feasible semiconductor for DSSC such as (i) the low intrinsic conductivity of the film, (ii) the small size of the nanocrystalline particles does not support a built-in electric field and (iii) the electrolyte diffuse into the porous film all the way to the back-contact created the semiconductor/electrolyte interface essentially three-dimensional.⁶⁹ TiO₂ normally occurs in three crystal structures, namely; rutile, anatase and brookite. While rutile is the thermodynamically stable phase, anatase is preferred for dye sensitized solar cells, due to its larger band gap ($E_g = 3.2$ eV for anatase compared to $E_g = 3.0$ eV for rutile).⁷⁰ The high refractive index of TiO₂ ($\varkappa = 2.5$ for anatase) results in efficient diffuse scattering of the light inside the porous photoelectrode, which significantly enhances the light absorption.^{71,72}

Additionally, mesoporous TiO₂ photoelectrode has a high internal surface area to support the monolayer of a dye sensitizer and its conduction band edge lies slightly below the excited state energy level (LUMO) positioned of many dyes sensitizer. This condition is required for efficient electron injection in the conduction band of semiconductors to transport across TiO₂ film by diffusion toward the transparent conducting oxide (TCO).^{69,71} The high dielectric constant of TiO₂ ($\epsilon = 80$ for anatase) provides good electrostatic shielding of the injected electrons from the oxidized dye molecule attached to the TiO₂ surface, thus reduced their recombination before
reduction of the dye by the redox electrolyte.^{68,71} The common techniques employed in the preparation of TiO₂ films include the doctor blade technique, screen printing, spin coating, tape casting method etc. In order to increase the DSSCs performance, an intensive research has been going on to increase the optimum porosity of the film.

5.2. Dyes

An efficient dye must fulfil certain requirements for DSSC applications:^{30,54,73,74}

- 1) A strong absorption in the visible region.
- 2) Strong adsorption onto the semiconductor surface.
- 3) Efficient electron injection into the conduction band of the semiconductor.
- It should possess several O or –OH groups capable of chelating to the Ti(IV) sites on the TiO₂ surface.
- 5) High thermal and electrochemical stability.
- 6) It must be rapidly regenerated by the mediator layer to avoid electron recombination processes and be fairly stable, both in the ground and excited states.
- It must absorb all light below a threshold wavelength of about 900 nm, which is equivalent to a semiconductor with a band gap of 1.4 eV.⁷⁵

The finest photovoltaic performance in terms of both conversion yield and long term stability, has so far been achieved with polypyridyl complexes of Ruthenium (Ru) developed by the Grätzel group. The most used are N-3 or N-719, which differ in the number of protonated caboxylate groups (figure 6). N-719 is a modification of N-3 dye by substituting the tetrabutylammonium group (TBA⁻) which can result in increased cell voltage. These two dye molecules absorb light in a wide range of visible wavelength.



Figure 6- Molecular structure of the dyes.⁷⁶

Carboxylate anchor groups bind strongly with anatase, leading to the dye absorption on the semiconductor surface. Depending on the dye structure and semiconductor interface, different modes of coordination bond can take place between carboxylate anchor groups and TiO₂.^{77–79}



Figure 7- Possible binding modes of a carboxylic acid group $toTiO_2$. (a) Ester linkage, (b) chelate binding, (c, d) bidentate bridges, (e, f) hydrogen-bonding interactions and (g) monodentate binding through CO.⁷⁹

Further to superior light harvesting properties and durability, a significant advantage of these dyes lie in the metal–ligand charge transfer transition through which the photoelectric charge is injected into TiO₂. In Ru (II) complexes, this transfer takes place at a much faster rate than the back reaction, in which the electron recombines with the oxidized dye molecule rather than flowing through the circuit and performing work.⁸⁰ However, the use of these expensive Ru metals, derived from relatively scarce natural resources corresponds to a relatively heavy

environmental burden and also due to their multistep synthesis and the need for complex purification methods.^{81,82} Hence, it is possible to use Ru-free dyes as alternative photosensitizers with appreciable efficiencies. Organic dyes such as coumarin, hemicyanine, merocyanine, squarylium, cyanine etc. are regarded as promising sensitizers for DSSCs because of their tuneable absorption in the red to near-infrared region as well as their high.^{83–86} However, metal-free sensitizers present some drawbacks, which are responsible for the lower power conversion efficiency compared with metal complexes. These are mainly the narrower absorption spectra, the increased recombination dynamics as a consequence of surface aggregation phenomena, and in some cases low thermal and photo stability, dye desorption due to electrolyte, cis–trans photoisomerization is one of the major decay pathways for some ionic dyes.^{87,88} The best efficiency reported for lab-scale DSSC using a Ru dye is 12.2%.⁵⁴ However, organic dyes also showed promising results with an efficiency over 10%.⁸⁹

5.3. Counter electrode

In DSSCs, the counter electrode is used to transfer electrons from the external circuit to the electrolytes and it should have a low charge transfer resistance and high exchange current densities for the reduction of the oxidized form of the charge mediator.⁹⁰ The counter electrode serves to transfer electrons arriving from the external circuit back to the redox electrolyte. It also has to carry the photocurrent over the width of each solar cell. Hence, it must be very conducting and exhibit a low overvoltage for reduction of the redox couple. Presently, platinum (Pt) is the best catalyst for I_3^- reduction because it reduces charge transfer over-voltages at the counter electrode.^{91,92} An interesting low cost alternative for Pt is carbon (C), because it combines sufficient conductivity and heat resistance as well as corrosion resistance and electrocatalytic activity for the I_3^- reduction but the cell performance are weaker.^{72,93} Porous carbon electrodes are easily prepared from graphite powder, which can be deposited easily aligned in the plane of the counter electrodes, resulting in a high conductivity in this plane. Pt/C black counter electrode for DSSC and achieved 6.72% efficiency under one sun illumination. Pt/C black electrode have reported the same efficiency and lower cost compared with Pt electrode alone.⁹⁴ On the other hand, plastic substrates are investigated as flexible counter-electrode material but chemical and thermal stability required for photovoltaic applications makes it expensive.^{54,95}

5.4. Blocking layer

In DSSC, TiO₂ blocking layer (BL) refers to the individual layer between mesoporous TiO₂ network and the charge collector in DSSC anodes.^{96,97} The BL plays a crucial part in the DSSC because it prevents carriers from directly contacting the conductive substrate and thereby avoiding the short-circuiting of the device. Two mechanisms have been proposed to explain this behaviour, a decrease in the electron-hole recombination at substrate/electrolyte interface and an enhancement in the electronic contact between the mesoporous TiO₂ network and the charge collecting electrode.⁹⁸ However, the effect is relatively low for the I_3^-/Γ electrolyte based DSSC,⁹⁸ since the regeneration of the sensitizer by Γ is significantly faster than the charge transfer from TiO₂ to the oxidized dye.⁹⁹ Polymer electrolytes have been employed as an alternative redox couple for DSSCs.^{100,101} As the diffusion constant of the I_3^- in polymer electrolyte is lower than the I_3^-/Γ in liquid electrolyte, the BL can play an important role in DSSC performance. TiO₂ is the most frequent BL material used, although ZnO, SrTiO₃, Nb₂O₅, SnO₂, Sb₂S₃ are also performing materials.¹⁰²⁻¹⁰⁶

It has been reported that the thickness of the TiO_2 BL a crucial role in the cell efficiency. BL must not exceed certain values in order to prevent the layer from acting as a charge trap site.¹⁰⁷ Kim et al presented a range of thickness of BL from 25 to 400 nm.¹⁰⁸ This wide range is normally affected by the method and conditions used for depositing the films. The thicker the BL, the poorer the photocurrent, and therefore, only thin BLs lead to an better photovoltaic performances.¹⁰⁹ The thickness of the BL also affected the internal series resistance of the solar cells, influencing their fill factor.¹⁰⁹ Spin coating and spray pyrolysis are two representative solution processes used to prepare BLs, although atomic layer deposition, thermal oxidation, and TiCl₄ chemical bath deposition, sputtering, dip coating etc. have also been reported in the literature.^{110–119} Ideally, a BL should be crack-free, dense and very thin to avoid additional resistive losses. In practice, spin coating is very facile way to produce the thin films and Ultrasonic Spray Pyrolysis (USP) can produce perfectly covered and dense films.

6. TiO₂ Porous layer

The preparation of mesoporous TiO_2 thin film is not new. The mesoporous TiO_2 has to present several characteristics for DSSC application:

- Mesoporosity that provides high surface area and hence, more adsorption of photoactive dye. Therefore, numerous efforts have been made to improve the surface area by simply playing with the film mesostructure (pore size and continuous pores) while keeping the optimum thickness of the film.^{27,72,74,120}
- 2) Efficient electrons transfer from the excited dye to the conduction band of TiO_2 and further transfer.
- 3) Well interconnected pores, robust, crystalline, adhesive and stable under cell operation.

Instead of having all the advantages, the mesoporous films still hold a challenge when tested with viscous electrolyte materials. This problem can certainly be improved by increasing the pore size with continuous pores. In order to fulfil the demand on high surface area, specific pore size or pore channel arrangements, increasing attention has been paid to attune the pore systems of such types of materials. Some works were focused on one of the exciting areas, namely bimodal materials. Currently, several methods have managed to synthesize bimodal TiO₂, e.g. utilizing surfactants, and polystyrene based templates.¹²¹⁻¹²³ Expanding mesopore size beyond a 10 nm diameter is a big challenge for developing applications on mesostructured mesoporous thin films. To fabricate these films, accurate tuning of pore size distribution (small mesopores 5-10 nm and large pores 20-150 nm diameter) is needed. Currently, doctor blade method, screen printing, and dip coating are most frequently used technique to prepare nanocrystalline TiO₂ films for DSSC.^{23,124–126} Recently, Henrist et al and Kaune et al, reported the spin coating technique to synthesize the bimodal TiO₂ films using soft and dual templates.^{127,128} These synthesis techniques normally deploy organic surfactant (soft) and polymers (hard) as templates. Combining template-assisted approach with sol-gel coating technique provides an interesting way to fabricate fine nanostructure of desired features.¹²⁹⁻¹³³ However, this kind of films possesses some limitations such a poor quantity of active material, poor adhesion. Therefore, the multilayer process must be optimized in order to have better films with high thickness. In the synthesis process, the major role of the surfactants is to organize precursor phases within micellar structures. In subsequent developments for bimodal material, surfactant (soft templates) is combined with more rigid moieties (hard templates), such as colloidal dispersions, colloidal crystals, porous membranes etc.^{134–136} Here, each set of templates acts as a space filler or a structure director at a given length scale, and after removal of the templates, materials with hierarchical pore structure are obtained. Zukalova reported that Pluronic-123 surfactant can be used as soft templates to produce the films with high surface area but with quite small pore diameters.^{137,138} Similarly, some publications report that polystyrene beads (PS) can be used to prepare films with larger pores.^{121,139,140}

6.1. Soft Templates

The sol-gel process of titanium precursors is distinguished from that of silicates by their higher chemical reactivity resulting from the lower electronegativity of titanium and its ability to exhibit several coordination states so that coordination expansion occurs spontaneously upon reaction with water or even moisture.¹⁴¹ Thus, titanium precursors tend to fast hydrolyze and form dense precipitates, which affect the cooperative assembly with surfactants, leading to phase separation. For example, the hydrolysis rate of titanium alkoxides is about five orders of magnitude faster than that of silicate ones. Therefore, the critical issue for preparing mesoporous TiO₂ under the guiding of surfactant templating is to control the hydrolysis and condensation rates of titanium precursors to effectively match the cooperative assembly with templates. In addition, the recovery of mesoporous TiO₂ without framework collapse should be paid much attention to during the template removal and crystallization. The self-structuration of surfactants can produce mesostructures by the spontaneous organization of Ti⁴⁺ around auto mounted micelle structures; usually in aqueous medium. The soft-templating method consists in the use of a template in the liquid phase, being widely used in the sol-gel processes based on titanium oxide precursors.

Studies have suggested that three mechanisms are related to the formation of mesoporous materials via soft-templating method.^{142–145} The first, known as Cooperative self-Assembly (CA), the second Liquid Crystal Template (LCT) and third the Evaporation-Induced Self-Assembly (EISA). In CA, there is a simultaneous aggregation between the inorganic precursor and the surfactant, with the formation of a liquid crystal-like phase with cubic, hexagonal or lamellar arrangement, containing both micelles and the inorganic precursor (figure 8, top). On the other hand, in the LCT mechanism the concentration of surfactant is so high that a liquid-

crystalline phase is formed without the presence of inorganic precursors (figure 8, middle). In both, LCT and CA, it is essential that the precursor does not condense too rapidly or interfere with the self-assembly of the surfactants into a liquid crystal. While, EISA is used extensively for the synthesis of mesoporous thin films and in multiple templating (figure 8, bottom).



Figure 8- Schemes detailing the soft templating process.¹³⁶

EISA can be understood to be closely related to LCT, there are additional interactions (like those at the solid–liquid interface) that impact the process.¹⁴⁶ To conduct an EISA synthesis, one must

use a dilute solution that contains a volatile solvent like ethanol, an inorganic/organic precursor, and a surfactant. In some cases nanoparticle precursors can also be used, provided that these crystals are small enough (<5 nm) to participate in self-assembly.¹⁴⁷ The solution is then spread over a large area and allowed to evaporate. In all the mechanisms mentioned above, after formation of the material it is necessary to remove the template for obtaining the porosity. For this, the procedure most commonly used is the calcination.¹⁴² On the basis of above synthetic mechanisms, a large number of mesoporous TiO₂ have been successfully prepared by using conventional titanium precursors (e.g., TiCl₄, titanium alkoxides, TiOSO₄, TiO₂ nanocrystals). The critical issue is to control their sol-gel process and the cooperative assembly with amphiphilic templates, thus ensuring the formation of ordered mesostructures. Various surfactants are utilized as a template such as organic amines, cetyltrimethylammonium bromide (CTAB), tetradecyl phosphates, diblock polymers (e.g., Brij 56, Brij 58), triblock copolymers (e.g., P123, F127), and lab-made block copolymers (e.g., Poly(o-hydroxypoly(ethylene-cobutylene)-co-poly(ethylene oxide) block copolymer, (KLE)). These templates play key roles in modulating the mesostructure, surface area, pore size and wall thickness, as well as thermal stability of the resultant mesoporous TiO₂.^{126,148} The soft templating method was used to fabricate high quality TiO₂ mesostructures by various researchers for DSSCs.^{149,150} Dewalque et al. established a multilayered deposition process with different soft templates, in order to obtain crack free and adherent mesopores films using various soft templating and were tested successfully in DSSCs.¹²⁶ Recently, Mirkhani et al. synthesized ordered and disordered TiO₂ mesostructured film up to 7 µm by the EISA process using spin and dip coating.¹⁵¹ The crack free films were obtained by optimizing the stabilization and calcination steps and DSSCs based on photoanode made of ordered mesostructure from dip coating showed the maximum efficiency of 8.33%.

6.2. Hard Templates

Different steps are needed to synthesize a porous material from a hard template (figure 9), starting with the synthesis of a precursor solution. For the formation of a templated inorganic material, the simplest solution-based precursor is a salt dissolved in a polar solvent. Metal alkoxides dissolved in aliphatic alcohols are also commonly used as precursors. Step two consists of filling or coating a hard template with a precursor. Further consolidation of the network of the templated material is often needed via temperature thermal treatment. Removal of

the template is the final and sometimes optional step. Chemical etching is a viable option for many different templates, including oxide templates. With polymeric templates, a common option for this final step is thermal treatment (calcination).



Figure 9- Schemes detailing the hard templating process.¹³⁶

In the hard-templating method the solid is formed around a template, usually zeolites and meso and macroporous silica, polystyrene beads, via interactions between the template and the precursor.¹⁴⁸ However, it is highly effective in obtaining mesoporous structures.¹⁵² By applying this methodology nanostructures are formed on surface of the templates.¹⁵³ In order to improve the photoconversion efficiency of DSSCs, a promising route is to control the pore size in order to have better light scattering and pore infiltration of viscous polymer by using hard templates such as PS beads.^{154,155}

6.3. Dual templates

The combination of soft and hard templating can induce considerable changes in the templated macrostructure as shown in figure 10. If the liquid crystal template is confined in a hard template with nanometric-scale dimensions, packing constraints can alter the structure of the liquid crystal.^{147,156} Confinement also enhances interactions between hard and soft templates.¹⁴⁷ Illustrative examples of multiple templating are given to provide a broad overview of the area and outline methods for tuning pore morphology.



Figure 10- Scheme detailing a multiple templating approach.¹³⁶

One of the key considerations in fabricating solid state Dye sensitized solar cells (ss-DSSCs) is to enable deep infiltration of large volume solid electrolytes into the TiO_2 photoanode, which largely depends on the pore structure and morphology of TiO_2 . A colloidal crystal template and holographic lithography have been introduced to produce well-organized TiO_2 photoanodes, but their surface areas were not high enough to load a large amount of dye molecules.^{154,157}

The Dual templating method has been used to fabricate high quality TiO_2 bimodal films by various researchers for DSSCs.^{158,159} Recently, Kim et al. demonstrated the synthesis of bimodal porous TiO_2 with large surface area, high porosity, good interconnectivity, and excellent light-scattering properties.¹⁶⁰ The films were synthesized via a facile one-step method using a self-assembled blend template consisting of an amphiphilic poly(vinyl chloride)-g-poly(oxyethylene methacrylate) (PVC-g-POEM) graft copolymer and a hydrophobic poly(vinyl chloride) (PVC) homopolymer. The bimodal films were tested with electrolytes composed of poly(ethylene glycol), 1-methyl-3-propylimidazolium iodide, Lithium Iodide and Iodine dissolved in acetonitrile and the fabricated DSSC showed the efficiency of 7.6% which was higher than reference mesoporous TiO₂ films (5.8%).

Use of a commercially available block copolymer, e.g., Pluronic P123 as soft templates, often leads to TiO_2 pore sizes smaller than 10 nm due to the low molecular weight of the copolymer, which hinders thorough infiltration of solid electrolytes and impedes the complete crystallization while maintaining structural integrity.¹⁶¹ In order to have dual porosity, polystyrene latex can be employed as hard-templates along with P123 as soft templates to build bimodal structures. For this reason, the combination of macro- and mesopores constitutes a very attractive strategy to produce thin films with highly structured interface, high specific surface, accessible and ordered pores as well as facilitated entry of viscous or hindered chemical species.

6.4. Spin coating process

In this present work, porous TiO₂ templated films are synthesized by spin-coating (figure 11).



Figure 11- Key stages of spin coating process.

During this stage, the solution is dropped on rotating substrates from micropipette and the substrate is accelerated to the desired speed. Spreading and drying of the solution takes place due to centrifugal force. The combination of spin speed and time selected for this stage will generally define the final film thickness.^{162,163} In general, higher spin speeds and longer spin times create thinner films. The spin coating process involves a large number of variables that tend to cancel and average out during the spin process and it is best to allow sufficient time for this to occur. Last step is the drying and stabilization at certain temperature for few minutes.

6.5. Film crystallization

Calcination is a key process during sol-gel preparation of TiO_2 film. The film prepared at ambient temperature is normally in its amorphous state accompanied with crystalline imperfection. Therefore, calcination can lead to the formation of oxides crystallite and also can help in making remedies for structural defects. Thermal treatment has to be applied to the spin coated film in order to fully condense and crystallize inorganic network, and complete removal of the organic material to provide the porosity as shown in figure 12. TiO_2 films prepared with or without hard templates can be calcined at 500 °C to have crystalline structure. However, the calcination temperature has to be perfectly tuned to limit the crystallite growth, preserve porosity and prevent cracks.^{164–166}



Figure 12- Pores generation in mesoporous and bimodal films by thermal treatment.

6.6. Scattering Properties

Light scattering has been applied to DSSCs in order to enhance optical absorption of the photoelectrode film. In general, there are two approaches that have been conventionally adopted to introduce light scattering into the photoelectrode film of a DSSC. The first method is called double-layer structure where the large particles are placed on the top of the nanocrystalline film to form a light scattering layer, so that the incident light can be reflected back to the film, resulting in more light absorption (figure 13). In these structures, the nanocrystalline film functions as the primary absorber to provide a sufficient surface area for dye adsorption, while

the large-size (submicron-sized TiO₂ particles) particles which are introduced to generate light scattering will however ineluctably cause a loss of internal surface area of the photoelectrode film in the case of a mixed structure, or increase the internal resistance of the solar cells and hinder charge transport within the solar cells in the case of a double-layer structure. A typical double-layer structure is shown in figure 13A-B, where the nanocrystalline film with a thickness of 8 μ m is made of ~ 20 nm TiO₂ nanocrystallites and the scattering layer (~ 3 μ m in thickness) is comprised particle size greater than 100 nm.¹⁶⁷ The photoelectrode with such double layer structure has been able to increase the photocurrent density of DSSCs.^{167,168}



Figure 13- Double-layer structure DSSC photoelectrode. (A) Schematic drawing of a double layer structure photoelectrode formed by a nanocrystalline film and a light scattering layer, and (B) a cross-sectional SEM image of the photoelectrode.

Spherical voids, a kind of hollow structure purposely introduced into nanocrystalline films, can also be employed as light scattering centres for DSSCs as shown in the figure 14B. To fabricate spherical voids in a nanocrystalline film, according to the method described by Hore et al., polystyrene spheres with radius of 200 nm was mixed with TiO_2 colloidal paste in a ratio of 1:5 by volume.¹⁶⁹ With a model of electrolyte-filled spherical voids surrounded by a medium of TiO_2 and using Mie theory, the optimal sizes of the voids were determined to be in the range of 50–100 nm, giving rise to the most intensive light scattering and the fabricated DSSCs resulted in a 25% improvement in the conversion efficiency. In addition to playing a role in generating light scattering, the spherical voids with a hollow structure had been also demonstrated the advantage

of allowing the liquid electrolyte to permeate into the nanocrystalline film, making it possible to use an electrolyte with high viscosity or low ion diffusion constant in DSSCs.^{158,169}



Figure 14- Schematic drawing of A) mesoporous and B) bimodal films.

6.7. Pore Infiltration

The two main issues thought to be responsible for the relatively poor operation of polymer based DSSCs are an inability to effectively infiltrate semiconducting polymers into random porous networks and ineffective charge transport within the polymer phase due to non-crystalline, unorientated polymer chains.^{170,171} Several techniques such as X-ray photoelectron spectroscopy (XPS)^{172,173}, Rutherford backscattering spectrometry (RBS)¹⁷⁴, spectroscopic ellipsometry and optical reflectometry^{161,175} have been studied to successful utilized to study the pore infiltration of hole transporting materials such as Spiro-OMeTAD, P3HT. However, these techniques were limited to very thin films. In the present work, our focus lies mainly on quantitative investigation of infiltration of the polymer electrolytes into titania nanostructures. Moreover, high viscous electrolytes make these techniques even more tedious. There have been reports of SEM being used to quantify the pore infiltration of ionic polymer electrolytes based on hexylimidazolium iodide.¹⁷⁶ Figure 15 exhibits the cross-section SEM images of TiO₂ electrode with and without the ionic polymer introduced by in situ polymerization (polycondensation between N,N'bis(imidazolyl) hexane and 1,6-diiodohexane). Figure 15 displays a porous and rough structure of as-prepared TiO₂ film. After electrolyte is introduced, the TiO₂ nanoparticles became indistinct and the porous character disappeared, suggesting good interfacial contact between polymer and TiO_2 film. The elemental mapping on the rectangular area shown in figure 15 demonstrates excellent distribution of iodine atoms throughout the 8 µm thick porous TiO_2 film.



Figure 15- Cross-section SEM images of TiO_2 photoanode without (a) and with (b) polymer electrolyte; (c) elemental mapping by energy dispersive spectroscopy for a rectangular area indicated in (b).¹⁷⁶

However, several conditions are necessary for *in situ* preparing chemical cross-linking electrolytes.¹⁷⁷

- (i) Polymerization must take place at a temperature below dye decomposition.
- (ii) Polymerization has to be completed without generating any by-products that could reduce the photovoltaic performance.
- (iii) Polymerization must take place in the presence of iodine.
- (iv) Polymerization can proceed without an initiator because the by-products of the initiator may decrease the photovoltaic performance.

This problem can certainly be improved by creating the dual porosity with small and large, simultaneously, in order to fulfil the demand of both high surface area, and improved pore infiltration as demonstrated by figure 16.



Figure 16- Schematic diagram of A) mesoporous, B) bimodal TiO₂ films showing pore infiltration with viscous polymer.

7. Electrolytes

Electrolyte, the key component of dye-sensitized solar cells, remarkably affects the stability and DSSC efficiency. Generally, electrolytes are divided into four main classes: liquid electrolyte, inorganic semiconductor, electronic conducting polymer (hole transporting material with electronic conductivity) and ionic polymers, solid ones or gelled ones using organic solvent or ionic liquid (named as quasi-solid state electrolyte).

In the groundbreaking article O'Regan and Grätzel, the efficiency reported for the first DSSC was 7.12%, with the standard Γ/I_3^- mediator and a Ru complex as sensitizer.²³ Over the years, the great efforts have been spent on materials and devices engineering permitted to achieve efficiencies exceeding 11% for liquid DSSCs fabricated with standard components (Γ/I_3^- mediator and Ru complexes).²⁴ The introduction of new redox couples based on Co-complexes and porphyrin dyes allowed to achieve the benchmark value of 13%.^{26,178} Indoor and outdoor applications of DSSCs based on liquid electrolytes is limited due to some practical problems, such as leakage and volatilization of solvent, photodegradation and desorption of dye, corrosion of counter electrode, and ineffective sealing of the cells.¹⁷⁹

When it comes to solid-state dye-sensitized solar cells, the electrolytes solution is replaced by a wide band gap inorganic semiconductor of p-type polarity, such as CuI or CuSCN^{10,54,180}, or a hole-transporting polymer, for example, Poly(3-hexylthiophene) (P3HT), an amorphous organic arylamine and its derivatives, Spiro-OMeTAD^{47,181–183}. The excited dye injects electrons into the n-type oxide, and it is regenerated by hole injection in the p-type material. Efficiency of solid-state electrolyte is lower than liquid electrolyte due to poor penetration into the meso-porous TiO₂, the low electron transfer from the dye molecules, and the faster recombination. One of the methods to solve these problems is using quasi-solid-state electrolytes.

7.1. Quasi-solid-state electrolytes (QSSE)

Quasi-solid (semisolid) state is a special state of a substance between solid and liquid states. Quasi-solid-state electrolytes (QSSE) always possess, both the cohesive property of solid and the diffusive property of liquid, which mean better long-term stability than liquid electrolytes and have the merits of liquid electrolytes including high ionic conductivity and excellent interfacial contact property. Due to their excellent characteristics, quasi-solid electrolytes are widely used in DSSCs¹⁸⁴, batteries¹⁸⁵, sensors and actuators¹⁸⁶, fuel cells¹⁸⁷ and super-capacitors¹⁸⁸. Although the efficiencies of the DSSCs with QSSEs are often lower than those of the DSSCs with liquid electrolytes. The quasi-solid electrolytes become possible alternatives to liquid electrolytes owing to improved stability and better sealing ability. The operating principle of quasi-solid state DSSC is in corresponding with that of liquid state DSSC. They are comprised of macromolecular system with or without the addition of solvent or ionic liquid showing high up to ionic conductivity (~ 10^{-3} S cm⁻¹).^{184,189} Due to their similar properties as liquid electrolytes and improved stability, QSSEs are widely used in DSSCs application.¹⁸⁴

QSSEs are divided into four main types: thermosetting polymer electrolytes¹⁹⁰, composite polymer electrolytes¹⁹¹, thermoplastic polymer electrolytes¹⁹² and ionic liquid (or polyionic liquid) electrolytes¹⁹³. This classification is based on features, formation mechanisms, and physical states of the electrolytes.

7.1.1. Thermoplastic Polymer electrolytes (TPE)

In order to improve ionic conductivity, solid polymer electrolyte are generally swelled by a liquid electrolyte.^{51,194} Sometime additives are also used along with the salts. Solvent provides the medium for the mobility of ionic species. It decreases the polymer-polymer chain interaction, and increases the free volume and segmental mobility of the system. This type of electrolytes are called thermoplastic polymer electrolyte (TPE) because these electrolytes can change from soluble state to the gel state or vice versa by controlling the temperature. Due to the large amount of solvent introduced, the TPE shows the liquid electrolyte feature with high ionic conductivity, good interfacial wetting and filling with a limitation of the leakage problem. Polymer matrix is a key component of TPEs. Linear polymers are often used as matrix, including poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), poly(vinyl pyrrolidinone) (PVP), polystyrene (PS), poly(vinyl chloride) (PVC), poly(vinylidene ester)(PVE), poly(vinylidene fluoride) (PVDF), and poly(methyl methacrylate) (PMMA), etc.¹⁹⁵ Main of these matrices has not solvation ability versus ionic species, the conduction is assumed by the solvent, whereas the polymer assumes the mechanical properties.

Wang et al. prepared a quasi-solid state electrolyte using poly(vinylidenefluoride-cohexafluoropropylene), (PVDF-HFP) (6 wt%) as gelator showed efficiency comparable to the liquid electrolytes based on acetonitrile and 3-methoxypropionitrile (MPN).¹⁹⁶ The open-circuit voltage increases substantially and stability of DSSCs are improved when polymer gel electrolytes was employed. Using the same polymer, in 2009, Hongsheng et al. reported in-situ ultra-thin porous (PVDF–HFP) membranes were prepared by a phase inversion method on TiO₂ electrodes coated with N-719 dye.¹⁹⁷ These membranes were then soaked in the organic liquid electrolyte to form the in-situ ultra-thin porous (PVDF–HFP) membrane electrolytes. DSSCs using the membrane electrolyte exhibited efficiency of 8.35% under 1 sun.

Lan et al. prepared gel polymer electrolyte by a mixture of poly(methyl methacrylate) (PMMA) as polymer host, ethylene carbonate, 1,2-propanediol carbonate and dimethyl carbonate as organic mixture solvents, sodium iodide and iodine as source of I^{-}/I_{3}^{-} source. The prepared polymer electrolyte showed high ionic conductivity of 7×10^{-3} S cm⁻¹ and the DSSC showed efficiency of 4.78%.¹⁹⁸

Contrarily to PMMA and PVDF based polymer, PEO has the ability to conduct ionic species, and was often used as polymer electrolyte, despite its low electrochemical stability in oxidation i.e. 3.9 V vs Li⁺/Li. Shi et al. used a high molecular weight PEO as polymer host and liquid electrolyte to form a polymer gel electrolyte; the DSSC with the polymer electrolyte (PEO 10 wt%) showed a conversion efficiency of 6.12%.¹⁹⁹ Pavithra et al. prepared polymer electrolytes by adding different weight percentage of acetamide to PEO in the presence of LiI, I₂, acetonitrile, and propylene carbonate (PC).²⁰⁰ Among the electrolytes with different ratio, PEO with 5 wt% acetamide shows the highest efficiency (9.01%) compared to original polymer electrolyte without acetamide (5.7%) under 85 mW cm⁻² illumination. PEO with 5 wt% acetamide showed an improvement of V_{oc}, J_{sc} and performance which is due to i) the reduction of the recombination reaction and ii) the increase in the electron life time upon incorporation of acetamide on the PEO.

Stathatos et al. prepared a novel quasi-solid state electrolyte for DSSCs through an amine alkylation reaction.²⁰¹ Two oligomers of poly(propylene oxide) with several molar weight (APPG230/400) and one block oligomer of poly(ethylene oxide)/poly(propylene oxide) diamine (Jeffamine®ED-600) reacted with iodoethane resulting in a gel material and iodide as counter ion. The use of different oligomers for the alkylation reaction showed also differences in the electron recombination and conduction band shift of the TiO₂ photoelectrodes. The electrolytes which do not contain any plasticizers, solvents or other additives were applied in the DSSCs

where competitive efficiencies were obtained with a 3.7% maximum overall efficiency recorded in the case of ED-600.

In order to manage the functional properties of electrolyte, and in particular to improve mechanical properties, blend polymers were investigated. The blending of two polymers has been largely paid attention due to the simplicity of preparation. However, the compatibility of the polymers is very important in order to have homogenous mixing. Many POE-based blends have been studied e.g. PEO/PPO, PEO/PVP, PEO/PAN, PEO–PVDF.^{198–202} Poly (vinylidenefluoride-co-hexafluropropylene) (PVDF-HFP) and poly (acrylonitrile-co-vinyl acetate) (PAN-VA) blends have been used to prepare gel polymer electrolytes for DSSC.²⁰⁶ It was seen that the viscosity of the blends was less than the one of pure polymer and maximum efficiency of 6.3% was reported with 75 wt% (PVDF-HFP) and (PAN-VA) dissolved in liquid electrolyte based on acetonitrile.

In 2015, Aram et al. prepared polymer blend electrolytes based on polyethylene oxide (PEO) and poly(methyl methacrylate) (PMMA) as host polymers with various weight ratios, dissolved in liquid electrolyte solvent of EC, PC and DMC with a volume ratio of 4:2:1 containing salts such as 0.5 M LiI, 0.05 M I₂ and 0.5 M of 4-tert-butlpyridine (TBP), followed by heating at 55 $^{\circ}$ C for 6h.²⁰⁷ The prepared polymer electrolyte was successfully employed in DSSC with a power conversion efficiency of 4.9% which was very similar to the device made with liquid electrolyte. In order to improve the mechanical properties and to limit phase separation block copolymer was also investigated.

Manfredi et al. introduced the first use of $(PS_n-b-PEO_{136}-b-PS_n)$, block copolymer (PS = polystyrene, PEO = poly(ethylene oxide)) as solid hosts for iodine/iodide electrolytes in DSSCs. DSSCs based on the new block copolymer electrolytes presented power conversion efficiencies comparable with that of the conventional liquid cell prepared under similar conditions. The best values were obtained for the smaller PS bocks.²⁰⁸

7.1.2. Thermosetting polymer electrolyte (SPE)

In order to limit the creeping of the gel polymer, thermosetting polymer electrolyte can be used. A thermosetting polymer is a 3D polymer network formed by covalent cross-linking. In order to improve the ionic conductivity, the network is often swelled by liquid electrolyte.^{22,194,209} In these electrolytes the change is not thermally reversible so that's why they are called thermosetting Solid Polymer Electrolyte (SPE). Despite having solid like appearance, they are classified as quasi-solid-state electrolytes because they contain liquid electrolytes.

SPE based on poly(acrylic acid)-(ethylene glycol) (PAA-PEG) was prepared by polymerization. It is known that PAA is a superabsorbent with 3D networks using hydrogen bonding structure and hydrophilic groups, it can absorb large amount of liquid. However, pure PAA is not a good absorbent for conventional organic solvents used in DSSC. By modifying with amphiphilic polyethylene glycol (PEG), the PAA-PEG shows a high absorbent ability for liquid electrolytes. Thermosetting gel electrolyte was prepared by soaking the synthesized copolymer in liquid electrolyte. The latter was composed of 0.5 M NaI and 0.05 M I₂ in mixed organic solvents including γ -butyrolactone (GBL) and N-methyl pyrrolidone (NMP).¹⁹⁰ This cross-linked SPE showed high conductivity and long-term stability because of a large quantity of liquid electrolyte adsorbed in the PAA–PEG networks. The DSSC based on this SPE, with a conductivity of 6× 10⁻³ S cm⁻¹, successfully brought out the efficiency of 6.1% under AM 1.5 irradiation, which was higher than liquid electrolytes (5.7%) with good long-term stability.

Wang et al. prepared a necklace-like polymer gel electrolyte containing latent and chemically cross-linked gel electrolyte precursors and injected it into an already set DSSC.²¹⁰ The gelation was carried out in the cell by heating at 80 °C, which triggered an *in situ* quaternization reaction and the formation of a 3D network. These cells exhibited efficiency of 7.72% due to improved J_{sc} .

Methacrylate function was very often used as cross-linking agent in SPE. Indeed, Hayase group reported the chemically cross-linked SPE prepared by photoinduced in situ polymerization.177,211-213 The electrolyte precursor, poly(ethylene oxide-co-propylene oxide)trimethacrylate was directly injected into the assembled cells.²¹⁴ A 3D polymer network was formed inside the device after being heated at 90 °C for 90 min. After quasi-solidification of the solution, the electrode was immersed in liquid electrolyte for one hour followed by

attachment of Pt counter electrode. The DSSC with this electrolyte acquired a high efficiency of 8.1% due to improved V_{oc}.

Using near the same strategy, Parvez et al. injected PEG and bifunctional PEGDA [poly(ethylene glycol) diacrylate] monomer electrolyte solution into the TiO₂ porous film of DSSC, followed by in-situ cross-linking upon UV light illumination.²¹⁵

Park et al. developed also in situ surface-induced polymerization method using methacrylate polymer and diacrylate cross-linking agent and demonstrated that cross-linking polymerization on the surface of nano-crystalline TiO_2 resulted from the encapsulation of the TiO_2 particles. The resulted device showed an efficiency of 7.1%, which increased to 8.1% after 30 days.²¹⁶

7.1.3. Composite polymer electrolytes (CPE)

Composite polymer electrolytes (CPE) can be prepared by addition of materials, such as TiO_2 , ZnO, SiO_2 , Al_2O_3 , carbon, gelators in polymer electrolyte or in ionic liquid. The addition of nanoscale inorganic fillers such as nano-particles, nanotubes, carbon nano-oxide, nanoclays permits to improve the mechanical, interfacial, and conductivity properties of the polymer electrolytes. The introduction of inorganic fillers does not only reduce the crystallinity and melting point but may also increase moderately the dielectric constant.^{217–219}

In 1998, Scrosati et al. first proposed that the addition of inorganic nanoparticles into polymer electrolytes can increase the ionic conductivity of polymer electrolyte especially at room temperature.^{220,221} It was shown that the addition of TiO_2 and Al_2O_3 nanopowder caused significant increment in the conductivities of PEO–LiClO₄ electrolyte, essentially due to some reduction of the crystallization kinetic. Mostly CPEs are prepared by an addition of TiO_2 nanoparticles to polymer electrolytes.^{222–224}

Falaras et al. prepared electrolyte by the addition of TiO_2 nanoparticles to the polymer electrolyte containing poly (ethylene oxide) (PEO), LiI, and I₂ and this composite electrolyte was tested for DSSCs which resulted an overall conversion efficiency (4.2%) under direct sunlight illumination.²²⁴ SiO₂ as gelator was widely investigated after the achievement of 7% efficiency by Wang et al. in 2003. SiO₂ nanoparticles were used to solidify ionic liquid-based electrolytes which resulted in the improvement in the efficiency.²²⁵ Meng et al. prepared composite

electrolytes by adding SiO_2 nanoparticles in liquid electrolyte and efficiency of 6.1% was recorded.²²⁶

Xia and coworkers used an interesting approach to make a composite polymeric electrolyte. First, the polymer, poly(ethylene glycolmonomethyl ether) with a molar mass of 350 g mol⁻¹ was grafted on to the surface of ZnO nanoparticles through covalent bond formation. The electrolyte was composed of KI and I₂ dissolved in polymer and 24 wt% of the polymer-grafted ZnO nanoparticles were used to solidify the electrolyte. This electrolyte system, showed an ionic conductivity of 3.3×10^{-4} S cm⁻¹ and DSSC showed the overall power conversion efficiency of 3.1% at AM1.5 direct irradiation of 75 mW cm⁻².²²⁷ DSSC fabricated with this novel gel electrolyte displays better thermal stability than those solidified with the conventional ZnO nanoparticle.

Chen et al, used a new copolymer, poly(acrylonitrile-co-vinyl acetate) (PAN-VA), as the solidification agent to prepare solid-state redox electrolytes with TiO₂ nanofillers for DSSCs.²²⁸ The composite polymer was composed of 20 wt% of PAN-VA dissolved in acetonitrile containing 0.1 M LiI, 0.5 M 4-tert-butylpyridine (TBP), 0.6 M 1-propyl-2,3-dimethylimidazolium iodide (DMPII) and various concentration of I₂. It was found that the TiO₂ nanofillers in the electrolyte greatly enhanced the charge transfer at the electrolyte/Pt interface and maximum efficiency of 8.65% was reported.

Carbon materials have been widely investigated as gelators in composite polymer electrolytes^{229–234} and showed good performance as compare with pure ionic liquid electrolytes. Recently, poly(acrylonitrile) (PAN)/LiI/activated carbon composite polymer electrolyte prepared by hot pressing method was employed in DSSC.²³³ The quasi-solid electrolyte showed the electrical conductivity of 8.7×10^{-3} S cm⁻¹ at ambient temperature and the device exhibited a high efficiency of 8.42%.

Generally, compared to the DSSCs based on liquid electrolytes, the DSSCs based on polymer gel electrolytes have lower J_{sc} and higher V_{oc} ; the former is due to the lower conductivity coming from the lower mobility of redox couple components, and the latter is due to the suppression of dark current by polymer chains covering the surface of TiO₂ electrode.²⁰⁹

7.2. Use of ionic liquids

An ionic liquid (IL) has multifunction. ILs are used as solvent for the preparation of liquid electrolytes but also used as ionic conductor in quasi-solid-state electrolytes.¹⁹³ ILs possess high chemical and thermal stability, wide electrochemical window, low volatility, good chemical stability, high ionic conductivity, attractive ability to dissolve various solutes and relative non-flammability.^{193,235–237} Their physical and chemical properties can be tuned by the modification of the anionic and/or cationic components. ILs are composed of aromatic or aliphatic organic cations and various anions as shown in figure 17A.



Figure 17- Examples of the A) cationic and anionic parts of ionic liquids, B) ILs.¹⁹³

ILs based on imidazolium salts have been widely used as solvents for DSSCs. ILs show relatively high viscosity which appears to limit their use because of transport limitations: diffusion coefficients of the redox-couple components (I_3^-) in ionic liquid electrolytes are about 1–2 orders of magnitude lower than those in volatile organic solvents. However, as shown in figure 18, ILs can be tuned with different anions to tune properties such as:

1) An IL composed of 1-methyl-3-propylimidazolium-iodide (MPI I) as source of iodide and increases the ionic conductivity.^{238–240}

2) An IL composed of 1-methyl-3-propylimidazolium bis(trifluoromethanesulfonyl)imide (MPITFSI) can reduce the viscosity and hence helps in increasing the ionic conductivity and diffusion coefficient.^{240,241}



Figure 18- Chemical structure of (A) MPI I and (B) MPITFSI ionic liquids.

A large number of electrolyte based on ILs have been investigated in DSSCs¹⁹³, some of them are presented in more details in the next paragraph. ILs such as 1-hexyl-3-methylimidazolium iodide (HMII) in combination with the ruthenium-based dye N-3 were utilized in order to examine the performance characteristics, the stability and the mass-transfer effects in DSSCs. Cell performance showed high stability.²³⁸ An investigation has been carried out on the physical–electrochemical properties of HMII and its mixtures with organic solvents, such as acetonitrile, and with other lower viscosity ILs, such as 1-ethyl-3-methylimidazolium triflate (EMITf). It was shown that I_3^- might be transferred to the counter electrode not only by diffusion, but also by a Grotthus-like, non-diffusional hopping mechanism.²³⁹ The effect of the viscosity of ILs such as HMII, EMITf and EMITFSI (figure 17B) on electrolyte has been investigated and it was found out that the performance of the DSSC was increased with decreasing viscosity of the ILs. A conversion efficiency of 2.1% was observed for a cell using EMITf in combination with the ruthenium-based N-3 dye.²³⁹

An ionic liquid electrolyte composed of 1-propyl-3-methylimidazolium iodide (PMII), 1-ethyl-3methylimidazolium dicyanamide (EMIDCN), and Lithium iodide (LiI) was combined with an amphiphilic polypyridyl ruthenium-based sensitizer (Z-907), to obtain a solar cell based on a solvent-free electrolyte that had an efficiency of 6.6% at 100 mW cm⁻².²⁴² A significant enhancement in the device efficiency was observed after adding the LiI to the ionic liquid electrolyte. The improved efficiency could be ascribed to an increase in the electron injection yield and dye regeneration rate.

Chi et al. prepared I₂-free electrolyte by mixing of 1-methyl-3-propylimidazolium iodide (MPII) and a Silyl based IL-modified Al_2O_3 nano-particles and this electrolyte showed efficiency of 7.6%, when used along a nanocrystalline TiO₂ bottom layer.²⁴³ Al_2O_3 nanoparticles were covalently surface modified with MPII to improve their miscibility with MPII. The hybrid electrolytes were prepared by dissolving MPII and 5 wt% IL- Al_2O_3 nanoparticles in acetonitrile and subsequently casting the solution onto the photoelectrode.

Bidikoudi et al. demonstrated a series of redox electrolytes prepared by using binary mixtures of MPII with 1-alkyl-methylimidazolium tricyanomethanide, C_n mimTCM (n = 2, 4, 6, 8) ILs to lower the high viscosity of MPII.²⁴⁴ These ILs allowed a systematic exploration of the effect of the alkyl chain length on the physicochemical properties such as density, viscosity and diffusion coefficient of ionic liquid electrolytes based on MPII blends and on their photovoltaic performances. The best performance was observed for cells based on the MPII/C₂mimTCM blend, where the efficiency reached 5.23% due to its higher diffusion coefficient.

In 2015, Ozawa et al. demonstrated that the alkyl chain length of imidazolium iodide in the electrolyte solution can affect the performance of the DSSC.²⁴⁵ It was reported that the J_{sc} increased and the fill factor (FF) decreased with increasing the alkyl chain length of the imidazolium iodide (see table 1).

In 2002, Wang et al. demonstrated that ILs based electrolyte can be gelled with polymer in order to prepare a quasi-solid state electrolyte for DSSCs. The polymer gel electrolyte was composed of 1-methyl-3-propyl-imidazolium iodide (MPII) and the polymer, poly(vinylidenefluoride-co-hexafluoropropylene, (PVDF–HFP). The DSSCs based hydrophobic Z-907 dye coated nanocrystalline TiO₂ with this electrolyte showed efficiency similar to the one using liquid electrolyte.²⁴⁶ Similar electrolytes based on 1-propyl-2,3-dimethylimidazolium iodide and (PVDF-HFP) (5 wt%) showed an overall conversion efficiency of 6.1% and long term stability with the Z-907 dye.²⁴⁷

Ionic liquids have two applications in electrolytes in DSSCs. One is acting as ionic solvents and another is functioning as organic salts in quasi-solid-state electrolytes. Table 1 shows some examples for using ionic liquids in polymer electrolytes for DSSCs.

Table 1- Photovoltaic Performance of ss-DSSC based on ILs Electrolytes under simulated solar light irradiation with intensity of 100 mW cm⁻², AM 1.5 (see list of acronyms).

Composition of electrolytes	σ	$\mathbf{J}_{\mathbf{sc}}$	Voc	FF	ղ	Ref
	(mS cm ⁻¹)	(mA cm ⁻²)	(V)	(%)	(%)	
40 g/L of gelator, I_2 (8.7 wt %) in HMII	-	11.8	0.63	70	5.0	248
PVDF-HFP (10 wt %), I ₂ /NMBI in MPII	-	11.29	0.66	71	5.3	246
PVDF-HFP (5 wt %), 0.6 M DMPII, 0.1 M I_2 , 0.5 M NMBI in MPN	-	12.5	0.67	73	6.1	247
DMII/EMII/EMIB(CN) ₄ /I ₂ /NBB/GNCS (mol ratio12/12/16/1.67/3.33/0.67)	-	15.93	0.71	75	8.50	249
0.12 M I ₂ , 0.5 M KI, 0.9 M BMII, in GBL, 35 wt % of PVP	2.3	15.72	0.62	55	5.41	250
0.1 M I2, 0.1 LiI, 0.45 NMBI in PMII/EMIDCN (13 : 7 v/v)	-	12.80	0.71	73	6.6	242
I ₂ (7.1 mg), MgI ₂ (0.02 g), Hex ₄ N ⁺ I (0.10 g), PAN (0.10 g), EC (0.40 g) and PC 0.40 g	-	8.60	0.79	52	3.5	251
0.1 M LiI, 0.45 M NMBI, 0.4 M DMPII, PEO/PVDF-HFP (2:3 wt %) 20 wt % in ACN	21.18	14.12	0.68	72	6.97	252
0.1 M LiI, 0.9 M EMII/SN, 0.1 M I_2 , 0.5 M TBP in ACN/MPN (vol ratio 1/4)	1.27	14.80	0.67	75	7.46	253
0.1 M LiI, 0.2 M I ₂ , 0.4 TBP in MPII: C2mimTCM (13:7, v:v)	-	12.48	0.67	63	5.2	244
0.1 M LiI, 0.2 M I ₂ , 0.4 TBP in EMIDCA- [C1C1Im]I: [C1C1Im]I (7:13, v:v)	-	11.26	0.71	69	5.5	254
0.1 M LiI, 0.5 M TBP, 0.6 M DMPII, 0.08 M I ₂ , 20wt% of PAN-VA in ACN	2.72	9.77	0.80	68	5.27	228
KI (1.5g), I ₂ (0.254g), MPII (0.75g), PVP-co- VAc in 3 g of EC:PC (1:1, v:v)	3.13	11.98	0.59	66	4.7	255
HPC (0.5g), MPII (0.5g), NaI (0.5g) in 10g of EC: PC (1:1, v:v)	7.37	13.73	0.61	69	5.79	256
0.05 M I ₂ , 0.02 M LiI, 0.6 M 0.3 M TBP, 0.05 M THAI in ACN:THF (95:5, v:v)	10.9	22.2	0.71	73	11.5	245
I ₂ (0.06g), THAI (0.26g), PVP-co-VAc (0.33g), EC (0.175g), PC (0.175g) in 4 g of BMII	1.05	12.37	0.69	58	3.95	257

7.3. Use of poly(ionic liquids) (PILs)

In recent years, polymeric ionic liquid (PILs) have attracted a growing attention because they are a new class of polymers combine both the novel properties of ionic liquids and improved mechanical durability and dimensional control of polymers as shown in figure 19.^{258–260}



Figure 19- Chemical structures of the (A) ionic liquid and (B) poly(ionic liquid).²⁶¹

Ionic liquid part of the PILs give rise to high ionic conductivity, tuneable chemical structure, and electrochemical and thermal stability.^{262,263} One of the other advantage of PILs, it's that just Γ and I_3^- are mobile, whereas the cations are bound to the polymer matrix. PILs having different onium cations have been studied but imidazolium salt type PILs tended to show higher ionic conductivity.²⁶⁴ More recently, PILs have been successfully applied as electrolytes in various energy devices, including lithium batteries, dye-sensitized solar cells (DSSCs), fuel cells, supercapacitors, light-emitting electrochemical cells and field effect transistors.^{262,265}

Table 2 exemplifies PILs based electrolytes used in DSSCs. It's difficult to compare the performances obtained and to deduce general rule, as PILs based electrolytes are composed of many components (PIL, IL, salt, solvent, additive). As an example, in 2008, an N-alkyl-4-vinylpyridineiodide/poly(N-alkyl-4-vinyl-pyridine)iodide composite polymer electrolyte combined with iodine retained a high ionic conductivity of 6.4×10^{-3} S cm⁻¹, and the efficiency of the fabricated DSSC reached as high as 5.64%.¹⁰⁰

Table 2- Photovoltaic Performance of ss-DSSC based on PILs Electrolytes under simulated solar light irradiation with intensity of 100 mW cm⁻², AM 1.5 (see list of acronyms).

Composition of electrolytes	σ	$\mathbf{J}_{\mathbf{sc}}$	Voc	FF	η	Ref
	(mS cm ⁻¹)	(mA cm ⁻²)	(V)	(%)	(%)	
0.5 M LiI, 0.05 M I ₂ , 0.5 M NMBI, 10 wt %	0.4	15.5	0.62	64	6.1	266
P(MOEMICI) in HMII/EMIBF ₄ (v/v, 2/1)						
poly(ViPrDII) (40 wt%), 0.6 M in LE	-	6.52	0.79	54	2.8	267
containing 0.6 M DMPII, 0.03 M I ₂ , 0.1						
GNCS, 0.5 M TBP in ACN/Valeronitrile						
(85:15, V:V)						
Poly(1-ethyl-3-	0.36	9.75	0.84	65	6.1	268
(acryloyloxy)hexylimidazoliumiodide) (PEAII)						
Poly((1-(4-ethenylphenyl)methyl)-3-butyl-	0.2	18.1	0.64	51	5.9	269
imidazolium iodide) (PEBII) in ACN (10 wt%)						
[PBVIm][TFSI] (25 wt%), 0.1 M I ₂ , 0.1 M LiI,	0.41	10.57	0.61	68	4.4	48
0.5 M TBP in PMII: MITFSI ((13 : 7, v:v)						
0.1MI ₂ , 0.5 M NBB, 0.1 M GNCS,	5.8	12.9	0.67	68	5.62	270
EMII/PMII/EMISCN (vol ratio 6/6/7) in						
poly[BVIm][HIm][TFSI] (25 wt %)						
P(MMA-VI) (20 wt%) in LE containing I ₂	5.8	10.54	0.72	69	5.16	271
(0.15 mol^{-1}) , DMPII (0.9 mol^{-1}) in MPN:						
MeOx (1:1, wt:wt)						
P(TFEMA-VI) (20 wt%) in LE containing I ₂	6.6	11.69	0.71	69	5.73	271
(0.15 mol^{-1}) , DMPII (0.9 mol^{-1}) in MPN:						
MeOx (1:1, wt:wt)						
P(TFEMA-4VPy) (20 wt%) in LE containing	5.1	10.03	0.69	70	4.84	271
I_2 (0.15 mol ⁻¹), DMPII (0.9 mol ⁻¹) in MPN:						
MeOx (1:1, wt:wt)						
P(MMA-4VPy) (20 wt%) in LE containing I ₂	4.5	7.85	0.68	67	3.57	271
(0.15 mol^{-1}) , DMPII (0.9 mol^{-1}) in MPN:						
MeOx (1:1, wt:wt)						
PMAPII (16.wt %) 0.05 M I ₂ , 0.05 M TBP in	4.9	14.7	0.79	70	8.12	272
GBL						
Poly(1-propyl-3-vinylimidazolium iodide) in	1.86	12.48	0.59	69	5.08	273
0.4 M ACN						
0.1 M LiI, 0.05 M I ₂ , 0.5 M TBP and 0.3 M	10.48	13.97	0.78	66	7.19	274
POEI-II in ACN/MPN (1:1, V:V)						
[PBVI][TFSI] (20 wit%), GO (2%) in solution	0.78	8.84	0.72	71	4.83	275
containing 1M PMII, 0.1 M 12, 0.2 MLiTFSI,						
0.5 M TBP						

Similarly, the PILs, bis-(imidazolium)-based poly(ILs) also gave a cell efficiency of 5.94% with an iodide-based IL electrolyte.²⁷⁶ Poly(1-butyl-3-(1-vinylimidazolium-3-hexyl)-imidazolium bis(trifluoromethanesulfonyl)imide) and poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide were synthesized and dissolved in ionic liquids (ILs) to form DSSCs. The electrolyte permitted to reach an efficiency of 5.92%, due to high conductivity and diffusion coefficient.

In 2015, Lin et al. prepared poly(ionic liquid)/ionic liquid/graphene oxide composite gel electrolytes containing poly(1-butyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide) (poly(IL), 1-propyl-3-methylimidazolium iodide (PMII) and graphene oxide (GO).²⁷⁵ The conductivity of the composite electrolyte is significantly increased by adding appropriate amounts of 2 wt% GO of 8×10^{-4} S m⁻¹. The DSSC based on composite electrolytes with GO (2wt %) showed an efficiency of 4.83% with outperformed the DSSC without GO (1.46%).

Recently in 2017, Wang et al, reported a novel PILs prepared by in situ low-temperature polymerization of N,N"-bis(imidazolyl) hexane and 1,6-diiodohexane without initiator at 40 $^{\circ}$ C and used as the electrolyte to fabricate solid-state DSSCs.²⁷⁷ As a result, a good interfacial contact between ionic polymer electrolyte and TiO₂ photoanode was achieved. The incorporation of 70 wt% of DMII in PILs lead to a great increase in the conductivity and overall efficiency was reported to be 6.55%.

PILs was also investigated using solvent, using this strategy, Chang et al. synthesized a novel PILs, poly(oxyethylene)-imide-imidazole complex coupled with iodide anions (POEI-II), and used for preparing the gel electrolyte for quasi-solid-state dye-sensitized solar cells.²⁷⁴ POEI-II acted simultaneously as a redox mediator and also as a polymer for the gelation of an organic solvent-based electrolyte. The concentration of POEI-II in the gel electrolyte was 0.3 M (see table 2), which rendered its DSSC the highest cell efficiency. The DSSC with the synthesized POEI-II gel electrolyte showed an efficiency of 7.19%.

The distinctive properties of ILs, PILs and PILs/ILs such a nearly negligible volatility, excellent ability to dissolve a large number of organic and inorganic compounds, tuneable physical and chemical properties such a viscosity, conductivity inspired us to explore more in this area in DSSCs applications.

7.4. Polysiloxane based polymer electrolytes

Modification with polysiloxane materials has been considered as the most effective method to improve the excellent optical transparency and thermal stability of electrolytes of the DSSCs. As shown in figure 20, different polysiloxane have been used for high performance electrolytes of DSSCs. Polysiloxanes have highly flexible backbone, with the barrier energy to bond rotation being only 0.8 kJ mol⁻¹, as well as very low T_g (-123 °C) and high free volumes, therefore polysiloxanes-based electrolytes have received much attention.²⁷⁸ However, the polysiloxane-based polymer electrolytes are gums at room temperature rather than solids, and recent efforts have been focused on the design and synthesis of polymers with both high ion transport and good dimensional stability.



Figure 20- Structure of polysiloxane based electrolytes used in DSSCs.

In 2001, Ren et al. introduced polysiloxane based electrolyte for DSSCs application for the first time.²⁷⁹ The novel electrolyte (*Si-1*) was cross-linked to have internal plasticizing PEO chains. Briefly, polymethylhydrosiloxane precursor with Si-H and PEO (macromonomer) were mixed with LiI (20 wt %), EC/PC (3:1, v:v) and a crosslinker trimethylolpropane- toluene diisocyanate (TMP TDI), and heated at 80 °C for 30 min. Then I_2 (5 wt %) was added. The energy conversion efficiency of the DSSC was recorded to be 2.9%. Preliminary results also showed that the polymer electrolyte was physically stable and quite retentive to the organic solvent PC and EC.

In 2004, polysiloxane containing quaternary ammonium group (*Si*-2), I₂ and 50 wt% of EC/PC (8:2) (w/w) was used as an electrolyte. The ambient conductivity of this plasticized electrolyte reached up to 1.9×10^{-3} S cm⁻¹ and the DSSC showed performances comparable to the liquid electrolyte.²⁸⁰

In 2010, Jung et al. synthesized an ionic siloxane hybrid electrolyte by thermal polymerization of iodide-oligosiloxane resin (*Si-3*). The nano sized iodide-oligosiloxane was synthesized by a simple sol gel condensation of 3-iodopropyltrimethoxysilane and diphenylsilanediol. It is found that the composition and concentration of the oligosiloxane used in the electrolyte affect the performance of the DSSCs. DSSCs based on this electrolyte showed efficiency of 5.2%, which was comparable to that afforded by a liquid electrolyte.²⁸¹

In 2012, Bae et al. fabricated a stable DSSC employing an oligosiloxane gel electrolyte by introducing a novel in situ gelation of liquid electrolyte (*Si-4*). The alkoxysilane monomers are capable of gelling the liquid electrolyte through a sol–gel reaction, resulting in effective infiltration and contact. The DSSC showed reduced charge recombination, and an efficiency of 5.8% with long-term stability.²⁸²

In 2013, Lee et al. used oligosiloxanediimidazolium iodides (SiDII1, SiDII2, and SiDII3) having different viscosity (*Si-5*).²⁸³ Organic solvent based three different liquid type electrolytes were prepared by dissolving 0.5 M of each siloxane diimidazolium iodides (SiDII1, SiDII2, SiDII3) with 0.1 M guanidinium thiocyanate, 0.05 M I₂ and 0.5 M TBP in MPN. The electrolytes based on SiDII1 and SiDII2 electrolytes showed a maximum efficiency of 6.2% and 6.0% which was due to their superior ionic conductivity. Later in the same year, Lee group developed electrolytes based functionalized oligosiloxane electrolytes by replacing the oligosiloxanediimidazolium

iodides with pyridinium iodides ((*Si-6*).²⁸⁴ The SiDPI2 electrolyte showed a maximum efficiency of 6.8% due to its superior diffusion coefficient.

In 2014, Manca et al. reported the implementation of poly[(3-N-methylimidazoliumpropyl)methylsiloxane-co-dimethylsiloxane]iodides (*Si-7*) as suitable polymeric hosts for a novelclass of in situ cross-linkable iodine/iodide-based gel-electrolytes for dye-sensitized solarcells.²⁸⁵ The electrolytes were prepared by dissolving the polymer (40 wt%) in liquid electrolyteconsisted of I₂, LiI, 1,2-dimethyl-3-propylimidazolium iodide (DMPII) dissolved in MPN. Theoverall value of iodide species in electrolyte was kept constant up to 0.9 M. A stoichiometricamount of bis(3-aminopropyl)-terminated poly(dimethylsiloxane) was then added to thepolymeric solutions and acted as a cross-linking agent. The polymers are first partiallyquaternized and then a thermal cross-linking. DSSCs based on the electrolyte and organicsensitizer showed a maximum efficiency of 5.84%.

Recently, the same group, reported the synthesis of an ion conductive polysiloxane, named poly[(3- N -methylimidazoliumpropyl)methylsiloxane-co-dimethylsiloxane]iodide (IP-PDMS) (*Si-8*), which was successfully employed as electrolyte in DSSCs.²⁸⁶ The electrolyte was preparing by dissolving about 40 wt % of synthesized IP-PDMS in liquid electrolytes consisted of 0.9 M of DMPII ionic liquid and 0.15 M I₂ in MPN. The final amount of the solvent in the prepared electrolyte is about 60 wt% and led the fabricated DSSCs to show a maximum conversion efficiency of about 6.45%.

In the latest work, a hybrid polymer gel electrolyte $(HPG)^{287}$ was reported as shown in figure 20. The HPG as the matrix, which was synthesized from 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) monomers and ILs mixture of 1,3-dimethylimidazolium iodide, and 1-ethyl-3-methylimidazolium iodide as the electrolyte salt. As the product of the synthesis, the HPG consisted of siloxane Si–O–Si chain networks that are also crosslinked by methacrylate chains. The electrolyte (*Si-9*) is composed of the polymer and IL mixture with an addition of propylene carbonate (PC) at several weight ratios of HPG:ILs:PC (20:20:20). DSSCs based on the electrolyte and organic sensitizer showed a maximum efficiency of 5.86%.

As expected, the literature results show that the addition of ionic liquids or organic solvent plays an important role in enhancing the performance of polysiloxane polymer which motivated us to study the influence to carry out the study in more details. An alternative way is definitely to use plasticizer. The effect of polar solvating plasticizer in polysiloxane has been reported to increase ionic conductivity by facilitating the dissociation of ions.²⁸⁸ However, there is few published research on the effect of plasticizer (such as ethylene carbonate (EC)) on polymer electrolytes based on polysiloxane and their influence on photovoltaic properties. It is well known that (EC) is a high-viscosity solvent with high dielectric constant, which is favorable for ionization of salts and resulting in high ionic conductivity. Owing to these properties of EC, there have been plenty of research groups utilizing the concept of plasticization.^{289–293} It has been shown that when a small amount of plasticizer is added in a polysiloxane electrolyte, an increase in ionic conductivity and a decrease in the glass transition temperature (T_g) is observed.^{288,294}

Therefore, in our work we extensively chose ionic liquids (MPII and MPITFSI) and EC in order to study the properties and employment with DSSC.

8. Key aspects for the electrolyte improvement

8.1. Electrochemical stability

The electrochemical stability of the electrolyte is one of the important parameters for the performance of dye sensitized solar cell. A number of factors affect the electrochemical stability of redox active ions and molecules in an electrolyte solution. They are connected with (i) the intrinsic electronic properties of both oxidized and reduced forms of a given redox couple, and (ii) their interactions with environment. The latter are largely determined by the structural changes of the surrounding electrolyte solution accompanying the electron transfer reaction.

8.2. Conductivity

The investigation of polymer electrolytes began in the 1970s, after the pioneering measurements of ionic conductivity in polymer–salt mixtures done by Wright and co-workers and the proposal of Armand and co-workers that these systems could be used in secondary batteries.^{295,296} Apart from electrochemical stability, high ionic conductivity is another critical factor in the development of efficient DSSCs. The conductivity of the electrolyte depends on two parameters; the number of charge carriers and their mobilities. The number of charge depends on the salt concentration and the salt dissociation. The ionic mobility is related to the viscosity of the electrolyte associated with the interactions ion /solvent and solvent/solvent. In the case of highly

concentrated salt, solvent cannot dissociate the ions completely, then ionic pairs exist (figure 21) that do not contribute the current transport. Furthermore, the formation of aggregates can occur at high salt concentration. The conductivity of the polymer electrolyte increases initially with an increase in the salt concentration and then decreases after reaching the maximum conductivity. The conductivity increase in the initial stage is easily comprehensible, and the conductivity decrease in the subsequent stage can be explained by the pair ions model and the increase in viscosity.^{184,297}



Figure 21- Various types of ion pair in an electrolyte solution.¹⁸⁴

Ion transport mechanism can be explained by two models.

I). Arrhenius model

The Arrhenius formula describes the conductive behaviour that mobile ions hop through energy favourable sites of the framework lattice (sublattice).²⁹⁸ For semi-crystalline polymer electrolytes at temperature below the melting temperature ($T < T_m$) or amorphous one below T_g , the conductivity is followed by Arrhenius law.

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{RT}\right) \tag{6}$$

Where σ is the conductivity (S cm⁻¹), σ_0 is pre-exponential factor (S cm⁻¹), E_a is activation energy (J mol⁻¹), *R* is perfect gas constant (R = 8.314 J mol⁻¹ K⁻¹) and *T* is temperature (K).

II). Vogel Tammann-Fulcher (VTF) model

The VTF formula interprets the conductive phenomena that carrier transports through free volume and assisted by segmental motion.²⁹⁸ Liquid electrolytes, molten salts, gels, amorphous polymer above the glass transition temperature ($T > T_g$) and semi-crystalline polymer above the melting point shows VTF dependence and the conductivity is varied in function of temperature as the following relationship.

$$\sigma = \frac{A}{\sqrt{T}} \exp(\frac{-E_a}{R(T - T_0)})$$
(7)

Where *A* is a pre-exponential factor related to the number of charge carriers (S cm⁻¹ K^{1/2}), E_a is pseudo activation energy (J mol⁻¹). T_0 is the ideal glass transition temperature at which ion mobility goes to zero (K). Above T_0 , thermal motion of the polymer chains initiates the transportation of ions. T_0 is usually found to 50 K or 25 K below T_g .

8.3. Diffusion coefficient

Besides ionic conductivity, diffusion coefficient is very important parameter since it determines the electron transfer rate. In DSSCs, under illumination the electrons are injected into the nanocrystalline TiO_2 film from the dye molecule and then transported through the film toward the FTO substrate contact where they are collected. During the transport, photoinjected electrons may recombine with the oxidized species in the electrolyte. These processes, characterized by the diffusion coefficient of iodide/triiodide, are key efficiency factors determining the performance of the DSSCs. In liquid or polymer electrolytes, the diffusion is due either to ion hopping or to liquid like diffusion of one ionic species.²⁹⁸ For the diffusion process, the host backbone local dynamic is determinant. The general diffusion coefficient can be expressed by the Einstein-Stokes equation.^{299,300}

$$D_{gen} \propto \frac{k T}{\mu R_{ion}}$$
 (8)

Here, k is the Boltzmann constant, T is the temperature, μ is the viscosity of the solvent and R_{ion} is the spherical radius of diffusion species; thus, a large solute ion radius and high fluidity $(1/\mu)$ are expected to cause high ion mobility.

For amorphous polymer electrolytes above the glass transition temperature the ions diffuse through the free volume promoted by polymer segmental motion. The ion diffusion coefficients in the amorphous polymer electrolytes are obviously higher than those in the crystalline polymer electrolytes below their melting point.^{301–304} The free volume is defined as the unoccupied space between the polymer chains.³⁰⁵ The free volume dependence of the diffusivity can be represented by Cohen and Turnbull equation.^{306,307}

$$D_{fv} = D_0 exp\left[B\left(1 - \frac{1}{f}\right)\right] \tag{9}$$

Here, *f* is the free volume fraction of the total volume, D_0 is the reference diffusivity and *B* is related to the critical voids for transportation. Thus, fast ion diffusion in a system with large free volume fractions can be expected.^{308,309} In high viscous system, generally obtained at high iodide concentration carrier transportation through an electron exchange mechanism (Grotthus-like mechanism) was proposed because of the formation of polyiodides.^{238,310,311}

$$I_3$$
 + Γ Γ \longrightarrow I_2 \longrightarrow Γ Γ + I_3

The Grotthus-like mechanism reasonably explains the unexpected high photocurrent density obtained for high viscous electrolyte in DSSCs.

8.4. Viscosity

In DSSC, the viscosity of electrolytes plays an important role as it directly affects the three crucial parameters such as ionic conductivity, diffusion coefficient and pore infiltration of TiO_2 photoanode. According to the Einstein-Stokes (equation 8), the ionic conductivity and diffusion coefficient of the electrolytes are largely depend on the viscosity. Even though the solid polymer electrolyte has many intrinsic advantages over the liquid electrolyte, its ionic conductivity, diffusion coefficient and mesopores filling are much poorer due to high viscosity. A highly
viscous polymer electrolyte does not readily penetrate into the mesopores of the dye-decorated TiO₂, resulting in poor contact with dyes and consequently low energy conversion efficiency.



Figure 22- Influence of viscosity.

Note that the average size of the photoanode mesopore is around 15-20 nm depending on the TiO₂ nanoparticles used, whereas many polymers have a coil shape in solution with a diameter much bigger than the mesopore size. The poor contact between the dyes and the polymer electrolyte is mostly associated with poor penetration of the polymer electrolyte simply due to the size difference between the TiO₂ mesopore and the polymer coil in a given solvent. Generally, in highly efficient DSSCs, the mesoporous TiO₂ layer has a typical pore size of about 20 nm. The liquid electrolytes can easily penetrate through the dye coated TiO₂ pore, resulting in efficient dye regeneration and consequently leading to high cell performance. However, the viscous polymer electrolytes suffer from poor TiO₂ pore-infiltration. This can cause dye regeneration to deteriorate, resulting in a decrease of the photocurrent. As we explained earlier sections that the ionic conductivity and diffusion coefficient of solid polymer electrolytes can be improved by incorporating ILs or plasticizer in to polymers, with bonus decrease in viscosity.

9. Objective and Aim of the thesis

The solid solid-state dye-sensitised solar cell (ss-DSSCs) based on polymer electrolytes was originally designed to avoid electrolyte-specific problems, such as evaporation of the electrolyte and electrodes corrosion by the redox mediator. However, the efficiencies of TiO_2 -Dye sensitised solar cells with polymer electrolytes are relatively lower than for the device comprising liquid electrolyte.

Thus, the objective of the present work is to perform a systematic study of the performance limiting factors emerging from the solid-state concept and to provide strategies/solutions to address these limitations, as well as to exploit the potential of polymer electrolytes in improving DSSC efficiency and durability. The study is mainly of experimental nature, supported by different characterization techniques.

The manuscript is divided in six chapters and started with the Introduction and Literature survey.



Chapter I gives an insight of the context of the work. A thorough literature review of the stateof-the-art polymer electrolytes and TiO_2 nanostructures was provided. DSSCs encompassing TiO_2 nanostructures and polymer electrolytes were also presented.

Chapter II is devoted to the synthesis and characterizations of polysiloxane based poly(ionic) liquid (PILs). An extensive study has been done on PIL's blends with ionic liquids and ethylene carbonate.

Chapter III is mainly dedicated to the photovoltaic properties of DSSCs containing various poly(ionic)liquid and their blends with ionic liquids and ethylene carbonate synthesized in chapter II. All the cells were fabricated on thick commercial photoanode (Dyesol). Prior to device assembly the polymer electrolytes properties were thoroughly investigated.

Chapter IV is dedicated to the porosity tuning in TiO_2 films and optimization of PS beads size for obtaining good electrolyte permeability and increased light harvesting while still preserving a high specific surface for dye loading. Influence of porosity and thickness on dye loading, light scattering and photovoltaic performance is studied.

Chapter V explains the effect of the blocking layer on the photovoltaic performance of DSSCs comprising the TiO_2 photoanodes optimized in chapter IV.

In **Chapter VI** the influence of PILs viscosity on electrolyte penetration into the mesoporous and dual photoanode electrodes with various thicknesses is studied. Finally, all these aspects were considered during the performance evaluation of DSSCs.

Finally, some conclusions and perspectives are drawn.

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CHAPTER – II

Electrolytes based on blends of polysiloxane based poly(ionic)liquid/ionic liquids/plasticizer: high ionic conductivity and improved diffusion coefficient for implication in solar cell

Abstract

Poly(ionic)liquids (PILs), Poly(1-N-methylimidazolium-pentylpolydimethylsiloxane)iodide (PDMSXIm⁺I⁻), having different ratio of pentyl-imidazolium iodide moieties have been prepared and characterized. In order to develop highly stable and efficient polymer electrolytes for dye sensitized solar cell (DSSCs) applications, the PILs/ILs blends were prepared with ionic liquids (ILs), 1-methyl-3-propylimidazolium iodide (MPII) and 1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide (MPI TFSI). The physiochemical and electrochemical properties of these PILs and their blends with ILs, including density, glass transition temperature, viscosity, ionic conductivity and diffusion coefficient were determined. The addition of ILs significantly lowers the viscosity, increases the conductivity, and increases the diffusion coefficient of the PILs. The investigation of the physicochemical properties of the mixtures as a function of temperature has shown that both viscosity and conductivity strongly depend on mixing ratio of the polysiloxane with ILs. Furthermore, the effect of ethylene carbonate (EC) on the physicochemical and electrochemical properties of PILs was studied. The evolution of the glass transition, ionic conductivity, and diffusion coefficient were evaluated. The addition of EC led to significant improved in conductivity and diffusion coefficient of the PILs, which is significantly higher than for the pure PILs.

Keywords: PILs, ILs, electrolytes, viscosity, ionic conductivity, glass transition temperature, diffusion coefficient

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1. Introduction

In 1991, the ground-breaking article by O'Regan and Grätzel on dye sensitised solar cell (DSSC) opened up the possibility to use the devices based on molecular components for the fabrication of cost effective, large scale solar electricity production.^{1,2} DSSC is more commonly composed of nano-porous dye sensitised TiO₂ photoelectrode, a platinum counter electrode and an electrolyte.^{3,4} The electrolyte is one of the most critical components in the DSSC as it is responsible for the charge carrier transport between electrodes and continuously regenerates the dye and itself during DSSC operations.^{5,6} The electrolytes have great influence on the light to electricity conversion efficiency and long term stability of the devices. The efficiency of the DSSC is determined by its photocurrent density (J_{sc}), photovoltage (V_{oc}), and fill factor (FF).² All of these parameters are remarkably affected by the electrolytes based DSSC has always been a topic of concern due to the leakage and evaporation of the solvent such as acetonitrile⁷ and their permeation through sealant⁸.

Thus in order to overcome these drawbacks, alternative sealing methods, replacing with P type semiconductor such as conducting polymer and CuI or CuSCN,^{9,10} ionic liquids,^{11,12} nanocomposites and polymer electrolytes^{13–18} have been utilized. However, for DSSCs incorporating these electrolytes, the solar to electricity conversion efficiencies are decreased relative to those of the corresponding liquid electrolyte based DSSC. The lowered efficiency is attributed to a decrease in the mobility of ions in the electrolytes and poor infiltration of the high viscous electrolytes into the pores of the TiO₂ films.

Among the various solid electrolytes, the solid polymer electrolyte is the most attractive due to its flexibility¹⁹ and that it can be laminated on a large scale compared to inorganic solid electrolytes. In 1973, Wright and co-workers discovered that poly(ethylene oxide) (PEO) could be used as an ion conductor upon the addition of lithium salt.²⁰ Therefore, they have been under intensive attention for potential applications in wide variety of solid state electrochemical cells devices, such as lithium battery, electrochromic cell, and DSSCs have received an upturn of interest.^{21–23}

The ionic conductivity of a SPE based on polyacrylonitrile-polyethylene oxide $(PAN-PEO)^{24}$ have been reported to be $10^{-6} - 10^{-4}$ S cm⁻¹ and increases with the molecular weight of PEO due to

the higher probability of interaction of ether oxygens with the ions such as Lithium.²⁵ Indeed, amorphous polymers with low T_g exhibit ionic conductivity whereas crystalline polymers, below the melting point, most likely behave as insulator. The ionic conductivity in amorphous polymer is due to the movement of ions, occurred by the local segmental motion of the polymer chain above its glass transition temperature (T_g). The ionic conductivity occurring in the polymer is too low at room temperature to be used in electrochemical and photoelectrochemical devices for energy conversion and storage. In order to increase ionic conduction at low temperature, polymer electrolytes are usually mixed with ionic liquids and organic solvents to achieve high conductivity value near 3×10^{-3} S cm⁻¹ at room temperature²⁶, although, this leads to some deterioration of the mechanical properties.

Polysiloxane based electrolytes have received a great attention because of the high flexibility of the Si–O bond, which permit to obtain the lowest glass transition temperature ($T_g = -123$ °C) and good thermal and chemical stability.²⁷ However, this low T_g is accompanied by almost liquid behaviour. The polysiloxane based SPEs have been used effectively for many potential application such as, lithium battery, DSSCs etc.^{23,28,29} Hooper et al. have reported that the lithium salt doped polysiloxane polymer prepared from the condensation of bis-[oligo(ethylene glycol) ether propyl] dichlorosilane showed ionic conductivity $\sim 10^{-4}$ S cm⁻¹ at 25 °C.³⁰ Walkowiak et al reported the highest ionic conductivity obtained with polysiloxane based polymer electrolytes at room temperature which is reported to be 10^{-3} S cm⁻¹, close to the level of a liquid organic electrolyte and meets the requirements for industrial application.³¹ More recently, growing attention has been paid to poly ionic liquids (PILs) because they have the properties of ILs and improved mechanical strengths.³² Moreover, compared with non-ionic polymers, PILs usually have higher ionic conductivity. Recently, PILs has been used as solid polymer electrolytes for solid state DSSCs.³³ However, these PILs are dissolved in organic solvents to fabricate the devices,^{34,35} the solvent is then evaporated. On the other hands, polysiloxane based electrolytes are gums at room temperature and can be cross linked within the device. In this work, new imidazolium modified polysiloxane electrolytes are synthesized as PILs and their ionic conductivity, viscosity, thermal properties and the iodide diffusion coefficient have been evaluated. Blending is an effective method to obtain the desired properties. So, the synthesized PILs have been mixed with ILs and non-volatile solvent such as ethylene carbonate (EC).

2. Experimental Part

2.1. Materials and solvents

Poly(dimethylsiloxane co methylhydrosiloxane) copolymer (H-PDMSX) precursors with different Si-H functionality, (X = 1, 2, 3 for respectively Si-H functionality 6% to 7%, 15% to 18% and 30% in mol%) were purchased from GelestInc (Morrisville, PA, USA) and dried at 80 $^{\circ}$ C during 6 h prior to use. Pt catalyst, (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex) was purchased from ABCR GmbH and was stored in the refrigerator. The reactants sodium hydride, imidazole, 5-bromo-1-pentene, bis(trifluoromethane)sulfonimide lithium salt (LiTFSI), and iodomethane, iodopropane were purchased from Sigma-Aldrich. The solvents, toluene and tetrahydrofuran (THF), were purchased from sigma Aldrich and were distilled prior to use.

2.2. Polysiloxane Functionalization

The synthesis of PILs, performed in 3 steps, is presented in Scheme 1. **Scheme 1**- Functionalization of polysiloxane polymer (H-PDMSX).



2.2.1. Synthesis of bromo-pentylpolydimethylsiloxane polymer (Br-PDMSX)

The bromo-pentylpolydimethylsiloxane polymers (Br-PDMSX) were synthesized using hydroxylation reaction. Approximately, 15 ml of toluene was taken into the three-neck conical flask and the toluene was dried at 110 °C until the left volume of the dried toluene was about 10 ml. The temperature of the reaction was reduced to 80 °C. 4.2 ml of polydimethylsiloxane (H-PDMSX) was added into the dried toluene while stirring. Pt catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex) was added to the above solution. The amount of the Pt catalyst added was 0.3, 0.5, and 0.7 ml for X = 1, 2, and 3, respectively. And then, 1.2 equivalents, *vs* the Si-H functionality, of 5-bromo-1-pentene was added to the above solution drop-wise under constant stirring. The reaction was refluxed at 80 °C for 3 hours and then cooled to room temperature. Resulting dark brown solution was washed by heptane and filtered until the solution became transparent. The reaction yield is 90%. The final product was dried under vacuum at 60 °C for 18 hours.

¹H NMR (400 MHz, Acetone-*d*) δ3.48-3.53 (m, 2H, BrCH_{2e}), 1.88-1.92 (m, 2H, CH_{2d}), 1.4-1.6 (m, 4H, CH_{2c}), 0.61-0.64 (m, 2H, SiCH_{2b}), 0.09-0.20 (s, 45H, SiCH_{3a}).



Figure 1-¹HNMR spectra of Br-PDMS2.

2.2.2. Synthesis of Imidazolium-pentylpolydimethylsiloxane polymer (Im-PDMSX)

The incorporation of the imidazolium function was performed by nucleophilic substitution. In typical procedure 0.95 equivalents of NaH was introduced in 10 ml of distilled THF under argon

atmosphere. 1.05 equivalents of imidazole dissolved in 5 ml distilled THF was added drop by drop in the NaH solution. The reaction was carried under stirring at room temperature for 3 hours. Then 1 equivalent of the synthesized Br-PDMSX polymer was added to the above solution and the temperature was increased up to the THF refluxing point during 18 hours. Resulting yellowish brownish solution was washed and filtered by using solvents, heptane and THF. The reaction yield is 40%. The final product, Imidazolium-pentylpolydimethylsiloxane polymer (Im-PDMSX) was dried under vacuum at 60 °C for 18 hours

¹H NMR (400 MHz, Acetone-*d*) δ 7.49 (s, 1H, CH_f), 7.08 (s, 1H, CH_g), 6.89 (s, 1H, CH_h), 4.00-4.04 (m, 2H, CH₂N_e), 1.77-1.80 (m, 2H, CH_{2d}),1.26-1.53 (m, 4H, CH_{2c}), 0.56-0.59 (m, 2H, SiCH_{2b}), 0.04-0.25 (s, 45H, SiCH_{3a}).



Figure 2-¹HNMR spectra of Im-PDMS2.

2.2.3. Synthesis of Poly(1-N-methylimidazolium-pentyl polydimethylsiloxane)iodide polymer (PDMSXIm⁺I⁻)

The quaternization reaction was conducted under ultrasonication and constant mechanical stirring in ice bath. In a typical procedure 1 equivalent of prepared Im-PDMSX and 1.2 equivalents of the methyl iodide were mixed and kept under ultrasonication for 2 hours. The reaction yield was 70%. Resulting highly viscous dark brownish final product, PDMSX-Im⁺T was dried under vacuum at 60 °C for 18 hours.

¹H NMR (400 MHz, Acetone-*d*) δ 10.01(s, 1H, CH_f), 7.47 (s, 1H, CH_g), 7.31 (s, 1H, CH_h), 4.25-4.34 (m, 2H, NCH_{2e}), 4.1(s, 3H, CH_{3i}),1.88-1.90 (m, 2H, CH_{2d}),1.33-1.40 (m, 4H, CH_{2c}), 0.45-0.55 (m, 2H, SiCH_{2b}), 0.04-0.20 (s, 45H, SiCH_{3a})



Figure 3- ¹HNMR spectra of PDMS2Im⁺I⁻.

Similarly, the PILs, PDMSXIm⁺I⁻ with (X =1 and 3 for respectively Si-H functionality 6% to 7%, and 30% in mol%) were also synthesized. Figure 4 shows the PILs having different functionality. Depending on the functionality; the PILs are a viscous liquid or an amorphous solid.



Figure 4- Sample type of PILs.

2.3. Synthesis of Ionic liquids

The synthesis of ILs, performed in 3 steps, is presented in Scheme 2.





2.3.1. Synthesis of 1-methyl-3-propylimidazolium-iodide (MPI I)

The reaction was done under ultrasonication and constant mixing. The mixtures of equimolar amount of 7.3 ml of methyl iodide and 12.5 ml of iodopropane were placed in flask under inert atmosphere. The reaction is kept on mechanical stirring under sonication overnight. The resulted reddish viscous product is washed several times with ether. The reaction yield is 85%. The resulted product was dried in vacuum for one day at 50 °C and 2 days at 80 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 9.82 (d, *J* = 1.9 Hz, 1H), 7.53 (dt, *J* = 19.9, 1.9 Hz, 2H), 4.24 (q, *J* = 7.5, 5.9 Hz, 2H), 4.10 – 4.02 (m, 1H), 4.04 (s, 2H), 1.91 (p, *J* = 8.3, 7.4 Hz, 2H), 1.00 – 0.87 (m, 3H).

2.3.2. Synthesis of 1-methyl-3-propyl-limidazolium-Bis(trifluoromethane)sulfonimide(MPI TFSI)

The 5 grams of prepared MPI I and 7.5 grams of Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) were mixed in 10 ml of water. The mixture was kept under stirring for one day. The yield of the light yellowish product is about after purification alumina column chromatography is 70%. The resulted product was dried in vacuum at 80 °C for 2 days.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 7.31 (dt, J = 5.4, 2.0 Hz, 2H), 4.22 – 4.13 (m, 2H), 3.98 (s, 3H), 2.19 (s, 1H), 1.94 (h, J = 7.4 Hz, 2H), 1.00 (t, J = 7.4 Hz, 3H).

2.4. Measurements

The densities of the PILs, PDMS1Im⁺I⁻, PDMS2Im⁺I⁻ and PDMS3Im⁺I⁻ and their blends with ILs were determined by taking the average value of mass per unit volume (Table 1). In order to have a precise value at least 3 measurements were performed. Attenuated total reflectance Fourier transform Infrared (ATR/FTIR) spectra were collected in the 4000-550 cm⁻¹ range using a Nicolet IS5 spectrometer (Thermo Fisher Scientific) equipped with a transmission or with a diamond attenuated transmission reflectance (ATR) device. Spectra were obtained in transmission or ATR mode as results of 32 spectra. Spectra were analyzed with ONIUMTM (Thermo Fisher Scientific) software. Glass transition temperature, T_g and melting point, T_m of the samples were recorded using differential scanning calorimeter, (DSC 1- Mettler-Toledo). Each sample was scanned at a cooling rate of 10 °C min⁻¹ within an appropriate temperature range (150 °C to 40 °C) under nitrogen atmosphere. Viscosity of the polymer electrolytes and their blends with ionic liquids and solvents was measured using Rheometer (ARG2). The viscosities (μ) were measured between 20 °C and 80 °C. Ionic conductivity of the electrolytes was measured using electrochemical impedance spectroscopy using an HP 4192A Impedance Analyzer in the frequency range 5Hz- 13MHz. The samples were placed between blocking electrodes. Measurements were done on successive increase and decrease of temperature in the range of 80 $^{\circ}$ C to 20 $^{\circ}$ C. The diffusion coefficient of I₃ was measured using a three electrode electrochemical configuration at 22-23 °C. The microelectrode (25 µm diameter) Pt electrode was used as working electrode along with Pt electrodes being used as pseudo reference and counter electrode respectively.

3. Results and discussion

3.1. Fourier transforms infrared spectra

Figure 5 shows the FTIR-ATR spectra of the H-PDMS and modified PDMS with their characteristic bands (different reaction stages for the chemical modification of the H-PDMSX).^{36,37} The sharp bands at 2961 and 2903 cm⁻¹ correspond to asymmetric and symmetric C-H stretching vibrations of Si-CH₃, 1411 and1259 cm⁻¹ owing to asymmetric and symmetric C-H deformation vibrations of Si-CH₃.³⁶ The presence of strong vibration band from 1000 cm⁻¹ to 1200 cm⁻¹, is attributed to Si-O-Si, in the spectrum of PDMS.³⁸ The adsorption peak at 2155 cm⁻¹ is attributed to the Si-H group which disappears after hydrosilylation reaction.³⁹ During the

hydrosilylation reaction, performed in our study, the intensity of the adsorption band attributed to the Si-H group, decreases, while new adsorption broad bands appeared at 2,920 and 2,850 cm⁻¹ attributed to the $-CH_2$ - group, suggesting that pentyl-bromide had been grafted onto the H-PDMS backbone by hydrosilylation.³⁹

The imidazolium moieties in Im-PDMS2 and PDMS2Im⁺T are determined by the existence of the peak at 1570, 1467 cm⁻¹, corresponding to stretching vibration of imidazole ring. The absorption band at 1470-1445 cm⁻¹ can be assigned to the C-C stretching and in plane C-N-H bending vibrations.⁴⁰ In addition to the imidazole ring, the frequency of the C-H stretch (2850-3000 cm⁻¹) of the terminal methyl group³⁶ confirmed the addition of imidazole.



Figure 5- FTIR spectrum of H-PDMS2, Br-PDMS2, Im-PDMS2, and PDMS2Im⁺I.

The FTIR-ATR spectra (figure 6) of the ILs are in accordance with literature data.⁴¹ The peaks at 1177, 1166 cm⁻¹ are assigned to the symmetric and asymmetric stretching vibrations of C-N of

imidazole rings.⁴² The peak at around 1570, 1460 cm⁻¹ can be ascribed to the C=N stretching vibration belonging to the imidazole ring. Compared with MPI Iodide, new bands corresponding to the TFSI anion is observed at1129, 1051, 739 cm⁻¹ as well as to stretching bands of sulfonyl group $(S=O)^{42}$ at 1329, 1347 cm⁻¹ in the IR indicating the successful anion exchange and formation of MPI TFSI.⁴³ The main TFSI vibrational bands observed are O–S–O asymmetrical stretch modes near 1350 cm⁻¹, CF₃ out-of-plane bending and C–F stretching modes around 1250 cm⁻¹, S–N–S asymmetrical stretch and O–S–O symmetrical stretch modes near 1170 cm⁻¹ and near 1080 cm⁻¹, S–N–S bending and CF₃ bending modes in the range 770–820 cm^{-1.44}



Figure 6- FTIR spectrum of ILs, MPI Iodide and MPI TFSI.

3.2. Density

Table 1 shows the density values for electrolytes based on polysiloxane PILs with different functionalization degree, i.e. different ratios of imidazolium iodide (PDMS1Im⁺ Γ , PDMS2Im⁺ Γ ⁻ and PDMS3Im⁺I⁻). The density of the PILs increases with the increase of the functionalization

degree of polysiloxane. This behaviour can be explained by the increase of, (i) the content of iodine, that is the heaviest element, and (ii) the ionic interactions between the chains, with PILS functionalization degree in polysiloxane). Concerning the ILs, the MPI I has slightly higher density than that of MPI TFSI (Table 1) and this can be attributed to the presence of iodine. The density of the mixtures was calculated with the Flory-Fox equation. The measured and calculated densities for the PDMS2Im⁺T + ILs based electrolytes are presented in table 2. Same evolution can be reported for the others PILs. The measured and calculated density values are very close; it seems that there is no specific interaction between the PILs and the two ILs.

Samples	Ionic concentration (mol/L)	Density (g cm ⁻³)
PDMS1Im ⁺ I ⁻	0.75	1.09
PDMS2Im ⁺ I ⁻	1.44	1.13
PDMS3Im ⁺ I ⁻	2.25	1.21
MPI I	6.28	1.58
MPI TFSI	3.69	1.49

Table 1- Density values and ionic concentrations of PILs and ILs.

Table 2- Density and molar concentration	n of PDMS2Im ⁺	[•] I and its mixtures	with ILs.
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Samples	(mol/L)	Measured density (g cm ⁻³)	Calculated Density (g cm ⁻³)	
PDMS2Im ⁺ I ⁻ : MPI I				
1:0.5	3.05	1.24	1.25	
1:1	3.86	1.31	1.32	
1:2	4.67	1.38	1.39	
1:3	5.07	1.42	1.44	
1:4	5.31	1.45	1.46	
PDMS2Im ⁺ I ⁻ : MPI TFSI				
1.05	2.19	1.23	1.23	
1:1	2.56	1.29	1.28	
1:2	2.94	1.34	1.35	
1:3	3.13	1.37	1.38	
1:4	3.24	1.39	1.40	

3.3. Thermal Properties

The glass transition temperature (T_g) of the PILs and its blends with ILs, MPI TFSI and MPI Iodide were measured by Differential Scanning Calorimeter (DSC). The glass transition

temperature (T_g) allows to evaluate the dynamic of the molecule chain and then the mobility of the ionic species which is often correlated to the electrolyte dynamic: lower the T_g , the higher may be the ionic mobility at a given temperature.⁴⁵ Table 3 compiles the T_g value of H-PDMSX, Br-PDMSX, Im-PDMSX and PDMSXIm⁺T. H-PDMSX polymer have amorphous character, with a T_g close to -131 °C, -110 °C and -50 °C for X = 1, 2 and 3, respectively. The increase of T_g vs the functionality can be related with hydrogen bond interaction. The hydroxylation of the H-PDMSX with the introduction of a long and flexible alkyl chain induces a neat decrease of the T_g especially for the highest functionalised polymer. The incorporation of the bulky imidazolium group and afterward quaternization increases notably T_g values. PDMSXIm⁺T exhibit T_g values of -123 °C, -85 °C, -47 °C for X = 1, 2, 3 respectively, the T_g increases notably with the polymer functionality which is coherent with ionic interaction which limits the PILs mobility then increase the viscosity and the T_g value.

Samples	T _g (° C)
H-PDMS1	-131
Br-PDMS1	-126
Im-PDMS1	-124
PDMS1Im ⁺ I ⁻	-123
H-PDMS2	-107
Br-PDMS2	-117
Im-PDMS2	-88
PDMS2Im ⁺ I ⁻	-71
H-PDMS3	-50
Br-PDMS3	-109
Im-PDMS3	-61
PDMS3Im ⁺ I ⁻	-47
MPI Iodide	-64
MPI TFSI	-90

Table 3- Glass transition temperature (Tg) of the each steps of polymer functionalization.

The T_g of the MPITFSI is lower than the MPI I one, respectively, -90 °C and -64 °C which is in accordance with the soft and flexible properties of TFSI anion.⁴⁶ The PIL (PDMSXIm⁺I) and ILs (MPI I and MPI TFSI) are miscible, except for the less functionalised polymer, PDMS1Im⁺I⁻ that seems to be immiscible with the MPI I. For PDMS1Im⁺I⁻ + MPI I mixtures, two T_g were clearly

observed, whatever the composition, with the lowest T_g , at -124 °C close to the one of pure PDMS1Im⁺I⁻ polymer.

For miscible electrolytes, the T_g value deceases with the increase of ILs amount in accordance with their lowest T_g value (Table 4). From the three PDMSXIm⁺ Γ , the PDMS3Im⁺ Γ has the highest T_g and the T_g values obtained with its blends are higher than the ones obtained with the two other polymers. In presence of MPI I, the measured T_g values are lower than the one calculated with the relation used for the determination of miscible mixtures T_g (equation 1) and even lower than the T_g of the two compounds in PDMS3Im⁺ Γ based electrolyte.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{1}$$

Where, w_1 , w_2 are weight fraction, T_g is in Kelvin. The presence of the second compound (IL or PILs) seems to decrease the ionic interaction presented in both the pure ILs and PILS, which may be due to the introduction of local disorder.

PDMSXIm ⁺ I ⁻ : MPI	T_{g}	Calculated	PDMSXIm ⁺ I ⁻ : MPI	T_{g}	Calculated
TFSI	(°C)	T _g (°C)	Iodide	(°C)	$T_{g}(^{\circ}C)$
X=1					
2:1	-88	-110			
1:1	-91	-108			
1:2	-90	-100			
1:3	-91	-99			
1:4	-95	-97			
X=2			X = 2		
2:1	-74	-76	2:1	-71	-68
1:1	-83	-81	1:1	-75	-67
1:2	-84	-82	1:2	-73	-66
1:3	-87	-86	1:3	-76	-66
1:4	-88	-87	1:4	-78	-65
X=3			X = 3		
2:1	-69	-56	2:1	-56	-52
1:1	-78	-71	1:1	-60	-56
1:2	-81	-79	1:2	-63	-58
1:3	-82	-81	1:3	-65	-60
1:4	-82	-82	1:4	-73	-51

Table 4- Glass transition temperature (T_g) of the PILs, PDMSXIm⁺ I (X= 1, 2, and 3) and their blends with ILs, MPI TFSI and MPI I (w/w).

3.4. Viscosity properties

3.4.1. PILs viscosity

Poly(siloxane) exhibits a range of unique properties that make them desirable for development as stable polymer electrolyte. The Si-O bond of siloxanes is about 30% stronger than C-C bonds presented in hydrocarbons.⁴⁷ Furthermore, the Si-O bond length is about 7% greater than a typical C-C bond. In most polysiloxanes, branch substituents are attached to the silicon atom, thereby giving them great flexibility as well as low viscosity.⁴⁸

Figure 8 plots the variation of viscosity as a function of temperature for each modification steps of H-PDMS polymer. The viscosities (μ) were measured between 20 °C and 70 °C, at shear rate of 0.3 s⁻¹ and ramping rate of 2 °C min⁻¹. Indeed, the polymers have non-Newtonian behaviour, with viscosity value decreasing with shear rate, PDMS based polymer has a lubricant behaviour.⁴⁹ A stabilisation of the viscosity is obtained up to 0.3 s⁻¹, that is why this shear rate was chosen for the viscosity comparison. Figure 7 shows an example of the evolution of viscosity *vs* shear rate.



Figure 7- Viscosity dependence on shear rate for PDMS1Im⁺I⁻ at 20 °C.

The addition of a long alkyl chain in H-PDMS to produce Br-PDMS causes a decrease in the viscosity by a factor of two for PDMS2 based polymers in the temperature range due to the free volume increase by the incorporation of flexible lateral chain and the disappearance of hydrogen bond. This decrease in viscosity corroborates with the decrease in the T_g value. The substitution of the bromide by imidazole ring induces a clear viscosity increase, which can be correlated with the bulkiness of the imidazolium function, and it is in accordance with the T_g value evolution. Quaternization of Im-PDMS2 induces a large increase of viscosity by a factor more than one hundred, which is associated with the addition of ionic interactions in the medium.⁵⁰ As expected, the viscosity decreases with increase in temperature, this change is more significant to the most viscous medium. This effect is attributed the increased Brownian movement of the molecules.⁵¹



Figure 8- Viscosity variations with functionalization in PDMS2 based polymer.

Figure 9 shows the evolution of the viscosity vs temperature for the three PILs, PDMS1Im⁺I, PDMS2Im⁺I⁻, and PDMS3Im⁺I⁻, respectively. It is observed that the viscosity increases significantly with the polymer functionality, and follow the same trend like the evolution of T_g values of this series, i.e. -123 °C, -71 °C and -47 °C for X = 1, 2 and 3, respectively. This behaviour can be attributed by the ionic interaction enhancement.



Figure 9- Viscosity comparison with different ionic functionality ratios in different PILs.

3.4.2. PILs -ILs mixtures viscosity

As expected, the viscosity of ILs decreases with increasing temperature due to the increased Brownian movement of the molecules of ILs.⁵¹ However it can be point out that this decrease is more significant for the most viscous ILs. Hence the viscosity of the MPI TFSI is about 20 times smaller at 20 °C while at 80 °C is only 4 times (figure 10) lower than MPI I ones.



Figure 10- Viscosity of ILs, MPI TFSI and MPI I.

The viscosity measurements were performed only on PDMS2Im⁺T based mixtures, indeed the same evolution is expected for the other miscible mixtures. Figure 11-12 present the viscosity of PDMS2Im⁺T - ILs as a function of temperature. The addition of MPI TFSI to PDMS2Im⁺T causes a drastic decrease in the viscosity which is attributed to the low viscosity of MPI TFSI. Such a decrease can be beneficial from a technological point of view when high viscosities limited the mass transfer process.⁵² The 1-1 in wt% of PDMS2Im⁺T/MPI TFSI exhibits a viscosity of 0.49 Pa.s at $T = 25^{\circ}$ C which is nearly 260 times less than the one of the pure PIL (127 Pa.s).

On the other site, addition of MPI I to PDMS2Im⁺T induce a more moderate decrease in the viscosity. The 1-1 in wt% of PDMS2Im⁺T/MPI I exhibits a viscosity of 5.08 Pa.s which is nearly 25 times less than the one of pure polymer. However, it can be pointed out that the viscosity ratio between the mixtures1-1 wt% PDMS2Im⁺T/MPI I and 1-1 wt% PDMS2Im⁺T/MPI TFSI (ratio equal to 10) is lower than the viscosity ratio of the pure ILs (MPI I and MPI TFSI).



Figure 11- Viscosity of PDMS2Im⁺T and its blends with MPI TFSI (w/w).



Figure 12- Viscosity of PDMS2Im⁺I⁻ and its blends with MPI I (w/w).

A real mixture does not behave as a perfect mixture and it is interesting to quantify the deviation from ideality, to highlight specific interactions between ionic molecules. The viscosity of an ideal mixture is calculated using the equation 2.

$$\mu_{th} = \mu_1 \chi_1 + \mu_2 \chi_2 \tag{2}$$

Where, μ_{th} is viscosity of ideal mixture, and μ_1 , μ_2 , χ_1 , and χ_2 are the mole fractions and viscosities of the two components in a binary mixture. The difference was estimated using two parameters; one is the viscosity of excess $\Delta \mu$, defined as the difference between the experimental viscosity and the ideal viscosity:

$$\Delta \mu = \mu_{exp} - \mu_1 \chi_1 - \mu_2 \chi_2 \tag{3}$$

The excess viscosity, determined at 30 °C, is very large (Table 5); indeed the experimental viscosity values are one order of magnitude lower than the expected ones for an ideal mixture, without specific interaction. The addition of ILs screens the ionic interactions between polymer chains inducing a sharp decrease in viscosity. This evolution is in good accordance with the evolution of the T_g .
	MPI I			MPI TFSI		
PIL/IL wt/wt ratio	μ_{exp} / Pa s ⁻¹	$\mu_{th}/Pa s^{-1}$	$\Delta \mu$ Pa s ⁻¹	μ_{exp} / Pa s ⁻¹	$\mu_{th}/Pa s^{-1}$	$\Delta\mu$ / Pa s ⁻¹
1:0	106	106	0	106	106	0
1:1	3.57	25.9	-22.3	0.38	36.0	-35.6
1:2	1.68	14.9	-13.2	0.23	21.7	-21.4
1:3	1.25	10.5	-9.2	0.14	15.5	-15.4
1:4	0.47	8.2	-7.7	0.09	12.1	-12.0
0:1	0.34	0.34	0	0.036	0.036	0

Table 5- Excess viscosity determination of PIL/IL mixtures.

As shown in figures 11-12, the viscosity of PILs, ILs and their mixtures decreases with the temperature increase attributed to increase in Brownian motion of the constituent molecules.⁵¹ Temperature dependencies of the viscosity values, μ , were fitted using Vogel-Tamman-Fulcher (VTF) equation for viscosity (equation 4).

$$\mu = \mu_0 exp\left[\frac{B'}{R(T-T_0)}\right] \tag{4}$$

Where the pre-exponential term μ_0 (mPa.s), corresponds to the viscosity at infinite temperature. *B*' (J mol⁻¹) is usually considered to be the pseudo-activation energy and corresponds to the slope of the VTF plots, *R* is the universal gas constant, T_0 (K) is the ideal transition temperature.^{53–55}

The best fit parameters μ_0 (mPa.s), B' (J mol⁻¹) and T_0 (K) are given in the table 6. Pure PILs exhibit higher pseudo-activated energy, B' (J mol⁻¹) than the ILs and their mixtures, in accordance with their higher viscosity. The pseudo-activated energy, B' (J mol⁻¹) of PILs/ILs are very close for all the mixtures and near the ones obtained for ILs. The empirical parameter T_0 is usually referred to "ideal glass transition temperature" and it has been given theoretical significance both through the free volume theory of Cohen and Turnbull⁵⁶ and the configurational entropy approach of Adam and Gibbs.⁵⁷ Below T_0 the product exhibits no free volume and has no mobility. Experimentally, this thermodynamic equilibrium cannot be attained, and the experimental glass transition, T_g , is observed instead, as a sudden change in properties such as heat capacity, volume or viscosity. In this study, the T_0 , is nearly equal to the T_g determined by DSC. The T_0 evolution with the PILs functionality and the ILs addition is in good agreement with the T_g values evolution.

Samples	μ_0 (mPa.s)	B ' (J mol ⁻¹)	T ₀ /K
PDMS1Im ⁺ I ⁻	4.1 ± 0.4	4200 ± 400	145 ± 4
$PDMS2Im^+I^-$	8.9 ± 0.1	10800 ± 400	197 ± 5
PDMS3Im ⁺ I ⁻	41 ± 10	23800 ± 200	222 ± 9
MPI I	0.48 ± 0.1	5200 ± 100	211 ± 2
MPI TFSI	0.36 ± 0.1	4500 ± 900	176 ± 5
$PDMS2Im^+ I^- : MPI I$			
1:1	2.7 ± 0.8	6400 ± 500	193 ± 5
1:2	2.8 ± 1	5900 ± 600	194 ± 6
1:3	0.8 ± 0.2	6500 ± 300	194 ± 5
1:4	0.7 ± 0.6	5300 ± 100	201 ± 1
PDMS2Im ⁺ I ⁻ : MPI TFSI			
1:1	$1.9\pm~0.1$	5800 ± 200	184 ± 5
1:2	1.7 ± 1.0	5000 ± 100	183 ± 2
1:3	1.1 ± 0.1	4900 ± 100	180 ± 2
1:4	0.6 ± 0.1	4100 ± 100	181 ±5

Table 6- VTF equation parameters of Viscosity data for PILs and ILs.

3.5. Ionic Conductivity

The ionic conductivity (σ) was calculated from the bulk resistance obtained from the complex impedance plot.⁵⁸ The ionic conductivity of PILs and ILs is mainly related to their viscosity and molar concentration (taking into account the density and molecular weight) of ionic species. These two phenomena are antagonists for conductivity, the increase in viscosity decreases the mobility of the ions, while the increase of the molar concentration induces an increase in charge carrier thus in conductivity, whereas the ion dissociation decreases as the ion concentration increases.

The conductivities were determined in the temperature range 25 °C to 80 °C, every 5 °C. Figure 13 shows the ionic conductivity of pure PILs, PDMS1Im⁺T, PDMS2Im⁺T, and PDMS3Im⁺T at various temperatures. At 25 °C, PDMS1Im⁺T and PDMS2Im⁺T show nearly the same ionic conductivities, with $\sigma = 9 \times 10^{-6}$ and 8×10^{-6} S cm⁻¹, respectively, whereas PDMS3Im⁺T exhibits the highest conductivity ($\sigma = 1.6 \times 10^{-5}$ S cm⁻¹). At high temperature, the difference in conductivity values is more important, with the highest conductivity value reached for the highest ionic concentration (with 6.3×10^{-5} , 1.5×10^{-4} , 4×10^{-4} S cm⁻¹ for X = 1, 2 and 3, respectively), in accordance with the less detrimental effect of viscosity at high temperature. Despite having a

high viscosity at room temperature, the conductivity obtained for PDMS3Im⁺I at room temperature is comparable to any class of PILs at room temperature.^{59–63}



Figure 13- Comparison of conductivity of PILs.

In order to compare the ionic conductivity at the same ionic concentration, the molar conductivities were determined and plot versus the temperature. The molar conductivity Λ_m (S cm² mol⁻¹) was obtained by dividing the ionic conductivity by the ionic concentration according to the following equation 5.

$$\Lambda_m = \frac{\sigma}{c} \tag{5}$$

Where, σ and *c* are the conductivity and the ionic concentration (mol cm⁻³) of the electrolyte. The molar conductivities of the PILs are very close even if PDMS3Im⁺T exhibits viscosity two order of magnitude higher than the PDMS1Im⁺T one. This decorrelation between viscosity and ionic conductivity may be explained by the formation of nanoscale segregation and phase separation between the hydrophobic siloxane backbone and the ionic lateral chains. The higher ionic function concentration of the PDMS3Im⁺T may induce more favourable pathway for ionic conduction through a better percolation of ionic nano-domains. The less viscous PIL, PDMS1Im⁺T, exhibits, as expected, the lowest activation energy.



Figure 14- Comparison of molar conductivity of different PILs.

Despite a lower molar concentration of MPI TFSI, the conductivities are higher than those of MPI I as shown in figure 15, especially at low temperature which is coherent with the viscosity of these two ILs, MPI TFSI exhibits a viscosity 20 times lower than MPI I at 25 °C.



Figure 15- Comparison of conductivity of IL, MPI TFSI and MPI I.

Temperature dependencies of the conductivity (σ) have been fitted using the Vogel–Tamman– Fulcher (VTF) equation 4.^{53–55}

$$\sigma = \sigma_0 exp \left[\frac{-B}{R(T - T_0)} \right] \tag{4}$$

Samples	σ_0 (S cm ⁻¹)	B (J mol ⁻¹)	T ₀ /K
$PDMS1Im^+I^-$	0.04 ± 0.005	12000 ± 500	125 ± 9
$PDMS2Im^{+}I^{-}$	0.06 ± 0.05	10000 ± 500	180 ± 5
PDMS3Im ⁺ I ⁻	0.07 ± 0.01	7000 ± 200	210 ± 5
MPI I	0.8 ± 0.05	5100 ± 100	215 ± 5
MPI TFSI	1.2 ± 0.3	4600 ± 200	175 ± 5

The T_0 values are in good accordance with the ones determined with the viscosity measurement (table 6), whereas the pseudo activation energy seems to be more or less disconnected.

3.5.1. Conductivity of PILs +IL mixtures

Figure 16-17 show the ionic conductivity of PDMS2Im⁺T and their blends with ionic liquids, MPI TFSI and MPI I in function of temperature. Addition of ionic liquids improved notably the ionic conductivity of PILs electrolytes at given temperature, even with only 30 wt% of IL. Indeed, the incorporation of the ionic liquid in the polymer decreases the viscosity, increases the ion concentration and introduces more mobile ionic species. Due to the lower viscosity of MPI TFSI, conductivities of the blends PDMS2Im⁺T + MPI TFSI are the highest.



Figure 16- Conductivity of PDMS2Im⁺I⁻ and its blends with MPI I (w/w).



Figure 17- Conductivity of PDMS2Im⁺I⁻ and its blends with MPI TFSI (w/w).

Indeed, the other PILs (X = 1, and 3) + ILs mixtures show the similar behaviour as presented with PDMS2Im⁺T and the effect of the addition of IL on the ionic conductivity for the different PILS is compared in Figure 18.



Figure 18- Conductivity versus the amount of IL for the different PILs at 30 °C.

With the addition of IL, the blend PILs/IL conductivity is weakly dependant of the PILs functionality and depends on both the IL nature and its amount. The difference in conductivity of the pure PILs is mitigated with the addition of IL. As for PILs, and ILs, the conductivity of the mixtures can be fitting by the VTF equation.^{53–55} The VTF fitting parameters of the ionic conductivity for the PILs, ILs and their mixtures are summarized in table 8 for the PDMS2Im⁺T based electrolyte in order to compare with viscosity evolution (Table 6).

Samples	$\sigma_{o}(S \text{ cm}^{-1})$	B (J mol ⁻¹)	T ₀ /K
PDMS2Im ⁺ I ⁻	0.06 ± 0.05	10000 ± 100	180± 5
MPI I	0.8 ± 0.05	5100 ± 100	215 ± 5
MPI TFSI	1.2 ± 0.3	4600 ± 200	175 ± 5
$PDMS2Im^{+}I^{-}:MPII$			
2:1	0.23 ± 0.05	7200 ± 100	193 ± 5
1:1	1.12 ± 0.13	8000 ± 300	191 ± 2
1:2	0.9 ± 0.6	7500 ± 1600	198 ± 17
1:3	0.69 ± 0.15	5700 ± 500	208 ± 5
1:4	0.9 ± 0.2	5400 ± 500	209 ± 5
PDMS2Im ⁺ I ⁻ : MPI TFSI			
2 :1	0.22 ± 0.04	6400 ± 500	182 ± 7
1:1	0.18 ± 0.11	7000 ± 900	189 ± 10
1:2	0.15 ± 0.12	4800 ± 800	187 ± 5
1:3	0.16 ± 0.04	4400 ± 400	187 ± 10
1:4	0.27 ± 0.04	4800 ± 300	176 ± 16

Table 8- VTF equation parameters of conductivity data for PDMS2Im⁺ I⁻, ILs and their blends.

As the ionic concentration of the two ILs is higher than the one of the PDMS2Im⁺T, the global ionic concentration should increase with the addition of ILs in PILs and then, σ_0 should also increase. Indeed, experimentally, a notable increment is observed when ILs is introduced to PDMS2Im⁺T. The adjustable pseudo-activation energy constant, *B*, can be seen as the energy barrier for the rotational motion of polymer segment and the value is predicted to decrease with the addition of ILs,⁶⁴ due to the decrease in viscosity. Experimentally, the predicted evolution was observed for high ILs amount. Moreover, the evolution of the pseudo activation energy, *B*, is in good agreement with those determined with viscosity for PDMS2Im⁺T, ILs and their mixtures (Table 6), indicating that the ionic conductivity, in presence of IL, is mainly governed by viscosity. As for viscosity data analysis, the ideal glass transition temperature, *T*₀, is nearly equal to the *T*_g determined by DSC and its evolution is the expected one.

3.5.2. Molar conductivity of PILs + ILs mixtures

To compare the conductivity of the PILs/ILs mixtures at the same molar concentration, the molar conductivity, Λ_m was determined at 25 °C and plots on the figure 19 for the PDMS2Im⁺ Γ based mixtures.



Figure 19- Molar conductivity of PDMS2Im⁺I⁻ + ILs.

As the viscosity of the two ILs added is very different, the evolution of the molar conductivity *vs* the molar concentration is notably separated. For each IL based mixtures, monotonous increase of the molar conductivity *vs* the ionic concentration can be noticed, with the increase of the IL proportion in the mixture the conductivity tend to the ones of the IL. This evolution may be explained by the large decrease of the viscosity of the mixtures associated with the incorporation of ILs which, in the same time, increases the ionic concentration. As previously said, it's the amount of IL which governs the conductivity. The same conclusions can be given with the others PILs.

The Walden plot was used to appreciate the ionicity in ionic liquids. In this approach, data for a 0.01 M KCl solution provides a useful calibration point. If the viscosity and conductivity of the electrolyte obeys Walden's rule, the ionic conductivity is correlated to viscosity using the qualitative approach of Angell et al (equation 5).⁶⁵

$$\Lambda \mu^{\alpha} = C \tag{5}$$

Where, *C* is a temperature-dependent constant, which is called the Walden product. Alpha (α) is the slope of the line in the Walden plot, α is a constant between zero and one, while $\alpha = 1$ indicates ideal behaviour of the solution (i.e., viscosity is the only force impeding the mobility of ions).⁶⁶ The Walden rule is explored using a plot of the log of molar conductivity (Λ_m) versus the log of fluidity (μ^i). The data takes the form of a straight line where the slope of the line is equal to α . Dilute aqueous KCl solutions generally give α value near 1, as it is completely dissociated (only free ion). In addition, the position of data points on the Walden plot reflects the behaviour of the ion conducting system. For example, data points on or above the ideal Walden line ($\alpha = 1$) indicate the behaviour of good ionic liquid. Data below the ideal Walden line are generally termed poor ionic liquids. For the unit chosen, the ideal line runs from corner to corner of a square diagram.⁶⁷ According to the Walden rule, electrolytes that possess strongly interacting ions are usually located below the KCl ideal line, due to partial association of neighbouring ions.

Each data point in figure 20 represents the molar equivalent conductivity (Λ_m) versus the fluidity at a common temperature. All data points except the PDMS3Im⁺T are below the ideal Walden line, indicating that the ionic conductivities are somewhat diminished as a result of ion-pair formation.⁶⁸ PDMS3Im⁺T is positioned slightly above the PDMS1Im⁺T and PDMS2Im⁺I. Indeed,

as we comment previously, some nanoscale phase separation can occur in polysiloxane based PILs due to the hydrophobicity of the siloxane backbone, inducing some viscosity and conductivity decoupling, which can be more efficient (a better percolation of ionic domains) for the highest functional polymer.

The ionicities of the two ILs are very close, indicating similar ionic dissociation. The ionicity of the PILs seems to be not so far (even weakly higher) from the one of the imidazolium ionic liquid, indicating that the ion dissociation may be close. In conclusion, the difference in conductivity values is largely correlated to the viscosity (much larger for the PILs) and nano-structuration of the electrolyte.



Figure 20- Walden plot for PILs and ILs at 25 °C.

Figure 21 shows that the molar equivalent conductivity (Λ_m) of PDMS2Im⁺T - IL mixtures is almost the same. So, all the PDMS2Im⁺T - ILs mixtures fall below the ideal KCl line. The ionicity of the PDMS2Im⁺T - IL mixtures are between the ones of the PIL and ILs, then weakly decrease with the IL amount.



Figure 21- Adjusted Walden plot for PDMS2Im⁺I⁻ -ILs mixtures at 25 °C.

3.6. Diffusion Coefficient

The ionic diffusion coefficient of tri-iodide (I_3^-) was determined using a microelectrode. The measurements of the diffusion coefficient of I_3^- is carried out by cyclic voltammetry at 25 °C ± 2 in glove box (less than 2 ppm of water), the polymer and the mixtures contain approximately 0.05 M I_2 to form I_3^- . The limiting current recorded at the microelectrode during cyclic voltammetry is given by the following equation.^{69–71}

$$I_{ss} = 4.n. \, c.r. F. D_{app} \tag{6}$$

Where, *n* is the number of electrons transferred per molecule, *F* is the Faraday constant, D_{app} is the apparent diffusion constant, ϕ is the bulk concentration of the electroactive species (I₃⁻) and r is the radius of the microelectrode. The reaction occurring at the Pt electrode is described as:⁷²

$$3I^- \quad \leftrightarrow \quad I_3^- \ + \ 2e^- \tag{7}$$

The diffusion coefficient of $D(I_3^-)$ assesses the mobility of I_3^- into the electrolyte. The value of the diffusion coefficient can measure the efficiency of transport. It is therefore essential to compare I_3^- mobility values obtained as a function of the iodide concentration in the mixtures of PILs/ILs

and to analyse these data with regard to the conductivity and viscosity values. High iodine concentration in the electrolyte is suspicion to reduce the efficiency of DSSC due to increased light absorption by I_3^- and an enhancement of recombination processes.⁷³ Due to that and the fact that there is no real concentration dependant enhancement of I_3^- , the systems of PILs and ILs were examined with an iodine concentration of 0.05 M.

In viscous electrolyte, the mobility of I_3^- is governed by two mechanisms the Grotthus mechanism (hopping process) which is prevalent in viscous medium and the diffusion mechanism which is predominant in fluid medium.⁷⁴ If we compare the diffusion coefficient of I_3^- in the different polymer, a maximum is obtained for PDMS3Im⁺T, in good accordance with its good conductivity despite its high viscosity. Due to the very high viscosity of this polymer, the Grotthus mechanism seems to be very efficient.

PILS: ILs	Diffusion coefficient (I ₃ ⁻)								
		$(cm^2 s^{-1})$							
wt:wt	1:0	2:1	1:1	1:2	1:3	1:4	0:1		
PDMS1Im ⁺ I ⁻	3.0×10 ⁻⁹	1.2×10^{-7}	1.6×10 ⁻⁷	2.6×10 ⁻⁷	2.0×10^{-7}	1.6×10^{-7}	-		
/MPI TFSI									
PDMS2Im ⁺ I ⁻	2.5×10 ⁻⁹	-	7.2×10 ⁻⁸	1.1×10 ⁻⁷	1.3×10 ⁻⁷	1.0×10^{-7}	2.0×10^{-7}		
/MPI I									
PDMS2Im ⁺ I ⁻	2.5×10 ⁻⁹	-	1.4×10^{-7}	2.7×10 ⁻⁷	3.2×10 ⁻⁷	3.3×10 ⁻⁷	-		
/MPI TFSI									
PDMS3Im ⁺ I ⁻	8.0×10 ⁻⁹	-	6.5×10 ⁻⁸	1.0×10 ⁻⁷	9.0×10 ⁻⁸	1.7×10^{-7}	2.0×10^{-7}		
/MPI I									
PDMS3Im ⁺ I ⁻	8.0×10 ⁻⁹	-	1.1×10 ⁻⁷	2.0×10^{-7}	2.7×10^{-7}	4.2×10^{-7}	-		
/MPI TFSI									

Table 9-Diffusion coefficient of PILS, ILs and their blends.

If now, we compared polymer and ionic liquid, the diffusion coefficient $D(I_3^-)$ in PDMS3Im⁺ Γ is 25 times lower than in MPI I, whereas the conductivity is more than 2 order of magnitude lower and the viscosity more than 3 order of magnitude higher. The diffusion coefficient is less affected by the increase of the viscosity. The presence of the hopping process explains the relative high diffusion coefficient were obtained in such viscous medium.^{74,75}

The value of $D(I_3^-)$ measured in PILs/IL mixtures increases with the proportion of MPI TFSI and MPI I up to the proportion of 1:2 or 1:3 depending of the PIL (Table 8), afterward near constant values were obtained. In addition the diffusion coefficient is mainly governed by the IL nature and amount, indeed similar values was obtained for PDMS3Im⁺ Γ and PDMS2Im⁺ Γ based electrolyte. For PDMS1Im⁺ Γ , we cannot exclude some phase separation occurring at high MPI TFSI concentration due to the low functionality of the PIL.

For the PIL/MPI I mixtures, the diffusion coefficient tends to the one of pure MPI I, which is expected. However for pure PILs and their mixtures with MPI I, the increase in diffusion coefficient is much lower than the one observed in conductivity, a factor between 10 and 20 for diffusion coefficient whereas the conductivities increase by a factor between 180 and 50 for respectively for 1:2 PDMS2Im⁺T and PDMS3Im⁺T mixtures.

Regarding the addition of MPI TFSI due to its low viscosity, a huge improvement in diffusion coefficient can be noticed, which may be associated essentially with diffusion process. In addition, the addition of MPI TFSI induces a neat decrease of Γ concentration, which limit the hopping process.

3.7. Polymer electrolytes and its blends with ethylene carbonate (EC)

3.7.1. Thermal Properties

Since the first example of electrochemical cell based on poly(ethylene oxide) PEO, many efforts has been made to improve the ionic conductivity by using gel polymer electrolytes.^{20,76} A common method is to add liquid solvent such as ethylene carbonate (EC) to the polymer matrix.^{77,78} The solvent has a role of plasticizer, with the increase of the chain mobility (i.e. decrease of viscosity) and then an increase of the ionic conductivity. In addition, plasticization has been identified as one of the effective and efficient routes available for enhancing the amorphous nature of the polymer electrolytes.^{79,80} The EC has been our first choice due to its superior properties such as high dielectric constant, high donor number, and high boiling point.⁸¹ Choi et al. showed that low molecular weight poly(ethylene glycol), (PEG600) can be used to enhance the ionic conductivity of polysiloxane based single ion conductor.⁸² The substantial improvement in ionic conductivity on the addition is due to plasticization and solvation. In this work, the PIL, PDMS3Im⁺T is mixed with ethylene carbonate and the physical properties such as

thermal properties, conductivity and I_3^- diffusion were evaluated. Indeed as the addition of solvent dilutes the ionic concentration, the experiments were done only on the highest concentrated PIL i.e. PDMS3Im⁺I⁻.

The results obtained with the addition of EC are given in Table 10. A marked decrease of T_g values was obtained up to a proportion of 2:1. Indeed, as the high T_g value of PDMS3Im⁺T is associated essentially with the strength ionic interactions. The decrease in T_g values may be related to the ionic dilution in addition to the incorporation of a plasticizer. For larger solvent amounts, an increase of T_g is observed; this effect is presumably associated with the huge excess of solvent, that is not more in interaction with the PILs and at low temperature a nanophase separation can take place leading to the EC crystallization. The crystallization of EC/salt complexes is observed for all the compositions except for the lower EC amount (up to PILs/EC =8/1). However, the melting point and the crystallinity content increase with the amount of EC, indeed the interaction between the ionic function of the PIL and EC inhibits the EC crystallisation. Some measurements were performed with the others PILs, and as expect, due to their lower ionic concentration, the complete crystallisation of EC is observed with lower proportion of EC, for a proportion 1:2 for PDMS2Im⁺T and PDMS1Im⁺T.

PDMS3Im ⁺ I ⁻ : EC	$T_{g}(^{\circ}C)$	$T_{f}(^{\circ}C)$	Crystallinity content of EC (%)
1:0	-47	-	-
8-1	-70	-	-
4-1	-72	-2	16
3-1	-75	4	4
2:1	-81	11	20
1:1	-70	15	10
1:2	-60	19	14
1:3	-59	29	97

Table 10- Glass transition temperature (T_g) and melting temperature (T_f) of the PIL, PDMS3Im⁺T and their blends with EC (w/w).

3.7.2. Ionic conductivity

The temperature dependence of the conductivity of PDMS3Im⁺I⁻EC mixtures is plotted in Figures 22. Addition of EC in PDMS3Im⁺I⁻ induces a large increase in conductivity which may be associated with both a decrease of viscosity and an increase of ion dissociation due to the high

dielectric constant of EC. For a large amount of EC added, up to the proportion 1:1, the ionic conductivity becomes constant. Indeed, the decrease in viscosity is mitigated by the ionic concentration decrease. At low temperature, a neat decrease of the conductivity is observed when the amount of EC is higher than 33 wt% (i.e. PDMS3Im⁺T/EC 2:1). The decrease in conductivity is associated with the crystallinity of EC, characterized previously by DSC.



Figure 22- Conductivity of PDMS3Im⁺I⁻ and its blends with ethylene carbonate solvent (w/w).

The temperature dependence of the ionic conductivity has been fitted with the Vogel–Fulcher–Tamman (VTF) equation (equation 4). Table summarizes the best fit factors.

Samples	σ_0 (S cm ⁻¹)	B (J mol ⁻¹)	T ₀ /K
PDMS3Im ⁺ I ⁻	0.07 ± 0.01	7000 ± 200	211 ± 5
PDMS3Im ⁺ I ⁻ : EC			
4:1	0.1 ± 0.01	3800 ± 300	194 ± 5
3:1	0.077 ± 0.02	3300 ± 200	204 ± 5
2:1	0.15 ± 0.03	5000 ± 500	190 ± 8
1:1	0.14 ± 0.03	4400 ± 500	160 ± 8

Table 11- VTF equation parameters of conductivity data for PDMS3Im⁺ I⁻ and its blends with EC.

The pseudo activation energy, B, of PDMS3Im⁺I⁻ weakly decreases with the addition of EC and is close for all the electrolytes PDMS3Im⁺I⁻ + EC (no logical evolution); in parallel, the ideal glass transition temperature, T_0 , decreases with the addition of EC. For the large amount of EC, the crystallisation of EC prevents the determination of the VTF law parameters with a sufficient precision. The two variations are consistent with the viscosity decrease with solvent addition.

3.7.3. Diffusion Coefficient

The same protocol that the one explained for PILs and PILs + ILs mixtures was used. Figure 23 shows the diffusion coefficients obtained with the PDMS3Im⁺T + EC electrolytes. As expected, the diffusion coefficient is highly improved by the addition of EC and the highest value, 2×10^{-6} cm² s⁻¹, is obtained for the highest concentration of EC. With the addition of only 20 wt% of EC, the diffusion coefficient is increased by a factor 10, and a diffusion coefficient of 10^{-7} cm² s⁻¹ is reached at room temperature. Contrary to thus obtained with IL, a good accordance is obtained between the increase in conductivity and the increase in diffusion coefficient, indeed the ionic conductivity is also increased by near a factor 10 with the addition of 20 wt% of EC. Due to the large decrease in viscosity, the large increase in mobility of I₃⁻ by diffusion process may mask the decrease of the hopping process. Therefore, the conductivity and the diffusion coefficient are largely related to viscosity evolution.



Figure 23- Diffusion coefficient of PDMS3Im⁺I⁻ and its mixtures with ethylene carbonate (EC).

4. Conclusion

А series of new polymer electrolytes based on poly(1-N-methylimidazoliumpentylpolydimethylsiloxane)iodide, poly(ionic) liquids (PILs) with different ionic functionality have been synthesized and characterized. The ionic functionality influenced the miscibility, glass transition temperature, viscosity, ionic conductivity and diffusion coefficient of the polymers. Aiming at materials that could be employed in quasi-solid-state-DSSC, we studied the binary mixtures of the synthesized poly(ionic)liquid with ionic liquid such as MPI TFSI and MPI I to achieve some interesting properties such as high conductivity, low viscosity associated with low T_g, improved diffusion coefficients of the triiodide. For the highest functionalized PIL (PDMS3Im⁺I⁻) nanophase separation seems to occur, which explain the high ionic conductivity obtained despite a very high viscosity. The determined triiodide diffusion coefficients for the PILs with 0.05 M iodine and varying ionic liquids amount showed a large improve of the diffusion coefficient with the addition of IL. The incorporation of ethylene carbonate (EC) solvent in PIL has been studied. With up to 33 wt% of EC, T_g of polymer decreases; but for a larger amount of solvent some phase separation takes place. The addition of 20-25 wt% EC is sufficient to have high conductivity values of 1.1×10^{-3} S cm⁻¹ and diffusion coefficient of 10^{-7} cm² $\rm s^{-1}$ at 25 °C. The photovoltaic performances of the PILs and PILs/ILs or PILs/EC will be tested in chapter III.

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CHAPTER-III

Ionic liquid-like polysiloxane electrolytes for highly stable quasisolid-state-dye sensitized solar cells

Abstract

In order to develop highly stable and efficient polymer electrolytes for dye sensitized solar cell (DSSCs) applications, a series of new poly(ionic)liquids (PILs), namely poly(1-Nmethylimidazolium-pentylpolydimethylsiloxane)iodide different ratios with of pentylimidazolium iodide moieties have been studied. The substituent functionality ratio influences several properties such as glass transition temperature, viscosity, conductivity and diffusion coefficient. PILs were further mixed with two types of ionic liquids (ILs), namely1methyl-3-propylimidazolium iodide (MPII) and 1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide (MPI TFSI), and a plasticizer such as ethylene carbonate (EC) in order to lower their viscosity and to increase the diffusion coefficient and ionic conductivity. Finally, PILs, PILs/ILs and PILs/EC blends are employed as gel electrolytes by being dissolved in acetonitrile/valeronitrile in DSSCs. Solar cells with an active area of 0.2064 cm², prepared using the gel electrolytes, showed light-to-electricity conversion efficiencies up to 6%. After 250 days, PILs-based cells retain 84% of their initial efficiency.

Keywords: PILs, ILs, electrolytes, blends, viscosity, ionic conductivity, glass transition temperature, diffusion coefficient

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1. Introduction

Dye-sensitized solar cells (DSSCs) have the attractive features of high efficiency, low cost and easy processing.¹ Such cells consist of a TiO₂ working electrode which acts as an electron acceptor and transport layer coated with a monolayer of a dye for light harvesting and electron injection into the conduction band of TiO₂. The electrolyte in DSSCs is very important because it provides the required ionic conductivity and diffusion coefficient if the redox mediators and helps dye regeneration through charge transfer reactions with the dye molecules. The electrolyte usually employed in DSSCs is the Γ/I_3 redox couple which acts as redox mediator i.e. regenerates the photo-excited dye molecules by reduction, leading to a certified record efficiency of 11.9%, reported by the National Renewable Energy Laboratory (NREL).^{2,3} In 2011, Yella et al. utilized cobalt-based redox electrolyte as an alternative to the iodine based electrolyte and the efficiency obtained in DSSC was 12.3%.⁴ Currently, a solar-to-electricity conversion efficiency of up to 14.3% has been achieved by employing an cobalt-based liquid electrolyte.⁵ Unfortunately, such electrolytes demonstrate much lower long-term stability trends if compared to the traditional Γ/I_3 redox couple.

More generally, the disadvantages of liquid electrolytes are corrosion, sealing, long-term stability etc., which reduces the performance of DSSCs.⁶ To overcome these problems, solid and gel materials such as p-type inorganic semiconductors^{7,8}, inorganic and organic hole transport materials ^{9–14}, and polymer-based gel electrolytes ^{15–19} have been exploited to replace the liquid electrolytes. However, the diffusion coefficient of the solid and gel electrolytes are usually less (~10⁻⁷cm⁻² s⁻¹) than that of a liquid electrolyte (~10⁻⁴ - 10⁻⁵ cm⁻² s⁻¹) and, therefore, the conversion efficiencies of solid and gel-state DSSCs are lower than their liquid counterparts.²⁰

One of the methods to solve these problems is using quasi-solid-state electrolytes (QSSEs). QSSEs have long-terms stability like solids and ionic conductivity and excellent interfacial contact property like the liquid electrolytes.^{21–24} More recently, growing attention has been paid to poly(ionic liquids) (PILs) because they are a new class of polymers that combine both the novel properties of ionic liquid (IL) and improved mechanical durability and dimensional control after polymerization.²⁴ PILs have been successfully applied for quasi-solid-state DSSCs which yielded high power conversion efficiency and excellent stability.^{25,26}

In the present work, we have chosen to work on polysiloxane-based PILs. Polysiloxanes have highly flexible backbone, very low glass transition temperature (Tg) and high free volumes, therefore polysiloxanes-based electrolytes have received much attention.²⁷ However, the polysiloxane-based polymer electrolytes are gums at room temperature rather than solids, and recent efforts have been focused on the design and synthesis of polymers with both high ion transport and good dimensional stability. Hooper et al. have reported that the lithium salt-doped polysiloxane polymer prepared from the condensation of bis-[oligo(ethylene glycol) ether propyl] dichlorosilane has ionic conductivity of $\sim 10^{-4}$ S cm⁻¹ at 25 °C.²⁸ Walkowiak et al. have reported the highest ionic conductivity obtained with polysiloxane-based polymer electrolytes at room temperature, 10⁻³ S cm⁻¹, which is close to the level of a liquid electrolytes and meets the requirements for industrial application.²⁹ In 2001, a DSSC assembled with a gel network polymer electrolyte based on polysiloxane and PEO, containing 20 wt% of LiI, 5 wt% of I₂ and 150 wt% of the mixture ethylene carbonate (EC)/propylene carbonate (PC) (3:1 v/v) was reported. The energy conversion efficiency of the cell was recorded to be 2.9%.³⁰ Recently, Manca et al. have successfully employed an ion conductive polysiloxane-based polymer electrolyte for DSSCs application: the DSSC assembled with 40 wt% of polysiloxane electrolytes dissolved in MPNbased ionic liquid solution has shown an efficiency of 6.37%.³¹

studied a series of new poly(1-N-methylimidazolium-In this work. we have pentylpolydimethylsiloxane)iodide as PILs (synthesized in chapter II), having different ratio of pentylimidazolium iodide moieties for the photovoltaic applications in DSSCs. Generally, the major shortcomings associated with utilizing pure PILs as electrolytes in DSSCs is the low ionic conductivity and diffusion coefficient which causes the poor photovoltaic performance in DSSCs. Incorporating the ILs with PILs is believed to enhance the ionic conductivity and diffusion coefficient.^{32,33} So, the synthesized PILs have been mixed with ILs such as 1-methyl-3propylimidazolium iodide (MPII) and 1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide (MPITFSI).

An alternative way is definitely to use a plasticizer. The effect of polar solvating plasticizer in polysiloxane has been reported to increase ionic conductivity by facilitating the dissociation of ions and their mobility.³⁴ However, there is not much research done on the effect of plasticizer such as ethylene carbonate (EC) on polymer electrolytes such as polysiloxane and their influence

on photovoltaic properties. It is well known that (EC) is a high-viscosity solvent with high dielectric constant, which is favourable for ionization of salts and resulting in high ionic conductivity. Owing to these properties of EC, there have been plenty of research groups utilizing the concept of plasticization.^{35–39}

In this work we study the influence of these physicochemical and electrochemical properties on their photovoltaic performances when assembled as quasi-solid-state DSSCs. Such fabricated quasi-solid-state DSSCs show high level of efficiency with long term stability for polysiloxane-based polymer electrolytes.

2. Experimental part

2.1. Materials

Fluorine Tin Oxide-coated glass substrates (FTO) (TEC15:15 ohm/sq) and TiO₂ colloidal pastes (18 NRT and T-Nanoxide R/SP) were purchased from Dyesol. N-719 dye and the Surlyn (60 μ m) spacer was purchased from Solaronix. Acetonitrile was purchased from ABCR GmbH and Co. The 3-methoxypropionitrile (MPN), 1-butyl-3-methylimidazolium iodide, iodine, guanidine thiocyanate; 4-tert-butylpyridine, valeronitrile, acetylacetone (AcAc), Titanium isopropoxide (TTIP) and ethylene carbonate were purchased from Sigma-Aldrich.

2.2. Fabrication of PILs-based electrolytes

The synthesis of PILs and ILs is described in Chapter *II* and in our recent article.⁴⁰ PILs electrolytes were prepared from three synthesized PILs: PDMS1Im⁺T, PDMS2Im⁺T, and PDMS3Im⁺I⁻ as shown in figure 4 of chapter *II*. The polymer mixtures (as shown in Table 1) were dissolved in a very small amount of acetonitrile/valeronitrile (1/1, v/v). Nine different types of polymer electrolytes are illustrated in the Table 1.

Sample code	PILs/ILs or EC (wt:wt ratio)	I ₂ (M)
P1	PDMS1Im ⁺ I ⁻	0.05
P2	PDMS2Im ⁺ I ⁻	0.05
P3	PDMS3Im ⁺ I ⁻	0.05
P2:MPII(2:1)	$PDMS2Im^{+}I^{-}:MPII(2:1)$	0.05
P2:MPII(1:1)	$PDMS2Im^{+}I^{-}:MPII(1:1)$	0.05
P2:MPITFSI(2:1)	PDMS2Im ⁺ I ⁻ : MPI TFSI (2:1)	0.05
P2:MPITFSI(1:1)	PDMS2Im ⁺ I ⁻ : MPI TFSI (1:1)	0.05
P3: EC (8:1)	$PDMS3Im^{+}I^{-} : EC(8:1)$	0.05
P3: EC (3:1)	PDMS3Im ⁺ I ⁻ : EC (3:1)	0.05

Table 1- Composition of the polymer electrolytes.

As presented in chapter *II*, PILs based electrolytes have been largely characterized, the more relevant data for the application is resumed in Table 2.

Electrolyte	$T_{g}(^{o}C)$	μ (Pa s)	σ (S cm ⁻¹)	$D(I_3)(cm^2 s^{-1})$
Reference ⁴¹	-	-	-	7.0×10 ⁻⁶
P1	-123	13	9×10 ⁻⁶	3.0×10 ⁻⁹
P2	-71	100	8×10^{-6}	2.5×10 ⁻⁹
P3	-47	1200	1.6×10 ⁻⁵	8.0×10 ⁻⁹
P2:MPII(2:1)	-71	-	1.3×10 ⁻⁴	-
P2:MPII(1:1)	-75	5.1	1.5×10^{-4}	7.2×10^{-8}
P2:MPITFSI(2:1)	-74	-	4.0×10 ⁻⁴	-
P2:MPITFSI(1:1)	-83	0.5	6.9×10 ⁻⁴	1.4×10^{-7}
P3:EC(8:1)	-70	-	1.8×10^{-4}	1.1×10^{-7}
P3:EC(3:1)	-75	-	1.1×10^{-3}	2.8×10 ⁻⁷

Table 2- Thermal and physiochemical properties of PILs-based electrolytes at 25 °C.

The "reference" redox liquid electrolyte was composed of 0.6 M 1-butyl-3-methylimidazolium iodide 0.03 M iodine, 0.1 M guanidine thiocyanate and 0.5 M 4-tert-butylpyridinein acetonitrile/valeronitrile (85/15, v/v).⁴¹

Appropriate weights of the components (PILs, IL, I_2 , and solvent) were mixed in a closed bottle and then continuously stirred at 50 °C until everything was dissolved. The resulting blends are further designated as "electrolyte".

2.3. Fabrication of DSSC

To fabricate the devices, a blocking layer TiO_2 layer (BL) was first deposited on FTO substrates. The property of BL was reported to show significant influence on the overall device performance.⁴² The TiO₂ BL of around 70 nm was prepared by spin coating of titanium(IV) isopropoxide (TTIP) solution in TTIP-AcAc solution at 2000 RPM for 60s and thermally stabilized at 150 °C for 15 min (studied briefly in Chapter V). Subsequently, a porous layer of TiO_2 was deposited by spin-coating from TiO_2 -nanocrystals based paste (Dyesol 18 NRT dispersed in ethanol) at 1500 RPM for 60 s and then stabilized at 180 °C on a hot-plate for 20 min. This spin-coating procedure was repeated several times till the desired film thickness was obtained. Finally an additional scattering layer was deposited by the use of a Dyesol T-Nanoxide R/SP colloidal paste (dispersed in ethanol) by spin-coating at 1500 RPM for 60s. Subsequently, the photoanodes were sintered at 500 °C for 30 min to generate the porous structure. The overall thickness of the TiO₂-mesoporous electrodes utilized in this work was kept around 11 μ m (8 μ m of photoanode $+ 3 \mu m$ of scattering layer). To ensure the connectivity between grains, the porous films were treated by soaking in a 0.04 M TiCl₄ aqueous solution at 60 °C for 30 min. After drying, the photoanodes were sintered again in air for 30 min at 450 °C. The freshly sintered photoanodes were sensitized with dye molecules by immersing overnight in 2.7×10^{-4} M N719 alcoholic solution at room temperature. The dye loading on the TiO₂ films was realized by desorbing the dye, and the amount of uptake dye was estimated to be 1.976×10^{-9} mol mm⁻². Finally, the dyed photoanodes were washed with ethanol and dried, then assembled in a sandwich configuration with a counter-electrode with Surlyn (60 µm) as a spacer. The counter-electrode consisted in a platinized FTO with a hole drilled from the uncoated side. The polymer electrolytes were introduced into the cell by vacuum back filling through the hole. Prior to sealing, the volatile solvent has been removed by heating the cell at 100 °C for 15 min on the hot plate followed by vacuum drying overnight. The electrolyte injection hole was firmly sealed with Surlyn and a microscope cover glass. A mask of black plastic tape was applied on the cells with an active area of 0.2064 cm^2 .

2.4. Characterizations

The PILs and their blends were characterized by the techniques mentioned in Chapter II.⁴⁰ The scanning electron microscopy (SEM) was used estimate the thickness of the TiO₂ photoanodes, as well as electrolyte infiltration. Energy-Dispersive X-ray spectroscopy (EDX) elemental mapping was used on cross sections of assembled cells to assert the pore filling. The photocurrent-voltage (J–V) characteristics of the DSSCs were measured by a solar simulator purchased from Newport Spectra **Physics** coupled with Keithley 2400 a Source Meter under a simulated Air Mass 1.5 G solar spectrum with an aperture mask of 0.2064 cm². The irradiance of the source was around 0.7 sun. The dye uptake was estimated by desorption from the dyesensitized electrodes in a 10^{-3} M KOH solution in water, and measuring the absorption spectrum of the resulting dye solution using a UV-visible spectrophotometer (Perkin Elmer UV-Vis Spectrometer Lambda 14P). The Incident Photon to Charge Carrier Efficiency (IPCE) data were collected in the 300 - 800 nm range using a Xe lamp associated with a monochromator (Triax 180, JobinYvon). No bias light was employed to illuminate the cell. The current produced was measured by steps of 2 nm after 2 s of radiation exposure with a Keithley 6487 picoammeter in order to be in steady state conditions. The incident photon flux was measured with a 6-in. diameter calibrated integrated sphere (Labsphere) and a silicon detector. Electrochemical impedance spectroscopy was performed using a BioLogic SP-200 potentiostat (Science Instrument) and data were analyzed with the EC-lab software. EIS spectra were recorded over a frequency range of 10 mHz to 100 kHz under dark conditions at room temperature by applying a bias equal to the V_{oc} value determined from the J-V curves.

3. Results and discussion

3.1. Photovoltaic Performance of DSSCs

Photocurrent density-voltage characteristics (two to three dummy cells for each electrolyte) under ~ 0.7 suns are presented in the figure 1A and Table 3. The device based on the liquid electrolyte (reference) showed J_{sc} of 10.04 mA cm⁻², V_{oc} of 0.75 V, FF of 68%, and gave a conversion efficiency of 7.69%. Among the three PILs the highest energy conversion efficiency was obtained for P2 (3.04%) followed by for pure P1 (2.47%) which is higher than that of for pure P3 (0.24 %). The highest conversion efficiency for pure P2 can be correlated to its high ionic conductivity (8×10⁻⁶ S cm⁻¹), better diffusion coefficient (2.5×10⁻⁹ cm² s⁻¹), and compromised viscosity (100 Pa s). On the contrary, P3 shows the lowest efficiency due to the poor pore infiltration caused by highest viscosity (1200 Pa.s) at room temperature.⁴³ The J_{sc} of the reference liquid electrolyte is higher than that of pure PILs electrolytes (P1, P2, and P3). The limitation of J_{sc} of the DSSCs using the pure PILs as compared to reference electrolyte is mainly attributed to the limited ion conduction restrained by the polymer viscosity. Besides, the V_{oc} of the polysiloxane-based PILs devices was significantly decreased (0.65 V to 0.11 V) compared with that of reference liquid-based device (0.75 V). The decrease in the V_{oc} is due to a shift in the

conduction band caused by the accumulation of oxidized species near TiO_2 surface. Indeed, the low I_3^- mobility of polysiloxane-based electrolyte causes a build-up near the TiO_2 and increases the probability of electron recombination. In solid-state or quasi-solid-state electrolyte systems, the main drawback of PILs is their high viscosity, which makes the ions diffusion rather slow. Therefore, transport of I_3^- ions to the counter electrode in a polysiloxane-based matrix can constitute a rate-limiting step in DSSCs;⁴⁴ as a consequence, depletion of I_3^- at the counter electrode takes place, and an over-potential that lowers the voltage output of the solar cell is observed.



Figure 1- J-V curves of DSSCs based on the Dyesol photoelectrode and liquid electrolytes and PILsbased electrolytes under ~ 0.7 sun illumination (A) and in dark (B).

Table 5 - Photovoltaic	parameters of th	e DSSCs contai	ining PILs and u	neir biends und	$er \sim 0.7 sun$
illumination.					

Electrolyte	Voc	\mathbf{J}_{sc}	FF	Average	Best efficiency
	(V)	$(\mathbf{mA \ cm}^{-2})$	(%)	Efficiency (η %)	(ղ %)
Reference (liquid)	0.75	10.04	68	7.69	7.96
P1	0.65	4.21	62	2.47	2.69
P2	0.56	5.71	63	3.01	3.04
P3	0.11	5.85	25	0.24	0.24
P2:MPII(2:1)	0.61	8.20	66	4.86	4.95
P2:MPII(1:1)	0.62	9.94	62	5.63	5.94
P2:MPITFSI(2:1)	0.57	6.85	66	3.79	3.99
P2:MPITFSI(1:1)	0.61	8.96	66	5.33	5.56
P3:EC(8:1)	0.55	3.76	63	1.93	2.09
P3:EC(3:1)	0.65	9.83	64	6.05	6.30

Imidazolium iodide based ILs have been widely used effectively for DSSC applications.^{41,45-48} In this work, MPII and MPITFSI were selected to study the influence of ILs on polymer electrolyte, P2 and its perspective photovoltaic behaviour. Furthermore, it has been reported that the MPII provides excellent efficiency and good stability in DSSCs.⁴⁷ The P2 containing 33 wt% of MPII, ((P2:MPII(2:1)) shows significant enhancement of DSSC efficiency compared with pure P2. Energy conversion efficiencies of 4.86% and 5.63% were achieved with the incorporation of 33 and 50 wt% of MPII, respectively, which is comparable to efficiency reported by Manca et al.^{31,49} We noted that the small of amount (33 wt%) of MPII is sufficient to have a 1.6 fold efficiency increment. This is due to a highly improved ionic conductivity, drastically reduced viscosity, and improved diffusion rate with the addition of MPII. The raise found for the value of V_{oc} in P2/ILs blends-based electrolytes could be ascribed to the remarkably higher diffusion coefficient, and conductivity of the electrolyte than with the pure polymer. The value of V_{oc} for DSSCs with Γ/I_3^- redox electrolyte can be represented by the following equation.⁵⁰

$$V_{oc} = \frac{kT}{e} \ln\left(\frac{I_{inj}}{n_{cb} k_{et} [I_3^-]}\right)$$
(1)

Where, *k* and *T* are the Boltzmann constant and absolute temperature, respectively, I_{inj} is the injection current from dye to semiconductor, n_{cb} is the electron density on the conduction band of the semiconductor, and k_{et} is the rate constant for I_3^- reduction. According to the equation 1, the higher V_{oc} of the P2/ILs-based electrolyte is related to the suppression of the dark current at the TiO₂ electrode/electrolyte interface (figure 1B).⁵¹ It has been demonstrated that the dark current originates from the reduction of I_3^- by conduction band electrons from TiO₂.⁵² The decrease of the I_3^- reduction rate should lead to an increase of V_{oc} according to the following equation 1.

The PILs/ILs with TFSI ions have been already used effectively in DSSCs and showed higher inherent (neat) ionic conductivity.^{26,53} We observed that the addition of 33 wt% of MPI TFSI to P2 caused very slight improvement in the photovoltaic parameters. Addition of about 50 wt% MPITFSI to P2 causes around 1.8 fold improvement in the efficiency. The improved performance of P2:MPITFSI-based cells can be attributed to the improved diffusion coefficient, higher ionic conductivity and lower viscosity. Slight improvement in the V_{oc} of P2:MPI TFSI-based devices

can be assigned to the suppression of the dark current at the TiO₂/electrolyte interface as shown in figure 2B.^{54,55} Energy conversion efficiencies of 3.79% and 5.33% were achieved with the incorporation of 33 and 50 wt% of MPITFSI, respectively. In addition to that, both the ILs led to the PILs infiltration into the working TiO₂ electrode. The P2/MPII blends showed higher J_{sc} due to extra release of Γ from MPII despite having inferior conductivity and diffusion coefficient than the one obtained with P2/MPITFSI, showing higher efficiency in DSSC. We presume that extra MPII can act as both source of redox electrolytes and lone charge transfer intermediate which leads to increase in photovoltaic performance.^{56,57}

The increase of ionic conductivity observed with the addition of EC is caused by decrease of viscosity and increase of ionic dissociation due to an increase of the dielectric constant and solvating ability of EC.⁵⁸ Therefore, the ionic conductivity increased with increase in amount of EC in the P3. The DSSCs assembled with increasing wt% of EC-containing electrolyte report highly improved FF and V_{oc} than the DSSC assembled without EC. The increase of V_{oc} for the DSSCs with 11 and 25 wt% of EC is related to the reduction of back electron transfer reaction and suppression of dark current as shown in figure 1B. The higher value of J_{sc} for the DSSCs with 25 wt% of EC-containing electrolyte may originate from their highly improved ionic conductivity and diffusion coefficient. The dependence of J_{sc} on the composition of EC in the electrolyte can be explained on the basis of the shift of flat band potential of TiO₂. As shown in figure 1A the P3:EC(3:1) based cells shows highly improved J_{sc} , largely improved V_{∞} and FF owing to its high ionic conductivity (1.1×10^{-3} S cm⁻¹) and diffusion coefficient (2.8×10^{-7} cm² s⁻¹), due to the Grotthus and diffusion mechanisms. The device based on the P3:EC (25 wt%) combination showed a J_{sc} of 9.83 mA cm⁻², V_{oc} of 0.65 V, FF of 64%, and exhibited an efficiency of 6.05%, which is 25 times higher than the pure P3.

3.2. Incident photon-to-current conversion efficiency (IPCE)

The IPCE curves of these DSSCs are shown in the figure 2. The maximum IPCE value at 530 nm is 23%, 39%, 37%, 42% for pure P2, P2:MPII(1:1), P2:MPITFSI(1:1) and P3:EC(3:1)-based electrolytes, respectively. The broad feature appears covering the visible spectrum from 450 nm to 600 nm. The IPCE values of these devices are consistent with the photoelectric conversion efficiency (η). The improvement of IPCE is expected to enhance charge-generation efficiency and inhibit electron recombination.⁵⁹



Figure 2- IPCE curves of DSSCs containing different electrolytes.

3.3. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was used to evaluate the charge transfer resistance at the $TiO_2/dye/electrolyte$ and the diffusion resistance. The Nyquist and Bode phase plots of the DSSCs comprising the P2, P2:MPITFSI(1:1), P2:MPII(1:1) and P3:EC(3:1) electrolytes are shown in figure 3A-B and C, respectively. In the case of the Nyquist plot the graphs were brought to the same origin for comparison, indeed the resistances measured at high frequency are not logically associated with the electrolyte resistance, and are significantly modified by the erratically and poor contact between the cell and the cable, that's why it is more useful to remove it in the graph.

In literature, the EIS spectrum of a DSSC shows three responses in the studied frequency range (10 mHz to 100 kHz). The first and second semicircles correspond to the charge-transfer resistances at the counter electrode (R_{ct1}) and TiO₂ (R_{ct2}) interfaces, respectively, while the third one represents the diffusion process of the I_3^- from the Γ/I_3^- redox electrolyte.⁶⁰ In our study, the circuit Rs + R1//Q1 + R2//Q2 + W_{d3} (// symbolizes a connection in parallel and + a connection in series) was used to fit the EIS spectra. The values of series resistance (R_s) which represented the electrolyte resistance and contacts/wires resistance, charge transfer resistance at the counter electrode (R_{ct1}) and charge transfer resistance at the TiO₂/dye electrode (R_{ct2}) are given in Table



4. Even the Bode plot confirms the clear separation of three phenomena according to their relaxation times.

Figure 3- The EIS Nyquist plots (A-B) and Bode phase plots (C) measured in dark for DSSC with different electrolytes. The continuous line represents the fit while the dotted line represents the raw data.

It can be seen that both R_{ct1} and R_{ct2} decrease with the addition of ILs due to the enhanced Γ/I_3^- mobility in the polymer⁶¹, as confirmed by the I_3^- diffusion coefficient values (see Chapter *II*). The decreased R_{ct2} upon addition of ILs and EC, ensured low recombination resistance at the photoanode/electrolyte interface are in agreement with the published study.⁶² The DSSC with P3:EC(3:1) electrolyte shows the lowest R_{diff} owing to its high ionic conductivity and diffusion

coefficient, resulting in a very high V_{oc} of 0.65 V. The R_{diff} values of the DSSCs are consistent with the dark current, FF and J_{sc} variation of the corresponding DSSCs.

Device	$R_s(\Omega)$	$\mathbf{R}_{\mathrm{ct1}}\left(\Omega\right)$	$\mathbf{R}_{\mathrm{ct2}}\left(\Omega\right)$	$\mathbf{R}_{\mathrm{diff}}\left(\Omega ight)$	f_{\max} (Hz)	τ_{e} (ms)
P2	55	19	40	21	11	14
P2:MPII(1:1)	48	6	21	21	8	19
P2:MPITFSI(1:1)	43	8	16	10	21	7.5
P3:EC(3:1)	51	4	12	7	17	9

Table 4- Parameters obtained by fitting the EIS of the DSSCs fabricated by different electrolytes.

The effective lifetime of electrons (τ_e) before the recombination in TiO₂ photoelectrodes can be determined from the equation 2.⁶³

$$\tau_e = \frac{1}{\omega_{max}} = \frac{1}{2\pi f_{max}} \tag{2}$$

Where ω_{max} is the frequency angle of the middle-frequency peak associated with TiO₂ electrode response and f_{max} is the maximum frequency of the middle-frequency peak. The f_{max} and lifetime of electrons are also summarized in Table 4. We assume that after the P2 electrolyte complete penetration the electron will be crossing the TiO₂ from grain to grain rather than through the TiO₂/electrolyte interfaces (which in this case are more rare), as opposed to the case with less viscous electrolyte when charge transfer and recombination at the TiO_2 /electrolyte interface is more likely to take place due to the electrolyte facile percolation between the TiO_2 particles. The electron lifetime (τ_e) for the P2 based cells (determined in dark condition), comprising the most viscous electrolyte, is higher (14 ms) than the P2:MPITFSI(1:1) based cells (7.5 ms) despite having lower viscosity and higher diffusion coefficient. It can be seen from figure 3C, that the addition of that upon the addition of MPITFSI, this character frequency shifts to a higher frequency range indicating that the electron lifetime has been shortened and these are in agreement with the dark current. However, the addition of the MPII to P2 shifted the middle frequency peak to lower frequencies. This corresponds to the prolonged electron lifetime (19 ms). MPII was found to be able to move the conduction band of the TiO₂ photoanode positively causing the electrons to be able to recombine with the I_3^- in the electrolyte which causes the

electron lifetime at this interface to be prolonged.⁶⁴ However, the P3:EC (3:1) based DSSC shows the electron lifetime of 9 ms.

3.4. Pore infiltration

The good interfacial contact between photoanode and electrolyte is essentially required for efficient regeneration of dye after electron injection into TiO₂ conduction band and one of the key factors affecting the photovoltaic performances of quasi-solid-state solar cells. Therefore, SEM images were taken first to evaluate the penetration of P3:EC(3:1) into mesoporous TiO₂ photoanodes. Figure 4A shows a porous and rough structure of TiO₂ film. After filling with electrolyte, the cross-section of film is covered thoroughly by a layer of polymer (figure 4B). Individual nanoparticle cannot be distinguished and the porous character disappeared. This indicated the complete infiltration of polymer into TiO₂ film. This result is further confirmed by EDX elemental analysis. The element mapping, as shown in figure 4C, demonstrates homogenous distribution of silicon and iodine atoms across the 11 μ m of TiO₂ film, This result makes it possible to get an excellent photovoltaic performance.



Figure 4- Cross-section SEM images of TiO_2 photoanode before (A) and after (B) filling with P3:EC(3:1) and (C) EDX mapping of P3:EC(3:1) filled TiO_2 nanoparticle film taken from a disassembled DSSC.

3.5. Stability of DSSC

To investigate the long-term stability of the DSSCs, the cells fabricated with the liquid and polymers were stored in ambient conditions for an extended duration (several months). The photovoltaic parameters were measured approximately every 30 days as shown in figure 5. It can

be seen that the DSSCs based on PILs and PILs blends maintained nearly 80-90% or more of their initial performance after 250 days.



Figure 5- Evaluation of the long term stability of the cells containing liquid and different pure PILs electrolytes: evolution of photovoltaic parameters (V_{oc} , FF, J_{sc} , η) over a period of 250 days.

As can be seen that the efficiency of reference (liquid) electrolyte based DSSC was degraded by 87% of its initial efficiency, whereas pure polymer P1 and P2 retained about 93 and 60% of their initial efficiency. Interestingly, the highly viscous polymer (P3) based DSSC showed about 400% times raise due to improved diffusion of electrolytes into TiO₂ pores over an extended period of time. It should be noted that the addition of ILs and EC into polymer does not degrade the cells. The cells containing P2-ILs and P3-EC still retain most of their efficiency after 250 days of measurement (figures 6, 7 and 8B).


Figure 6- Evaluation of the long term stability of the cells containing liquid and different pure P2 + ILs electrolytes: evolution of photovoltaic parameters (V_{oc} , FF, J_{sc} , η) over a period of 250 days.



Figure 7- Evaluation of the long term stability of the cells containing liquid and different pure P3 +EC electrolytes: evolution of photovoltaic parameters (V_{oc} , FF, J_{sc} , η) over a period of 250 days.

As shown in figure 8 and Table 5, the P3: EC (3:1) based DSSC retains about 84% of its initial efficiency. However, the liquid electrolyte reference cell maintained only 13% of its initial performance. The efficiency of the cells with the liquid electrolyte decreased gradually because of possible electrolyte leakage. The similar device performance for 250 days old P3: EC (3:1) based DSSC can be obtained at both high (1 sun) and moderate (0.7 sun) simulated sunlight irradiance as shown in figure 8A.



Figure 8- (A) I-V curve of fresh and 250 days-aged DSSCs containing liquid electrolyte ("reference" cell) and P3/EC(3:1) electrolyte. Curves are obtained under 0.7 sun unless other label. Inset shows the reference and P3:EC cells after 250 days. (B) Efficiency losses over a period of 250 days.

Table 5- J-V values of DSSCs containing liquid and P3:EC(3:1) electrolytes after 1 and 250 days.

Cell	Sun	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	Efficiency (η%)
Reference (Fresh)	0.7	10.04	0.75	68	7.69
Reference (Aged)	0.7	2.09	0.71	44	1.02
P3:EC(3:1) (Fresh)	0.7	9.83	0.65	64	6.05
P3:EC(3:1) (Aged)	0.7	7.50	0.64	69	5.09
P3:EC(3:1) (Aged)	1	11.80	0.67	64	5.13

4. Conclusion

We presented a series polymer electrolytes based on the blends of new poly(1-N-methylimidazolium-pentylpolydimethylsiloxane)iodide, (PILs) having different viscosity as well as their blends with ILs and EC and their successful implementation as efficient polymer gel electrolytes for DSSCs. We observed that the synthesized electrolytes show high thermal stability and greater solvent retention capability. The addition of ionic liquids to the P2 causes an increase in V_{oc} and J_{sc} value and results in improved photovoltaic performances. The highest efficiencies of 5.63% and 5.33% were achieved with the incorporation of 50 wt% of MPII and 50 wt% of MPI TFSI. It has been demonstrated that MPII provides extra Γ ions and longer electron lifetime as compared to TFSI⁻ ions. EC was used as plasticizing solvent to enhance the conductivity. The

EC, thanks to the high dielectric constant, promotes ion dissociation in the polymer electrolyte system and hence a significant improvement of diffusion rate was found. The EC promotes also the ions homogeneous distribution over the photoanode thickness. As a conclusion the substantial improvement in the ionic conductivity and diffusion coefficient after the addition of EC is due to three effects: plasticization, homogenization, and solvation. Addition of EC to the P3 causes an increase in V_{oc} , J_{sc} value and FF and results in improved photovoltaic performances. The highest efficiency of 6.05% was achieved with incorporation of 25 wt% of EC which is, to best of our knowledge, the highest ever reported efficiency on polysiloxane-based PILs with the EC. The quasi-solid-state DSSCs exhibited a prolonged stability maintaining up to 85% of its initial efficiency after 250 days. These reported results demonstrate the high potential of PILs-ILs and PILs-EC blends and pave novel roads towards further optimization in industrial solar energy conversion devices and other energy related applications.

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CHAPTER-IV

Tuning bimodal porosity in TiO₂ photoanodes towards efficient solid state dye sensitized solar cells

Abstract

In this chapter, a cell architecture that achieves enhanced light harvesting with less dye quantity while simultaneously improving the performance of the dye sensitized solar cell (DSSCs) is described. We report the synthesis of bimodal mesoporous anatase TiO₂ films by a dual templating approach, combining the Pluronic template (P123 block-copolymer) and polystyrene nanospheres (PS) as soft and hard templates, respectively. The SEM, AFM and TEM analysis of TiO₂ films revealed a mixture of mesoporous and macroporous morphology in which dual porosity is generated by combustion of soft and hard templates. The size of the macropores was varied by employing PS beads with different diameters (62, 130 and 250 nm). The influence of the macropores size on the dye loading and charge transfer at the TiO₂/electrolyte interface was the main focus in this chapter. The bimodal porosity leads to increased light scattering, enhancing the optical path length and hence favoring the photons harvesting by the sensitizer. In addition, better pore infiltration of the polysiloxane electrolyte is achieved. The amount of dye uptake by the dual films is lower than that of soft films because the larger pore size reduces the total surface area. The optimum bimodal structure was obtained when combining P123 surfactant and the 130 nm PS beads and a high efficiency for DSSCs is reported with both liquid and polymer electrolytes. Even if the dye uptake was lower, the photovoltaic performance has been maintained and improved in some devices. The open circuit voltage and fill factor were improved, owing to a successful joining of different effects i.e. increased light harvesting, facile electrolyte penetration and reduced charge recombination.

Keywords: Thin films, templating, soft, bimodal, TiO₂, DSSCs

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1. Introduction

There is an increasing demand in developing economical and efficient technologies for the direct exploitation of the solar energy for generating electricity, water splitting, and sustaining applications like photodegradation.^{1–6} Over the past few years, porous materials have attracted increasing interest due to their potential applications in the fields of catalysis, photovoltaic, adsorption and separation.⁷ Tremendous efforts have been made in the synthesis of ordered micro-, meso-, and macroporosity coexisting together.^{8–10} Hierarchically ordered materials with both mesoporous and macroporous structures are truly useful for a wide range of dye sensitized solar cells (DSSCs). The ordered mesopores provide high surface area for dye adsorption while interconnected macropores can act as channels for viscous electrolytes infiltration. TiO₂ is a widely studied material, because of its low cost, chemical stability and electronical properties such as photo-induced electronic transfer associated with the anatase phase.^{11–15} Anatase thin films have attracted considerable attention in past years, being mostly used in applications such as photovoltaic, photocatalysis, gas sensors etc.^{13,16–19} In all the previously mentioned applications, porosity plays an important role.

Often nano-structured TiO₂ has been used because of its high surface area and mesoporosity which are mainly determined by the grains size, shape, and crystallinity, and the structuring agent.²⁰ Hence, controlling the morphology, crystallinity and porosity of nano-structured TiO₂ has been explored in DSSCs applications.¹⁶ Although, power conversion efficiencies of around 13% were reached, stability and leakage of the liquid electrolyte are still an issue.^{21,22} A promising approach for making cost effective photovoltaic cells is to fill mesoporous TiO₂ films with organic semiconductors or polymer electrolytes.^{23–27} Porosity strongly influences the dye adsorption and the polymer electrolyte penetration, critical parameters in DSSC functioning.²⁸ In DSSCs, the bimodal structure having dual size porosity was shown to improve the efficiency of the solar cell.²⁹ Materials with dual porosity are thought to be advantageous over individual macroporous or mesoporous counterparts since they contain large pores along with high surface area.^{30,31} Dual porosity of TiO₂ has been employed by few research groups which have reported: high surface area, better pore infiltration, favorable light scattering effects, faster electron transfer and lower charge recombination.^{32–34}

The most commonly used surfactant is the P123 Pluronic ($(PEO_{20}-PPO_{70}-PEO_{20})$) triblock copolymer.^{35,36} However, the use of P123 as a template often generates small pore size (less than 10 nm) due to its low molecular weight. This does not allow for deep pore infiltration of

solid electrolytes. Therefore, hierarchical bimodal structures have recently attracted attention due to the synergistic advantages of the mesoporous and macroscale morphologies. For example, assemblies of both mesoporous TiO₂ particles (with diameters of several hundred nanometers) and nanostructured TiO₂ fibers have been applied in this view.^{37,38} A polystyrene beads based approach could be a simple, and effective alternative method of preparing multiscale porous TiO₂ structures.^{9,39} Since structures with large pores lack the high surface area, bimodal structures combining both small and large pores present very interesting prospects.^{29,40,41} The small pores provide the high surface area and large pore acts as channels for the viscous electrolyte penetration.

Yang et al. has first synthesized bimodal silica using the P123 and F127 surfactants and colloidal crystals as templates in various patterned micromolds.⁴² Until now, a very limited number of bimodal TiO₂ has been reported.^{43,44} Fu et al. first attempted to synthesize the bimodal TiO₂ film with Ti(OBu)₄ as Ti⁴⁺ source and P123 and colloidal crystals as dual templates. However, only ordered macropores TiO₂ with 205 nm in size were seen.⁴⁵ Recently, our group attained dual structures comprising macropores and mesopores of around 150 and 10 nm, respectively, which were prepared using polystyrene beads (PS) as hard templates and P123 surfactant as soft template.²⁹

Inspired by this, we attempted to synthesize a series of dually structured TiO_2 by using PS beads of various sizes, while keeping the P123 soft template. The obtained films are used in DSSCs comprising either liquid or polysiloxane based polymer electrolytes. The impact of such a unique hierarchical structure on dye loading, light scattering and consequently power conversion efficiency has been studied and discussed within this chapter. To the best of our knowledge, there have been no reports on bimodal TiO_2 electrodes tested in DSSC including polysiloxane based electrolytes. The TiO_2 films were prepared by spin-coating, and several replicates of the films have been studied in order to have a conclusive study. The performance of the DSSCs comprising the liquid reference electrolyte and the newly synthesized polysiloxane electrolytes with mono-and bimodal structured layers are comparatively studied.

2. Experimental Section

2.1. Materials and Chemicals

The P123 Pluronic ((PEO₂₀–PPO₇₀–PEO₂₀)) surfactant (molecular weight = 5800 g mol⁻¹), titanium tetraisopropoxide (TTIP) and 1-butanol were purchased from Sigma Aldrich. Hydrochloric acid was purchased from Acros Organic. FTO substrates (15 ohm/sq) were purchased from Dyesol. Polystyrene nanospheres (dia 62, 130 and 250 nm) that were originally dispersed in water at 10 wt% were purchased from Bang Laboratories, the USA. The N-719 dye and the polymer spacer SX-1170-25 (25 μ m thick) were purchased from Solaronix. Acetonitrile was purchased from ABCR GmbH and Co. The 3-methoxypropionitrile, 1-butyl-3-methylimidazolium iodide, iodine, guanidine thiocyanate, 4-tert-butylpyridine, valeronitrile were purchased from Sigma-Aldrich.

2.2. Mesoporous thin film synthesis (SOFT TiO₂ films)

The Pluronic surfactant P123 has been used as soft template according to the procedure described in the literature.⁴⁶⁻⁴⁸ The procedure was adapted from Henrist et al with slight modifications aiming at increasing the film thickness and homogeneity as obtained by spincoating.²⁹ The sol-gel precursor solution was prepared by mixing a solution of P123 (1.005 g) in 1-butanol (11.2 ml) with a solution of TTIP (3.96 g) in concentrated HCl (2.07 mL) and the solution was stirred for 2 h. For a single coating, 150 µl of the resulting mixed precursor solution is deposited by spin coating on the substrate for 2 s at 1930 rpm, 2 s at 2500 rpm and finally 30 s at 6900 rpm. The stabilization is performed by heating the fresh film during 30 min on a hot plate pre-heated at 300 °C. The partial condensation of the inorganic network and structure stabilization will occur during this step, which prevents the film dissolution during the next spin coating step. Solvent evaporation, as well as partial contraction of the film and pore merging also takes place during the stabilization step. When the desired number of layers is reached, the film is then calcined during 30 min at 500 °C with a heating rate of 1 ^oC min⁻¹. The calcination step is required to fully condense the inorganic network, crystallize anatase and burn out all the organic residues, leading to a porous structure. The terms "SOFT" and "mesoporous" are used for the photoanode synthesized by soft templating only (single pore size).

2.3. Bimodal thin film synthesis (DUAL TiO₂ films)

The templates are combined in a mixed precursor solution: the widely studied P123 surfactant and 62, 130 and 250 nm PS nanospheres. To avoid uncontrolled hydrolysis of the TTIP, the water from the commercial nanospheres suspensions was evaporated by using freeze-drying at

very low temperature. Anhydrous PS beads were then re-dispersed in 1-butanol under ultrasound sonication giving a suspension concentration of 10 wt%.

Figure 1 shows the SEM images of the 130 nm PS beads. It can be seen that dried PS beads can retain their original structure after freeze drying process.



Figure 1- SEM images of the 130 nm PS beads A) as-purchased (dispersed in water) and B) after freeze-drying.

The PS suspension is mixed to the previously synthesized sol-precursor (section 2.2) in a 1.5:1 volume ratio and stirred for 1 hour prior to deposition. For a single coating, 150 μ l of the precursor solution is dropped on the FTO glass and spin-coated for 2 s at 1930 rpm, 2 s at 2500 rpm and finally 30 s at 6900 rpm. The stabilization is performed by heating the fresh film during 30 min on a hot plate pre-heated at 150 °C in case of dual templating. When the desired number of layers is reached, the film is calcined during 30 min at 500 °C at very slow heating ramp (1 °C min⁻¹). The labels DUAL-62, DUAL-130 and DUAL-250 were used for the films synthesized with PS beads of 62, 130 and 250 nm, respectively. It is to note that different thicknesses were obtained for the soft and dual templated layers. Films produced by dual templating are relatively thicker compared to films produced by soft templating due to extra porosity. The terms "DUAL" and "bimodal" are used to designate samples containing the two populations of pores resulting from such dual templating route.

2.4. Preparation of polymer electrolyte

Polysiloxane based poly(ionic)liquid (PIL), PDMS2Im⁺I⁻ (also referred as P2) were synthesized as explained in the Chapter *II* and reported in our recent published work.⁴⁹ For the sake of comparison, a reference liquid electrolyte solution was prepared with the following

composition: 0.6 M 1-butyl-3-methylimidazolium iodide, 0.03 M iodine, 0.1 M guanidine thiocyanate and 0.5 M 4-tert-butylpyridine in acetonitrile/valeronitrile (85/15, v/v).⁵⁰

2.5. Solar cell fabrication

A TiCl₄ treatment of the synthesized soft and dual TiO₂ photoanodes was performed by immersing the layers into a 0.04 M TiCl₄ aqueous solution for 30 min at 60 °C. After that, the electrodes were washed with deionized water and ethanol to remove residual TiCl₄, and then sintered at 450 °C in air for 30 min. Freshly sintered photoanodes were immersed in a 2.7×10^{-4} M solution of N719 dye ethanolic solution for overnight. The dye-impregnated photoanode was rinsed in anhydrous ethanol and assembled with a Pt counter-electrode in a sandwich configuration. The electrodes were separated by applying a polymer spacer under spring pressure and heating at 100 °C for 30 mins. The Pt counter electrode was deposited on the FTO glass by drop-casting of a H₂PtCl₆ solution followed by heat treatment at 450 °C for 30 min. The liquid or polymer electrolytes were introduced into the cell by vacuum back filling in a hole drilled in the Pt coated FTO electrode. Prior to sealing, the volatile solvent has been removed by heating the cell at 100 °C for 15 min on the hot plate, followed by vacuum drying overnight. The hole was firmly sealed with a piece of polymer spacer and a microscope cover glass.

2.6. Characterization Techniques

X-ray Diffractometry (XRD) was performed on a D8 diffractometer (Bruker) working in grazing incidence (CuK α). We used scanning electron microscopy (SEM) to estimate the thickness and surface morphology of the TiO₂ photoanode. The samples were sputtered with gold before being observed at 15 kV in a FEG-SEM (XL30, FEI). The porosity of films has been checked by transmission electron microscopy (TEM) on a Tecnai G2 TWIN (FEI) working at 200 kV. The topography of the samples was also examined by atomic force microscopy (AFM) under ambient conditions using a Digital Instruments Nanoscope III microscope (Veeco). The dye loading was measured by UV-vis spectroscopy in 1 mM KOH solution with a Perkin Elmer UV-vis Spectrometer Lambda 14P. The film area was precisely determined by image analysis (GIMP2 software). The film was soaked in dye solution during one night at room temperature. After rinsing and drying, it was dipped in a known volume of KOH solution for 1 h. A calibration curve was used to calculate the experimental extinction coefficients of N719 dye, which is 12900 (mol/L)⁻¹ cm⁻¹ at 500 nm. The dye loading of the films was then determined from the desorption solutions. Photovoltaic performances have been evaluated by solar simulator purchased from Newport Spectra Physics coupled with a

Keithley 2400 SourceMeter. Photocurrent-voltage curves were measured under simulated 0.7 SUN illumination (filter AM 1.5). The electrode active area was set to 0.145 cm² with a mask. Reflectance and transmittance of the photoanodes were done on Shimadzu 1600, UV-VIS-NIR spectrometer. The Incident Photon to Charge Carrier Efficiency (IPCE) data were collected from 300 to 800 nm using a Xe lamp associated with a monochromator (Triax 180, JobinYvon). No bias light was employed to illuminate the cell. The current produced was measured by steps of 2 nm after 2 s of radiation exposure with a Keithley 6487 picoampmeter in order to be in steady state conditions. The incident photon flux was measured with a 6-in. diameter calibrated integrated sphere (Labsphere) and a silicon detector.

3. Result and Discussion

3.1. Micro-structural characterization of TiO_2 films



Figure 2- Mechanism of formation of mesoporous ("SOFT") and bimodal ("DUAL") TiO₂ films.

The figure 2 illustrates the experimental procedure for fabricating the TiO_2 films used in this study. First, the use of P123 produces small pores after calcination, which consequently leads to high density packed mesoporous structure. Secondly, the use of larger PS beads helps to generate large pores. After TiO_2 PS beads calcination, a bimodal structure having dual porosity was successfully obtained and thicker films are finally prepared. Compared to the original sizes of the PS microspheres, the diameters of the spherical voids were reduced by 40-50%.

We synthesized four types of samples: SOFT samples, which contain only the P123 surfactant and DUAL-62, DUAL-130 and DUAL-250 samples which contain P123 as soft template and PS beads of 62, 130 and 250 nm, respectively as hard templates. Figure 3(A–D) shows the SEM images of the as-fabricated mesoporous and bimodal structured TiO₂ layers after the removal of PS templates. It was observed that the pores left after PS beads removal were smaller than the original PS beads that served as the templates. From the top view, it can be seen that the TiO₂ film forms interconnected three dimensional structures with defects being more and more present with increasing PS beads size, due to the thermal contraction of the TiO₂ network.



Figure 3- SEM images of TiO₂ films: A) SOFT, B) DUAL-62, C) DUAL-130, and D) DUAL-250.

AFM studies complement the results obtained from SEM images, allowing for a threedimensional nanoscale imaging and roughness measurements. Spherical large pores are clearly seen on samples DUAL-130 and DUAL-250 confirming the influence of PS templating (figure 4C-D). On sample DUAL-62, since the pore size is so close to the particle size, circular arrangements of 5-6 particles defining a space of around 30 nm in diameter in the between can be observed (some of the pores are represented by green dotted circle in



figure 4B). Figure 4 also shows that the porosity and roughness increase with the PS bead size.

Figure 4- AFM images of TiO₂ films (A) SOFT, (B) DUAL-62, (C) DUAL-130 and (D) DUAL-250.

Figure 5 shows the XRD patterns of mesoporous TiO₂ films deposited on FTO substrate after calcination at 500 °C. The main peak at $2\theta = 25.3^{\circ}$ corresponds to the (101) reflection of anatase phase (tetragonal, *I* 41/ amd, JCPDS 78-2486) and is identified in all the samples.



Figure 5- XRD of soft and dual templated TiO₂ layers coated on FTO substrate calcined at 500 °C.

Soft templated film have a stronger (101) anatase peak than the dual template films which is correlated to higher density of TiO_2 layer. This translates different preferential orientation of crystallites during the development of the structure upon calcination.

Under TEM observation (figure 6), detailed morphological structures and porosity can be seen. The TiO₂ framework was comprised of 8-10 nm pores for all the samples due to P123 templating.⁵¹ TEM imaging confirms the coexistence of macroporosity and mesoporosity in DUAL-130 and DUAL-250 samples; however, it is not so clear for sample DUAL-62. DUAL-250 film exhibits a clear hexagonal packing of macropores.



Figure 6- TEM images of A) SOFT, B) DUAL-62, C) DUAL-130 and D) DUAL-250 TiO₂ layers.

As expected, removal of PS nanospheres by calcination leads to pores with a diameter 40-50% smaller than the original bead size.^{52,53} Therefore, macropores of about 30-40 nm, 60-70 nm, 150-160 nm are obtained in case of samples DUAL-62, DUAL-130 and DUAL-250, respectively. The larger pore size open new possibilities for the use of polymer electrolytes, which can be easier infiltrated into the network. At the same time the small pores provide a high surface area, making the films promising for applications in photovoltaic.

For the preparation of thicker films, the complete spin-coating procedure of film formation was repeated. The evolution of film thickness for SOFT and DUAL-130 is shown in the figure 7A. The evolution of film thickness follows a linear trend. Not surprisingly, films produced by large PS templates are relatively thicker than films produced by soft or smaller PS templates due to extra porosity provided by PS beads (figure 7B).⁵⁴



Figure 7- Evolution of films thickness (A) as function of the number of layers for SOFT and DUAL-130 and (B) as a function of the templating agents (3 layers each).

A known method to improve the performance of the solar cells is a post-TiCl₄ treatment of the TiO₂ film in which an extra layer of TiO₂ is grown onto the TiO₂ nanoparticles constituting the film. Different explanations of the working principle of this coating have been reported. These hypotheses cover increased surface area, improved electron transport, light scattering and dye anchoring.^{55–57} The TiCl₄ procedure was reported not to influence the layer thickness with all changes taking place inside the film.⁵⁸ Indeed, the SEM and TEM imaging (figure 8 A-D) showed no visible morphological changes post TiCl₄ treatment when comparing with non-treated films (figures 3A, 3C, 6A and 6C).



Figure 8- SEM and TEM images of SOFT (A and C) and DUAL-130 (B and D) photoelectrodes after TiCl₄ treatment.

As shown by the figure 9A, TiCl₄ treated DUAL-130 films shows a slightly increased dye adsorption due to an increase of the TiO₂ surface area compared to the non-treated electrodes.⁵⁵ Presumably, the TiO₂ surface after the TiCl₄ treatment provides more specific binding sites and hence improves the photovoltaic performance.⁵⁹ We performed dye desorption experiment to quantify the amount of dye uptake in each films. Figure 9B shows the calculated dye adsorption for all the TiO₂ samples with respect to number of layers. The dual templated TiO₂ adsorbs less dye due to expected lowered surface area. The more the diameter of the PS beads increased, the lower the amount of dye molecule adsorbed on the TiO₂ surface. It has been reported that the post TiCl₄ treatment leads to increase in photovoltaic performance by increasing the photocurrent.^{28,60,61} Therefore, all the photoanodes for DSSCs were subjected to post-TiCl₄ in the present study.



Figure 9- Dye loading expressed in moles of N719 dye per mm^2 of the projected electrode area as a function of the number of layers for DUAL-130 with and without TiCl₄ treatment (A) and of the different TiO₂ samples subjected to TiCl₄ post treatment (B).

3.2. Scattering properties

Diffuse reflectance and total transmittance of hierarchically structured porous TiO₂ layers with and without adsorbed dye were measured using a UV-Vis spectrophotometer. The light scattering is an important factor that influences the performance of DSSCs. It is known that the ideal photoanode should have a higher diffuse reflectance and lower transmittance. Hore et al have demonstrated a method proving that the spherical voids (pores) can also be employed as light-scattering centers.⁶² Mie theory, the optimal sizes of the pores were determined to be in the range of 50–100 nm, giving rise to the most intensive light scattering.⁶³

The diffuse reflectance of the bare porous TiO_2 layers varies in the order SOFT<DUAL-62 < DUAL-130< DUAL-250 in the 450–800 nm wavelength range (figure 10A). As expected, all the dual templated samples have significantly lower transmittance compared to the SOFT samples (figure 10B). However, interestingly the reflectance of DUAL-62 is weaker than that of DUAL-130 in the range of 480–800 nm. This result may be related to layer homogeneity. Additionally, the diffuse reflectance and transmission of dye-adsorbed porous TiO_2 films has been measured and spectra are shown in figure 10(C and D). The transmittance spectra of the SOFT and DUAL dye loaded TiO_2 samples exhibit the same trend as for non dye loaded sample, with however lower transmittance values due to dye adsorption. The optical properties of mesoporous and bimodal TiO_2 films are better differentiated after dye loading (figure 10C) with reflectance increasing with increasing pores.



Figure 10- Diffuse reflectance and direct transmittance of porous TiO₂ layers, before (A and B) and after (C and D) N-719 sensitization.

3.3. Photovoltaic performance

The soft and dual templated films (3 layers each) were incorporated in DSSCs with liquid and polymer electrolytes. The photovoltaic parameters of the DSSCs with liquid and P2 polymer electrolyte are summarized in Table 1, and the corresponding photocurrent-density curves under ~ 0.7 suns are shown in figure 11A-B. From the table 1 it is evident that the porosity has a significant effect on the device performance. As a general trend, the porous structure exerts very low influence on the V_{oc} since all values lay within the same range (0.76 -0.79 V for liquid electrolyte and 0.62 -0.66 V for polymer electrolyte). An increase of J_{sc} is observed for the SR-0 device (SOFT + liquid electrolyte) which is correlated to the high surface area available for dye loading. The highest efficiency with liquid electrolyte is also obtained for this sample. The DUAL-130 TiO₂ layers seems to have the optimum structure in the case of polymer electrolytes, that favors both dye uptake (with electron injection from the dye to the TiO₂ layer giving a high J_{sc}) and efficient polymer electrolyte penetration within the TiO₂

layer. When the size of the PS beads is increased, the specific surface area is considerably reduced, explaining why for device DR-250 (DUAL-250 + liquid electrolyte), we obtain the lowest J_{sc} and efficiency, even if high V_{oc} and FF are obtained.

Photoanode	Dye loading (mol mm ⁻²)×10 ⁻¹¹	Electrolyte	Device Code	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	η (%)
SOFT	13.96	liquid	SR-0	2.25	0.76	62	1.58
		P2	SP-0	0.81	0.62	56	0.42
DUAL-62	13.09	liquid	DR-62	1.95	0.75	63	1.38
		P2	DP-62	1.02	0.62	59	0.55
DUAL-130	12.36	liquid	DR-130	2.02	0.79	60	1.44
		P2	DP-130	1.61	0.64	58	0.89
DUAL-250	11.04	liquid	DR-250	1.56	0.79	68	1.25
		P2	DP-250	1.38	0.66	55	0.75

Table 1- Photovoltaic performances TiO_2 films (3 layers each) prepared by soft and dual templating with liquid electrolyte (reference) and polymer electrolyte (P2) at 25 °C.

When the polymer electrolyte is used, lower efficiencies are obtained due to the lower diffusion rate compared to liquid electrolytes. However, for the larger PS beads (250 nm) the performance is lower indicating that the DUAL-130 photoanode is the optimum structure. The J_{sc} is improved with increasing the porosity (with overall lower values compared to liquid electrolytes) due to better pore infiltration, and most importantly due to increased light trapping inside the large pores. Furthermore, the large pores enhance the mass transport of triiodide in the viscous polymer, resulting in a decrease of the diffusion resistance and hence the increase of fill factor of the DP-62 and DP-130 devices. Interestingly for the DSSC containing 130 nm PS beads, despite the smaller surface area and lower dye loading, the photocurrent of the dual templated cell exceeds that of soft templated cell in presence of polymer dye loading, resulting in a slight enhancement of J_{sc} . Thus, in the current study we manage to get higher efficiency despite having lower dye uptake.

3.4. Incident-Photon-to Current Efficiency (IPCE)

IPCE was measured (figure 11C) to show the effect of light scattering on the device DSSCs based on SOFT and DUAL-130 TiO₂ photoanodes with polymer (P2) electrolyte (SP-0 and DP-130, respectively). The greater scattering properties of the dual template films are attributed to the size-distributed locally ordered structure comprising mesopores and macropores. The J_{sc} value also depends on the dye loading which is influenced by the surface area. The DUAL-130 based DSSC with polymer electrolyte (DP-130) showed higher J_{sc} value than the SOFT based DSSC (SP-0) and consequently, higher incident photon-to-current efficiency as shown in figure 11C. Furthermore, figure 11D shows a comparison of cell performance as function of pore size. As far as dual templating is concerned, the DP-130 devices show better performance with both liquid and polymer electrolytes, indicating the bimodal structured DUAL-130 TiO₂ photoanode as optimum.



Figure 11- J-V curves of DSSC devices based on different TiO_2 samples with (A) liquid and (B) polymer (P2) electrolyte, (C) IPCE of devices SP-0 and DP-130, and (D) evolution of efficiency for DSSCs with increasing pore size for liquid (black) and polymer (blue) electrolytes.

3.5. Pore infiltration

To prove that dye still allows filling of the whole bimodal layer, the SEM images of the DUAL-130 layer before and after filling with P2 electrolyte were compared (figure 12). The polymer fills the entire thickness of the sensitized film. Bare TiO_2 nanocrystals can be observed in figure 12A, while the filling with polysiloxane smoothens the edges of the crystals as observed in figure 12B proving the P2 electrolyte deep infiltration throughout all the layer thickness.



Figure 12- Cross-section SEM image of bare DUAL-130 photoanode (A) and of DUAL-130 layer filled with polymer P2, (B) after breaking the corresponing cell.

4. Conclusion

We have synthesized bimodal TiO₂ photoanodes with different macropores size by using PS beads with different sizes (62, 130 and 250 nm). The bimodal films exhibited good light harvesting properties due to the increased scattering effect inside the large pores. However, increasing the pores size resulted in a lower surface area and reduced dye loading. When considering the devices with small pores (SOFT and DUAL-62 photoanodes), the performance of DSSCs containing polymer electrolyte was lower than the DSSCs containing liquid electrolyte. However, this trend is inversed for large porosity. Although the amount of dye loaded on bimodal TiO₂ films was smaller, the power conversion efficiency was still maintained and even improved with respect to soft TiO₂ photoanodes for the same electrolyte. Among the dual templated photoanodes, the DUAL-130 gave the highest performance when tested with liquid and polymer electrolyte (P2) in DSSCs representing the best compromise between the decrease of dye loading and the improvement of the photon harvesting due to light scattering. The DUAL-130 photoanode will be further used to optimize the performance of DSSC as function of the P2 electrolyte composition (viscosity tuning by adding ionic liquids (ILs)) in chapter VI.

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CHAPTER-V

Effect of thin TiO₂ blocking layer on the performance of dye sensitized solar cells with poly(ionic)liquid electrolytes

Abstract

The deposition of a thin, blocking layer (BL) of TiO₂ on the conductive glass substrate in a DSSC prevents short-circuits by blocking the transfer of electrons between the electrolyte and the conductive substrate and thus enhances the device performance. In this chapter, the conventional spin-coating, using an alcoholic acetyleacetone-titanium-tetraisopropoxide precursor solution were used for TiO₂ layers coating and the final properties were compared. We demonstrate that a thin spin-coated blocking layer can reduce the electron recombination in the dye-sensitized solar cells (DSSCs) optimized in Chapter *IV* containing the DUAL-130 TiO₂ photoanode. For the first time, we demonstrate the influence of the BL on the performance of on DSSCs comprising polysiloxane polymer electrolytes. Electrochemical impedance spectroscopy (EIS) confirms that the resistance at the FTO/electrolyte interface slightly increases once the spin coated BL is applied onto the porous TiO₂ layer resulting in improved photovoltaic performance due to reduced electron recombination and reduced charge transfer resistance.

Keywords: Spin-coating, TiO₂ blocking layer (BL)

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1. Introduction

Dye sensitized solar cells (DSSCs) are regarded as promising next-generation alternatives to conventional silicon based solar cells due to their lower manufacturing cost and environmentally friendly characteristics.¹ The working photoelectrode of a DSSC is generally formed by a fluorine-doped tin oxide (FTO) glass substrate covered with a dye-adsorbed nanoporous TiO_2 film^{1,2}, while the counter electrode can be platinized FTO glass³, graphene⁴ or carbon⁵. Finally, the space between the two electrodes is filled with a redox electrolyte. Electron recombination process is one of the limiting factors of the performances of a DSSC that takes place at the FTO and electrolyte interface.⁶ Because of the porous nature of the TiO₂ layer, the FTO surface cannot be insulated from the electrolyte.

It has been demonstrated that a thin dense blocking layer (BL) of TiO₂ prevents these efficiency losses by inhibiting the contact between the FTO and the electrolyte.⁷ Besides the blocking effect, the higher density of the BL can provide more electron pathways from the photoelectrodes to the FTO substrate for photogenerated electrons.^{8,9} It has been reported that the crystalline nature of the BL also has a profound effect on the performance of the DSSC by forming an energy barrier that suppresses electron recombination from the FTO to the electrolyte.^{10,11} The importance of BL has been studied and some potential material has been suggested.^{12–15} In addition to TiO₂, other materials such as SnO₂¹⁶, MgO¹⁷, ZnO¹⁸, Nb₂O₅¹⁹ and calcium and barium carbonates^{20,21} are also known to be effective as a BL. However, these materials involve complicated fabrication processes; thus, TiO₂ is the most widely used material.

An ideal BL should completely cover the relatively rough FTO surface and its thickness must not exceed certain values in order to prevent the layer from acting as a charge trap.²² Kim et al reported a range of BL thicknesses of 25 to 400 nm as being effective.²³ This wide range is normally affected by the method and conditions used for depositing the films. Various methods have been used to deposit the TiO₂ BL, such as sputtering²⁴, screen-printing²⁵, atomic layer deposition²⁶, and spray pyrolysis²⁷. Spin-coating is probably the easiest of all when it comes to lab scale processing.^{28,29}

In this chapter, the preparation and characterization of thin TiO_2 blocking layer fabricated by spin-coating is presented. Alcoholic acetyleacetone-titanium tetraisopropoxide (TTIP) solution is used as starting material due to its good stability, low viscosity and good adherence on the FTO

substrates.^{30,31} The process parameters were optimized in order to obtain a blocking layer with appropriate homogeneity, density and thickness. Structural, morphological, optical and electrochemical performances of the resulting TiO₂ BLs were investigated using different characterization techniques. EIS was used as a tool to investigate the influence of the presence/absence of BL on the charge transfer resistance at the FTO/electrolyte and TiO₂/FTO interfaces, by characterizing the bare FTO and BL coated FTO. The performances of the DSSCs containing the DUAL-130 photoelectrode with and without blocking layer were compared. Finally, we confirmed that the blocking layer effectively improved the photoconversion efficiency of the DSSCs.

2. Experimental section

2.1. Materials

Titanium tetraisopropoxide (TTIP, Aldrich), acetylacetone (AcAc, Aldrich), and ethanol, acetone and isoporopanol were used without further purification. The water was purified using a Milli-Q water treatment system. The FTO (2.2 mm thick, TEC-15) substrates were purchased from Solaronix.

2.2. Preparation of the Ti⁴⁺ precursor

1.46 ml of AcAc was added drop-wise to 2.195 ml of TTIP under constant stirring and then 30 ml of anhydrous ethanol were added to the above solution. The resulting solution was filtered and stored in the refrigerator.

2.3. Preparation of substrates

FTO substrates were cleaned by sequential sonication in commercial detergent and DI-water, acetone and isopropanol for 10 minutes. TiO_2 layer was deposited onto clean FTO substrate using spin-coating and USP method as described in the following sections.

2.4. Spin-coating parameters

The titanium oxide BL is deposited on FTO substrates with a spin-coater (Specialty Coating Systems, Inc. Model P6700 series). Nearly 200 μ l of the solution is spin-coated dynamically at 2000 RPM for 60 s in ambient room conditions. The deposited single layer was stabilized for 10

min at 150 °C on a hot-plate, followed by calcination at 500 °C. The obtained blocking layers are called BL-2000. Similarly, BL-6000 films were dynamically spin-coated at 6000 RPM for 60s.

2.5. Bimodal TiO₂ thin film synthesis (DUAL-130)

The dual templated film (combined in a mixed precursor solution: P123 surfactant and 130 nm PS nanospheres) was deposited on both the thermally stabilized blocking layer (BL) and FTO as optimized in Chapter *IV*. The term DUAL-3L is used for 3 layers of porous film.

2.6. Fabrication of electrolytes and devices

The synthesis of liquid and polymer (P2) electrolytes, and device fabrication was already described in the Chapters *II* and *III*.

2.7. Characterization Techniques

The films deposited on glass/FTO substrates were characterized by X-ray diffraction with a Bruker D8 grazing incidence diffractometer (CuKa radiation, incidence angle of 0.5). The morphology and the relative amount of Ti in the films was studied by SEM microscopy (FEG-ESEM XL30, 15 kV, FEI and EDX spectrometer, Bruker). The relative amount of Ti in the films was extracted from their X-ray emission spectrum. More specifically, the intensity of Ti peak was recorded and compared to a pure Ti standard to calculate the so-called "k-ratio" of Ti atom in the films and the quantified thickness were compared with the one obtained with SEM. The morphology of the samples was examined by atomic force microscopy (AFM) under ambient conditions using a Digital Instrument Nanoscope III microscope (Veeco). The image acquisition was performed in tapping mode with a super sharp improved super cone tip (Team Nanotec, tip diameter 5 nm). The thickness of the blocking layer was estimated by SEM cross-section analysis with the FEG- ESEM XL30. The sheet resistance of the bare FTO was measured by Phys Tech, RH2035 Hallsystem (four-point probe method), while two point probe was used for the blocking layers. The dye-loading procedure and evaluation were previously described in Chapter IV, Section 2.6. The photocurrent-voltage (J-V) characteristics of the DSSCs were measured by a solar simulator purchased from Newport Spectra Physics coupled with a Keithley 2400 Source Meter under a simulated Air Mass 1.5 G solar spectrum with an aperture mask of 0.145 cm². The irradiance of the source was around 0.7 sun. The Incident Photon to Charge Carrier Efficiency (IPCE) data were collected from 350 to 800 nm using a Xe lamp associated with a monochromator (Triax 180, JobinYvon). The electrochemical analysis of the bare FTO and BL-

2000 coated FTO films was realized in a three-electrode configuration (WE- the photoelectrode, CE – Pt, RE – Ag/AgCl in 3M KCl saturated with AgCl) using a BioLogic SP-200 potentiostat (Science Instrument) and 0.1 M LiClO₄ in PC as electrolyte. The impedance measurements were carried out at 0V, in the 100 kHz – 1.0 Hz frequency range at 10 mV signal amplitude without light illumination. The system was stabilized for 5 min at open circuit potential.

3. Results and discussion

3.1. Stability of the Ti⁴⁺ precursor

Figure 1 shows the photographs of the fresh and 72 hours aged AcAc-TTIP alcoholic solutions. The solution appears to be clear with no trace of precipitation. The stability of the precursor solution is very important in order to have better reproducibility of the TiO_2 blocking layer.³²



Figure 1- Ti⁴⁺precursor solution, just prepared (A) and after 72 hours storing (B).

3.2. Properties of TiO₂ blocking layers

Figure 2 shows the XRD patterns of the bare FTO substrate and spin-coated TiO₂ blocking layers (BL-2000 and BL-6000) after annealing at 500 °C. The FTO peak intensity decreases confirming the deposition of the TiO₂ film. However, no characteristic peak of the TiO₂ is observed, due to the low thickness and/or lack of crystallinity of the deposited layers and strong contribution to the XRD signals from the highly crystalline FTO. After depositing BL, there is little shift from the peak from 25.65° to 25.4°, suggesting the anatase phase of TiO₂ (101) is being formed (JCPDS



89-4921). Indeed, the detection limit of a thin, crystalline layer is around 50 nm with the system used.

Figure 2- XRD patterns of the bare FTO substrate and BL spin-coated FTO after annealing at 500 °C.

The morphology of the blocking layers on FTO substrates was investigated by SEM. As shown in figure 3A, the bare FTO has a rough surface being composed of grains with irregular shapes and sizes ranging from tens to hundreds of nanometers. As shown in figures 3B and C, the structure of spin-coated TiO₂ blocking (samples of BL-2000 and BL-6000) are homogeneous and continuous with no visually observable defects, indicating a satisfactory surface coverage. The cross-section SEM of sample BL-2000 (figure 3A) shows the good contact of the TiO₂ layer with the FTO surface. The cross-section also reveals that the film is compact and with regular thicknesses. The thickness of the TiO₂ blocking layers deposited by spin-coating was corroborated with the ones estimated from EDX detection as shown in Table 1.



Figure 3- SEM images of (A) bare FTO substrate and calcined TiO_2 blocking layer deposited by spincoating at 6000 rpm (sample BL-6000) (B), and at 2000 rpm (sample BL-2000) (C). Cross-sectional SEM images of the TiO_2 blocking layers obtained by spin-coated sample BL-2000 (B). TiO_2 layer thickness is indicated on the figure.

The sheet resistance of bare FTO substrate is about 12 Ω sq⁻¹. However, the sheet resistance after depositing the TiO₂ blocking layers on FTO was increased confirming the layer deposition.

Sample	Thickness from SEM (nm)	Thickness from K-ratio (nm)	Sheet resistance
Bare FTO	-	-	$12.3\pm0.1~\Omega$
BL-6000	40 ± 10	45 ± 15	$244\pm20\;k\Omega$
BL-2000	75 ± 12	60 ± 18	$268\pm 30\;k\Omega$

Table 1- TiO₂ BL thickness obtained by different methods and sheet resistance.

Atomic force microscope (AFM) images in figure 4 indicates that the root-mean-square roughness (R_{rms}) of bare FTO surface was diminished from 18.4 nm to 11 and 8.0 nm after coating with the BL-6000 and the BL-2000 TiO₂ layers, following calcination. The surface
roughness is one of the important factors that influence optical properties and also the quality of interfaces in case of multilayers.



Figure 4- AFM images of (A) bare FTO (5×5 μ m²), (B) TiO₂ BL deposited by spin coating at 6000 rpm (sample BL-6000, 2×2 μ m²), and (C) at 2000 rpm (sample BL-2000 for 5×5 μ m²) and (D) zoomed BL-2000 (1×1 μ m²).

3.3. Investigation of charge transport properties

Electrochemical impedance spectroscopy (EIS) is very effective for studying the mechanism and kinetics of complicated electrode reaction.^{33–36} An equivalent circuit is proposed to describe the charge transfer at semiconductor/electrolyte interface. We have studied the effect of the BLs coating over the FTO substrate in the absence of a TiO₂ mesoporous film and dye. The electrochemical analysis of the films was realized in a three-electrode configuration cell as described in the sub-section 2.7. The Nyquist plots of BL-2000 and FTO layers are presented in figure 5. In both cases a half semicircle is observed in the high frequency range which is attributed mainly to the FTO/electrolyte interface. An extra contribution from the FTO/TiO₂ interface is expected in the high frequency range in case of TiO₂ coated FTO layers testing. The

second contribution in the mid-frequency range of sample BL-2000 coated FTO is attributed to the charge transfer at the TiO_2 /electrolyte interface. The corresponding reaction is:

$$Li^+ + TiO_2 + xe^- \rightarrow Li_xTiO_2$$
 (1)

This second contribution is also visible in the Bode plot of sample BL-2000 (figure 5C) with a distinct higher relaxation time which can be thus described by an R/C circuit.



Figure 5- A) Nyquist plots for the bare and BL-2000 coated FTO substrate in the frequency range 0.1 Hz – 500 kHz. The fit in the lower frequency range is shown for both samples, B) Zoom in the higher frequency range showing how the fit was done and C) The Bode plot for bare and BL-2000 coated FTO.



Figure 6- Equivalent circuit of used for the fitting of the EIS spectra for BL-2000 blocking layer.

Figure 6 shows the circuit used for fitting in which, R_s is the series resistance comprising essentially the electrolyte contribution and additionally wires and crocodile/sample contact, $R_1//Q_1$ cumulates the contributions of FTO/electrolyte and TiO₂/FTO interfaces, and $R_2//Q_2$ represents the resistance and capacitance of the double layer formed at the TiO₂/electrolyte interface. The values of the fitted circuit elements are summarized in the Table 2.

Table 2- TiO₂ BL thickness obtained by different methods and sheet resistance.

Sample	R _{TiO2/FTO}	Rs	R ₁	Q1	R ₂	Q ₂	X(10 ⁻³)
		(Ω)	(Ω)	$(\Omega.cm^2.s^{-(1-a)})$	(kΩ)	$(\Omega.cm^2.s^{-(1-a)})$	
FTO	-	580	810	1.4×10^{-9}	-	6.6×10 ⁻⁶	2.2
				a = 0.99		a = 0.95	
BL-2000	270	500	1090	1.4×10^{-9}	60	6.2×10 ⁻⁶	3.7
(BL)				a = 0.92		a = 0.92	

X is a term that describes the quality of fitting. $R_{TiO2/FTO}$ was determined by calculating the difference of the R_1 values.

It is important to notice that the R_1 value increases with respect to bare FTO due to the addition of the TiO₂/FTO contact resistance, which value was obtained by the subtraction of the two R_1 values (see Table 2). The addition of the BL-2000 on FTO modifies the low frequency response with the appearance behaviour of transfer reaction instead of blocking behaviour (equation 1). This proves that the Li⁺ penetration into TiO₂ is easier compared to the bare FTO electrode which is acting as a quasi-blocking layer.

3.4. Photovoltaic properties

The introduction of TiO₂ BL has been claimed to improve the performance of solar cell devices by decreasing the electron-hole recombination at substrate/electrolyte interface and an enhancement in the electronic contact between the porous TiO_2 network and the charge collecting electrode.²⁶ To study the effect of blocking layer, the photovoltaic response (J-V curves) of the four DSSCs comprising bare FTO and BL-2000 substrates with liquid and polymer electrolytes were measured under ~ 0.7 sun as shown in figure 7A-B. Short circuit current density (J_{sc}) , opencircuit voltage (V_{oc}), fill factor (FF) and overall power conversion efficiency (η) of the DSSCs are listed in Table 3. The measured photovoltaic performances (J_{sc}, η) of the liquid-DSSCs with bare FTO and BL-2000 photoanodes are (2.02 mA cm⁻², 1.44%) and (2.18 mA cm⁻², 1.55%), respectively which can be attributed to the suppression of parasitic charge transfer between FTO and electrolyte by BL, as proved by EIS measurements.³⁷ Similarly, the polymer electrolyte based-DSSCs with bare FTO and BL-2000 photoanodes show (1.61 mA cm⁻², 0.89%) and (1.89 mA cm⁻², 1.12%), respectively. The slight increment of both J_{sc} and η by introducing the BL-2000 TiO₂ blocking layer is justified by the retardation of unfavourable charge recombination process with redox species^{38,39}, but also by the increased dye loading. Other minor contributions to solar cell performance have been attributed to changes in series resistance associated to BL thickness which modifies the fill factor.



Figure 7- J-V curves of DSSCs based on FTO and blocking layer (BL-2000), comprising liquid (A) and polymer (P2) (B) electrolytes.

Electrolytes	Blocking	Dye loading	J _{sc}	Voc	FF	ղ
	layer	$(mol mm^{-2}) \times 10^{-11}$	$(\mathbf{mA} \ \mathbf{cm}^{-2})$	(V)		(%)
Liquid	-	12.36	2.02	0.79	60	1.44
Liquid	BL-2000	12.64	2.18	0.78	61	1.55
P2	-	12.36	1.61	0.64	58	0.89
P2	BL-2000	12.64	1.89	0.65	61	1.12

Table 3-: Photovoltaic performances of DSSC comprising the DUAL-130 (3 layers) with and without BL-2000 with liquid (reference) and polymer electrolyte (P2) at 25 °C.

Figure 8 shows the IPCE of DSSCs with and without BL-2000 blocking layer in the 350 nm and 800 nm wavelength range. It is clearly shown that the DSSC with a TiO_2 blocking layer (BL-2000) has a higher IPCE as compared to the DSSC without BL. The significant improvement in IPCE proves that the BL-2000 blocking layer increases the sunlight conversion in the visible wavelength range and thus the DSSC efficiency. This positive effect is due to the reduced parasitic reactions at the electrolyte/FTO interface, but also due to the increased dye loading.



Figure 8- IPCE of DSSCs based on DUAL-130 photoanodes with polymer electrolyte with and without BL-2000 blocking layer.

4. Conclusion

In conclusion, we demonstrated an efficient way to deposit dense, homogenous and thin blocking layer of TiO_2 for DSSCs application. A 70 nm thick TiO_2 blocking layer is obtained by spincoating the TTIP precursor. The blocking layer coating reduced the charge recombination and charge transfer resistance and increased dye loading thus improving the DSSCs photovoltaic performances. The optimized BL (BL-2000) will be utilized in all the photoanodes in the next chapter (chapter *VI*).

5. References

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CHAPTER-VI

Quasi-solid state dye-sensitized solar cells: influence of polymer electrolyte viscosity, photoanode thickness and porosity

Abstract

In this chapter, poly(ionic liquid) (PILs) electrolytes infiltration into mesoporous and bimodal TiO₂ thin films with different thickness will be discussed and the DSSC performance will be investigated. Four different PILs with various viscosities were tested. The mesoporous and bimodal TiO_2 films have been synthesized via a spin coating technique. The as-synthesized mesoporous films exhibit small mesopores of 8-10 nm formed by the P123 soft template removal exhibiting high surface area. The as-synthesized dual (soft/hard) templated films have unique bimodal porous structures comprising 8-10 nm mesopores and 60-70 nm macropores given by the P123 and PS templates, respectively. The SEM, AFM and TEM analysis of TiO₂ films revealed a mixture of mesoporous and macroporous morphology which increased the diffuse reflectance and thus light trapping by the sensitizer. Additionally, better pore infiltration of the PILs electrolyte is achieved when using the bimodal TiO₂ films. The DSSCs fabricated with bimodal-TiO₂ photoanodes exhibited higher energy conversion efficiencies i.e. 1.12% for the most viscous polymer (P2) than those of soft templated mesoporous TiO₂, 0.54%, despite having lower dye adsorption. The addition of ionic liquid to polymer electrolytes significantly lowered the viscosity, and increased the diffusion coefficient, resulting in noticeable improvement in photovoltaic performance. However, slightly lower performances were obtained for the dual templated films compared to the soft templated films when tested with less viscous polymer electrolytes. The cell performance increases with layer thickness, due to increased dye adsorption. This proves that increasing electrolyte infiltration and light harvesting can compensate for the lower dye adsorption.

Keywords: polymer electrolytes, TiO₂, dual templating, bimodal, pore filling

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been under intensive investigation as a low cost alternative to silicon solar cells.^{1,2} High efficiencies, over 11%, have been reported by either Γ/I_3^- or Co²⁺/Co³⁺ redox electrolytes dissolved in solvents like acetonitrile which are fluidic enough not to hinder a Γ/I_3^- or Co²⁺/Co³⁺ redox diffusion.³⁻⁶ However, the use of liquid electrolyte causes some limitations such as electrolyte evaporation and leakage which demands highly stable electrolytes such as polymer electrolytes. Thus in order to overcome these drawbacks, alternative sealing methods, replacing the liquid electrolytes with p-type semiconductor such as conducting polymer⁷ and CuI or CuSCN⁸, ionic liquids (ILs)^{9,10}, nanocomposites and polymer electrolytes¹¹⁻¹⁶ have been utilized. The solid polymer electrolyte is the most attractive due to its flexibility¹⁷ and its facile and large scale elaboration compared to inorganic solid electrolytes.

In polymer electrolyte-based DSSCs, extensive work has been invested in improving their overall energy conversion efficiency by increasing their ionic conductivity. The ionic conductivity was improved by decreasing their crystallinity, adding plasticizers and ILs.^{18–21}

In our present work, we chose to work on polysiloxane-based electrolytes due to their highly flexible backbone, with the barrier to bond rotation being only 0.8 kJ mol⁻¹, as well as very low T_g (-123 °C) and high free volumes and electrochemical stability and is easy to functionalize. One strategy is to use polysiloxane based electrolytes directly on synthesized mesostructured TiO₂ thin films having larger pores.

Hereby, ILs are used instead of solvents due to their interesting properties such a negligible vapor pressure, excellent chemical and thermal stability, non-flammability, and high ionic conductivity.²² Poly(1-N-methylimidazolium-pentylpolydimethylsiloxane)iodide, iodine (I₂), 1-methyl-3-propylimidazolium iodide (MPII) and 1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide (MPI TFSI) were used for preparation of non-volatile polymer electrolytes for DSSC applications.

In a DSSC cell, the polymer electrolyte may not infiltrate into the mesopores of the dyesensitized photoanodes which results in the poor contact with the dye and hence low performance of the device. It is noted that the average pore size of the commercial Dyesol TiO_2 is about ~ 20 nm, whereas, many polymer can be larger in size than the mesopores which results in poor penetration.²³ There have been efforts for eliminating such problems associated with pore infiltration by using photoanodes with large pores.^{24,25} Additionally, large pores can also exhibit the light scattering effect. Hore et al have demonstrated that the pores can also be employed as light scattering.^{26,27} The Mie theory proved that the spherical voids of about 50-100 nm could act as very good backscatters.²⁸ Since most applications of bimodal porous thin films of anatase rely on the interface between the porous semiconductor and an adsorbed dye so it is important to control the porosity and specific surface obtained when two pore sizes are combined in a single film.

The commercially available amphiphilic block copolymers (e.g. Pluronic P123 and F127 surfactants), which consist of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) chains have been widely used as structure-directing agents for well organized mesoporous structures 29,30 and have been employed for solar energy conversion $^{31-34}$. However, the use of Pluronics generates very small pores, typically with diameters of less than 10 nm, due to their low molecular weights. Such a structure is not favorable for pore filling of viscous and large molecular volume polymer electrolytes, resulting in poor photovoltaic performances of solidstate or quasi-solid-state DSSCs. Hierarchical bimodal structures have recently attracted attention due to the synergistic advantages of mesoporous and macroscale morphologies. For example, assemblies of both mesoporous TiO₂ particles (with diameters of several hundred nanometers) and nanostructured TiO₂ fibers have been applied in this regard.^{35–38} A polystyrene beads based approach could be a simple, and effective alternative method of preparing organized porous TiO₂ structures.^{25,39} As porous structures lack the high surface area, bimodal structures combining both small and large pores present very interesting prospects, since the small pores provide a high surface area and large pore acts as channel for viscous electrolytes penetration.40,41

This work describes the comparative investigation of mesoporous and bimodal porous TiO_2 thin films with different thickness in DSSCs comprising the newly developed PILs with different viscosities. The impacts of such TiO_2 hierarchical structures on dye loading, light scattering, charge transport properties, and consequent power conversion efficiency with the different PILs is discussed. To the best of our knowledge, there have been no reports on DSSC including dual porosity and polysiloxane-based electrolytes.

2. Experimental section

2.1. Materials and chemicals

P123 Pluronic ((PEO₂₀–PPO₇₀–PEO₂₀)) surfactant (molecular weight = 5800 g mol⁻¹), titanium tetraisopropoxide (TTIP) and 1-butanol were purchased from Sigma Aldrich. HCl was purchased from Acros Organic. FTO glasses (15 ohm/sq) were purchased from Dyesol. Polystyrene nanospheres (130 nm) that were originally dispersed in water at 10 wt% were purchased from Bang Laboratories, USA. The N-719 dye and the polymer spacer SX-1170-25 (25 μ m thick) were purchased from Solaronix. Acetonitrile was purchased from ABCR GmbH and Co. 3-methoxypropionitrile, 1-butyl-3-methylimidazolium iodide, iodine, guanidine thiocyanate, 4-tert-butylpyridine, valeronitrile were purchased from Sigma-Aldrich.

2.2. Mesoporous thin film synthesis (SOFT synthetic route)

Prior to deposit the mesoporous TiO_2 layer, a compact TiO_2 layer was first deposited on FTOcoated glass (TEC 15) as a blocking layer as described in chapter *V*. This blocking layer (BL) was reported to show significant influence on the overall device performance.⁴² The BL of thickness ~ 70 nm was prepared by spin-coating at 2000 RPM for 60 s from alcoholic solution of TTIP precursor containing acetylacetone as a stabilizer. The deposited BL was stabilized at 150 °C for 15 mins. The mesoporous films (P123 as templates) were deposited on pre-stabilized BLcoated FTO as explained in Chapter *IV*. The term SOFT-3L and SOFT-5L is used for 3 and 5 layers of porous film, obtained after calcination at 500 °C, respectively.

2.3. Bimodal thin film synthesis (DUAL synthetic route)

Similarly, the optimized bimodal film with P123 and 130 nm PS beads as templates was deposited on BL-coated FTO as previously described in Chapter *III* and *IV*. The term DUAL-3 L and DUAL-5 L is used for the samples comprising 3 and 5 layers, obtained after calcination at 500 °C respectively. It is to note that the soft and dual templated layers with different thickness were obtained.

Similarly, reference electrodes were prepared by spin-coating 150 μ l of an alcoholic solution of Dyesol paste at 2000 RPM for 30 s on the BL coated FTO glass, followed by stabilization at 200 °C for 15 mins. The reference films, DYESOL-1L and DYESOL-2L comprising 1 and 2 layers, were annealed at 500 °C. The average particle (and pore) size of the TiO₂ was ~ 20 nm.

2.4. Preparation of polymer electrolyte

The synthesis of PIL (PDMS2Im⁺T), (P2) and ILs is described in Chapter *II* and in our recent article.⁴³ Composition of the various polymer electrolyte mixtures are mentioned in the Table 1. The mixtures were dissolved in a very small amount of 3-methoxypropionitrile/valeronitrile (1/1, v/v) solvent. Amount of the solvent *vs* the amount of P2 in wt/wt ratio was kept to be (P2/ Solvent, 1/0.5, wt /wt). Appropriate weights of the components were mixed in a closed bottle and then continuously stirred at 50 °C until everything was dissolved.

Sample	PILs : ILs (wt:wt ratio)	I ₂ (M)
P2	PDMS2Im ⁺ I ⁻	0.05
P2:MPII(1:1)	$PDMS2Im^{+}I^{-}:MPII(2:1)$	0.05
P2:MPII(1:3)	$PDMS2Im^{+}I^{-}:MPII(1:1)$	0.05
P2:MPITFSI(1:1)	$PDMS2Im^{+}I^{-}:MPI TFSI (1:1)$	0.05

The "reference" redox liquid electrolyte was composed of 0.6 M 1-butyl-3-methylimidazolium iodide 0.03 M iodine, 0.1 M guanidine thiocyanate and 0.5 M 4-tert-butylpyridinein acetonitrile/valeronitrile (85/15, v/v).⁴⁴

Table 2- Properties of the polymer electrolytes at 25 °C.

Electrolyte	Diffusion Coefficient $D(I_3) (cm^2 s^{-1})$	Conductivity σ (S cm ⁻¹)	Viscosity µ (Pa s)
Reference ⁴⁴	7.0×10 ⁻⁶	-	-
P2	2.5×10 ⁻⁹	8.0×10^{-6}	100
P2:MPII(1:1)	7.2×10 ⁻⁸	1.5×10^{-4}	5
P2:MPII(1:3)	1.3×10 ⁻⁷	3.5×10 ⁻⁴	1.8
P2:MPITFSI (1:1)	1.4×10 ⁻⁷	7×10^{-4}	0.5

2.5. Solar cell fabrication

The TiCl₄ treatment and the dye loading of the synthesized soft and dual TiO₂ photoanodes, and DSSCs mounting were realized as described in Chapter *IV*, Section 2.5.

3. Results and discussions

3.1. Structural analysis of titania films

The main micro-structural characterization of the soft (with P123) and dual (with P123 and PS 130 nm beads) templated films are presented in the Chapter *IV*.

3.2. Multilayer film thickness and dye loading

For studying the influence of TiO₂ porous layer thicknesses on the infiltration of polymer electrolytes on DSSC performance, coatings with various thicknesses were prepared by spincoating. The films produced by dual templating are relatively thicker than films produced by soft templating due to extra porosity provided by the PS beads (as shown in figure 1A).⁴⁵ In the next step, the dye loading values were measured and plotted as function of layer thickness in figure 1B. As expected, dye loading increases with film thickness. Interestingly, SOFT and DUAL porous films show quite close values of dye loading (figure 1B, for 3 layers) despite strong difference in thickness, as if the DUAL structure was a "swollen version" of the corresponding SOFT film.



Figure 1- A) Evolution of thin films thickness and B) dye uptake as function of the no of TiO_2 layers prepared by soft and dual templating, and from commercial Dyesol paste.

However, SOFT films always exhibit slightly higher dye loading, due to their large number of small pores. A picture of the SOFT-5L and DUAL-5L TiO_2 layers before and after dye-loading is shown in figure 2.



Figure 2- Images of the SOFT-5L films before and after dye loading (A and C) and DUAL-5L films before and after dye loading (B and D).

In DSSC, the active material under visible light is the dye adsorbed onto the TiO₂ surface. However, strictly a monolayer of dye is required to raise the best photovoltaic performances and to avoid the risk of recombination losses due to multilayers. As proven in previous studies, the conversion efficiency is directly dependent on the accessible surface area of the anatase film.^{46,47} A high value of accessible porosity, combined with small pores, can lead to high dye loading and thus to an efficient light harvesting and subsequent high photoelectron production. Moreover, the pore accessibility is expected to promote a complete penetration of electrolyte into the film, making possible an efficient regeneration of oxidized dye molecule. The SOFT-3L (0.85 μ m), DUAL-3L (2.3 μ m), SOFT-5L (1.5 μ m) and DUAL-5L (3.6 μ m) have been selected for the solar cell assembly and study the layer thickness and electrolyte viscosity influence on the photovoltaic properties. The Dyesol TiO₂ layers, DYESOL-1L (0.9 μ m) and DYESOL-2L (1.6 μ m) were used as reference in DSSCs. The chosen samples DYESOL-1L and DYESOL-2L had similar dye loading as comparable to SOFT-3L and SOFT-5L, respectively.

3.3. Scattering properties

Diffused reflectance of all porous TiO₂ layers with different thicknesses, with and without dye adsorption was measured using a UV-vis spectrophotometer. As observed in the figure 3A, the diffuse reflectance of the undyed porous TiO₂ layer varied in the sequence SOFT-5L=SOFT-3L <DYESOL-2L<DYESOL-1L<DUAL-3L<DUAL-5L in 300–700 nm wavelength range. Dual templated films exhibited average diffuse reflectance of 35% (5L) and 25% (3L), while the soft templated films displayed reflectance of only 2.5%, indicating the dual templated TiO₂ films have a better light-scattering ability than those in the soft templated films. The increased reflectance along with the increasing pore size may be attributed to sufficient light scattering due to their porous architectures.^{28,48} Additionally, the diffused reflectance of dye-adsorbed porous TiO₂ films has also been investigated and spectra are illustrated in figure 3B. They show the same trend in the reflectance as the TiO₂ layer without dye loading.



Figure 3- Diffuse reflectance spectra of porous TiO₂ layers without (A) and with (B) N-719 sensitization.

3. 4. Investigation of charge transport properties

The EIS spectra in the 100 kHz - 1.0 Hz frequency range, were registered for the SOFT and DUAL-130 TiO₂ layers coated on FTO and compared to that of BL-2000/FTO substrates (figure A and B). The same circuit as the one presented in figure 6 of Chapter V was used for fitting. Indeed the Bode plot (figure 4C) reveals the presence of a second processes in the low frequency range (more obvious for samples BL and SOFT-3L with BL) with a distinct relaxation time, apart from the high frequency contribution, which is attributed to the charge transfer resistance at

the TiO_2 /electrolyte interface. Circuit components values are shown in Table 3 and their signification is already given in Chapter *V*.



Figure 4- (A) Nyquist plots and fit in the lower frequency range for the samples SOFT-3L, DUAL-130 and BL in the 0.1 Hz - 500 KHz frequency range, (B) Zoom in the higher frequency range showing how the fit was done and (C) Bode plot for the samples SOFT-3L, DUAL-130 and BL in the 0.1 Hz - 500 KHz frequency range.

Sample	R _{TiO2/FTO}	$\mathbf{R}_{s}(\Omega)$	$\mathbf{R}_{1}\left(\Omega ight)$	Q1	$R_2(k\Omega)$	$Q_2(\Omega.cm^2.s^{-(1-a)})$	X(10 ³)
				$(\Omega.cm^{2}.s^{-(1-a)})$			
FTO	-	580	810	1×10 ⁻⁹	-	7×10 ⁻⁶	2.2
				a= 0.99		a = 0.95	
BL-2000	280	500	1090	1×10 ⁻⁹	60	6×10 ⁻⁶	3.7
(BL)				a = 0.92		a = 0.92	
SOFT-3L	270	540	1080	1.5×10^{-9}	60	10.0×10 ⁻⁶	3.7
				a = 0.98		a = 0.88	
DUAL-3L	350	540	1160	1.5×10^{-9}	50	12×10-6	5.8
				a = 0.98		a = 0.84	

Table 3- Results of the EIS spectra fitting for the BL-2000, and SOFT-3L and DUAL-3L with BL-2000.

X is a term that describes the quality of fitting. $\mathbf{R}_{\text{TiO2/FTO}}$ was determined by calculating the difference of the R_1 value for each sample versus the bare FTO.

The lower TiO₂/FTO resistance in case of the soft templated layer compared to the bimodal one might be attributed to the better adhesion of the TiO₂ layer on the substrate. The charge transfer resistance (R_2) at the TiO₂/electrolyte interface decreases once the BL-2000 blocking layer is covered by a porous TiO₂ layer (samples with SOFT and DUAL-130 with BL). Moreover, it can be observed that the dual templated TiO₂ porous layer has a lower charge transfer resistance compared to the SOFT templated layer. The low charge transfer resistance (R_2) indicates much faster electron transport and it is closely related to the DSSCs efficiency.^{49,50}

3.5. Photovoltaic performances

In our work, synthesized TiO_2 films were incorporated in DSSCs using different polymer electrolytes.

3.5.1. Influence of pore size

The J-V curves under light (~ 0.7 suns) of the DSSCs based on TiO₂ photoanodes with different pore size and polymer electrolyte (P2) are shown in figure 5A, while the photovoltaic performances are listed in Table 4. Interestingly, the device P-D-3 (Polymer electrolyte (P2) with the DUAL-3L layer) attained better J_{sc} and efficiency (1.89 mA cm⁻² and 1.12%, respectively) as compared to the P-S-3 (polymer electrolyte (P2) with SOFT-3L layer) (1.04 mA cm⁻² and 0.52%, respectively) and P-R-1 (polymer electrolyte (P2) with DYESOL-1L layer) (1.61 mA cm⁻² and 0.89%, respectively). A 2.2 fold efficiency improvement can be attributed due to the improved pore infiltration of viscous P2 in dual templated films.⁴¹ Additionally, the gain from better light scattering overcomes the loss associated with slightly lower dye loading, resulting an enhancement in J_{sc} . Furthermore, increment of V_{oc} and FF are observed for DUAL-3L due to reduction of dark current and enhancement of mass transport of triiodide in viscous polysiloxane. The influence of the light scattering was analyzed by IPCE measurements and corresponding spectra are shown in the figure 5B.



Figure 5- A) J-V curves, B) IPCE curve of the DSSCs, P-D-3 (with DUAL-3L), P-R-1 (with DYESOL-1L) and P-S-3 (with SOFT-3L), respectively, fabricated with P2 electrolyte at 25 °C.

Again P-D-3 (polymer electrolyte with DUAL-3L layer) device proved to be more efficient in the wavelength region of 350-700 nm, than P-S-3 device (polymer electrolyte with SOFT-3L layer) and the P-R-1 (polymer electrolyte with DYESOL-1L) reference cell. Ruthenium dyes have poor light absorption at 600-700 nm, but the big pores increased light absorbing capabilities and thus improved the overall efficiency.^{28,51} When tested with liquid electrolytes as shown in figure 6A, the reference film DYESOL-1L, despite having a higher dye loading, yielded an efficiency of 1.45% (device R-R-1), which was lower than the one obtained for the SOFT-3L (device R-S-3) and DUAL-3L (R-D-3) based DSSCs i.e. 1.64 and 1.55%, respectively. The enhanced photovoltaic performance in templated films can be attributed to 3D-organization, pore size and better pores accessibility.³⁴

Photoanode	Thickness (µm)	Dye loading (mol mm ⁻²)×10 ⁻¹¹	Electrolyte	Device Code	$\frac{J_{sc}}{(mA cm^{-2})}$	V _{oc} (V)	FF	η (%)
DYESOL-1L	0.9	14.9	P2	P-R-1	1.61	0.64	58	0.89
			Liquid	R-R-1	2.23	0.79	55	1.45
			P2:MPII(1:3)	Q-R-1	2.67	0.69	58	1.59
SOFT-3L	0.85	14.3	P2	P-S-3	1.04	0.61	54	0.52
			Liquid	R-S-3	2.29	0.76	63	1.64
			P2:MPII(1:1)	Z-S-3	2.70	0.63	64	1.63
			P2:MPII(1:3)	Q-S-3	2.79	0.66	68	1.89
			P2:MPITFSI(1:1)	T-S-3	2.39	0.61	65	1.39
DUAL-3L	2.3	12.6	P2	P-D-3	1.89	0.65	61	1.12
			Liquid	R-D-3	2.18	0.78	61	1.55
			P2:MPII(1:1)	Z-D-3	2.23	0.66	62	1.37
			P2:MPII(1:3)	Q-D-3	2.63	0.67	68	1.79
			P2:MPITFSI(1:1)	T-D-3	2.26	0.62	65	1.36
DYESOL-2L	1.6	21.4	P2:MPII(1:3)	Q-R-2	3.01	0.67	67	2.03
SOFT-5L	1.5	24.9	Liquid	R-S-5	3.32	0.76	67	2.54
			P2:MPII(1:1)	Z-S-5	3.54	0.63	59	1.96
			P2:MPII(1:3)	Q-S-5	3.99	0.65	61	2.41
			P2:MPITFSI(1:1)	T-S-5	2.54	0.66	63	1.60
DUAL-5L	3.6	18.7	Liquid	R-D-5	3.09	0.74	66	2.27
			P2:MPII(1:1)	Z-D-5	3.09	0.61	60	1.73
			P2:MPII(1:3)	Q-D-5	3.36	0.65	61	2.24
			P2:MPITFSI(1:1)	T-D-5	2.38	0.66	64	1.49

Table 4- Photovoltaic performances of the TiO_2 films (3 and 5 layers each) prepared by soft and dual templating and Dyesol TiO_2 (1 and 2 layers each) with various electrolytes at 25 °C.

3.5.2. Influence of viscosity: addition of ILs

However, the polysiloxane-based polymer electrolytes exhibit very high viscosity, so blending with ionic liquids (ILs) is an effective way to utilize it as an electrolyte for DSSCs.²¹ The addition of ILs such as MPII to P2 caused drastic decrease in viscosity, increased conductivity and improved diffusion coefficient as shown in Table 2. The J-V curves under light and the

photovoltaic parameters of all the DSSCs tested with liquid and the less viscous electrolytes are shown in figure 6A-D and Table 4, respectively. It is observed that the devices prepared from both P2:MPII (1:1) and P2:MPII (1:3) showed a behavior similar to liquid electrolytes. The devices Z-S-3 and Q-S-3 based on SOFT-3L showed an efficiency of 1.63 and 1.89% with P2:MPII (1:1) and P2:MPII (1:3) electrolytes, respectively. Improvement in the performance can be attributed to the increase in conductivity and diffusion due to lowered viscosity. The dual templated devices, Z-D-3 and Q-D-3 showed an efficiency of 1.37 and 1.79%, respectively which is quite comparable with soft templated devices (devices Z-S-3 and Q-S-3) and commercial DYESOL (Q-R-1) ($\eta = 1.59\%$), despite having lower dye loading which is attributed to the better light harvesting. Influence of viscosity can be correlated with the studies done by Lee et al. where they compared three different siloxanes diimidazolium iodides having different viscosity, which consequently affected the photovoltaic performance of the DSSCs. However, these electrolytes were tested on DYESOL based TiO₂ with very thick films having very high dye loading.

Polymer electrolyte, P2:MPITFSI (1:1) based cells showed a lower efficiency than P2:MPII (1:1), despite having greater diffusion coefficient, conductivity, and lower viscosity. The superior efficiency of P2:MPII based electrolytes can be attributed to the significant raise of J_{sc} , due to the extra and facile iodide release from MPII. Interestingly, the dual templated films showed very similar values despite having low dye loading (Table 4). The devices T-S-3 and T-D-3, showed an efficiency of 1.39 and 1.36%, respectively. When comparing the SOFT-3L and DUAL-3L with the SOFT-5L with DUAL-5L, we observe similar J_{sc} values, despite having lower dye uptake. So, the higher cell efficiency can be attributed to the enhanced J_{sc} value resulting from the well-organized, interconnected structure with large pores and excellent light scattering ability as confirmed by UV-VIS measurements. Similar V_{oc} values also prove that there are recombination losses.

3.5.3. Influence of thickness

When moving from the 3 layers to 5 layers, one could observe that there is a noticeable increase of the photocurrent density due to higher dye loading, which is responsible for the higher efficiencies attained indicating that there are no recombination losses with thickness.⁵³ The photovoltaic performances of TiO₂ photoanodes with different thicknesses comprising the liquid and polymer electrolytes are listed in Table 4. The J_{sc} parameter is known to be largely determined by the dye loading and thus the surface area and the pores connectivity. With film thickness increase (figure 6A), the solar cells exhibit a continuous improvement in J_{sc} and consequently in efficiency due to increased dye uptake. When comparing the SOFT-3L and SOFT-5L with the DUAL-3L with DUAL-5L based DSSCs, we observe improved J_{sc} values, due to higher dye uptake. It was then shown that SOFT-5L/P2:MPII(1:3) is highly efficient when incorporated into DSSCs, attaining an overall power conversion efficiency of 2.41% which was attributed to highest dye loading. The influence of MPII on polymer electrolytes performance are in accordance with data reported by Khanmirzae et al.⁵⁴ The low viscosity of the blends can lead to the better pore infiltration in thick films and hence higher J_{sc}.



Figure 6- J-V curves of the DSSCs measured at 25 °C: (A) R-R-1 (with DYESOL-1L), R-S-3 (with SOFT-3L), R-D-3 (with DUAL-3L), R-S-5 (with SOFT-5L) and R-D-5 (with DUAL-5L), respectively, fabricated with liquid electrolytes. (B) Z-S-3 (with SOFT-3L), Z-D-3 (with DUAL-3L), Z-S-5 (with SOFT-5L) and Z-D-5 (with DUAL-5L), respectively, fabricated with P2:MPII (1:1) electrolytes. (C) Q-R-1 (with DYESOL-1L), Q-S-3 (with SOFT-3L), Q-D-3 (with DUAL-3L), Q-R-2 (with DYESOL-2L), Q-S-5 (with SOFT-5L) and Q-D-5 (with DUAL-5L), respectively, fabricated with P2:MPII (1:3) electrolytes. (D) T-S-3 (with SOFT-3L), T-D-3 (with DUAL-3L), T-S-5 (with SOFT-5L) and T-D-5 (with DUAL-5L), respectively, fabricated with P2:MPII (1:1) electrolytes.

4. Conclusion

A multilayer deposition process of SOFT and DUAL TiO_2 films was realized. The thickness was gradually increased up to few microns by repeating the spin-coating procedure. The soft and dual films (3 layers each) with similar dye uptake and were chosen and assembled in photovoltaic devices. Similarly, soft and dual films with 5 layers each were also studied to see the influence of

thickness on the photovoltaic performances. It has been shown that the SOFT templated TiO_2 photoanodes showed higher efficiency than DUAL templated TiO_2 photoanodes when tested with liquid electrolyte and less viscous polymer/ionic liquid blends (P2/ILs). However, interestingly, when used with a highly viscous polymer electrolyte (P2), the DUAL-3L photoanode gave the highest performance which can be correlated to the improved pore infiltration.

We observed that the addition of ionic liquids to the P2 caused increase in J_{sc} value and results in improved photovoltaic performances for both SOFT and DUAL templated TiO₂ films. The highest efficiency of 2.41% and 2.24% were achieved for the SOFT-5L and DUAL-5L with the incorporation of P2:MPII(1:3) electrolytes having similar performance with the reference liquid electrolytes. An efficiency of 2.41% for SOFT-5L/P2:MPII(1:3) was obtained only for a 1.5 µm film, which is one of the best efficiencies ever reported for such a small thickness with PILs/ILs based electrolytes. In summary, a bimodal structure combines the advantages of both large and small pores such as excellent transport properties, efficient light scattering, better pore infiltration of poly(ionic)liquid/ionic liquid based electrolyte. The DSSCs performance could certainly be improved by increasing the thickness of the photoanodes.

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General conclusions and prospects

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1. General conclusions

At the end of the last century, the possibility to use the devices based on molecular components for the construction of robust large-scale electricity production facility seemed non-materialistic. But the ground-breaking paper by O'Regan and Michael Graetzel in 1991, encouraged researchers to take on the challenge.¹ With the development of Dye Sensitized Solar Cells (DSSCs), conventional solid-state solar cell technologies are now challenged by devices functioning at the molecular and nano-level. The objective of the present work was to obtain the polymer based highly efficient and stable DSSCs. Indoor and outdoor applications of DSSCs based on liquid electrolytes are limited due to stability of the cells. For this reason, polymer electrolytes represent as promising alternatives. However, the efficiencies of the DSSCs with polymer electrolytes are often lower than those of the DSSCs with liquid electrolytes. In the present thesis, two important parts of the DSSC, i.e. the polymer electrolyte and the photoanode, were studied in order to achieve high efficiency.

In the first part, we presented a synthetic protocol for the preparation of solid polymer electrolytes based on novel poly(ionic liquid) (PIL), namely, poly(1-*N*-methylimidazolium-pentylpolydimethylsiloxane)iodide (Chapter *II*). In order to further improve the performance, we worked on a strategy on mixing the polymers with room temperature ionic liquids (ILs) and plasticizer such as ethylene carbonate (EC). The mixing process resulted in the significant enhancement of the ionic conductivity and diffusion coefficient, with the concomitant decrease of the viscosity. In addition, the fabricated solid state-DSSCs showed efficiencies comparable to liquid electrolytes with incredible long-term stability, as illustrated in Chapter *III*. The improved ionic diffusion and conductivity of the polymer electrolytes can help in accelerating the ion conduction *via* the Grotthus mechanism or an exchange reaction mechanism as explained in Chapter *II*, leading eventually to greater photovoltaic performances.^{2,3} Our target for the initial part of work was to synthesize stable polymer electrolytes with good conductivity and diffusivity at room temperature.

One of the main issues with polymer electrolyte has been the poor pore infiltration due to small pores of TiO_2 photoanodes. Poor penetration of the polymer electrolyte is mostly due to the small size difference between the mesopores in the photoanode and the coil size of the polymeric chain. Therefore, if the pore size of the photoanode can be increased, the polymer electrolyte

may penetrate into the pores deeply, resulting in a good contact between the electrolyte and the dye coated TiO_2 films. However, large pores have the disadvantages of lower dye loading due to the reduce surface area. In recent years, the photoanodes with dual porosity (meso and macropores) seem to be a viable compromise solution, allowing better pore infiltration of polymer electrolytes and increased light harvesting.^{4,5}

Therefore, our second part was dedicated to the synthesis of TiO_2 films with dual porosity. The spin-coating template assisted route was applied as an alternative strategy towards porous photoanode, in contrast to the most commonly employed methods such as doctor blade or screen printing. In chapter *IV*, we have successfully synthesized bimodal TiO_2 photoanodes with different macropore sizes by using PS beads with various diameters. A perfect balance between complete pore infiltration and high surface area was obtained by using both Pluronic surfactant (P123) and 130 nm PS beads. Furthermore, the synthesized bimodal films exhibited good light harvesting properties due to the scattering effect and exhibited lower charge recombination resistance. Successful assembly and reproducibility of solid-state DSSCs featuring bimodal films and polymer electrolytes was achieved with the standard dye N719, as illustrated in Chapter *VI*. It was also shown that the implementation of a thin TiO₂ blocking layer in DSSCs was useful in avoiding charge recombination and enhancing the efficiency as described in Chapter *V*.

2. Prospects

Throughout the manuscript, a few questions still remain which demand further experiments and investigations. We are convinced that polymer electrolytes present a huge potential as an alternative to liquid electrolytes. However, considering the solid-state nature of the polymers and the diffusion limited photocurrent, it will be a great challenge to reach efficiency values close to liquid solar cells. Bimodal DSSCs have already proved their capabilities as an alternative to the mesostructured and dyesol TiO_2 based solar cells. We firmly believe that the DSSCs performance could further be improved by optimizing the thickness of the bimodal photoanodes. Furthermore, the emphasis should be given to the deposition techniques such as Ultrasonic spray pyrolysis, etc. in order to have large scale industrial production of porous films.

Nevertheless, the reported efficiencies with polymer electrolytes, along with the stability results, can be considered very promising incentives and might motivate the researchers to bring these

devices to the market. Efforts should now be directed to up-scaling such devices and also to the assembly of flexible devices, combining the application of polymer electrolytes with flexible conductive substrates instead of the TCO glass routinely employed. Although, already commercialized in many companies such as Solaronix, Dyesol Ltd, Fraunhofer ISE, G24 Innovations, Ltd. etc. So, the large scale multilayer deposition process of porous films is costly and still needs to be improved.

To make DSSC technology more competitive, it is crucial to improve the device efficiency and stability, as well as to further reduce the material and manufacturing costs. To achieve these goals, models should be developed to quantitatively identify the promising semiconductors, dyes, and electrolytes, as well as their assembly. A well-developed model could be utilized to accelerate the development process with a substantial saving of experimental time and resources.

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Appendix

Electrolyte	T _g (°C)	μ (Pa s)	σ (S cm ⁻¹)	$D(I_3) (cm^2 s^{-1})$
liquid (reference)	-	-	-	7.0×10 ⁻⁶
P1	-123	13	9×10 ⁻⁶	3.0×10 ⁻⁹
P2	-71	100	8×10 ⁻⁶	2.5×10 ⁻⁹
P3	-47	1200	1.6×10^{-5}	8.0×10 ⁻⁹
P2:MPII(2:1)	-71	-	1.3×10 ⁻⁴	-
P2:MPII(1:1)	-75	5.1	1.5×10^{-4}	7.2×10 ⁻⁸
P2:MPII(1:3)	-76	1.8	3.5×10 ⁻⁴	1.3×10 ⁻⁷
P2:MPITFSI(2:1)	-74	-	4.0×10 ⁻⁴	-
P2:MPITFSI(1:1)	-83	0.5	6.9×10 ⁻⁴	1.4×10 ⁻⁷
P3:EC(8:1)	-70	-	1.8×10 ⁻⁴	1.1×10 ⁻⁷
P3:EC(3:1)	-75	-	1.1×10 ⁻³	2.8×10 ⁻⁷

Table S1- Thermal and physiochemical properties of PILs-based electrolytes at 25 °C.

Table S2- Photovoltaic parameters of the DSSCs with 11 μ m Dyesol TiO₂ comprising PILs-based electrolytes under~ 0.7 sun illumination.

Electrolyte	V _{oc}	J _{sc}	FF	Average	Best efficiency
	(V)	$(\mathbf{mA} \ \mathbf{cm}^{-2})$	(%)	Efficiency (η %)	(ղ %)
liquid	0.75	10.04	68	7.69	7.96
P1	0.65	4.21	62	2.47	2.69
P2	0.56	5.71	63	3.01	3.04
Р3	0.11	5.85	25	0.24	0.24
P2:MPII(2:1)	0.61	8.20	66	4.86	4.95
P2:MPII(1:1)	0.62	9.94	62	5.63	5.94
P2:MPITFSI(2:1)	0.57	6.85	66	3.79	3.99
P2:MPITFSI(1:1)	0.61	8.96	66	5.33	5.56
P3:EC(8:1)	0.55	3.76	63	1.93	2.09
P3:EC(3:1)	0.65	9.83	64	6.05	6.30

Photoanode	Dye loading	Electrolyte	Device	J _{sc}	Voc	FF	ղ
	(mol mm ⁻²)×10 ⁻¹¹		Code	(mA cm ⁻²)	(V)	(%)	(%)
SOFT	13.96	liquid	SR-0	2.25	0.76	62	1.58
		P2	SP-0	0.81	0.62	56	0.42
DUAL-62	13.09	liquid	DR-62	1.95	0.75	63	1.38
		P2	DP-62	1.02	0.62	59	0.55
DUAL-130	12.36	liquid	DR-130	2.02	0.79	60	1.44
		P2	DP-130	1.61	0.64	58	0.89
DUAL-250	11.04	liquid	DR-250	1.56	0.79	68	1.25
		P2	DP-250	1.38	0.66	55	0.75

Table S3- Photovoltaic performances TiO_2 films (3 layers each) prepared by soft and dual templating with liquid electrolyte (reference) and polymer electrolyte (P2) at 25 °C.
Table S4- Photovoltaic performances of the TiO_2 films with BL prepared by soft and dual templating (3 and 5 layers each) and Dyesol TiO_2 (1 and 2 layers each) with various electrolytes at 25 °C.

Photoanode	Thickness	Dye loading	Electrolyte	Device	\mathbf{J}_{sc}	Voc	FF	ղ
	(µm)	(mol mm ⁻²)×10 ⁻¹¹		Code	(mA cm ⁻²)	(V)		(%)
DYESOL-	0.9	14.9	P2	P-R-1	1.61	0.64	58	0.89
1L								
			Liquid	R-R-1	2.23	0.79	55	1.45
			P2:MPII(1:3)	Q-R-1	2.67	0.69	58	1.59
SOFT-3L	0.85	14.3	P2	P-S-3	1.04	0.61	54	0.52
			Liquid	R-S-3	2.29	0.76	63	1.64
			P2:MPII(1:1)	Z-S-3	2.70	0.63	64	1.63
			P2:MPII(1:3)	Q-S-3	2.79	0.66	68	1.89
			P2:MPITFSI(1:1)	T-S-3	2.39	0.61	65	1.39
DUAL-3L	2.3	12.6	P2	P-D-3	1.89	0.65	61	1.12
			Liquid	R-D-3	2.18	0.78	61	1.55
			P2:MPII(1:1)	Z-D-3	2.23	0.66	62	1.37
			P2:MPII(1:3)	Q-D-3	2.63	0.67	68	1.79
			P2:MPITFSI(1:1)	T-D-3	2.26	0.62	65	1.36
DYESOL-	1.6	21.4	P2:MPII(1:3)	Q-R-2	3.01	0.67	67	2.03
2L								
SOFT-5L	1.5	24.9	Liquid	R-S-5	3.32	0.76	67	2.54
			P2:MPII(1:1)	Z-S-5	3.54	0.63	59	1.96
			P2:MPII(1:3)	Q-S-5	3.99	0.65	61	2.41
			P2:MPITFSI(1:1)	T-S-5	2.54	0.66	63	1.60
DUAL-5L	3.6	18.7	Liquid	R-D-5	3.09	0.74	66	2.27
			P2:MPII(1:1)	Z-D-5	3.09	0.61	60	1.73
			P2:MPII(1:3)	Q-D-5	3.36	0.65	61	2.24
			P2:MPITFSI(1:1)	T-D-5	2.38	0.66	64	1.49