

Synthesis and Characterization of Gel Electrolytes



Submitted to
The Faculty of Science
University of Calicut in partial fulfillment of
the requirements for the degree of

DOCTOR OF PHILOSOPHY

By
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April 2018

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Under the Guidance of
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CERTIFICATE

This is to certify that the thesis entitled “**Synthesis and characterization of gel electrolytes**” is a bona-fide record of research work carried out by Ms. Nijisha. P., under my supervision in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy in Nanoscience and Technology of the University of Calicut. The plagiarism check is carried out and this work or the part thereof has not been presented before for the award of any other degree. Also certify that she has incorporated the suggestions and corrections pointed out by the examiners in the revised thesis.

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DECLARATION

Certified that the thesis bound herewith is an authentic record of the work on **“Synthesis and characterization of gel electrolytes”** carried out by me under the supervision of Dr. Sindhu .S, Assistant Professor, Department of Nanoscience and Technology, University of Calicut in partial fulfillment of the requirements for the award of the degree of the Doctor of Philosophy of the University of Calicut, and further that no part thereof has been presented before for any other degree.

University of Calicut

Nijisha. P

Date

Dedicated to
Amma & Achan

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Preface

Electrolytes play a vital role in the proper functioning of all electrochromic devices. The biggest problem faced by these devices for the past few decades was their lack of stability which arises due to the usage of liquid electrolyte. Gel electrolyte formed by the complexation of polymer matrix with ionic salt resulted a breakthrough in the field of electrochromic devices. Where the problem of leakage and stability is improved with respect to liquid electrolytes. However, the performance of gel electrolyte based devices were poor compare to the corresponding liquid electrolyte. This drawback can be overcome by adding fillers to enhance the electrical, thermal and other properties of the gel electrolyte. Use of filler incorporated gel electrolyte gives better device performance.

An attempt was made to immobilize the liquid electrolyte by adding polyvinyl alcohol and polymethyl methacrylate. The synthesized gel electrolytes were characterized with various techniques to study their properties. QSDSSC was fabricated with these electrolytes and their performances were compared. Inorganic semiconductor oxides like commercial TiO_2 and ZnO were chosen as the filler. ZnO was synthesized via a simple co-precipitation method. A time dependent stability study of all the synthesized polymer gel electrolytes were performed for a period of one month. Finally QSDSSC was fabricated with the filler incorporated polymer gel electrolyte and their performances were compared.

Chapter wise detail of the thesis is added below.

Chapter 1: Introduction

In this introductory chapter an overview of world energy demand and the importance of seeking renewable energy source is reported. Among the alternative energy sources, a special interest is devoted to photovoltaics. The generations of solar cell are discussed with special attention to third generation solar cell, for example, Dye sensitized solar cell. Structure, components and functioning of a DSSC is briefed, followed by the description about different electrolytes used in DSSC, and the need for a new electrolyte material and the importance of quasi solid state electrolytes are thoroughly presented. Last section of this chapter highlights the aim, objectives, and the methodologies of this thesis work.

Chapter 2: Characterization Techniques and Theory

This chapter describes the characterization techniques employed to study the properties of the materials developed for the work. A brief outline of the theory involved in each techniques is discussed. The morphology of the sample was obtained from scanning electron microscopy. The formation of the sample was confirmed from the x-ray diffraction studies. The optical properties of the sample were studied by performing diffuse reflectance spectroscopy, Tauc plot and photoluminescence spectra. To get an idea about the network structure of the gel electrolyte FT-IR is performed. The impact of temperature on the polymer matrix on gelation was studied by performing the thermogravimetric analysis. The electrical conductivity of the electrolytes were studied by performing the electrochemical impedance spectroscopy.

The current-voltage characteristics and the electrochemical impedance measurements were adopted to evaluate the photovoltaic response of the device is also explained in detail.

Chapter3: Synthesis of PVA and PMMA Gel Electrolytes, its Characterizations and Application

This chapter describes the synthesis of gel electrolytes using two polymer matrices – polyvinyl alcohol and polymethyl methacrylate. The synthesized gel electrolyte was characterized to study its properties and was applied to QSDSSC. A detailed overview of QSDSSC components and architecture is presented. A comparison of electrolyte properties and their comparative performance is evaluated. A time dependent stability study, for one month, is also performed. Finally the performance of QSDSSC is compared with the corresponding DSSC and the results are discussed in detail.

Chapter 4: Synthesis, Characterization and Application of Filler Incorporated PVA Gel Electrolyte

This chapter deals with the synthesis of filler incorporated PVA gel electrolyte, its characterization and application in QSDSSC. ZnO synthesized via a simple co-precipitation method and its basic characterizations were performed. Different weight percentage of commercial TiO_2 and ZnO were introduced as filler particles in the polymer gel electrolytes. These electrolyte combinations were characterized and an optimized electrolyte combination was finalized for both TiO_2 and ZnO incorporated

electrolytes. The objective of improving the performance of the gel electrolyte on filler incorporation was proved. The stability study of the best performing gel electrolyte was done and compared with filler free system. QSDSSC was fabricated with gel electrolyte containing different weight percentage of fillers and the performance was compared with the filler free system.

Chapter 5: Synthesis, Characterization and Application of Filler Incorporated PMMA Gel Electrolyte

In this chapter the synthesis of filler incorporated PMMA gel electrolyte, its characterization and application is reported. Two different fillers - commercial TiO_2 and ZnO of different weight percentage was added. Characterization of the filler incorporated gel electrolytes are carried out. A time dependent stability study of the optimized electrolyte composition was done. QSDSSC was fabricated with these filler incorporated electrolytes and the performance was compared with the corresponding filler free system.

Chapter 6: Conclusion

In the concluding chapter a compilation of the important findings of the entire work is reported. A comparison in properties and performance of the polymer gel electrolytes has been discussed in detail. Suggestions were given to proceed this work further for the stable performance of filler incorporated PMMA gel electrolyte.

Scope of the Work

Polymer gel electrolytes were synthesized and characterized for QSDSSC application. Immobilization of liquid electrolyte by adding polymers can solve almost all the problems confronted while using the liquid electrolyte. Semiconductor oxide incorporated polymer gel electrolyte can perform equally well as the corresponding liquid electrolyte.

Properties of the polymer gel electrolyte is found to be altered on introducing fillers. So optimizing the properties of the filler like size, introducing new fillers like conducting polymers can give a better performance. Doping of the conducting polymers with iodine shows a drastic enhancement in its conductivity. Solvents has an important role in forming a stable polymer network structure, enhancing conductivity, and performance of the electrolyte. So attempting different solvents in polymer gel electrolyte can enhance the properties of the electrolyte. Attempts can be taken to improve the stability of these gel electrolyte by minimizing the photoactivity of the fillers. Also optimizing the fabrication procedure of the photoanode and counter electrode can improve the device performance. Other than solar cells, these gel electrolytes can be tested for different applications by replacing the liquid electrolytes.



Abbreviations:

<i>DSSC</i>	<i>Dye-sensitized solar cell</i>
<i>QSDSSC</i>	<i>Quasi-solid state dye sensitized solar cells</i>
<i>ITO</i>	<i>Indium doped tin oxide</i>
<i>FTO</i>	<i>Fluorine doped tin oxide</i>
<i>TiO₂</i>	<i>Titanium dioxide</i>
<i>ZnO</i>	<i>Zinc oxide</i>
<i>N719</i>	<i>Ru sensitizer</i>
<i>AN</i>	<i>Acetonitrile</i>
<i>DMSO</i>	<i>Dimethyl sulfoxide</i>
<i>EC</i>	<i>Ethylene carbonate</i>
<i>PC</i>	<i>Propylene carbonate</i>
<i>I⁻/I₃⁻</i>	<i>Iodide-triiodide redox couple</i>
<i>I⁻</i>	<i>Iodide ion</i>
<i>I₃⁻</i>	<i>Triiodide ion</i>
<i>TBP</i>	<i>4-tert butyl pyridine</i>
<i>GuSCN</i>	<i>Guanidinium thiocyanate</i>
<i>Pt</i>	<i>Platinum</i>
<i>FE-SEM</i>	<i>Field emission scanning electron microscopy</i>
<i>EDX</i>	<i>Energy dispersive X-ray spectroscopy</i>
<i>XRD</i>	<i>X-ray diffraction</i>
<i>DRS</i>	<i>Diffuse reflectance spectroscopy</i>
<i>PL</i>	<i>Photoluminescence</i>

<i>FT-IR</i>	<i>Fourier transform infrared spectroscopy</i>
<i>TGA</i>	<i>Thermogravimetric analysis</i>
<i>EIS</i>	<i>Electrochemical impedance spectroscopy</i>
<i>LSV</i>	<i>Linear sweep voltammetry</i>
<i>J-V</i>	<i>current density- voltage</i>
<i>J_{sc}</i>	<i>Short-circuit current</i>
<i>V_{oc}</i>	<i>Open circuit voltage</i>
<i>FF</i>	<i>Fill Factor</i>
<i>Eff</i>	<i>Efficiency</i>
<i>PVA</i>	<i>Polyvinyl alcohol</i>
<i>PMMA</i>	<i>Polymethyl methacrylate</i>
<i>PGE</i>	<i>Polymer gel electrolyte</i>
<i>KI</i>	<i>Potassium iodide</i>
<i>I₂</i>	<i>Iodine</i>

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List of Publications

1. **Nijisha P**, Dharsana M.V, Sindhu Swaminathan Synthesis and Electrochemical Characterization of Physically Cross-Linked Gel Electrolyte for QSDSSC Application, *Materials and Design* 101 (2016) 270–276.
2. **Nijisha P**, Bhabhina. N.M, Sindhu Swaminathan Application of gel electrolyte in dye sensitized solar cells, *Nanosystems: Physics, Chemistry, Mathematics* 7 (4) (2016) 752–754.
3. Rajita Ramanarayanan, **Nijisha P**, Niveditha C.V, Sindhu Swaminathan Natural dyes from red amaranth leaves as light-harvesting pigments for dye-sensitized solar cells, *Materials Research Bulletin* 90 (2017) 156–161.
4. Bhabhina. N.M, **Nijisha P**, Sindhu Swaminathan Anchoring of polymeric precursor on oxygen deficient ZnO nanotubes: A chelation assisted combined nucleation-growth-dissolution synthesis strategy, *Materials & Design* 130 (2017) 426–432.
5. Niveditha C V, Aswini R, Jabeen Fatima M J, Rajita Ramanarayanan, **Nijisha P**, Sindhu S, Feather like active Co_3O_4 electrode for supercapacitor application: A potentiodynamic approach, *Materials Today Express* (Accepted)
6. Bhabhina N M, **Nijisha P**, Niveditha C V, Rajita Ramanarayanan, Sindhu S, Inorganic-organic semiconductor hybrid nanocomposite for anticorrosion applications, *Mater. Today Proceedings*, 2017(Accepted)
7. **Nijisha P**, Bhabhina N.M, Sindhu Swaminathan Scrutinize the dye anchoring effect on the performance of quasi solid state dye sensitized solar cell : A comparative approach *Solid State Ionics* (Under review)

Conferences Attended

1. **Nijisha. P**, Bhabhina. N.M, Sindhu Swaminathan, Application of gel electrolyte in dye sensitized solar cells, International conference on Nanomaterials and Nanotechnology NANO-15, KSR College of Technology.
2. **Nijisha. P**, Sindhu .Swaminathan, Quasi-solid state electrolyte: An alternative to liquid electrolyte based DSSC, 4th International Conference on Nanoscience and Technology COCHIN NANO 2016, CUSAT.
3. **Nijisha. P**, Niveditha. C.V, Rajita R, Sindhu Swaminathan, Immobilization of Liquid Electrolyte with Polymeric Matrix for the Long Term Stability and Durability of Dye Sensitized Solar Cells, 4th International conference on Nanoscience and Nanotechnology ICONN-2017, SRM University.

1

INTRODUCTION

1. INTRODUCTION

1.1 Global energy demand

Nobel Laureate Richard E Smalley, in 2003 pointed that the top challenge faced by humanity is the global energy problem which is closely related to three ever growing issues: the increasing energy demand to support economic growth, depletion of fossil fuels and its soaring price, and the greenhouse gas emission and global warming caused by fossil fuel combustion¹⁻³. To meet the rising energy demand nuclear energy has become an alternative which is cost-effective low emission energy source. But the disposal of the radioactive waste became a serious challenge in the nuclear energy industry. So it became a prerequisite to find out cheap and obtainable resources to meet the rising energy demand. Renewable energy sources like solar energy, wind energy, hydropower, biomass etc., have the potential to meet the energy demand and can move the world to a more secure, reliable and sustainable energy system. Among the renewable energy sources solar energy is the most abundant permanent energy resource on earth⁴. The supply of energy from sun to earth is 3×10^{24} joules a year⁵. Converting 0.1% of this energy would satisfy our present need.

The International Energy Agency projected that solar power could provide "one third of the global final energy demand after 2060, while CO₂ emissions would be reduced to very low levels"⁶. Solar energy technology⁷ includes solar photovoltaics, solar heating, concentrated solar power and solar architecture. Among these, photovoltaic production featured an annual growth rate of more than 20% within the

last few decades making it the world's fastest growing energy technology^{8,9}. Some of the attractive features of these photovoltaic cells are: they are inexhaustible, does not lead to secondary environmental pollution, has no exhaust that produce greenhouse gases, has zero nuclear waste products. These cells do not require mechanical movement or movable parts to generate electricity and hence can continuously work free from maintenance for a longer period of time than other solar energy technologies.

1.2 Development of solar cells

A photovoltaic cell or solar cell is an electrical device that directly convert solar energy into electrical energy by photovoltaic effect. The development of solar cells begins with the discovery of photovoltaic effect by the French scientist Edmond Becquerel (1839) while experimenting with an electrolytic cell and found that electricity generation increased when exposed to sunlight¹⁰. In 1883 first solar cell was developed by Charles Fritts by coating Selenium with a thin layer of gold and achieved an efficiency of 1%. It was in 1954, first silicon solar cell of efficiency 6% was introduced by Daryl Chapin, Calvin Fuller and Gerald Pearson at Bell Labs¹¹. In 1985, The Center for Photovoltaic Engineering at the University of New South Wales developed a Silicon solar cell of 20% efficiency¹². These crystalline silicon solar cells (monocrystalline and polycrystalline) are typically referred to as 1st generation solar cell and they dominant the commercial production of solar cells. The benefit of this solar cell relies in their good performance (25% efficiency in 2008; 34.5% in 2016) and high stability. However the demand of high purity silicon for manufacturing the cell restricts their widespread application in the future. Figure 1.1 shows the

classification of solar cell on the basis of materials used for device fabrication and the current trends.

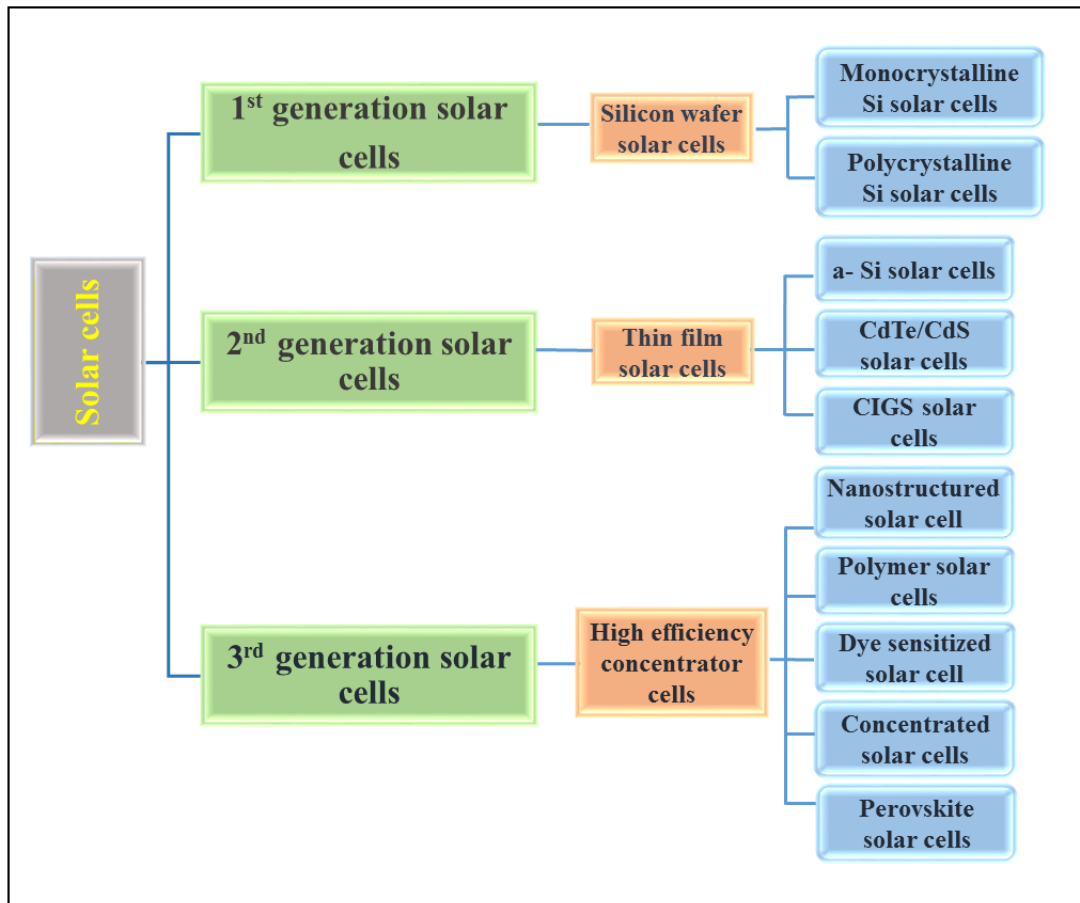


Figure 1.1: Classification of solar cells and current trends of development

2nd generation solar cells are thin film solar cells made on amorphous silicon, Copper indium gallium selenide (CIGS) and Cadmium telluride (CdTe). The consumption of material for thin film technology was less which significantly reduce their production cost in contrast to 1st generation solar cells. However their conversion efficiency was less ranging between 10-15%. Moreover the scarcity and toxicity of the raw materials are the other major disadvantages that limits their large scale production and commercialization.

The development of 3rd generation solar cell focused mainly on improving the shortcomings of 1st and 2nd generation solar cells. Three major issues to be improved was to increase light to electric energy conversion efficiency, to enhance the long term stability and to decrease the cost of production. 3rd generation solar cell are quite different from the previous semiconductor devices where traditional p-n junction separate photo-generated charge carriers. This 3rd generation solar cell includes organic solar cell, perovskite solar cells, dye sensitized solar cells, nanocrystal solar cell and are still in research phase¹³⁻¹⁵.

Organic solar cells or polymer solar cells are generally flexible cells in which the active layer that absorbs the solar light is an organic material-conducting/conjugated polymer. The active layer is comprised of a donor and acceptor material for charge separation and transportation¹⁶. The first polymer solar cell was invented by the research group of Tang *et al.* at Kodak Research Lab¹⁷. The major advantage of these devices are their ability to be produced from solutions. i.e., they can be printed or coated. But the efficiency and the stability of these devices are still far behind traditional technologies. Also these organic compounds decompose under light reducing the lifetime to the order of months or weeks rather than years¹⁵.

In sensitized photovoltaics, organic dyes are used as sensitizers (DSSC). Natural organic dyes from plant extracts shows poor performance and hence synthetic dyes are mostly preferred. The best performance is shown by Ruthenium based dye with an efficiency of 13% and a current density of 20 mAcm⁻². As the development progressed, these dyes were replaced by quantum dots or nano-sized semiconductor

crystals with a short band gap and a high extinction coefficient and hence these are named as Nanocrystal based solar cells or generally Quantum dots solar cells (QDSSC)¹³. The band gap of these quantum dots are highly tunable across a wide range of energy levels by changing their size. This property makes quantum dots attractive for multi-junction solar cells, where a variety of materials are used to improve efficiency by harvesting multiple portions of the solar spectrum¹⁵. In DSSC iodine based redox mediators are used. Whereas QDSSC works well with polysulfide based redox mediators. Later during 2009, these quantum dots were replaced by perovskite material and a record efficiency of 21% was attained. These perovskite solar cells use hole-conductors instead of redox mediators. However, perovskites are very moisture-sensitive materials and fabrication must be done in very clean and controlled conditions¹⁸.

1.3 Dye sensitized solar cell

It was in 1988, Dye sensitized solar cells were developed by Michael Gratzel and Brian O' Regan based on nanocrystalline titania which then became a milestone in the history of photovoltaic technology. At the present stage DSSC's are far behind the efficiency value of conventional Si-solar cells (app 25%)¹. But the low cost, easy fabrication, lower purity demand on raw materials, environmental benignity subjects them to undergo intense research and development ¹⁹.

Unlike other semiconductor p-n junction solar cells the light absorption and charge transport mechanisms are done by two separate components in DSSC. Here,

photons are absorbed by the sensitizer molecules and the charge transport is carried out in the semiconductor oxide and electrolyte.

1.3.1 DSSC components and working

A typical DSSC consist of three components²⁰-a photoanode, electrolyte and a counter electrode. Schematic representing the structure of a typical DSSC is shown in figure 1.2.

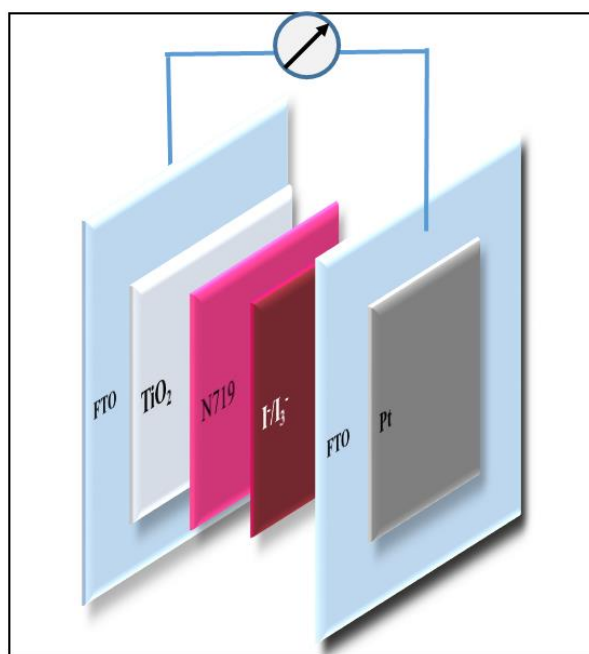


Figure 1.2. Schematic showing the structure of a typical DSSC

Photoanode consist of 1) a transparent conducting oxide as substrate material (mainly ITO and FTO) which allows light to pass through the active material beneath and acts as an ohmic contact for charge carrier to transport out of photovoltaic devices²¹. 2) A mesoporous layer of wide band gap semiconductor oxide (mainly TiO_2) spread uniformly on the substrate which functions as electron acceptor and electronic conductor. The thickness of the film should be around $12\mu\text{m}$. Other metal

oxides such as ZnO, SnO and Nb₂O₅ were also of great interest due to their wide band gap^{22,23}. Ternary oxides like SrTiO₃²⁴ and Zn₂SnO₄²⁵ and core shell structures- ZnO coated SnO₂ were also successfully investigated in DSSC by Hagfeldt et al., in 2010.

3) A monomolecular layer of sensitizer (mainly ruthenium complexes) is chemisorbed on the oxide layer to harvest the incident sunlight. The energy level of the sensitizer should be above the conduction band of the semiconductor-oxide to ensure efficient charge injection. Charge injection takes place from the highest occupied molecular orbital of the anchoring group to the oxide 3d-orbital²⁶. An ideal sensitizer is the one that should absorb all the light below a threshold wavelength of about 920 nm. Mainly two types of sensitizers are employed: metal complexes (Ru based dyes) and metal free organic sensitizers. Ru complexes like N719, N3, black dye etc., have been used from the beginning of DSSC research. Organic sensitizers like D35, TH305, C229 etc., have also been investigated in DSSC.

Electrolyte consist of an organic solvent and a redox mediator (usually iodide/triiodide couple) for dye regeneration. Counter electrode²⁷ is again a transparent conducting oxide (mainly ITO and FTO) coated with a catalytic material (mainly Pt) to catalyze the regeneration of the electrolyte redox couple by collecting electrons from the external circuit. Other alternative to Pt include carbon based materials (graphite, graphene, carbon black, single walled and multi walled carbon nanotubes etc.), conducting polymers, nitrides and sulfides based materials. But all these alternatives have got poor electro-catalytic activity than Pt²⁸.

Working principle: The stepwise charge transport in DSSC is schematically shown in figure 1.3 and their corresponding representation is given in equation 1 to 6.

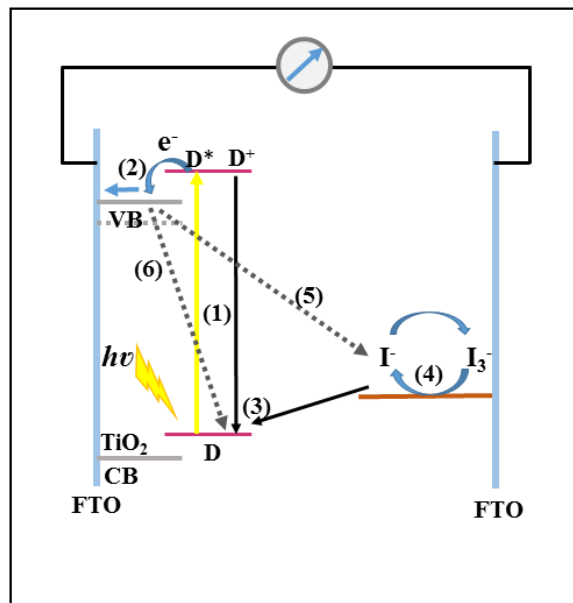
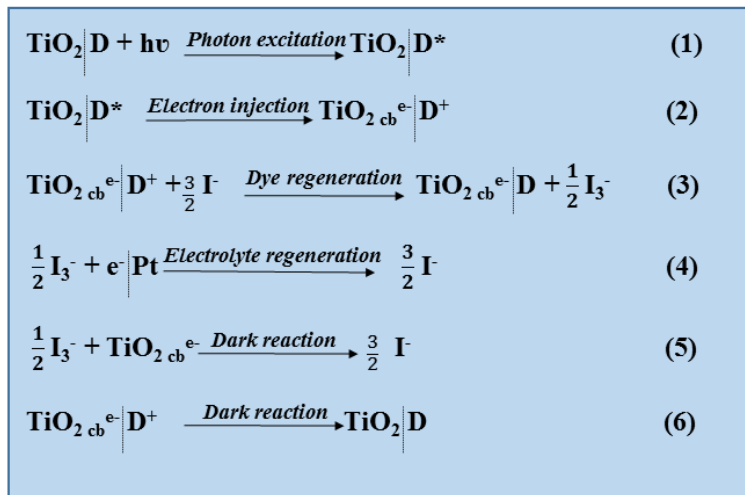


Figure 1.3. Schematic diagram showing the charge transport mechanism in a typical DSSC

The operational steps are as follows^{1,29}:



On illuminating the DSSC, the sensitizer get photo-excited from its highest occupied molecular orbital to its lowest unoccupied molecular orbital - equation (1).

The excited dye molecule inject an electron to the conduction band of the semiconductor material and itself get oxidized - equation (2). The injected electron is then transported across the TiO_2 film towards the transparent conducting oxide substrate and then to the external circuit. The oxidized dye molecule get regenerated by snatching an electron from the reduced component of the redox couple - equation (3). Now the reduced component of the redox couple get oxidized and is transported towards the catalyzed counter electrode which collects the electron from the external circuit. The regeneration of the redox couple takes place at the surface of the counter electrode - equation (4) and the entire cycle is repeated. Equation (5) and (6) are dark reactions or charge carrier recombination reactions which are the important loss mechanisms taking place within the closed system that adversely affect the overall performance of the cell. For efficient performance of the cell, the electron injection reaction should be faster than dye regeneration step. Dye regeneration step should be faster than the dark reaction taking place between the injected electron and dye cation and also between injected electron and the oxidized component of the electrolyte. Also the counter electrode must guarantee the fast regeneration of the electrolyte components²⁹.

1.4 Electrolytes in DSSC

Electrolytes are materials that provides pure ionic conductivity between the positive and the negative electrodes in an electrochemical device. The expected behavior of electrolyte remain the same in capacitors, supercapacitors, electrolytic cells, fuel cells or batteries i.e., the medium for the transport of the charge carriers

between the electrodes. Some of the basic requirements that the electrolyte should possess for the stable operation of DSSC's are^{30,31}:

- † It must be able to transport the charge carriers between the photoanode and the counter electrode. Once the photo-excited dye injects electron to the conduction band of the semi-conductor, the dye get oxidized and must be regenerated by grabbing an electron from the redox couple in the electrolyte. So the electrolyte preference should take into account the dye redox potential and regeneration of itself
- † The redox couple must be completely reversible and it should not exhibit significant absorption in the same spectral region as the dye
- † The electrolyte should permit the fast diffusion of the charge carriers and a good interfacial contact with the electrode surfaces
- † The electrolyte must be stable at the electrode surface preventing the desorption and degradation of the dye from the oxide surface and also the corrosion of the counter electrode
- † Electrolyte should have long term stability, including chemical, optical, thermal and interfacial stability

A successful electrolyte plays multiple roles like dissociation of ion pairs, transport of the active species, penetration and wetting of the porous chemically stable electrodes, should not leak or vaporize during device operation and storage, chemically robust and must be stable under normal operating voltage range. To find a single material

fulfilling all the above mentioned qualities is quite difficult. So always a combination of two or more constituents contributes a successful electrolyte in all electrochromic devices.

1.4.1 Classification of electrolytes

Electrolytes play an important role in the light-to-electricity conversion in DSSC. Depending upon the physical state and composition, electrolytes in DSSC can be classified into three: Liquid electrolyte, solid state electrolyte and quasi solid state electrolyte^{1,29,30}. Their merits and demerits are highlighted in Figure 1.4.

1.4.1.1 Liquid electrolytes

Liquid electrolytes are the most widely used transport medium for DSSC since 1991 when Michael Gratzel introduced the first DSSC with a light-to-electricity conversion efficiency of 7.1%³². Still the most widely used transport medium in DSSC is liquid electrolyte. This is mainly because of some of its features like ease of preparation, low viscosity, high conductivity and good interfacial contact between electrodes and electrolyte and hence high efficiency. The highest efficiency so far reported in DSSC is 13% (2014) by M. Gratzel and Nazeeruddin utilizing liquid electrolyte as the transporting medium³³. The performance of the electrolyte depends upon the properties of the electrolyte constituents. Liquid electrolyte in DSSC constitutes two basic components: solvent and redox couple.

Solvent is the basic component in liquid electrolytes. It acts as the medium for the dissolution and diffusion of the ionic conductor. Water is the universal solvent and

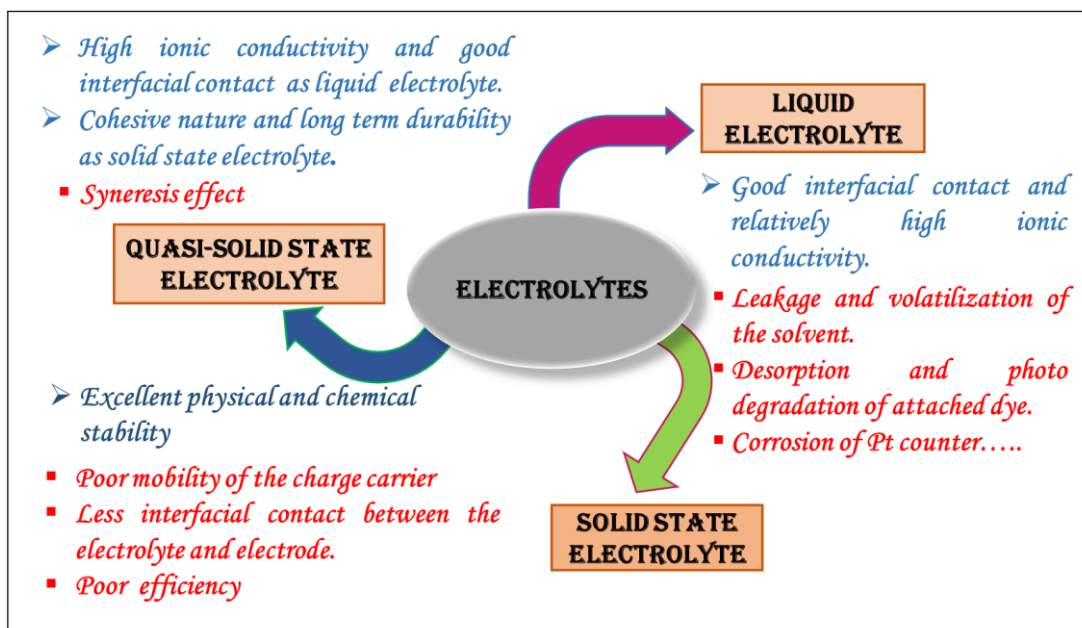


Figure 1.4: Classification of electrolyte for DSSC, their merits (in blue) and demerits (in red)

during the initial stage of DSSC research, water was used as a solvent³⁴. O' Regan et al. from his findings pointed out that addition of 20% water to a non-aqueous solvent enhanced the efficiency of DSSC from 5.5% to 5.7% and on further addition of water, the efficiency was found to decrease³⁵. The maximum efficiency attained for DSSC using pure aqueous electrolyte was 2.4%. This may be due to the oxidation of iodide to iodate (IO_3^-)³⁶, which cannot be reduced at the counter electrode and hence the triiodide concentration reduces resulting in poor cell performance. Also there is a chance for hydrolysis of the dyes in presence of water and mild alcohol and therefore water is not a perfect choice as solvent in DSSC. So water was replaced by organic solvents. The physical constituents of organic solvents that affect the photovoltaic performance of DSSC include dielectric constants, viscosity, melting point, boiling point, donor number etc.

Selection of organic solvents for DSSC should fulfil some of the basic requirements like³⁰:

- † High dielectric constant - so that the added electrolyte salts get completely dissociated
- † Low viscosity – so that the electrolyte possess high conductivity
- † Low melting point and high boiling point – so that the electrolyte will not evaporate under operating conditions
- † Chemically inert towards sealant material, dye-metal oxide surface and counter surface
- † Low light absorption
- † Low toxicity and low cost

Acetonitrile (AN) is the preferred organic solvent for DSSC due to its good chemical stability, good solubility and low viscosity. The first DSSC in 1991 was reported with AN as the organic solvent and the DSSC with highest efficiency reported in 2014 (13% efficiency)³³ utilized the same AN as the organic solvent. But the low boiling point and high toxicity limits it from industrial applications. Other nitriles like 3-methoxypropionitrile (MPN), methoxyacetonitrile etc., have also been widely studied in DSSC. Solvents like ethylene carbonate (EC), propylene carbonate (PC), γ -butyrolactone (GBL), N-methyloxazolidinone (NMO) etc., are other solvents studied in DSSC. Physical properties of some of the common organic solvents used in DSSC's are listed in table 1.1^{1,37}. No single solvent can satisfy the aforementioned

requirements for DSSC application. So always a mixture of two or more solvents are taken to obtain an optimal performance in DSSC.

Table 1.1: Physical properties of some of the common organic solvents used in DSSC

Solvent	MP (°C)	BP (°C)	Viscosity (η)	Dielectric constant (ϵ)
Acetonitrile (AN)	-44	82	0.33	36
Propionitrile (PPN)	-93	97	.39	27
Valeronitrile (VN)	-96	139	0.78	21
3-methoxy-propionitrile (MPN)	-63	164	2.5	36
Butyrolactone (GBL)	-44	204	1.7	42
N-methylpyrrolidone (NMP)	-24	203	1.65	32.2
Ethylene carbonate (EC)	38	244	1.90	89
Propylene carbonate (PC)	-55	240	2.53	64.6
Dimethyl acetamide (DMA)	-20	165	1.93	37.8
Dimethyl formamide (DMF)	-61	153	0.80	36.7
Dimethyl sulfoxide (DMSO)	18.4	189	1.1	45

The redox couple regenerates the photoexcited dye and get oxidized itself during the functioning of a DSSC. This oxidized state then diffuses towards the counter electrode and is reduced and the cycle repeats. The commonly used charge mediator in an electrolyte is the I^-/I_3^- redox couple for DSSC application. Some of the remarkable characteristics of I^-/I_3^- redox couple are^{38, 39}:

- † I^-/I_3^- redox couple exhibit an electrochemical redox potential suitable for the reduction of several oxidized dyes
- † They promote rapid dye regeneration and slow back recombination at the photanode-electrolyte interface (TiO_2 to I_3^-) and hence long electron diffusion length through TiO_2 with cent percent charge collection efficiency
- † Highly soluble in an array of organic solvents and high conductivity
- † I^-/I_3^- is highly reversible and stable under device operation condition

Apart from these remarkable performance of I^-/I_3^- redox couple, they have got several limiting factors^{40,41} such as highly corrosive to many sealing material, relatively high vapour pressure of iodine make it difficult for device assembly, I_3^- ion and other polyiodide if present absorbs a portion of visible light may reduce the light absorption by the dye, the mismatch between the typical sensitizer and I^-/I_3^- redox couple leads to an internal potential loss in DSSC.

As an alternative, cobalt (Co) complexes were tried for the first time by Gratzel group and an efficiency of 12.3% was reported⁴². DSSC's with Br^-/Br_3^- redox couple exhibited higher photovoltage than I^-/I_3^- system but lower current density⁴³. The choice of suitable dye for this system remains as the bottleneck for the expected outstanding performance of the device. Pseudohalogen redox couples like $(SCN)_2/SCN^-$ and $(SeCN)_2/SeCN^-$ were tested with Ru dye-N3 and got an efficiency of 7.5%. However when coming to device performance, the cell exhibited lower efficiency and this can be correlated to the comparative slower regeneration of the photoexcited dye and their

poor stability which limits further study and application^{44,45}. Inter-halogen redox system such as I^-/IBr_2^- and I^-/I_2Br^- in combination with Ru sensitizer gave an efficiency of 6.4%⁴⁶.

Other metal complexes and clusters like Ni (III)/Ni (IV), Cu (I)/Cu (II) and Fc/Fc⁺ have also been investigated. All these redox couples gave an average cell performance of 7 to 7.5% efficiency⁴⁷. An organic redox disulfide/thiolate was successfully tested with a ruthenium based dye- Z907 and got an efficiency of 6.44%⁴⁸ and an efficiency of 7.9% was obtained with PEDOT counter electrode⁴⁹.

Additives in liquid electrolytes:

Additives or coadsorbents are component added to the liquid electrolyte in DSSC in order to optimize the photovoltaic performance. 4-tert-butylpyridine (TBP) was the first additive added in iodine/iodide electrolyte by Gratzel's group soon after the development of DSSC in 1991⁵⁰. A dramatic increase in the photovoltage of the cell was observed when TBP was introduced into the liquid electrolyte. Thereafter nitrogen containing heterocyclic compounds like pyridine, alkylaminopyridine, benzimidazole, pyrazole, quinolone etc., as additives in DSSC electrolytes have been explored extensively by various research groups. The role of additives in photovoltage increase can be ascribed to two reasons: i) shifting of oxide conduction band towards higher energy ii) suppress the back recombination of the injected electron in the oxide conduction band with the electrolyte, and hence longer electron life time in the oxide conduction band⁵¹. Huang et al. found that these nitrogen heterocyclic compounds reduce the recombination by 1-2 orders of magnitude. Another additive that studied

by different research groups include specific cations like guanidinium ions (guanidinium thiocyanate) and lithium ions. An enhancement in short-circuit current density (J_{sc}) was observed in DSSC with cation additives. Cation additives get adsorbed on to the oxide surface and reduces the dark reaction taking place at the photoanode-electrolyte interface⁵². Adsorption of a cation additive on the oxide surface shift the oxide conduction band downwards resulting an increased electron injection from the excited dye molecule to the semiconductor oxide. Though these two additives perform different function with respect to the oxide conduction band, they are often simultaneously used in electrolyte to obtain an optimal photovoltaic performance.

Ionic liquids:

Room temperature ionic liquids (RTIL) are attractive alternatives to the volatile organic solvents in DSSC. These are organic salts composed of aromatic and non-aromatic cations with various anions⁵³. These are molten salts with low volatility, good chemical and thermal stability, non-flammability and high ionic conductivity. ILs used in DSSC are of imidazolium based and non-imidazolium based. Most widely used RTILs are alkyl imidazolium salts, trialkyl methyl sulfonium salt, alkyl pyridinium salt, etc^{30,54}. DSSC using an ionic liquid, methyl-hexyl-imidazolium iodide (MHImI), as involatile electrolyte was first demonstrated by Papageorgiou in 1996 and showed an outstanding stability. By using ethyl-methyl imidazolium selenocyanate (EMImSeCN) an efficiency of 7.5-8.3% was obtained for Wang et al. and group.

However the conversion efficiency of DSSC based on non-imidazolium ILs are normally lower than imidazolium based electrolytes owing to their relatively high viscosities and mass transport limitations. Pure IL are highly viscous than the organic solvents. The diffusion coefficient of the redox species are lower in magnitude than those of the volatile organic solvents. This is the main disadvantage of the ILs. As a result the reduction of the sensitizer get delayed and hence lowers the cell efficiency. In order to reduce the mass transport limitation of ionic liquids, these are usually diluted with organic solvents¹. But the mass transport limitation is not only the factor that limits its use in DSSC. It was found that⁵⁵ in the presence of high concentration of imidazolium iodides, effective quenching of dye molecules were observed and so the electron injection to the semiconductor conduction band will not takes place effectively. Studies also suggests that when compared to volatile organic solvents, a high recombination and lower rate of electron injection probably due to the conduction band shift of TiO₂, slower dye regeneration, faster self-recombination of the dyes limits the use of this pure ILs in DSSC⁵⁶.

The highest efficiency of 13% in DSSC was achieved using Co (II/III) redox species in acetonitrile solvent and zinc-porphyrin sensitizer with a Voc of 0.91 V, Jsc of 18.1 mAcm⁻² and FF of 78%. DSSC showed the best performance when liquid electrolyte was employed as the charge carrier transporters. But the commercialization and outdoor application of these device is still a problem to the scientific world due to the lack of long stability and durability. The problem of leakage and volatilization of the solvent, ineffective sealing, photo-degradation and desorption of the attached dye,

corrosion of the counter electrode etc. are some of the major impediments confronted when using the liquid electrolyte^{1,57,58}. By using the viscous IL, high efficiency was obtained but the problem of sealing and leakage still exist. As an alternative solid state electrolytes are introduced.

1.4.1.2 Solid state electrolytes

Solid state DSSC (SS-DSSC) are of two kinds in which one utilizes hole transporting material (HTM) as medium and in the second one iodide/triiodide redox couple acts as the medium. In the former case the dye is restored by accepting an electron from the hole conductor which in turn is regenerated at the counter electrode⁵⁹. The transport mechanism in cells with HTM is typically electronic³⁰. Inorganic salts like CuI⁶⁰, CuSCN⁶¹ CuBr etc., or organic molecular solids and polymers including conducting polymers are widely used as HTM for SS-DSSC. First SS-DSSC was introduced by Tennakone in 1995 based on CuI HTM and reported an efficiency of 2.4%^{60,62}. In 1998, SS-DSSC with organic HTM 2,2',7,7'-tetrakis(N,N-di-*p*-methoxyphenylamine)9,9'-spirobifluorene (OMeTAD)⁶³ was developed with an efficiency of 0.74%. Overall the efficiency of SS-DSSC was less when compared to traditional DSSC using liquid electrolyte and this is mainly due to two major reasons: low intrinsic conductivity of HTM and poor contact between the dye molecule and HTM.

In solvent-free polymer electrolytes with iodide/triiodide redox couple as the medium, the structure and operational principle is similar to that of DSSC using liquid electrolyte. The conduction mechanism in polymer electrolyte results from a solvation

– desolvation process along the chains that occur in the amorphous polymer phase³⁰. Superior performance of polymer electrolyte when compared to HTM in SS-DSSC is due to the efficient regeneration of the dye ground state by the I^-/I_3^- redox couple and better interfacial contact properties. But these solid state electrolytes are not an ideal electrolyte material for DSSC. By introducing solid state electrolyte some of the problems like leakage and volatilization of the solvent, sealing problem and hence the stability and durability of the device was improved. But they also confronted some major problems when the device got assembled such as less interfacial contact between the electrode-electrolyte interfaces, poor mobility of the charge carriers³⁰ and hence lower cell performance. So it became a prerequisite to find a new electrolyte with the benefits of both the liquid and solid state electrolyte and ‘quasi solid state electrolyte’ or ‘gel electrolyte’ was introduced.

1.4.1.3 Quasi solid state electrolyte/ Gel electrolyte

In Latin the word ‘gel’ means ‘freeze’. Gels are colloids constituting solid component as dispersion medium and liquid as the dispersed phase. During gel formation, loose framework is woven by the interlocking of solid dispersion medium inside which the liquid is entrapped^{64,65} and the process of gel formation is called gelation. Cooked egg white is an example of gel from our day today life. The proteins in egg open up from their natural folded shape and then bind to one another to give the gel.

Gel electrolytes possess features intermediate between liquid and solid state electrolytes. Gel electrolytes are defined as the system which consist of a polymer

matrix swollen with liquid electrolyte⁶⁶. Generally a salt-solvent-polymer hybrid in which salt solution is immobilized with a suitable polymer. The polymer matrix that forms the framework is often referred to as ‘gelator’. The uniqueness of the gel electrolyte lies in its ability to switch its property between solid state electrolyte and liquid electrolytes. They simultaneously possess the cohesive property of solid electrolyte with low liquid fluidity, reducing the leakage and vaporization of the solvent and thereby improves the durability and long term stability and diffusive transport property of the liquid that helps in the proper wetting of the electrode surfaces and high ionic conductivity^{30,67,68}.

Depending upon the cross-linking (interaction) formed during gelation, they can be classified into two^{30,29} (i) thermoplastic gel electrolytes and (ii) thermosetting gel electrolytes.

Thermoplastic gel electrolytes (TPGE)

Polymeric network structures were found to be highly beneficial to the entrapment of a large volume liquid electrolyte. Polymers are giant molecules with large number of segments entangled to form a tightly folded random coils. There are numerous cohesive and attractive forces acting between different segments of the same molecular coils as well as neighboring coils. Forces like dispersion, induction, dipole-dipole interaction and hydrogen bond hold the molecular coils and segments together. Because of these strong attractions and entangled structure the dissolution of polymers occurs very slowly. When a polymer fragment comes in contact with a solvent, force of attraction/dispersion start acting between them. When solvent-solute interaction

become more intense than solute-solute attraction, the force holding the polymer segment together become weak and breaks the segment-segment interaction. During this process a few segment of the coil here and there unfolds and the solvent penetrate into the intersegmental space thus vacated. As more solvent penetrate, segment-segment interaction get weakened and the coiled segments get completely solvated by unfolding. Gel formation or gelation takes place by the association of the polymer segments in solution to form a three dimensional network with solvent in the interstices. During gelation a dilute heterogeneous mixture of polymer-electrolyte solution is converted into a homogeneous system of infinite viscosity, i.e., a transition from a sol state to gel state⁶⁹.

The network formed via a physical cross-linking is called ‘entanglement network’. These physical cross-linking (interaction) is temperature dependent and therefore the gels obtained are thermo-reversible. Hence they are termed as thermoplastic gel electrolyte^{29,30}. The polymer chains can move more freely because of the presence of weak intermolecular forces. Figure 1.5 (a) shows schematic representation of physical interaction between the polymer chains on gelation. First experiment on quasi solid state dye sensitized solar cell was done by Cao et al. using a mixture of poly(acrylonitrile), ethylene carbonate, propylene carbonate, acetonitrile and NaI and the gel was obtained after three days⁷⁰. QSDSSC based on TPGE gave almost same efficiency as the corresponding DSSC. Moreover the long term stability of the device was greatly improved. Most studied gelators are mainly linear polymers including PEO, PAN, PVP, PS, PVC, PVE, PVDF, PMMA etc¹.

Organic molecules are also used as gelators for preparing TPGE. Yu et al. incorporated cyclohexane carboxylic acid-[4-(3-octadecylureido)phenyl]amide⁷¹ to MPN based liquid electrolyte and C105 dye and obtained a conversion efficiency of 9.1%. TPGE without gelator was reported by Yang et al., by adding 1-alkyl-3-carboxypyridinium iodide molten salt into AN-MPN liquid and lithium salt. Here gel electrolyte is formed by the complexation between organic iodide and inorganic ions without any nanoparticles, oligomers or polymer matrix⁷².

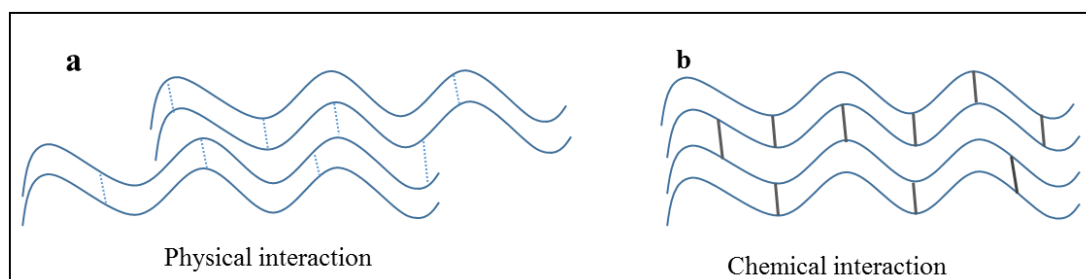


Figure 1.5: Physical interaction in thermoplastic gel electrolyte (a) and chemical cross-linking in thermosetting gel electrolyte (b)

Thermosetting gel electrolytes (TSGE)

Thermosetting gel electrolytes obtained as a result of chemical cross-linking or covalent cross-linking. These type of gel electrolyte cannot reversibly change with temperature and hence the name thermosetting gel electrolyte^{29,30}. The cross-links hold the polymeric chains in place and cannot move freely. Figure 1.5 (b) shows schematic representation of chemical interaction between the polymer chains on gelation. The conductivity of TSGE is lower than TPGE, but still considered as an optional electrolyte material for DSSC because of its physical, chemical and thermal stability when compared with TPGE. These TSGE are usually prepared via three methods⁷³⁻⁷⁶:

1) light induced in situ polymerization 2) heat induced in situ polymerization and 3) liquid electrolyte adsorption method. For in situ chemical or covalent cross-linking to occur certain conditions are necessary⁷³. i) polymerization should occur at a temperature below dye decomposition ii) there should be no byproduct formation throughout the polymerization iii) polymerization should occur in the presence of iodine iv) polymerization should proceed without an initiator because the initiator or its byproducts may decrease the photovoltaic performance.

The first TSGE was introduced by Matsumoto in 2001 via a photoinduced in situ polymerization of α -methacryloyl- ω -methoxyocta (oxyethylene) and obtained a conversion efficiency of 2.62%⁷⁴. There are also gels that liquefy on shaking and reset on being allowed to stand. These gels are called thixotropic gels and the reversible sol-gel transition is called thixotropy.⁷⁶

One of the major disadvantages of gel systems is that they are highly unstable thermodynamically. When the gels stands for a long time contraction begins with the loss of the liquid trapped within. This contraction or shrinking of gel cause the separation of trapped liquid electrolyte and this is called ‘*syneresis*’ or ‘*weeping*’⁷⁷. This solvent exudation upon long storage under open atmospheric condition lowers the ionic conductivity and hence cell performance³⁰.

1.5 Aim of the thesis

Leakage and volatilization of the liquid electrolyte is the major setbacks of conventional DSSC. This thesis aims to prepare quasi-solid state electrolyte to subdue the problems confronted while using liquid electrolyte. The main objectives include:

- ⊖ Synthesis of quasi solid state electrolytes for QSDSSC application via a simple gelation method. The preferred polymer matrix are

Polyvinyl alcohol

Polymethyl methacrylate

- ⊖ To modify the properties of the synthesized gel electrolyte by incorporating additives and the selected additives are

4-tertbutyl pyridine and guanidinium thiocyanate

Commercial TiO₂

ZnO (synthesized)

The synthesized polymer gel electrolyte and the filler incorporated polymer gel electrolyte has to be characterized to study the structural, thermal and electrical properties. Fourier transform infrared spectroscopy is an efficient tool to study the structural identification of the synthesized sample. The thermal property and stability can be understood by performing thermogravimetric analysis on the samples. The diffusion of the ionic species can be studied from linear sweep voltammetry and the total ionic conductivity of the system can be understood by exploring the electrochemical impedance spectra. Finally the application study of these gel electrolyte has to be carried out by fabricating QSDSSC.

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2

CHARACTERIZATION TECHNIQUES AND THEORY

2. CHARACTERIZATION TECHNIQUES AND THEORY

2.1 Characterization Techniques

The morphology, structure, optical, thermal and electrical properties of the synthesized samples were analyzed by using different characterization techniques. Finally, the application of gel electrolytes in solar cell design was analyzed. The formation and phase purity of the samples were confirmed from X-Ray diffraction analysis and energy dispersive spectra. The morphological and structural studies were performed using scanning electron microscopy and Fourier-transform infra-red spectroscopy. The thermal stability of the sample was studied by performing thermogravimetric analysis. The electrical properties were measured using electrochemical impedance spectroscopy and linear sweep voltammetry. The optical characterizations were carried out by performing the diffuse reflectance spectrum, tauc plot and photoluminescence measurements. The gel electrolytes were then applied in QSDSSC and monitored the photovoltaic performance of the device from the I-V and EIS measurements.

The major characterization tools used for the analysis and application study are listed below and the theory involved in each technique is discussed in detail in the following paragraphs.

- *Field-emission scanning Electron Microscopy*
- *Energy Dispersive Spectra*
- *X-Ray Diffraction analysis*
- *Diffuse Reflectance Spectroscopy*

- *Photoluminescence Spectroscopy*
- *Fourier Transform Infrared Spectroscopy*
- *Electrochemical Impedance Spectroscopy*
- *Linear Sweep Voltammetry*
- *Thermogravimetric Analysis*

2.1.1 Field Emission Scanning Electron Microscopy (FE-SEM)

FE-SEM is a powerful magnification tool that images a sample surface by raster scanning over it with a high energy electron beam. Electrons from a field emission source is accelerated in a high electrical field gradient. These primary electrons are focused and deflected by electronic lenses to produce narrow electron beam that hit the sample. As a result secondary electrons, that relates the surface structure of the object, are ejected. These ejected electrons are analyzed by a detector to produce an electronic signal that can be transformed to a digital image¹. The signals produced by the sample gives information about surface topography, composition etc. A typical SEM image is shown in figure 2.1. The morphology of the synthesized samples were examined with field emission scanning electron microscope (FEI-QUANTA-FEG250).

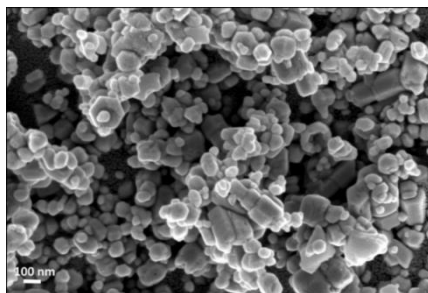


Figure 2.1: A typical SEM image

2.1.2 Energy Dispersive X-ray Spectroscopy

Energy dispersive X-ray spectroscopy (EDS or EDX) is a powerful technique used in conjunction with SEM to identify the surface elemental composition. It works by detecting the X-rays produced by sample placed in electron beam path. The sample is bombarded with a beam of electrons and the X-rays emitted from the sample is detected to obtain the elemental composition of the analyzed volume².

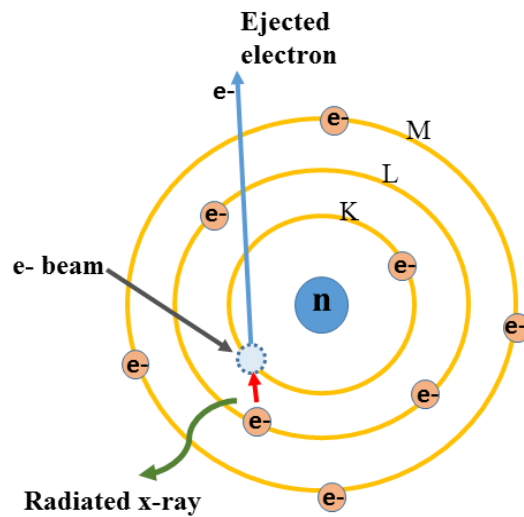


Figure 2.2: Schematic showing the principle of EDS

Figure 2.2 shows the schematic representation of EDS principle. When the SEM's electron beam hit the surface of the sample, electrons from the atoms at the surface get ejected. The vacancy thus created is filled by electrons of higher energy state with the emission of an X-rays to balance the energy difference between the two electronic states. These X-ray energies are the characteristic of each element. From the spectrum of X-ray energy versus count, the elemental composition of the sample analyzed is obtained.

2.1.3 X-ray Diffraction Analysis (XRD)

X-ray diffraction analyses are used to obtain the information about the crystal structure and atomic spacing of a material. The interaction of an electromagnetic wave with an object produces constructive interference when conditions satisfy Bragg's law³. The law gives a simple relation between the wavelengths of the X-rays, the interplanar distance in the crystal and the angle of reflection. The diffracted rays are then studied. The Bragg's equation is given by:

$$n\lambda = 2d \sin \theta \quad (1)$$

Where n can have values 1, 2, 3, etc., λ is the wavelength of the incident radiation, d is the distance between the planes and θ is the incident angle. Scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained. Conversion of the diffraction peaks to d-spacing helps to identify the material. Figure 2.3 represents the Bragg's reflections from a crystalline surface⁴.

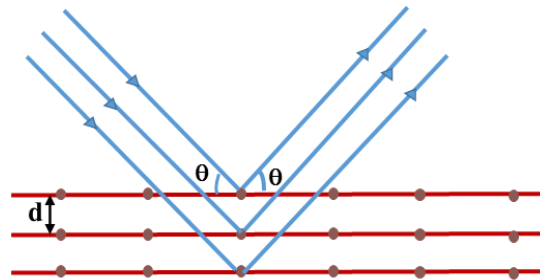


Figure 2.3: Bragg's reflections from a crystalline surface

Also the crystallite size of the sample can be calculated using Scherrer formula.

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (2)$$

Where D is the crystallite size, λ is the wavelength of the incident radiation, β is the full width at half maximum of the most intense peak and θ is the angle of incidence.

The formation, purity and crystallinity of the samples were obtained from the X-ray diffraction (XRD) with Cu-K α radiation. The obtained XRD pattern is then compared with a standard JCPDF data.

2.1.4 Optical Measurements

Optical characterization techniques explore the change on intensity, energy, phase, direction, or polarization of the light wave after interaction with the object being studied. UV-Visible absorption spectrum was measured at room temperature on a PerkinElmer Lambda 650 spectrometer and the photoluminescence spectrum was recorded using fluorescence spectrometer - PerkinElmer-LS55.

2.1.4.1 Diffuse Reflectance Spectrum (DRS)

DRS is a powerful spectroscopic tool to estimate the bandgap energy of powder sample. For bulk material it is difficult to obtain the absorbance and hence the reflection of the sample is taken. The theoretical description to diffuse reflectance spectroscopy is given by Kubelka-Munk theory. When a powder is irradiated with light, a portion of it get reflected and remaining enters the powder and diffuses. Figure 2.4 shows the diffuse reflection from the surface of a bulk sample.

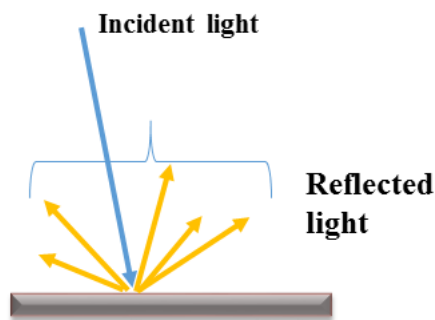


Figure 2.4: Diffuse reflection

The measurement of diffuse reflectance light at different wavelength gives the diffuse reflectance spectrum. Kubelka-Munk function is given as⁵:

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{k}{s} = \frac{Ac}{s} \quad (3)$$

Where, R = reflectance; k = absorption coefficient; s = scattering coefficient; c = concentration of the absorbing species; A = absorbance.

Tauc Plot:

Tauc plot is used to determine the optical band gap of semi-conductors. The data obtained from DRS is converted to data equivalent to absorption. The plot is obtained by taking $h\nu$ (photon energy) along abscissa and $(\alpha h\nu)^{1/n}$ along the ordinate. α is the absorption coefficient. For allowed direct transitions $n = 1/2$, allowed indirect transitions $n = 2$, prohibited direct transition $n = 3/2$, prohibited indirect transition $n = 3$. The resulting plot has a linear regime which on extrapolating to the abscissa gives the energy of the optical bandgap of the material.

2.1.4.2 Photoluminescence Measurement

Photoluminescence is the emission of light from the material under optical excitation and it helps to determine the bandgap, purity, crystalline quality and defect levels of semiconductors. When light is directed on to a sample, it absorbs certain amount of energy and the valence band electrons get excited to the conduction band. When the electrons return to their equilibrium state, the excess energy is dissipated through the emission of light (luminescence) or some other non-radiative processes. In radiative emission as the electrons relax to their band edges light is emitted⁶. Figure 2.5 shows the schematic representation of the principle of PL spectroscopy.

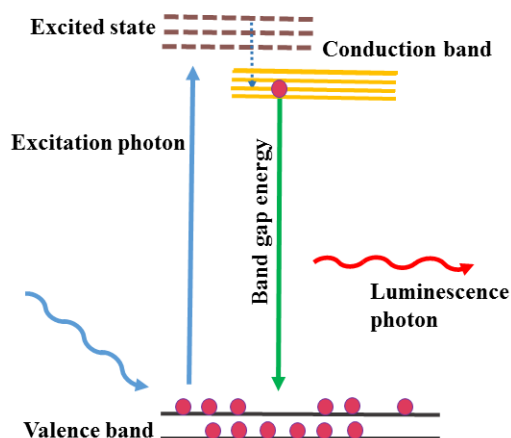


Figure 2.5: schematic showing the principle of photoluminescence

In semiconductors, the defects or impurity level take part in radiative transition and hence analysis of their PL spectrum helps to identify the defects or impurities present. The spectrum is a graph of emission intensity vs excitation wavelength⁷. Emission behaviour of the sample synthesized has been checked by recording the photoluminescence spectrum at room temperature.

2.1.5 Fourier Transform Infra-red Spectroscopy (FT-IR)

The technique is used mainly to identify the organic materials. When a molecule is irradiated with an infrared radiation, it absorbs some radiation and get excited. The absorption is due to the change in vibrational and rotational levels and causes the bonds to bend and stretch. Only those bonds which are accompanied by a change in dipole moment will absorb in the infra-red region. The absorption of radiation within the range 1500 cm^{-1} to 4000 cm^{-1} causes the bonds to stretch and absorption below 1500 cm^{-1} (fingerprint region) causes bending of the bonds. The absorbed radiation will be the characteristic of its molecular structure. The intensity of the transmitted or reflected light as a function of wavelength is measured. The interferogram obtained from the detector is analyzed with a computer using Fourier transforms to obtain the infra-red spectrum.

FTIR spectra of the samples were recorded at a resolution of 4 cm^{-1} in the range from 400 to 4000 cm^{-1} using Perkin Elmer Spectrum Two FT-IR spectrometer. The plot of FT-IR spectra is usually presented as transmittance vs wavenumber⁸.

2.1.6 Thermogravimetric Analysis (TGA)

TGA is a technique in which the change in mass of a sample over a range of temperature is measured in a controlled atmosphere. As the sample is heated, its mass changes. From the change in mass the composition of a material and its thermal stability can be predicted⁹. This change in mass may be due to weight loss (decomposition, evaporation or reduction) or weight gain (oxidation or absorption). A typical TGA curve is shown in figure 2.6.

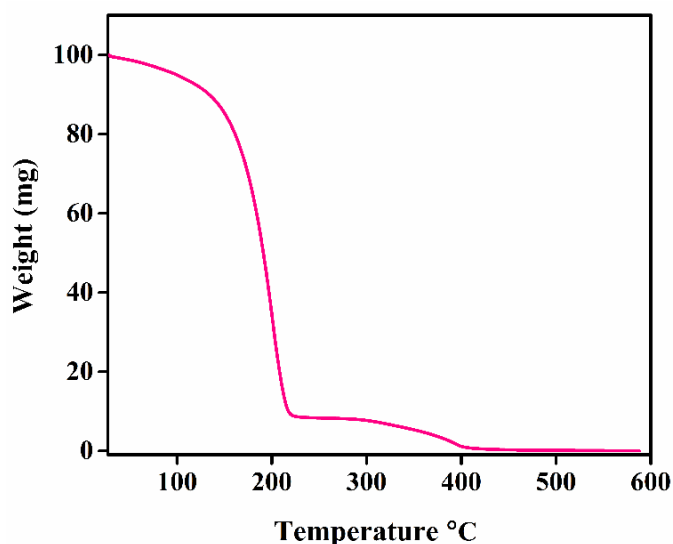


Figure 2.6: A representative TGA curve

Typically, polymers undergo three primary thermal decomposition processes, namely, depolymerization, elimination and cyclization¹⁰. The thermal stability of the synthesized samples were carried out in SDT Q600 V20.9 Build 20. The samples were heated in an alumina crucible from room temperature to 600 °C at a rate of 10 °C per min under nitrogen flow.

2.1.7 Electrochemical Impedance Spectroscopy (EIS)

EIS is a powerful tool to obtain information about the interfacial charge transfer at different interfaces in a solar cell or any electrochemical devices. EIS consists of measurement of ac current (I) at an angular frequency (ω) when certain ac voltage is applied (V) or vice versa¹¹.

$$Z(\omega) = \frac{V(\omega, t)}{I(\omega, t)} \quad (4)$$

Where Z is a vector quantity called the impedance, V is the voltage and I is current

In complex numbers, AC voltage can be described as $V_0 \exp(j\omega t)$ and the corresponding current as $I_0 \exp[j(\omega t - \theta)]$, where θ is the phase difference between $V(\omega, t)$ and $I(\omega, t)$ and $j = \sqrt{-1}$. Equation (4) can then be written as

$$Z(j\omega) = \frac{V_0}{I_0} \exp(j\theta) = Z_0 \exp(j\theta) \quad (5)$$

On applying Eurlers relationship and replacing Z_0 with $|Z|$, equation (5) becomes

$$Z(j\omega) = |Z| (\cos\theta + j\sin\theta) \quad (6)$$

In general, impedance can be expressed as,

$$Z(j\omega) = Z_{re} + jZ_{im} \quad (7)$$

$$Z = Z' + jZ'' \quad (8)$$

In an electrochemical impedance spectrum (Nyquist plot) the real part of the impedance (Z') is plotted on the X-axis and the imaginary part (Z'') is plotted on the Y-axis.

The EIS of a gel electrolyte is taken by fabricating a dummy cell and the cell structure is - [Pt/ (I^- / I_3^-) electrolyte/Pt]. The synthesized gel electrolyte is sandwiched between two Pt electrodes to obtain the dummy cell and the EIS measurement was carried out. Considering the various interfaces that are present in the dummy cell, it is possible to model an equivalent circuit. Figure 2.7 shows the Nyquist plot representation of a dummy cell and figure 2.8 shows the corresponding equivalent circuit. There will be resistance components and capacitive components. R_s is the series resistance. The two resistances R_1 and R_2 are the resistive components at the

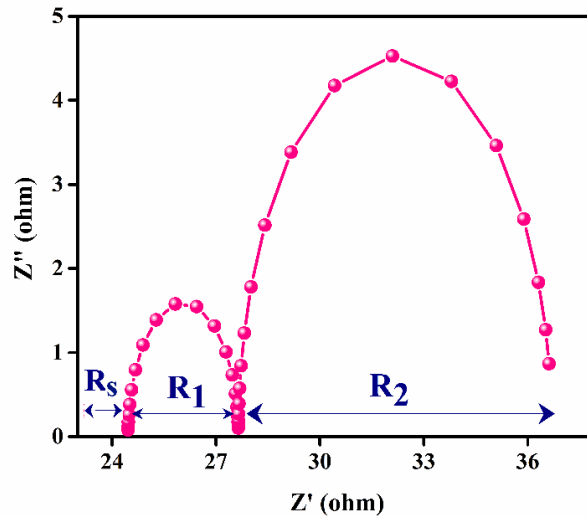


Figure 2.7: Nyquist plot for a dummy cell counter electrode-electrolyte interface and diffusion resistance in the electrolyte. The capacitance elements are due to the formation of electrical double layer at the interface. The data obtained from this measurement was fitted by simulation software – Z-fit, which proposed an equivalent circuit to model the data.

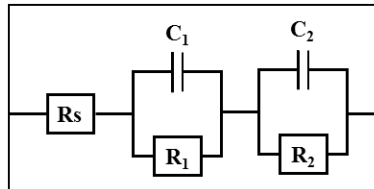


Figure 2.8: Equivalent circuit of a dummy cell

The total conductivity (σ) of the electrolyte can be calculated from the equation¹²:

$$\sigma = \frac{l}{AR_2} \quad (9)$$

Where l is the thickness of the film and A is the active area.

When coming to device, one more interface will be present. A typical Nyquist plot of a QSDSSC is shown in figure 2.9.

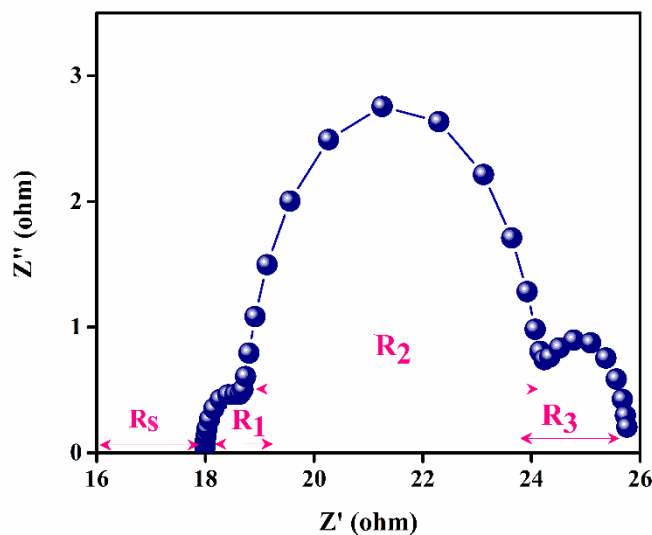


Figure 2.9: Typical Nyquist plot of QSDSSC

It consists of three semi-circles which indicate that electron transport taking place at each interface has different time constants¹³. The corresponding equivalent circuit is shown in figure 2.10.

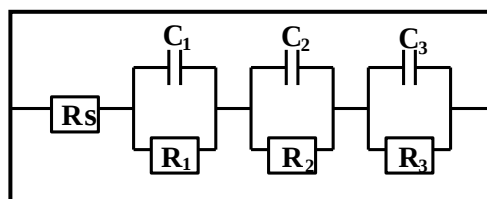


Figure 2.10: Equivalent circuit model of QSDSSC

R_s represents the sheet resistance of the FTO glass, contact resistance and wire resistance. R_1 shows the resistance at the counter – electrolyte interface, R_2 represents the resistance at the photoanode-electrolyte interface and R_3 is the Warburg impedance.

2.1.8 Linear sweep voltammetry (LSV)

Linear sweep voltammetry is an electroanalytical method where the current is measured as the potential is varied. It is a subset of cyclic voltammetry consisting of a single voltage sweep along one direction. A typical linear sweep voltammogram is shown in figure 2.11. The diffusion of iodide and triiodide in the electrolyte influence the light to electricity conversion in QSDSSC. From linear sweep voltammogram the limiting current density is obtained and by substituting the value in equation (10) gives the apparent diffusion coefficient of the limiting ion can be calculated¹⁴.

$$J_{lim} = \frac{2nFD^*C_0}{d} \quad (10)$$

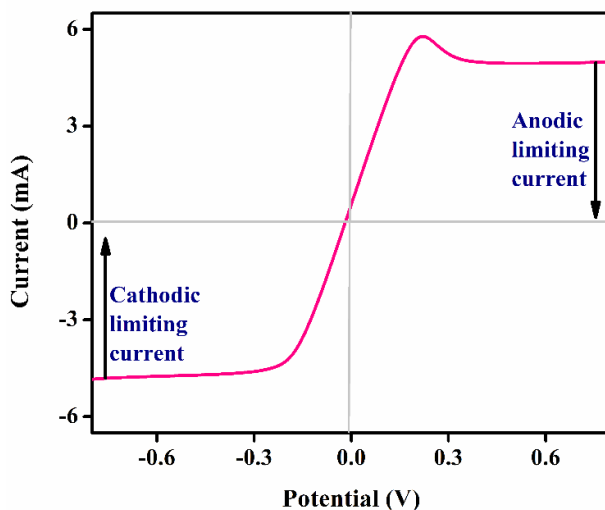
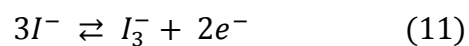


Figure 2.11: A typical linear sweep voltammogram

The LSV of a polymer gel electrolyte is done by fabricating a dummy cell. When a potential is applied to the cell, the following reaction occurs at the Pt surface:



In I^-/I_3^- electrolyte, an excess iodide concentration over I_3^- is taken, which ensures triiodide as the limiting current ions. Therefore limiting current density obtained in this case can be used to calculate the triiodide apparent diffusion coefficient.

2.1.9 Application

The synthesized gel electrolyte is applied to QSDSSC. The components of the device, working principle and fabrication is discussed in Chapter 1, section: 1.3.1 and Chapter 3, section 3.7.1. The photovoltaic performances and the charge transport and recombination properties of the device can be studied by performing the current-voltage measurement and the electrochemical impedance spectroscopy. The J-V measurements and EIS for the cells were done with Bio-Logic SAS SP-150 using Sciencetech SF 150B solar simulator as the light source with 100 mWcm^{-2} light output under AM 1.5 illumination.

2.1.9.1 J-V Curve

Figure 2.12 shows the typical J-V curve of QSDSSC. From the curve photovoltaic parameters like short circuit current, open circuit voltage, fill factor and efficiency of the device can be obtained and these parameters are discussed below in detail.

Solar cell terminologies:

Short-circuit current (J_{sc}): Short circuit current is the maximum current obtained from the cell when short circuited¹⁵ i.e, when the applied potential is zero. Current from a

cell is normally expressed as current density (J_{sc} - mAcm^{-2}) and is obtained by dividing the obtained short circuit current by the effective area of the cell.

$$J_{sc} = \frac{I_{sc}}{A} \quad (12)$$

Where A is the active area of the cell.

Open circuit voltage (V_{oc}): Open circuit voltage is the maximum voltage obtained from the cell when no current flows and is defined as the potential difference between the fermi level of semiconductor oxide and the redox potential of the electrolyte. V_{oc} is given by:

$$V_{oc} = \frac{E_{cb}}{q} + \frac{kT}{q} \ln\left(\frac{n}{N_{cb}}\right) - \frac{E_{redox}}{q} \quad (13)$$

The first two terms defines the quasi fermi level of the semiconductor oxide, n is the number of electrons in the semiconductor oxide, N_{cb} is the density of states and E_{redox} is the Nernst potential of redox mediator. V_{oc} is expressed in volts.

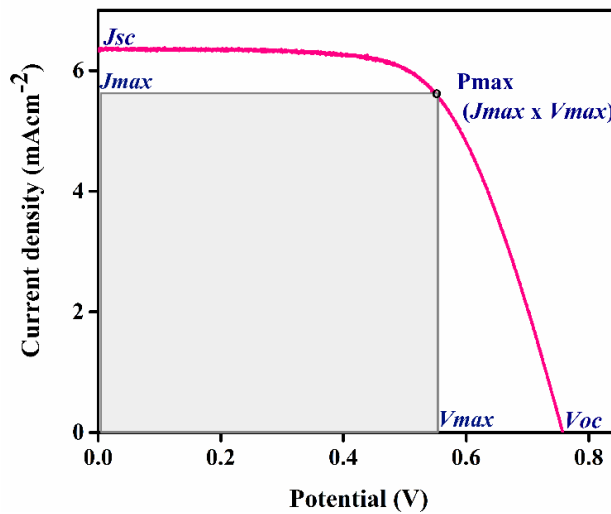


Figure 2.12: Typical J-V curve of QSDSSC

Fill factor (FF): Fill factor of a cell represent the squareness of the J-V curve and is the ratio of maximum power output to the product of short circuit current and open circuit voltage. It reflects the electrical and electrochemical losses occurring during DSSC operation.

$$FF = \frac{I_{max} \cdot V_{max}}{J_{sc} \cdot V_{oc}} \quad (14)$$

Where I_{max} and V_{max} are the current and voltage at maximum power point. FF being the ratio of same physical parameters, doesn't have a unit. It is a function of series and shunt resistance. FF ranges between 0 and 1. The value 1 corresponds to zero internal resistance cell.

Power conversion efficiency (η): Efficiency of a solar cell is obtained by taking the ratio of maximum power output to incident radiation power.

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_{in}} \quad (15)$$

Where P_{in} is the power input from the source. Efficiency is generally expressed in percentage.

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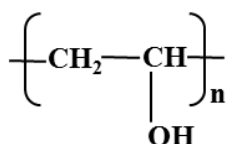
SYNTHESIS OF PVA AND PMMA GEL
ELECTROLYTES, ITS
CHARACTERIZATION AND
APPLICATION

3. SYNTHESIS OF PVA AND PMMA GEL ELECTROLYTES, ITS CHARACTERIZATIONS AND APPLICATION

3.1 Introduction

Polyvinyl alcohol (PVA)

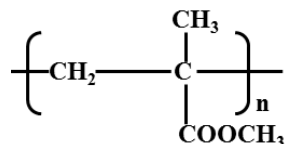
Polyvinyl alcohol is a water-soluble^{1,2} synthetic polymer with the chemical structure



The monomer, vinyl alcohol being unstable, the polymer PVA is prepared by the hydrolysis of polyvinyl acetate in presence of acid or alkali¹. PVA is a biodegradable, non-toxic polymer that have good optical features, physico-mechanical property, low-cost, and high dielectric constant^{3,4}. The polar functional group –OH present in PVA helps in the dissolution of the salt and is a source of hydrogen bonding. This helps in building interconnected network between the polymer chains with the help of the solvents and hence provide high chain flexibility⁵. Polyvinyl alcohol has excellent film forming, emulsifying and adhesive⁶ properties. It is also resistant to oil, grease and solvents⁷.

Polymethyl methacrylate (PMMA)

The polymethyl methacrylate is a synthetic polymer of methyl methacrylate and has the following chemical structure:¹



The full chemical name is poly(methyl 2-methylpropenoate)- $(\text{C}_5\text{O}_2\text{H}_8)_n$. It is sold under the trade names – Lucite, Acrylite, Plexiglass optix, Altuglas, Orgoglas, Perspex⁸. Polymethyl methacrylate is a lightweight, colorless transparent thermoplastic with good strength and excellent outdoor life. It is amorphous by nature, owing to the presence of bulky side groups in the molecule. Optical clarity is the main feature of this plastic. PMMA transmits up to 92% of visible light, and gives a reflection of about 4% from each of its surfaces due to its refractive index (1.4905 at 589.3 nm)^{1,9,10}. It is an excellent substitute for glass in many applications and has good mechanical property. PMMA is used to make head and tail light covers on passenger automobiles, illuminated signs, street lamp housings, aircraft windows and in other weight sensitive applications such as race cars, motorcycles and off-road vehicles. PMMA is also compatible with human tissue and is used for making prosthetics and transplants especially related to ophthalmology¹¹.

The current study discuss the synthesis of PVA and PMMA based polymer gel electrolytes, their network structure, basic characterizations and QSDSSC fabrication.

The study compares the performance of polymers – PVA and PMMA in making quasi-solid state electrolyte for QSDSSC application.

3.2 Synthesis of polymer gel electrolyte

Polymeric network structures were found to be highly beneficial for the entrapment of a large volume liquid electrolyte. During gel formation or gelation a few segment of the coil randomly unfolds and the solvent penetrate into the intersegmental space thus vacated. As more solvent penetrate, segment-segment interaction get weakened and the coiled segments get completely solvated by unfolding. There are numerous cohesive and attractive forces acting between different segments of the same molecular coils as well as neighboring coils. Forces like dispersion, induction, dipole-dipole interaction and hydrogen bond hold the molecular coils and segments together. Depending upon the extent of crosslinking, the network structure become too dense to store a fair amount of liquid electrolyte¹. In some cases, thermal energy is required to trigger or improve the solvent polymer interaction and to extend the polymer chains. Gelation occurs very slowly. At low temperature the molecular motion of the polymer chains decreases and makes the cross linking easier between polymer chains.

There are several factors which determines the properties and structure of polymer gel electrolyte formed, such as, molecular mass of polymer, initial concentration of polymer in the solution, chain tacticity, chemical structure of the polymer material, thawing rate, duration of storing in frozen state etc^{12,13}.

PVA and PMMA are the two polymer matrix chosen to immobilize the liquid electrolyte. The difference between the polymers lies in the group attached to the polymer backbone. In PVA, $-H$ and $-OH$ group are the side groups and in PMMA, $-H$, $-CH_3$ and $-COOCH_3$ are the side groups. Simple gelation technique was employed for the synthesis of polymer gel electrolyte. The synthesis, characterizations and application of the polymer gel electrolytes are discussed in the following sections.

3.2.1 Synthesis of PVA gel electrolyte

Materials

- Potassium Iodide (KI)
- Iodine (I_2)
- Ethylene carbonate (EC)
- Dimethyl sulfoxide (DMSO)
- Polyvinyl alcohol (PVA)

PVA gel electrolyte with different concentrations of KI and I_2 is prepared. An optimum electrolyte composition is essential to minimize the metal corrosion and visible light absorption by this I^-/I_3^- electrolyte, details discussed in section 3.7.3 of this chapter. By trial and error method the concentration of KI and I_2 is chosen as 0.3 M and 0.03 M respectively.

Method

Liquid electrolyte was first prepared by adding 0.3 M KI and 0.03 M I_2 into a mixture of DMSO and EC. DMSO is a polar protic solvent that helps in the dissolution

of the salts and EC acts as the plasticizer which when added to a polymer improves its flexibility, processibility and utility. The solution mixture was stirred until we get a homogenous mixture. To this liquid electrolyte 0.19 g of PVA was added and heated at 100 °C with stirring till the polymer get completely dissolved in the organic mixture. The result was a uniform highly viscous molten solution which on keeping for an overnight set to give a three dimensional network structure of free standing “*pudding thick*” PVA polymer gel electrolyte as shown in Figure 3.1. The sample is named as VA B (bare polyvinyl alcohol) throughout the thesis for simplicity. The following paragraphs briefs different parameter optimization for a better PVA gel electrolyte.

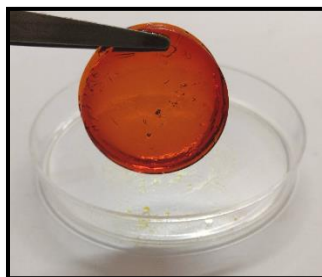


Figure 3.1: Free standing PVA gel electrolyte

3.2.1.1 *Gelation and Expected gel network structure*

The solvent was heated at 100 °C for the dissolution of PVA to get a highly viscous molten PVA gel electrolyte. On keeping this hot melt overnight, the temperature of the polymer solution decrease and the molecular movements of polymer chain will be reduced. As a result, intermolecular force of attractions in PVA strengthens and impart crystallinity to the polymer network. These force of attraction function as crosslinks and hold the adjacent molecular chains to form a free standing 3D PVA network. Tacticity and functional groups present in the polymer plays an

important role in forming the crosslinking. The hydroxyl group ($-OH$) present on the polymeric backbone forms intermolecular and intramolecular hydrogen bonding depending on the syndiotactic or isotactic nature of the polymer chain. During gelation, the presence of strong intermolecular and intramolecular hydrogen bonding along with other attractive forces restricts the molecular motion to some extent making the gel electrolyte a denser one¹⁴. The expected network structure of the PVA gel electrolyte is shown in figure 3.2.

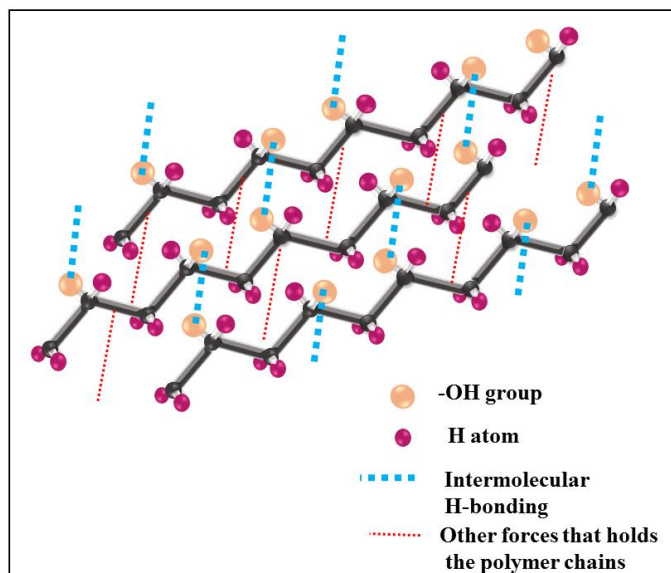


Figure 3.2: Schematic showing the interaction in PVA gel electrolyte

3.2.1.2 Polymer concentration optimization

The gel electrolyte was prepared with three different concentrations (1wt%, 2wt% and 3wt%) of PVA. Figure 3.3 shows the photograph of the three gel electrolytes prepared with 1, 2 and 3 wt% of PVA. All the three concentration formed a molten highly viscous solution after one hour of synthesis. This was kept for an overnight to get set. 1wt% of PVA results in a very dilute solution of polymer gel electrolyte. On

increasing the concentration (2wt%) of the polymer, the molecular chains get closer and a stable network is built holding the liquid electrolyte within. On further increasing the concentration to 3wt%, these polymer strands get closer and develop a strong molecular interactions resulting in the formation of an aggregated solid polymer gel electrolyte with a decrease in size of macro-pores. The degree of crystallinity increased by varying the concentration¹⁵. Based on the analysis 2wt% of PVA is chosen as an optimum concentration for the synthesis of polymer gel electrolyte and the same has been used for further studies. The sample is named as bare polyvinyl alcohol (VA B) throughout the thesis for simplicity.

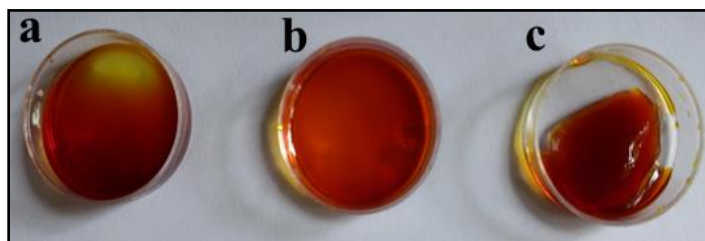


Figure 3.3: Polymer gel electrolyte synthesized with 1wt% (a), 2wt% (b) and 3wt% (c) of PVA

3.2.1.3 FT-IR of PVA powder and PVA gel electrolyte

Figure 3.4 shows the IR spectra of the gel electrolytes VA and VA B. The peak centered at 3446 cm^{-1} corresponds to the stretching vibration of -OH group. Both inter and intramolecular hydrogen bonding can be readily identified in IR technique. Intramolecular hydrogen bonds are sharp and well defined, whereas intermolecular hydrogen bonding gives rise to broad bands. In VA the peak is sharp and well defined

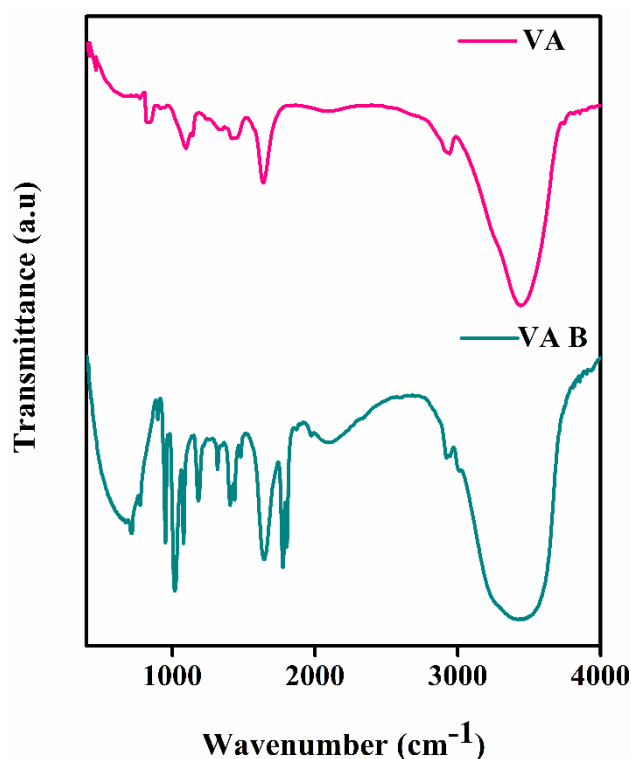


Figure 3.4: FT-IR spectra of pure PVA (a) and PVA polymer gel electrolyte (b)

whereas it was found broadened in VA B due to polymer association as a result of extensive intermolecular hydrogen bonding between the molecular chains. The peak at 2935 cm^{-1} is assigned to the $-\text{CH}_2$ stretching vibration mode and is found in both VA and VA B. Peaks at 1781 cm^{-1} in VA B is assigned to $\text{C}=\text{O}$ stretching of the plasticizer - ethylene carbonate which is absent in VA. Peaks at 1638 cm^{-1} is found in both VA and VA B corresponds to $\text{C}=\text{C}$ stretching of vinyl group. Peaks at 1433 cm^{-1} and 1323 cm^{-1} are found in both VA and VA B corresponds to $\text{C}-\text{H}$ vibration. 1138 cm^{-1} . Peak at 1095 cm^{-1} corresponds to $\text{C}-\text{O}$ stretching of alcohol. In VA B there is a slight shift in position of this peak i.e., at 1084 cm^{-1} , which may be due to the involvement of $\text{C}-\text{O}$ in forming hydrogen bond. Peak at 1019 cm^{-1} corresponds to $\text{C}-\text{O}-\text{C}$. The peak at 955 cm^{-1} corresponds to the vibration from the solvent DMSO. The

peak at 834 cm^{-1} in VA corresponds to C-C stretching. The peaks 1487 cm^{-1} , 1183 cm^{-1} , 899 cm^{-1} , 779 cm^{-1} and 725 cm^{-1} are present only in VA B corresponds to the vibration from ethylene carbonate^{2,16, 17}.

The FT-IR shows almost no change in the spectral features of PVA in terms of shifts in peak position or peak intensities except for peaks assigned to the hydroxyl group. This indicates that there is no complex formation and bulk of liquid electrolyte is trapped in the matrix.

3.2.2 Synthesis of PMMA gel electrolyte

Materials

- Potassium Iodide
- Iodine
- Propylene carbonate (PC)
- Polymethyl methacrylate (PMMA)

Method

Liquid electrolyte was first prepared by adding 0.3M KI and 0.03M I_2 to PC. Here PC acts both as a solvent and plasticizer. The solution mixture was stirred until we get a homogenous mixture. To this liquid electrolyte 0.19 g of PMMA was added and heated at $70\text{ }^{\circ}\text{C}$ with stirring till the polymer get completely dissolved in the organic mixture. The result was a uniform highly viscous molten solution which on keeping for an overnight set to give a three dimensional network structure of “honey

thick” PMMA polymer gel electrolyte and is shown in Figure 3.5. The sample is named as MA B throughout the thesis for simplicity.

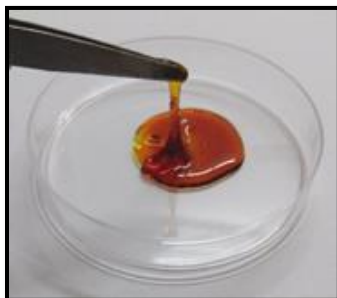


Figure 3.5: Honey thick PMMA gel electrolyte

3.2.2.1 Gelation and Expected gel network structure

PMMA chains are syndiotactic in nature with the substituents ($-\text{CH}_3$ and $-\text{COOCH}_3$) arranged alternate uniformly. These bulky side groups prevents the polymer molecular chains from approaching close to each other when the temperature of the melt decreases. As a result the crystallization of the polymer gel electrolyte get blocked. This causes PMMA to be amorphous in nature and hence we obtain a highly viscous gel electrolyte¹¹. In PMMA there is no hydrogen bonding and there exist some other cohesive and attractive forces that helps in building the network structure and making it more flexible.

The interaction between the PMMA chains in gel electrolyte is shown schematically in figure 3.6.

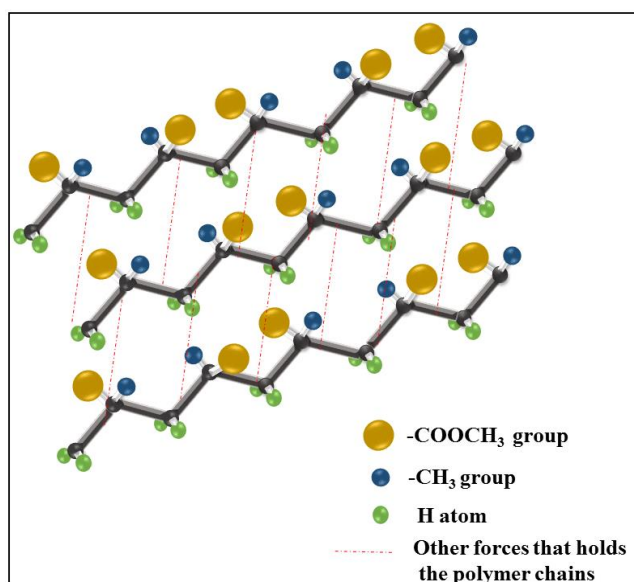


Figure 3.6: Schematic showing the interaction in PMMA gel electrolyte

3.2.2.2 Polymer concentration optimization

Three concentrations (1wt%, 2wt% and 3wt%) of the PMMA were taken and gel electrolyte was synthesized. Figure 3.7 shows the image of three concentration of PMMA gel electrolyte. All the three concentration formed a molten highly viscous solution after one hour of synthesis. This was kept for overnight to get set. The very next day the polymer matrix got separated from the liquid electrolyte for both 1wt% and 3wt%.

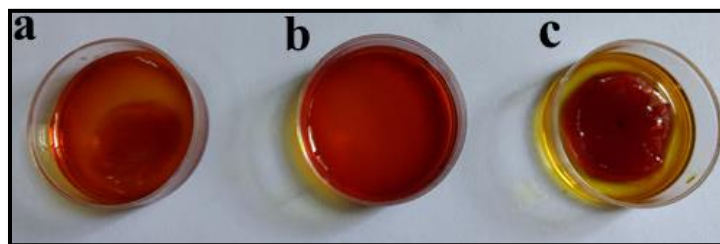


Figure 3.7: Polymer gel electrolyte synthesized with 1wt% (a), 2wt% (b) and 3wt% (c) of PMMA

From the images of three different concentration of the polymer matrix it is visible that 1wt% was not sufficient for building a network structure to hold the liquid electrolyte within. In the case of 3wt% PMMA, when the temperature of the hot melt is decreased, again strong interactions are established between the polymer chains resulting in chain overlapping and prevent the liquid electrolyte getting trapped within the network structure. In such cases the solvent fails to overcome the force of attraction between the polymer chains. Gelation was found to be successful for only 2wt% of polymer matrix and was fixed as optimum for further studies.

3.2.2.3 FT-IR of PMMA powder and PMMA gel electrolyte

FT-IR spectra of pure PMMA powder and PMMA polymer gel electrolyte is shown in Figure 3.8.

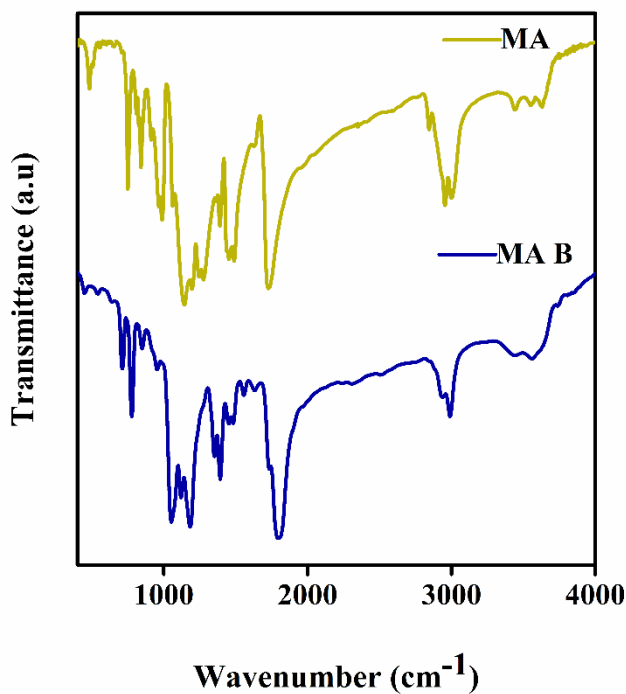


Figure 3.8: FT-IR spectra of pure PMMA (a) and PMMA polymer gel electrolyte (b)

The peak centered at 3631 cm^{-1} , 3566 cm^{-1} , 3435 cm^{-1} , 3002 cm^{-1} and 2945 cm^{-1} is assigned to the symmetric and asymmetric stretching modes of methyl ester. The peak at 1726 cm^{-1} corresponds to the C=O absorption of acrylate carboxyl group. The position of this C=O absorption is sensitive to ring and unsaturation due to conjugation. For carbonyl group of five membered ring the absorption occurs at higher wavenumber. In gel electrolyte this absorption was found at 1803 cm^{-1} along with a shoulder peak and is due to the C=O of both solvent-propylene carbonate and PMMA. A doublet is observed at 1487 cm^{-1} and 1456 cm^{-1} and it corresponds to the asymmetric bending vibration of $-\text{CH}_3$. The vibrational frequency at 1400 cm^{-1} in both MA and MA B corresponds to CH_3 symmetric deformation of PMMA. Peak at 1378 cm^{-1} is present in both MA and MA B and it corresponds to the C-H deformation absorption. Peaks at 1270 cm^{-1} , 1182 cm^{-1} and 1128 cm^{-1} can be attributed to the C-O-C stretching vibration of the ester group in PMMA. The bands at 1052 cm^{-1} , 975 cm^{-1} and 845 cm^{-1} corresponds to the bending vibration of C-H group. Peak at 779 cm^{-1} is found only in gel electrolyte which corresponds to the vibration from propylene carbonate. Peak at around 736 cm^{-1} in both MA and MA B corresponds to the $-\text{CH}_2$ rocking vibration¹⁸⁻²⁰.

3.3 Electrochemical impedance analysis

The ionic conductivity studies of the synthesized polymer gel electrolytes were done by fabricating the dummy (symmetric) cells.

3.3.1. Fabrication of symmetric cells (dummy cells)

Characterizations like linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) of the gel electrolyte were carried out by fabricating a dummy cell or symmetric cell. The dummy-cell structure is given as FTO/Pt//gel electrolyte//Pt/FTO. Two similar electrodeposited Pt electrodes were taken and the PGE is sandwiched in between the two electrodes. The electrodeposition details are mentioned in section 3.7.1. of this chapter. Electrodeposition of Pt was confirmed by taking the XRD of the film. Figure 3.9 shows the SEM image and XRD of electrodeposited Pt. The spectrum shows good crystallinity and the peaks matches with the JCPDS file no. 87-0647 of platinum. The characteristic peaks are obtained at 40(111), 46.2 (220), 68 (311) and 82 (222). The morphology of the deposited film was obtained from the SEM image. The particles deposited are highly uniform with a bud-rose structure. The image shows relatively good coverage of Pt on the FTO surface. The active area of the dummy cell was fixed to 0.25cm² for the following studies.

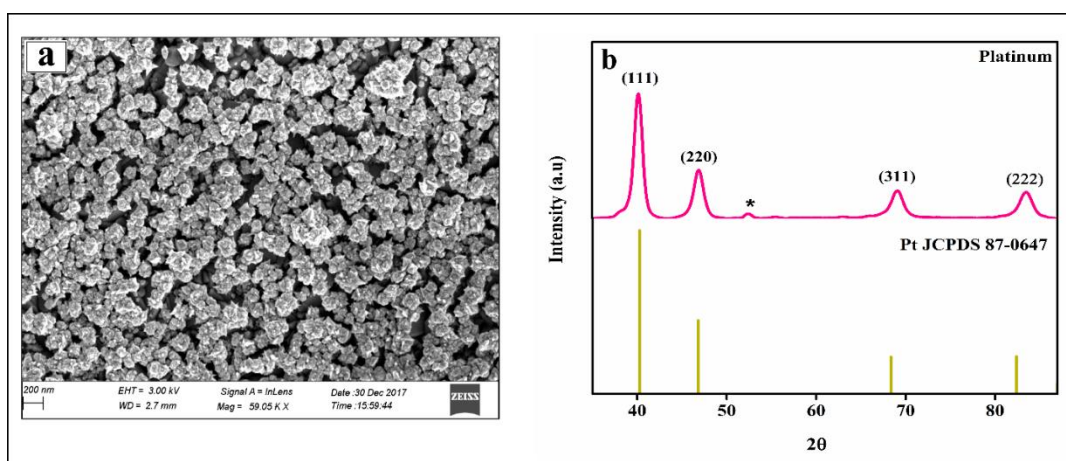


Figure 3.9: SEM image (a) and XRD (b) of Pt electrodeposited

Figure 3.10 shows the Nyquist plot of VA B and MA B gel electrolytes. From the plot the resistance offered by each interface to the electron transfer was obtained. The semicircle in the high frequency response is represented as R_1 and the one in the low frequency response as R_2 .

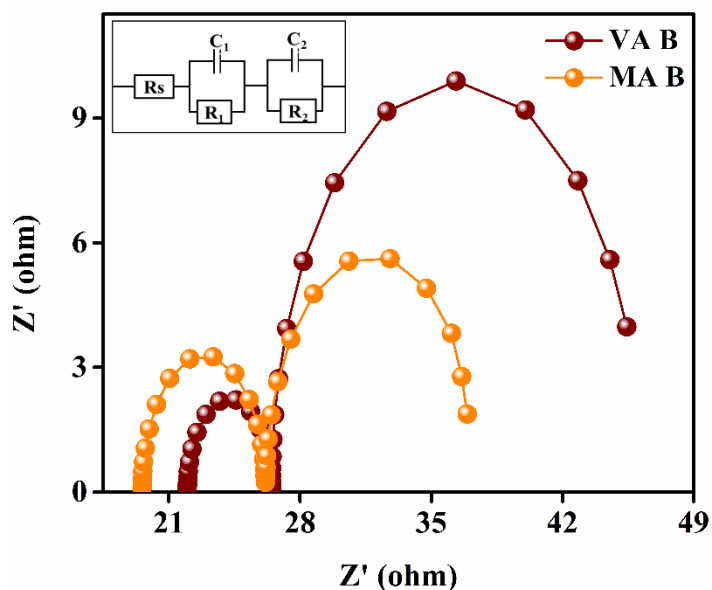


Figure 3.10: Nyquist plot of VA B and MA B measured on fabricating dummy cell

R_1 is the charge transfer resistance at the Pt-electrolyte interface and R_2 is the impedance due to Warburg diffusion. The data obtained by fitting the curve is given in the Table 3.1.

Table 3.1: Parameters obtained by fitting the EI spectra for PVA and PMMA gel electrolyte

Gel electrolyte	R_1 (Ω)	R_2 (Ω)	σ (mho cm^{-1})* 10^{-4}
MA B	6.57	10.67	14.99
VA B	4.50	18.93	8.45

The R_2 value of MA B is higher when compared to VA B. This can be explained by the less viscous nature of the gel electrolyte formed using PMMA. The major drawback of liquid electrolyte is the corrosion of counter electrode by I^-/I_3^- . For MA B the chances for the corrosion of counter electrode is high that can results in a poor catalytic activity of the counter electrode for the redox reaction $[I_3^- \leftrightarrow I^-]$ taking place at its surface.

The conductivity (σ) of the gel electrolyte is calculated using the equation 2 ^{21,22}:

$$\sigma = L/AR_b \quad (2)$$

Where R_b is the bulk resistance, L is the thickness of the film and A is the area of the sample (0.25cm^2).

The conductivity (σ) of the electrolyte depends on the mobility (μ) and carrier concentration (n). The mobility is related to viscosity (η) of the electrolyte by the equation:

$$\mu = q/6\pi r\eta \quad (3)$$

q is the charge and r is the radius of the ion.

3.3.2 Conduction mechanism in polymer gel electrolyte

Conductivity of the electrolyte solution generally can be explained via a diffusional ion migration. But in the presence of redox couple an electronic conduction and electron exchange between the redox couple is responsible for the effective

conductance in polymer gel electrolyte. The electron exchange occur between the I^- , I_3^- and the polyiodides through a chemical bond exchange. Thus a combined electron hopping and bond exchange between the iodide moieties can be expressed via a Grotthus type charge mechanism. A schematic showing the Grotthus like charge exchange between the redox couple is shown in figure 3.11^{23,24}.



Figure 3.11: Grotthus type conduction mechanism in I^-/I_3^- system

The conductivity of MA B calculated is higher when compared to VA B. This can be explained on the basis of the R_3 value of the PGEs. The R_3 value is related to the mass transfer in the electrolyte. Higher R_3 value means, a sluggish diffusion of triiodide ions towards the counter surface. VA B is highly viscous and is having higher R_3 value due to the restriction imparted by the dense crosslinking of the polymer network which decreases the mobility and hence the ionic conductivity of the electrolyte is found to be less. Whereas in the case of MA B, a higher void space is created between the polymeric chains by the bulky side groups which makes it less viscous that allows an easy triiodide diffusion and hence higher ionic conductivity.

3.4 Linear sweep voltammetric analysis

The light to electrical energy conversion efficiency of QSDSSC is influenced by I^-/I_3^- diffusion in the electrolyte. The charge transport behavior in the polymer gel electrolyte was studied by running the LSV of the dummy cell. The charge transport

between two electrodes in a dummy cell can be described by limiting current density as per the equation^{25, 26}:

$$J_{limiting} = \frac{2nFDappC}{d} \quad (1)$$

Where n is the number of electrons required for the reduction reaction (n=2), F is the Faraday's constant, Dapp is the apparent diffusion coefficient of triiodide, C is the concentration of triiodide ions and d is the thickness of the electrolyte. The diffusion limited current was measured at a scan rate of 100 mV/s and the potential was swept between -1.5 to 1.5 V. Figure 3.12 shows the LSV plots of PVA and PMMA gel electrolyte. The sigmoid representation indicates the redox reaction occurring at the Pt surface *i.e* $3I^- \leftrightarrow I_3^- + 2e^-$. Table 3.2 lists the limiting current density and I_3^- diffusion coefficient calculated from LSV response.

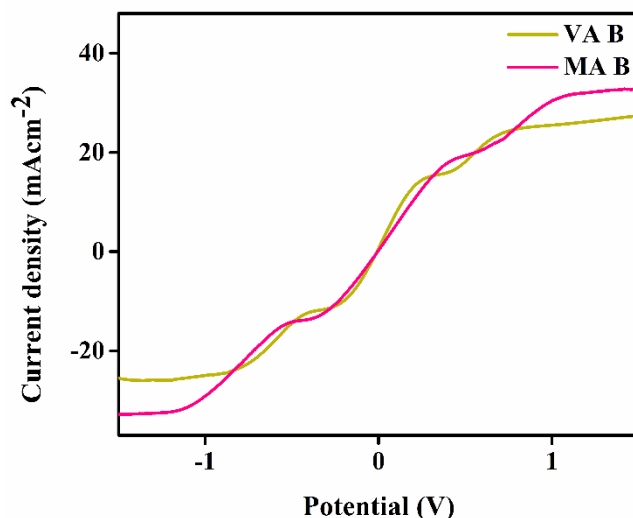


Figure 3.12: Linear sweep voltammograms of dummy cells with VA B and MA B gel electrolyte

Table 3.2: Limiting current density of VA B and MA B and their apparent diffusion coefficient

Gel electrolyte	$J_{lim} (mAcm^{-2})$	$DI_3- (cm^2S^{-1}) * 10^{-6}$
VA B	26.04	8.99
MA B	32.78	11.32

A limiting current density of 26.04 mA cm^{-2} and 32.78 mA cm^{-2} is obtained for VA B and MA B. The apparent diffusion coefficient of the VA B and MA B calculated is $8.99 \times 10^{-6} \text{ S}^{-1}\text{cm}^2$ and $11.31 \times 10^{-6} \text{ S}^{-1}\text{cm}^2$. The polymer PMMA is amorphous in nature and PVA is found to be semi-crystalline. The difference in values obtained for the two PGE can be well explained from the nature of the polymeric network formed. The restriction inflicted by the dense polymeric network structure of PVA hinders the motion of the triiodide ions resulted in the lower diffusion coefficient value for the VA B gel electrolyte than MA B gel electrolyte. The result accounts well with the lower short- circuit value (J_{sc}) and hence the performance of the QSDSSC with VA B (section 3.7.4).

3.5 Thermogravimetric analysis

Thermogravimetric analysis shows that polymer gel electrolytes are less stable than the pure polymers - PMMA and PVA. The polymer mechanical properties got diminished in polymer gel electrolyte due to the presence of high fraction of liquid components. With the loss of mechanical strength, a gain in ionic conductivity is accompanied. The inferior stability of the PGE may be due to the decomposition of polymer accelerated by the solvents presents.

All polymer host lose their mechanical strength when they get plasticized. Most of the polymers undergo complete decomposition before reaching 600°C. PMMA undergo three distinct step in thermal degradation. The bonds joining the end units are highly vulnerable to breakdown. The first two steps are associated with degradation starting from head to head linkages and unsaturated chains resulting in the formation of radicals. The third step is associated with the random scission of the PMMA chain²⁷⁻²⁸. The thermal degradation of powder PMMA (MA) and MA B are shown in Figure 3.13.

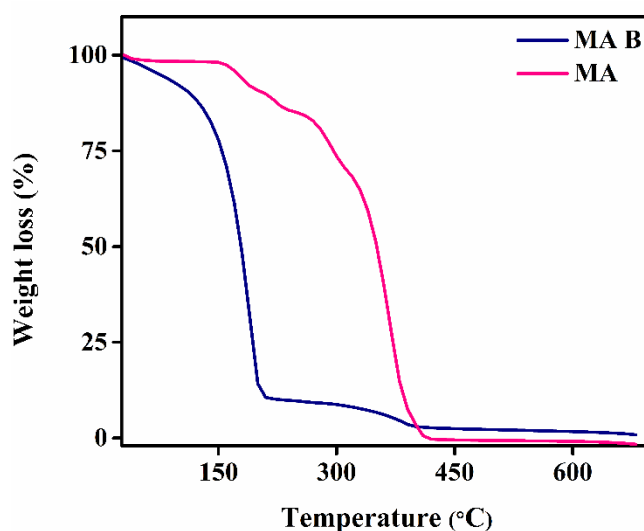


Figure 3.13: TGA of commercial PMMA polymer (MA) and PMMA gel electrolyte (MA B)

The thermal degradation of commercial PVA (VA) and VA B are shown in Figure 3.14. Initial weight loss for all PVA samples results in a rapid chain stripping with the elimination of water molecule and scission of some of the C – C bonds takes place to give carbonyl compounds. The second stage decomposition products are the hydrocarbons^{30,31}.

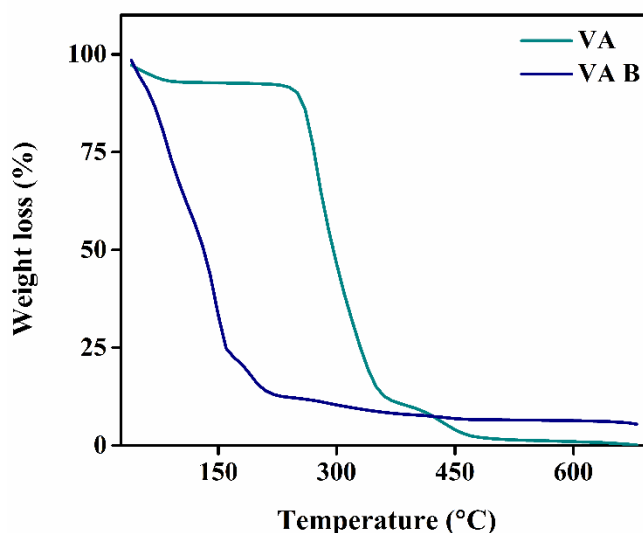


Figure 3.14: TGA of commercial PVA polymer (VA) and PVA gel electrolyte (VA B)

3.6 Time dependent stability study of PGE

Gel stability studies are done at regular intervals of time for a period of one month. Syneresis effect was the only factor that diminishes the performance of the PGE. As a result shrinkage of PGE takes place and the liquid electrolyte that got trapped within the network structure get evaporated at long time period. The effect of liquid electrolyte evaporation loss on their performance can be studied by measuring the conductivity of the PGE. This can be done by performing the EIS analysis at different time intervals such as, on the 1st day, 5th day, 10th day, 20th day and 30th day of the synthesis of gel electrolyte. The gel stability study was conducted with freshly prepared counter electrodes each day and the dummy cell is fabricated with the PGE synthesized on the first day. Figure 3.15 and figure 3.16 shows the EIS of both VA B and MA B and the data is listed in table 3.3 and 3.4 respectively. The best performance is given on the first day of synthesis for both VA B and MA B.

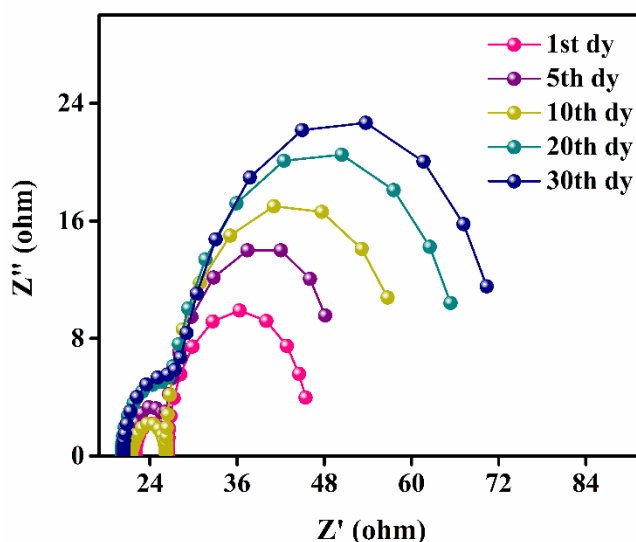


Figure 3.15: EIS of VA B showing time dependent stability study of one month by fabricating dummy cell

Table 3.3: Parameters obtained by fitting the EI spectra for VA B and ionic conductivity calculated for a period of one month

Time	$R_1 (\Omega)$	$R_2 (\Omega)$	$\sigma (\text{mho cm}^{-1}) * 10^{-4}$
Day 1	4.50	18.93	8.45
Day 5	4.84	22.12	7.23
Day 10	5.01	30.33	5.27
Day 20	6.40	38.83	4.12
Day 30	7.59	42.47	3.76

Both PGE's are found to be stable for first few days and a very slight decrease in performance was observed after fifth day of synthesis. When comparing the stability study performed on the two PGEs, MA B is found to be more stable and shows better performance than VA B and is least susceptible to syneresis. However, a slight decrease in performance can be found for MA B after each measurement and this

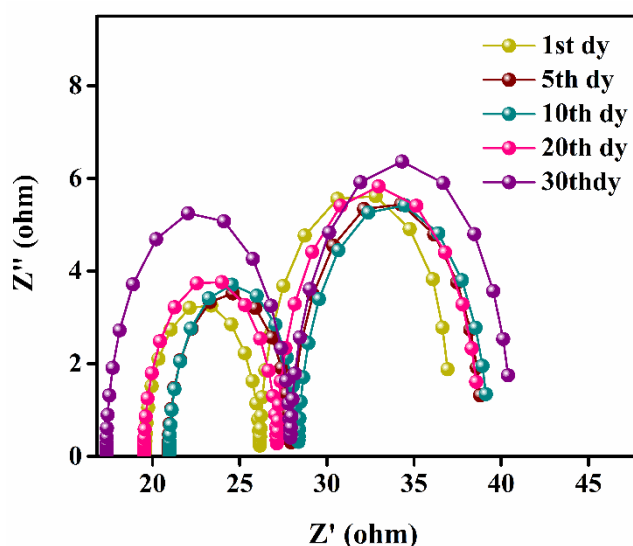


Figure 3.16: EIS of MA B showing time dependent stability study of one month by fabricating dummy cell

Table 3.4: Parameters obtained by fitting the EI spectra for MA B and ionic conductivity calculated for a period of one month

Time	$R_1 (\Omega)$	$R_2 (\Omega)$	$\sigma (\text{mho cm}^{-1}) * 10^{-4}$
Day 1	6.57	11.98	13.35
Day 5	7.02	10.80	14.81
Day 10	7.39	10.90	14.67
Day 20	7.68	11.52	13.88
Day 30	10.6	12.67	12.62

might be due to the ageing of PGE. VA B is highly vulnerable towards syneresis when compared to MA B. A countable falloff in performance was observed in the performance of VA B and is due to the solvent transudation upon storage in open condition which negatively affects the performance of the cell. Whereas this effect was found to be visibly zero in the case of MA B.

3.7 Application

To check the performance of the synthesized gel electrolytes, it was applied in QSDSSC. The device fabrication and assembly was discussed below.

3.7.1 QSDSSC fabrication and cell assembly

Figure 3.17 shows the schematic of a typical QSDSSC and its fabrication and assembly is discussed in detail below.

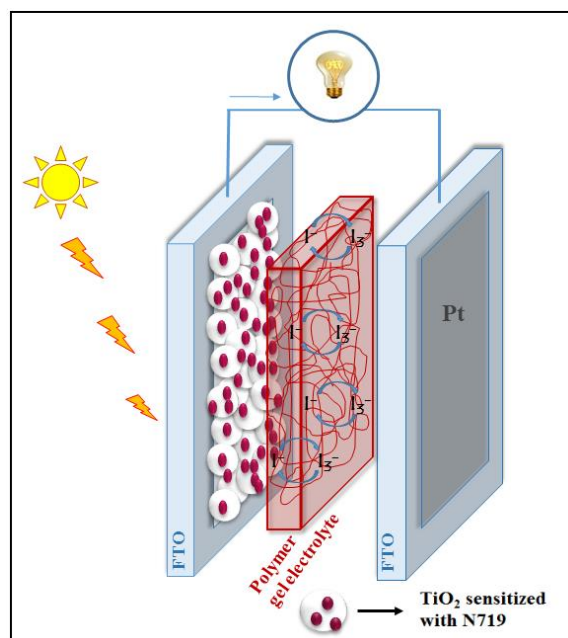


Figure 3.17: Schematic showing QSDSSC structure

Preparation of photoanode: FTO was the substrate material used for making the photoanode. A TiO_2 buffer layer was coated on the pre-cleaned FTO in order to avoid the direct contact of the electrolyte with the FTO. In classical nanoparticulate DSSC, a titanium tetrachloride (TiCl_4) treatment is usually used to improve solar cell efficiency. Stock solution was prepared by diluting 1M TiCl_4 with deionized water at 5°C .

Cleaned FTO was then immersed into this solution for 15 hrs. After air drying the substrate was sintered at 450°C. Pre-treatment strengthen the bonding between the FTO substrate and the porous TiO₂ film. This helps in reducing the charge recombination at the interface.

Highest energy conversion efficiency in DSSC was obtained for FTO coated with titania and hence was employed as the photoanode material throughout the work. Commercial Degussa P25 anatase titania is first thoroughly grounded in mortar and made into paste using ethanol. For good dispersion and adhesion Triton X-100 is chosen as the binder material. The paste was then spread uniformly on to the FTO surface by using a glass rod. This method is known as doctor-blading technique. The film was then dried under room temperature and kept for an overnight. The thickness of the film should not exceed beyond 15 micrometer for high absorption and lower recombination. The film was then subjected to sintering at 450°C for half an hour. This step helps to remove the organic contents present within giving rise to an electrically connected network of TiO₂ particle. After cooling the area of the film was confined to 0.25cm².

Sensitization of TiO₂ using N719 dye: Dye solution was prepared by dissolving 0.3mM N719 in methanol. The photoanode was first heated at 80 °C for half an hour and is dipped in the dye solution for 24 hours. Heating of the photoanode helps to prevent the capillary condensation of moisture from surroundings inside the nanoporous film which decrease the injection efficiency of the dye. After 24 hours the photoanode is rinsed with methanol to remove the dye aggregates at the surface and is

then dried under air flow³²⁻³⁴. N719 attachment on TiO_2 surface is shown in Figure 3.18.

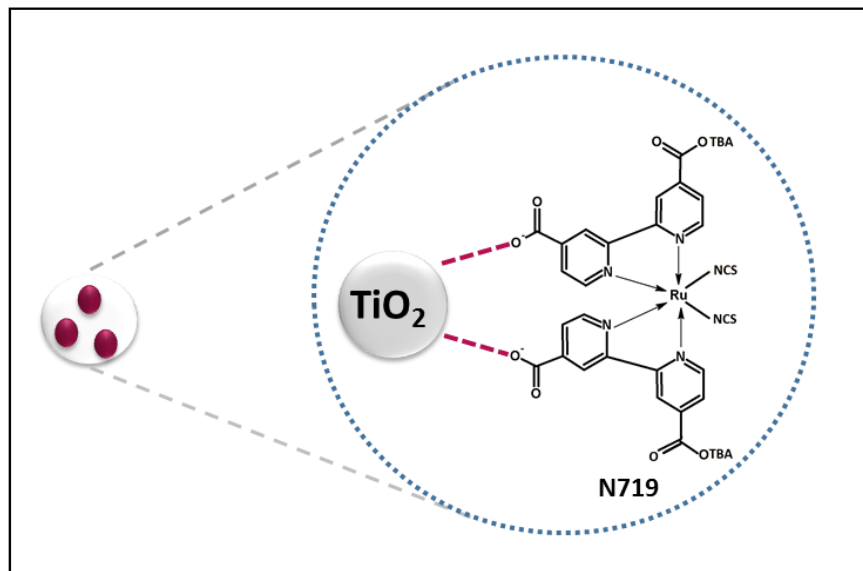


Figure 3.18: Schematic showing the N719 attachment on TiO_2 surface through carbonyl linkage

Preparation of electrolyte: Detailed preparation procedure of polymer gel electrolytes was given under section 3.2.1 and 3.2.2 of the same chapter.

Preparation of counter electrode: Counter electrode³⁵ was prepared by electrodepositing Pt from a solution of hexachloroplatinic acid (H_2PtCl_6) on FTO. 4mM precursor solution of H_2PtCl_6 was prepared and by using a three electrode system a uniform semi-transparent film of Pt was deposited with a scan rate of 20mV/s. The potential is swept from 0V to -0.45V. The electro-deposited Pt counter is then dried in the oven before cell assembly.

QSDSSC assembly

QSDSSC were assembled in a sandwich type configuration of photoanode and counter electrode facing each other with the quasi solid state electrolyte within. All four sides of the photoanode material was sealed with stripes of hot melt tape. It was then kept on the hot plate for the tape to melt. Required amount of polymer electrolyte was then placed on the photoanode and the assembling was completed by pressing counter electrode onto it. Figure 3.19 shows the QDSSC fabrication steps and device assembled.

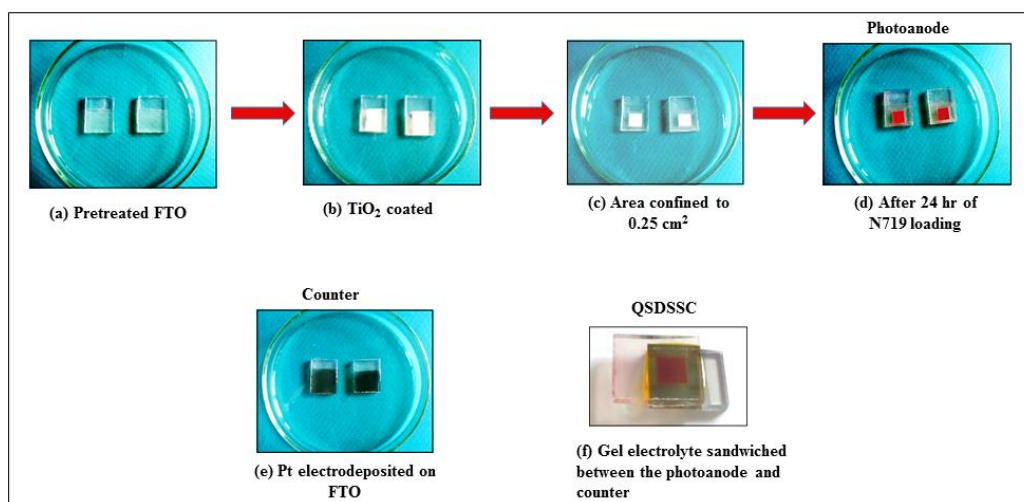


Figure 3.19: QDSSC fabrication steps and assembly

3.7.2 DSSC

To compare the performance of the synthesized polymer gel electrolyte a standard DSSC combination was first selected. Device was fabricated by mimicking the early version presented by O'Regan and M. Gratzel³⁶. Acetonitrile (AN) was used as the solvent, TiO_2 coated with Ru complex as photoanode and Pt coated conducting

glass as counter electrode. Liquid electrolyte composition includes, additives like 4-tertbutyl pyridine (4-TBP) and guanidinium thiocyanate (GuSCN), butylmethyl imidazolium iodide, Lithium iodide and iodine redox couple. The Current density-voltage plot (a) and the Nyquist plot (b) of DSSC is shown in figure 3.20. The photovoltaic parameters obtained from the analysis is listed in table 3.5.

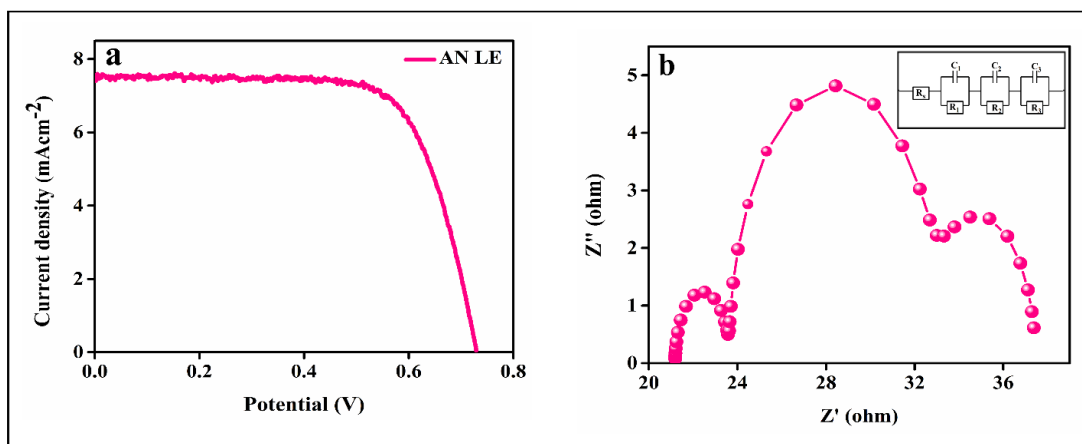


Figure 3.20: Current density-voltage plot (a) and the Nyquist plot (b) of AN based DSSC

From the J-V curve, AN based DSSC has got a J_{sc} value of 7.57 mA cm^{-2} , V_{oc} of 0.72 V, FF of 73 %, Eff of 4.01 %. The corresponding EIS spectra shows the resistance at each interface of the device. R_1 shows the resistance at the counter-electrolyte interface, R_2 shows the resistance at the photoanode-electrolyte interface and R_3 is the Warburg impedance and the values are listed in table 3.5.

Table 3.5: Photovoltaic parameters and the fitted impedance parameters for AN based DSSC

J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	Eff (%)	R_s (ohm)	R_1 (ohm)	R_2 (ohm)	R_3 (ohm)
7.57	0.72	73	4.01	21.18	2.37	9.57	4.25

4-TBP and GuSCN are the common additives added to liquid electrolyte in DSSC¹⁷ to enhance the cell performance. The role of additives/fillers in enhancing the performance of the device is discussed in detail in chapter four and chapter five. In the coming sections filler free liquid electrolyte and the polymer gel electrolyte were used to fabricate the DSSC and QSDSSC.

3.7.3 Optimization of salt concentration in gel electrolyte

The power conversion efficiency of the device greatly depends on the ionic conductivity of the electrolyte that will in turn depends on the concentration of the redox couple. KI and I₂ serves as the source of I⁻/I₃⁻ redox couple in the gel electrolyte. At high salt concentration, the I₃⁻ will react with injected electron and increases the dark current. In addition to this a chance of reductive quenching, deactivate the excited state of the sensitizer representing a loss channel^{37,38}. Because of all these negative effects, the concentration of these salts have to be optimized during electrolyte synthesis. For optimizing the salt concentration, I₂ concentration was fixed constant initially (0.03M) and KI concentration was varied from 0.1 M to 0.7 M. The concentration of KI in gel electrolyte was optimized by applying the synthesized gel electrolyte in QSDSSC. Figure 3.21 shows the current density – voltage response of PVA QSDSSC showing the effect of different KI/I₂ salt concentration. The photovoltaic parameters obtained from the plot is listed in table 3.6.

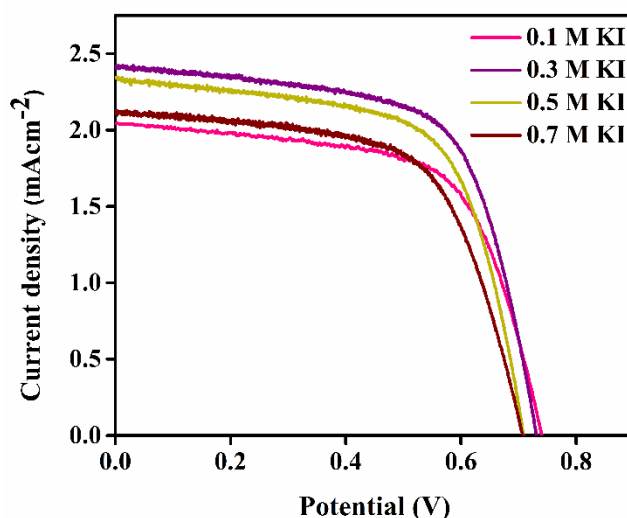


Figure 3.21: Current density- voltage plot of PVA QSDSSC showing the effect of different KI/I₂ salt concentration

Table 3.6: Photovoltaic parameters of PVA QSDSSC with different KI/I₂ salt concentration

KI concentration	J _{sc} (mAcm ⁻²)	V _{oc} (V)	FF (%)	Eff (%)
0.1M	2.03	0.74	65	0.99
0.3M	2.41	0.73	65	1.15
0.5M	2.33	0.71	64	1.07
0.7M	2.11	0.71	63.4	0.944

The performance efficiency of QSDSSC increases initially with an increase in the concentration of the KI and then decreases. At high KI concentration, the solvated ions get closer and there is a chance for them to exist as contact ions which contributes less to the cell performance. Also high salt concentration may tie down the segmental motion of the polymer chain and there is a chance for the shrinkage of polymer chain with the loss of solvent and hence phase disengagement³⁷.

3.7.4 VA B – QSDSSC and DSSC

The photovoltaic performance of the cell is done under 1 Sun illumination-100 mW cm⁻². The performance of the PGE was compared by fabricating DSSC with the corresponding liquid electrolyte. Figure 3.22 (a) shows the photocurrent density – voltage curve of cells with VA B- QSDSSC and the corresponding liquid electrolyte - DSSC. The DSSC and QSDSSC exhibit an overall power conversion efficiency of 1.44 and 1.19 % respectively. The efficiency mentioned here for DSSC is lower than that given in Table 3.7, due to the lack of additives in the electrolyte. The cell parameters for both DSSC and QSDSSCs including the electrolyte compositions are given in Table 3.7. Relatively lower cell parameter values obtained for QSDSSC can be explained on the basis of conductivity and the wetting property of the electrolyte. The viscosity of an electrolyte is inversely proportional to the mobility by the equation (3). The addition of polymer to the liquid electrolyte increases its viscosity and thereby decrease the mobility. The restriction offered by the polymeric network to the easy transport of the ionic species lowers the device performance. The presence of polymeric network structure also prevent the proper wetting of the electrode surfaces that disturbs the electron transfer kinetics at the electrolyte- electrode interface. Thus the overall kinetics of the cell reactions get lowered and hence exhibit a poor performance when compared to the corresponding liquid electrolyte.

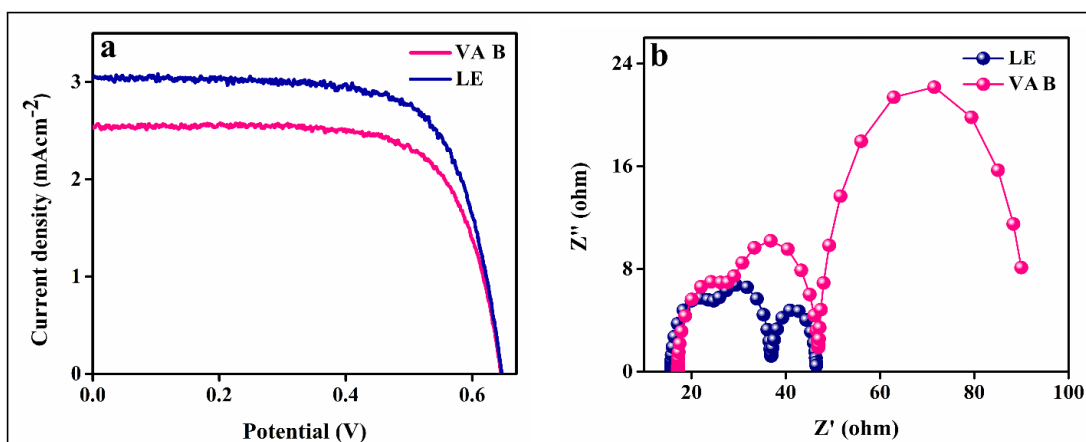


Figure 3.22: Current density-voltage plot (a) and the Nyquist plot (b) of VA B – QSDSSC and the corresponding DSSC

Table 3.7: Photovoltaic parameters of VA B – QSDSSC and the corresponding DSSC

Electrolyte	J_{sc} (mAcm^{-2})	V_{oc} (V)	FF (%)	Eff (%)
DMSO + EC + KI + I_2	3.05	0.65	73	1.44
PVA +DMSO + EC + KI + I_2	2.54	0.65	73	1.19

The resistance offered at different interfaces in the cell can be studied from Nyquist plot, which gives three semi-circles corresponding to the resistance generated at each interface of the cell and the Warburg diffusion. The appearance of multiple semicircles in the Nyquist plot indicates that electrochemical interfaces have got different kinetics for electron transfer. The Nyquist plot for VA B based QSDSSC and the corresponding LE-DSSC is given in figure 3.22(b) and the fitted data is listed in table 3.8.

Table 3.8: Fitted impedance parameters for VA B– QSDSSC and the corresponding DSSC

Electrolyte	R_s (ohm)	R_1 (ohm)	R_2 (ohm)	R_3 (ohm)
DMSO + EC + KI + I_2	15.80	9.11	12.25	9.27
PVA +DMSO + EC + KI + I_2	17.02	10.5	19.26	43.06

R_s gives the sheet resistance which corresponds to the TCO contact resistance and electron transfer at TCO/TiO₂ interface. The high frequency response corresponds to the electron transfer resistance at Pt-electrolyte interface (R_1), the middle frequency response corresponds to the resistance at the TiO₂/dye/electrolyte interface (R_2) and the low frequency response corresponds to Warburg impedance, arising from the diffusion of I^- and I_3^- (R_3)^{34, 37}. The R_2 value for QSDSSC is found to be higher than that of the corresponding DSSC. This can be explained by the sluggish electron transfer process taking place at the PGE-counter interface. The presence of the polymeric backbone at the interface prevents the fast reduction of the triiodide ions at the counter surface. A higher R_2 value for QSDSSC shows that at the photoanode-electrolyte interface a high resistance is imparted to the electron flow. In QSDSSC the presence of network structure prevents the direct contact of the I_3^- ions from TiO₂ surface by developing a temporary hindrance at the interface. Also there is a chance for interaction between the –OH side group of the PVA chain and the TiO₂ surface. This high resistance positively affect the device performance by promoting the photo-injected electrons to the external circuit. Thus the major recombination loss i.e. the regeneration of the electrolyte at the interface can be minimized by introducing polymer matrix to the liquid electrolyte. The higher R_3 value of QSDSSC is due to the

restriction to the easy diffusion of the triiodide ions towards the counter electrode by the polymer network. As a result the electrolyte regeneration at the counter surface become slower and hence a higher R_1 value.

3.7.5 MA B – QSDSSC and DSSC

The performance of MA B – QSDSSC is studied and compared with the corresponding DSSC. Figure 3.23 (a) shows the photocurrent density – voltage curve of cells with MA B- QSDSSC and the corresponding liquid electrolyte – DSSC and (b) shows their Nyquist plot.

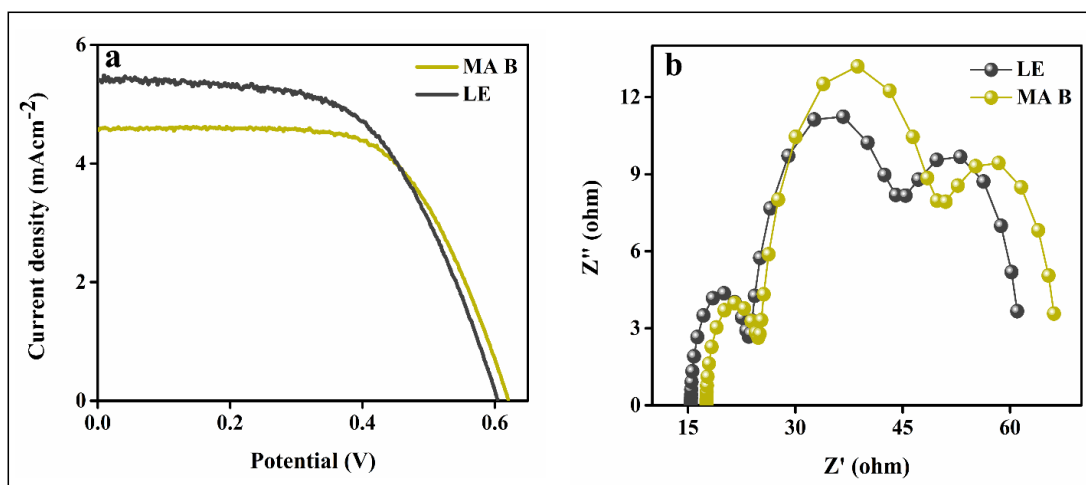


Figure 3.23: Current density-voltage plot (a) and the Nyquist plot (b) of MA B – QSDSSC and the corresponding DSSC

The parameters obtained from the J-V characterization and the EIS measurement for both DSSC and QSDSSCs are listed in the Table 3.9 and Table 3.10 respectively. The DSSC and QSDSSC exhibit an overall power conversion efficiency of 1.92 and 1.84 % respectively.

Table 3.9: Photovoltaic parameters of MA B – QSDSSC and the corresponding DSSC

Electrolyte	J_{sc} (mAcm ⁻²)	V_{oc} (V)	FF (%)	Eff (%)
PC + KI + I ₂	5.47	0.61	61.2	1.92
PMMA +PC + KI + I ₂	4.58	0.62	63.7	1.84

Table 3.10: Fitted impedance parameters for MA B – QSDSSC and the corresponding DSSC

Electrolyte	R_s (ohm)	R_1 (ohm)	R_2 (ohm)	R_3 (ohm)
PC + KI + I ₂	15.32	7.81	21.22	16.12
PMMA +PC + KI + I ₂	17.48	7.94	25.15	16.57

No significant change in R_1 and R_3 value could be observed when comparing the DSSC and QSDSSC performances. A higher R_2 was measured for MA B indicating a higher ability of the system in suppressing the recombination rate of the injected electrons in the TiO₂ with the electrolyte. This shows that the addition of PMMA to the liquid electrolyte does not adversely affect much in the device performance. The results shown by MA B – QSDSSC is highly comparable with that of the DSSC. This comparable results shown by the MA B can be explained on the basis of nature of gel formation. The branching on the carbon skeleton and the bulkiness of the side groups creates larger voids for the storage of the liquid electrolyte within the network and hence a less resistance is experienced for the diffusion of ionic species in MA B.

Comparing the R_3 values of VA B and MA B – QSDSSC's, VA B show a higher value. This can be explained on the basis of dense nature of the polymer gel electrolyte formed with PVA. The strong interaction between the polymer chains along

with the hydrogen bonding hold the polymer molecular chains close together giving the gel electrolyte a denser nature. As a result diffusion of the ionic species become difficult in VA B and hence the device experiences a higher R_3 value.

The photovoltaic parameters listed in the Table 3.7 and 3.9 shows that the lower performance of QSDSSC's is mainly due to the decrease in the J_{sc} values. The lower J_{sc} value shown by QSDSSC's can be connected with the lowered I_3^- diffusion coefficient. This can be well explained on the basis of higher viscosity of the polymer gel electrolyte when compared to the liquid electrolyte. The highly viscous nature of the polymer gel electrolyte hinders the easy diffusion of the ionic species between the electrodes. Thus the kinetics of dye regeneration get delayed. Also the diffusion of the triiodide ions towards the Pt counter surface for getting reduced will confront some resistance which in turn results in lowering of the J_{sc} . The data also suggest that the gelation does not alter the V_{oc} of QSDSSC. The introduction of polymers to the liquid electrolyte only affect the electrolyte conductivity. Both DSSC and QSDSSC has got almost same values for V_{oc} .

QSDSSC with PMMA gel electrolyte shows higher efficiency when compared to the PVA gel electrolyte. This can be explained on the basis of the viscosity of the electrolyte which in turn effects the penetration of the gel electrolyte into the mesoporous TiO_2 film. The lower viscosity of the PMMA based system is inferred to be the reason leading to its better performance and higher efficiency.

3.7.6 Effect of exposure time on cell performance (temperature effect):

The performance of QSDSSC becomes better upon prolonged exposure to light. This can be considered as a unique characteristics of gel electrolyte. On continuous exposure to sunlight, the quasi solid state of the electrolyte gradually turns to viscous state. This helps in improving the wetting of the electrode surface and hence QSDSSC performs like a conventional DSSC. Here the thermal instability of the gel electrolyte has become a blessing for the sustainable performance of the device¹⁴. The J-V curves of QSDSSC with PVA or PMMA based gel electrolyte shown in Figure 3.24 (a) and (b), explains the effect of exposure time on the device performance. On prolonged exposure to light, the FF of the cell is improved indicating proper wetting of the electrode surface by quasi-solid state electrolyte and hence improvement in cell performance.

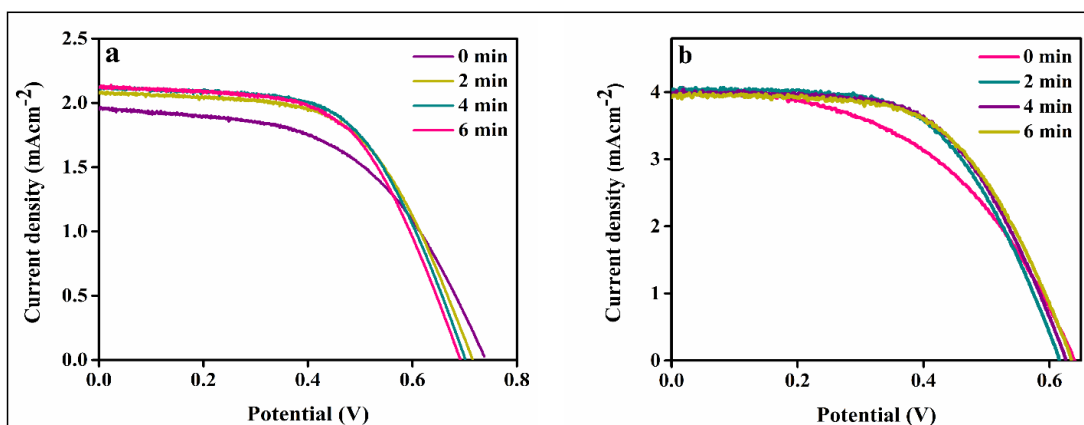


Figure 3.24: Current density-voltage plots of VA B - QSDSSC (a) and MA B - QSDSSC (b) showing the effect of exposure time on cell performance

3.8 Conclusion

PVA and PMMA based polymer gel electrolytes were synthesized via a simple gelation method. Its basic characterizations like conductivity measurements, thermal stability, time dependent stability studies were performed. Application study was done by fabricating QSDSSC with these electrolytes and their performance was compared with the corresponding liquid electrolytes.

Among the two polymers a better performance was given by PMMA based polymer gel electrolyte. Time dependent stability study shows that PVA polymer gel electrolyte was prone to syneresis effect and PMMA polymer gel electrolyte shows a better stability in ambient temperature. Based on the observations it is concluded that the gel electrolyte formed by PMMA can be considered as a stable framework and that formed by PVA can be considered as metastable framework. Application study also replicates the same trend in cell performance. The study has been extended to check the role of fillers or additives in gel electrolyte and their influence on cell performance.

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4

SYNTHESIS, CHARACTERIZATION
AND APPLICATION OF FILLER
INCORPORATED PVA GEL
ELECTROLYTE

4. SYNTHESIS, CHARACTERIZATION AND APPLICATION OF FILLER INCORPORATED PVA GEL ELECTROLYTE

The cell efficiency shown by QSDSSC compared to DSSC can be attributed to the inferior mass transfer rates in the highly viscous electrolyte medium and high electron transfer resistance at the electrode-electrolyte interface¹. One of the promising ways to improve the electrochemical properties of polymer gel electrolytes is by the addition of fillers². Efforts have been made to modify the properties of polymer gel electrolyte by adding inorganic fillers. The primary reasons to incorporate these fillers are:

- † Enlarges the amorphous phase in polymer gel electrolyte³
- † Reduce the degree of crystallinity and degree of self- aggregation of the polymer chain⁴
- † Increase the number of charge carriers due to enhancement of the salt dissociation⁵
- † Enhancement in ionic conductivity at low temperature by providing additional conductive pathway⁶
- † Improvement of the stability at the interface with the electrode⁷
- † Enhance the mechanical strength and stability of the polymer electrolyte⁸

Pyridine derivatives, especially 4-tertbutyl pyridine is used commonly as efficient additives in liquid electrolyte. In addition to this alkyl phosphonic or carboxylic acids, guanidinium derivatives etc⁹ are also reported as additives in liquid

electrolyte for improved charge transfer/transport process. The additives alter the performance by shifting the band edge position of the TiO_2 conduction band^{10,11}. They also change the rate of back recombination between the injected photoelectrons in the conduction band of TiO_2 and the electrolyte¹². Here, an attempt has been made to study the effect of fillers on enhancing the properties of the PVA gel electrolyte. As a first trial the common trio combination (4-TBP, GuSCN and IL) used in liquid electrolyte was added to the polymer gel electrolyte. Here the pyridine-iodide complex formation resulted in the loss of original function of the PVA gel electrolyte. Previous reports show that other than these common liquid electrolyte additives, high surface area semiconducting oxides, such as SiO_2 , TiO_2 , Al_2O_3 , ZnO ^{3,13}, ZrO_2 , CeO_2 , and MgO ¹⁴, were also used as fillers in gel electrolyte to enhance its electrical, thermal, mechanical and optical properties.

In the present study commercial TiO_2 -Degussa P25 and synthesized ZnO were added as fillers in PVA gel electrolyte to improve the electrical properties. The stability and performance were optimized by introducing different weight percentage of ZnO/TiO_2 in PVA gel electrolyte. Detailed study on the addition of 4-TBP, GuSCN and IL or metal oxides in PVA gel electrolyte is given in the following paragraphs.

4.1 Synthesis of TBP and GuSCN incorporated PVA gel electrolyte

Materials

- *Potassium Iodide*
- *Iodine*
- *4-tertbutyl pyridine*
- *Guanidinium thiocyanate*
- *Butyl-methyl-imidazolium iodide*
- *Ethylene carbonate*
- *Dimethyl sulfoxide*
- *Polyvinyl alcohol*

Method

Liquid electrolyte was first prepared by adding 0.3M KI, 0.03M I₂, 4-tertbutyl pyridine, guanidinium thiocyanate, butyl-methyl-imidazolium iodide into a mixture of DMSO and EC with constant stirring. To this liquid electrolyte mixture 0.2 g of PVA was added and stirred for 15 minutes for uniform distribution. The mixture was then heated at 100°C under stirring till the polymer get completely dissolved in the organic mixture. This resulted in a uniform, highly viscous molten solution, which set to a jelly texture on keeping for an overnight under ambient condition. However, the study took a different direction when it was observed that the obtained gel electrolyte was different in color than the previously obtained VA B prepared without any additives or ionic liquid. A golden brown colored polymer gel electrolyte was obtained on

gelation. On the second day of synthesis the color of the gel turns golden yellow and after three days of synthesis the color completely faded, and along with syneresis was observed and we got a transparent polymer gel electrolyte. Figure 4.1(a-d) shows the step wise color transformation observed in the polymer gel electrolyte formed in the presence of TBP, GuSCN and Butyl-methyl-imidazolium iodide.

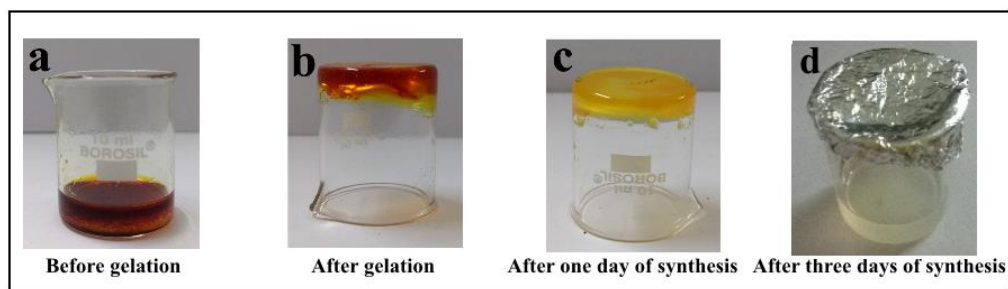


Figure 4.1. Pyridine-iodine Complex formation in polymer gel electrolyte

The dark brown color of the electrolyte was due to the formation of triiodide ion. The fading of the color may be due to the interaction of TBP and I_2 leading to the formation of molecular complexes. The presence of pyridine- I_2 complex and N-iodopyridinium cation have been reported in many journals¹⁵. Reports show that a charge transfer complex is likely to be formed between pyridine derivatives and iodine. In non-polar solvents $Py \cdot I_2$ complexes are formed and in polar solvents charge transfer complex is formed with various ionic products like $PyrI^+$, Pyr_2I^+ etc¹⁶. DMSO and EC are both polar solvents and charge transfer complex and ionic products are expected to be formed in our experiment as per the reaction,



The absence of free triiodide ion in the polymer gel electrolyte results in the loss of their original functions and cannot be used for the proper solar energy-to-electricity conversion of solar cell. Also these additives are specific for sensitized solar cells. So for the synthesis procedure followed in the thesis, the regular additives cannot be used and for further studies thermodynamically more stable inorganic fillers are used. These semiconductor oxide fillers are widely used to modify polymer gel electrolytes for all electrochromic applications like QSDSSC, Li-ion batteries², capacitors¹³ etc.

4.2 Synthesis of ZnO nanoparticle

Zinc Oxide

ZnO is a wide band gap semi-conductor with large exciton binding energy. It is one of the promising nontoxic and biocompatible semiconductor material, which has received extensive application due to its exceptional electrical and optical characteristics in fabricating nanoscaled electronic and optoelectronic devices^{17,18}. Owing to the properties stated above, it is expected to have applications in room temperature ultraviolet lasing¹⁹, biosensors²⁰, bioimaging²¹, drug delivery²², cosmetics²³, photocatalysis²⁴, piezoelectric transducers²⁵ etc. The non-centrosymmetry and polar surface of wurtzite ZnO structure helps in tuning its morphology. It can be synthesized into a variety of morphologies including nanowires, nanorods, nanosheets, nanotubes, nanobelts, nanoflowers and nanoparticles. ZnO can be synthesized via physical and chemical synthetic methods, such as thermal evaporation²⁶, pulsed laser deposition²⁷, ion implantation²⁸, reactive electron beam

evaporation²⁹, thermal decomposition³⁰, and sol-gel technique³¹. To obtain ZnO nanoparticle, we choose sol-gel method because of its simplicity, which offers a possibility of large yield at low cost. The particle size and crystal shape can be controlled by varying the temperature and duration of the process³²⁻³⁴.

ZnO was synthesized via a simple co-precipitation method using zinc acetate as the precursor material.

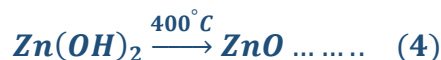
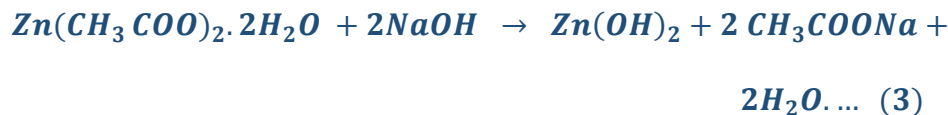
Materials

- *Zinc acetate*
- *Sodium hydroxide*
- *Distilled water*

Method

ZnO was synthesized by dissolving 0.05 M zinc acetate dihydrate ($(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$) in 200 mL of distilled water. The solution was stirred continuously for the complete dissolution of the precursor in water. To this a freshly prepared 0.5 M NaOH solution was added drop-wise until the pH of the solution became 8. A white turbidity begins to appear on the addition of NaOH and this shows the precipitation of zinc hydroxide ($\text{Zn}(\text{OH})_2$) in solution as per equation (3)³⁵. A constant temperature of 75° C was maintained for two hours under stirring and the solution mixture was kept for an overnight aging. The white colloidal precipitate settled down at the bottom is separated from the supernatant solution and was centrifuged and washed with distilled water for three to four times to remove the

byproducts bound with the Zn(OH)_2 . It was then air dried followed by annealing at 400°C for half an hour to obtain phase pure ZnO as per equation (4)



4.2.1 ZnO characterizations

4.2.1.1 X-ray diffraction study

X-ray diffraction study confirms the purity and crystallinity of the ZnO nanoparticles. Figure 4.2 shows the XRD pattern of calcined (at 400°C) ZnO nanoparticles which confirms the hexagonal crystal structure ($\alpha=3.2$, $\beta=5.2$) with intense reflection from (100), (002) and (101) planes coinciding with JCPDS Card No. 75-0576. The sharp diffraction peak indicates good crystallinity of the nanoparticles. No other peaks are observed in the XRD, thus ruling out other phases of ZnO or any impurity. The crystallite size of the sample has been determined by means of X-ray line broadening method with Debye Scherrer formula³⁵

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (1)$$

Where D is the average crystallite size, λ is the wavelength of Cu-K α radiation (1.54 Å), β is full width at half maximum (FWHM) of the peak corresponding to the plane (101) and θ is the angle corresponding to maximum intense peak in XRD. The crystallite size thus obtained is 55.49nm.

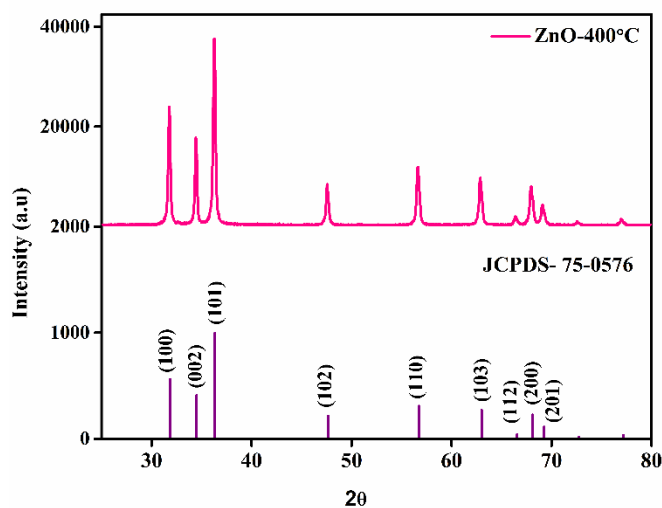


Figure 4.2: X-ray diffraction pattern of ZnO nanoparticle compared with JCPDS file no. 75-0576

4.2.1.2 SEM with EDS analysis

Formation of nanoparticles of ZnO is seen from the SEM image shown in figure 4.3.a. Energy dispersive spectrum (EDS) gives information about the elemental identification and their relative proportions. EDS indicates the presence of Zn and O in the sample without any impurities (Figure 4.3.b).

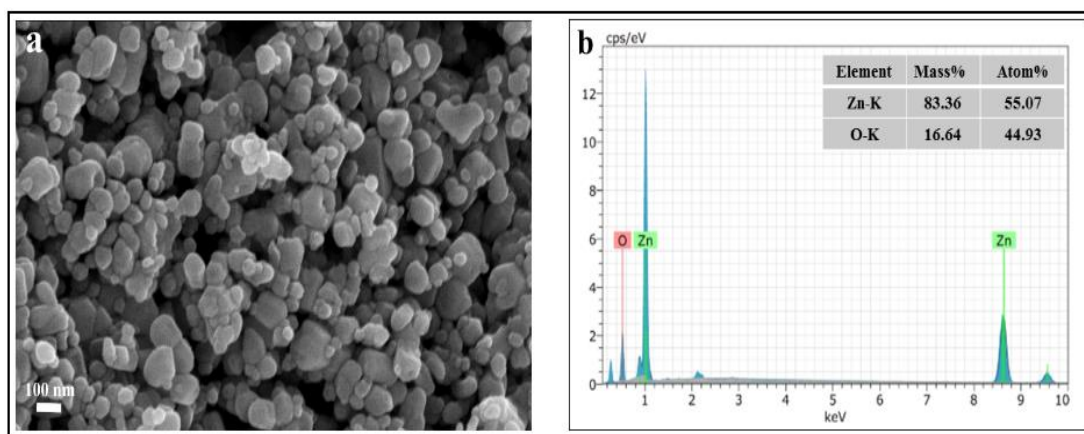


Figure 4.3: SEM image (a) and EDS (b) of ZnO nanoparticles

4.2.1.3 Optical properties

The absorption spectrum of the synthesized ZnO nanomaterial is given in figure 4.4. The band edge is found at 374 nm. Tauc plot gives a bandgap of 3.16 eV which is in good agreement with the already reported data³⁶.

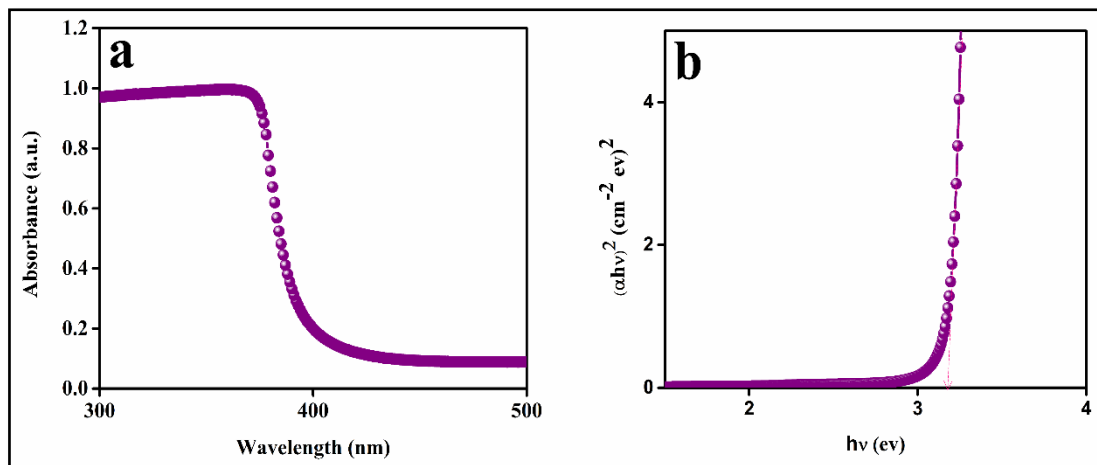


Figure 4.4: Photo-absorption spectrum (a) and the corresponding Tauc plot (b) of ZnO nanoparticles

ZnO nanomaterials have remarkable defect chemistry and these defects notably modify the grain boundaries of crystals as well as the I-V characteristics of the cell³⁷. The Gauss fitted deconvoluted photoluminescence (PL) spectrum of calcined zinc oxide nanoparticles (at 400°C), is shown in figure 4.5. The sample excited at 340 nm gives band edge emissions at 396 nm with other defect emissions at 420, 455, 487 and 526 nm.

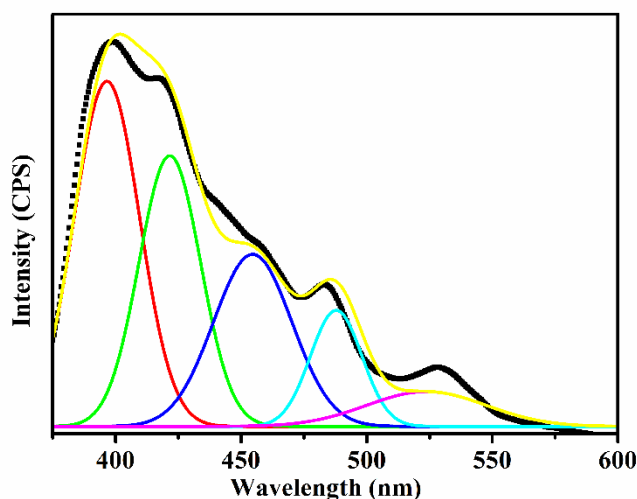


Figure 4.5: Gauss fitted de-convoluted photoluminescence spectrum of ZnO nanoparticles excited at 340 nm

The room temperature PL spectrum is normally characterized by near band edge UV emission and emissions due to deep levels called DLE. DLE refers to bands extending from 400nm to 750nm. ZnO possess a large number of deep level impurities and complex like oxygen vacancy (V_o), zinc vacancy (V_{zn}), zinc interstitial (Zn_i), oxygen interstitial (O_i) etc³⁷. Near band edge emissions at 420 nm corresponds to violet emission which originates from Zn_i and is due to the transition from Zn_i to valence band. The blue emission at 455 nm and 487nm is due to the V_{zn} and the recombination between Zn_i energy level and V_{zn} energy levels^{38,39}. Intense green emissions observed at 526 nm is due to oxygen vacancies created in the crystal lattice⁴⁰ and other intrinsic defects like Zn_i also contribute to green emission. The electron transitions from the deep trap levels to valance band give low energy green emissions^{41,42}.

4.3 Synthesis of filler incorporated PVA gel electrolyte

Commercial TiO_2 and ZnO are the two inorganic fillers of choice. These fillers are added during the initial stage of gelation for their uniform distribution in the polymer gel electrolyte. Different weight percentage of the fillers are added during synthesis to obtain an optimum concentration.

Materials

- *Potassium Iodide*
- *Iodine*
- *Ethylene carbonate*
- *Dimethyl sulfoxide*
- *Filler (ZnO / TiO_2)*
- *Polyvinyl alcohol*

Method

Liquid electrolyte was first prepared by adding 0.3M KI and 0.03M I_2 into a mixture of DMSO and EC. Required amount of filler was added (1wt%, 2wt%, 3wt% and 5wt %) to the above mixture and stirred. To this liquid electrolyte mixture 0.2 g of PVA was added and stirred for 15 minutes for uniform distribution, followed by heating at 100°C , till the polymer get completely dissolved in the organic solvent mixture. The result was a uniform, highly viscous molten solution which on keeping overnight set to give a free standing “pudding thick” filler incorporated PVA gel electrolyte. The sample is named as VAT 1, VAT 2, VAT 3 and VAT 5 for TiO_2

incorporated PGE and VAZ 1, VAZ 2, VAZ3 and VAZ 5 for ZnO incorporated PGE throughout the thesis for simplicity. Figure 4.6 and 4.7 shows the photographs of the TiO_2 and ZnO incorporated PVA gel electrolyte respectively.

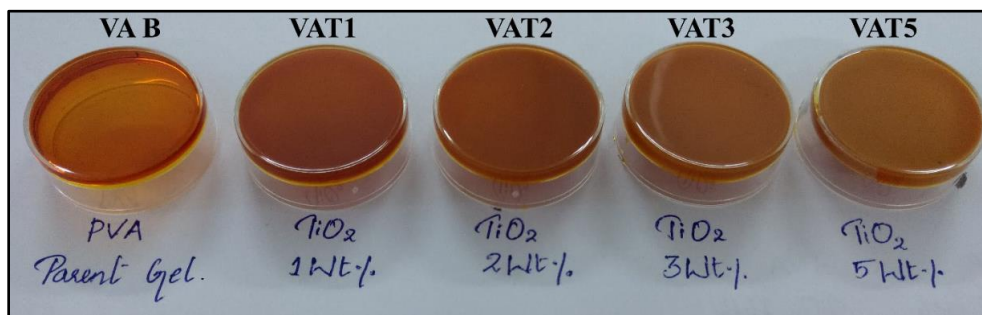


Figure 4.6: Photographs of PVA parent gel (VA B) and different weight percentage of Commercial TiO_2 incorporated PVA gel electrolyte

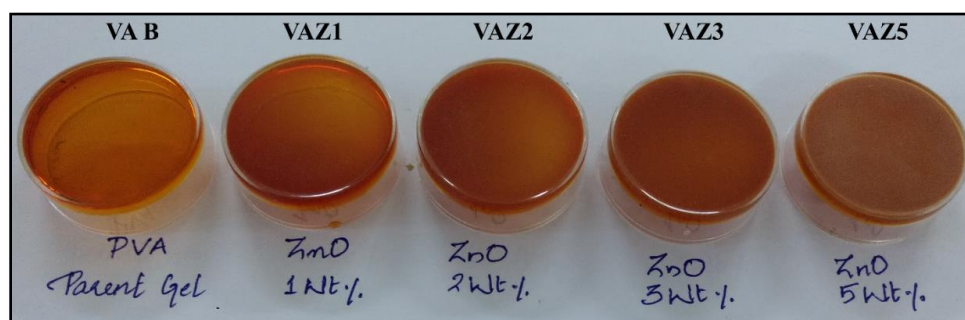


Figure 4.7: Photographs of PVA parent gel (VA B) and different weight percentage of synthesized ZnO incorporated PVA gel electrolyte

4.4 Characterization of filler incorporated PVA gel electrolyte

The properties of the filler incorporated polymer gel electrolyte depends on several factors like size of the particle, dispersion of the filler, the interaction between filler and polymer matrix as well as the preparation methods. The structural, electrical and thermal properties of the filler incorporated PVA gel electrolyte were studied and compared with the filler free electrolyte and the results are discussed in detail.

4.4.1 Fourier transform infrared analysis

The interaction of the PVA matrix with the added filler is studied by performing the FT-IR analysis and the spectra is compared with the filler free VA B. The spectral details of VA B is discussed in detail in section 3.2.1.3 of chapter 3.

4.4.1.1 FT-IR of TiO_2 incorporated PVA gel electrolyte

Figure 4.8 depicts the infra-red spectrum of VA B, TiO_2 and TiO_2 incorporated PVA gel electrolyte.

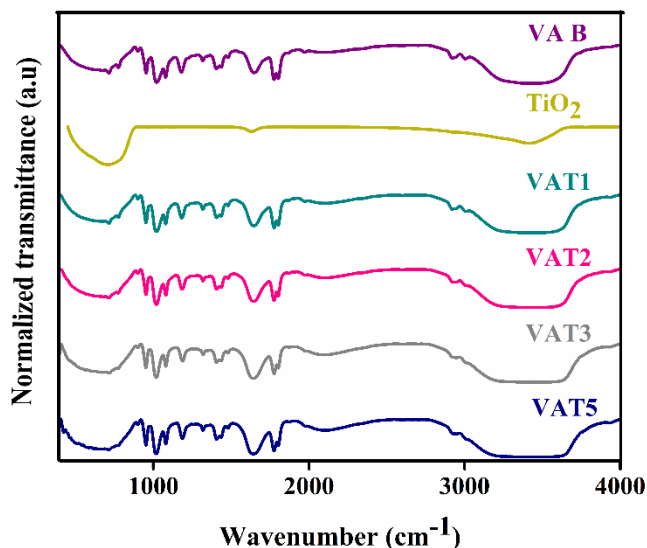


Figure 4.8: FT-IR spectra of VA B, TiO_2 and different weight % of TiO_2 incorporated VA B

In the IR spectrum of TiO_2 , the two sharp peaks present at 1634cm^{-1} and 3411cm^{-1} are attributed to the O-H bond of the adsorbed water molecule on the surface of TiO_2 . Absorption peak at 704cm^{-1} is the characteristic of TiO_2 . A comparison of the FTIR spectra of TiO_2 , filler free polymer gel electrolyte and TiO_2 incorporated polymer gel electrolyte show the following changes. In all filler incorporated systems, there is broadening of peak observed in the range 400cm^{-1} - 900cm^{-1} , which shows the

presence of these fillers in the polymer gel electrolyte. The peak at 3429cm^{-1} in VA B corresponds to the intermolecular and intra molecular hydrogen bonding present in the polymer host. This peak was found broadened in the filler incorporated system. This indicates weak hydroxyl interaction present between added filler and the $-\text{OH}$ group of the PVA network. No other shifting or peak broadening could be observed in filler incorporated system, confirming that there is no chemical interaction between the added filler and the polymeric chains⁴³.

4.4.1.2 FT-IR of ZnO incorporated PVA gel electrolyte

The infra-red spectra of VA B, ZnO and ZnO incorporated PVA gel electrolyte are shown in figure 4.9.

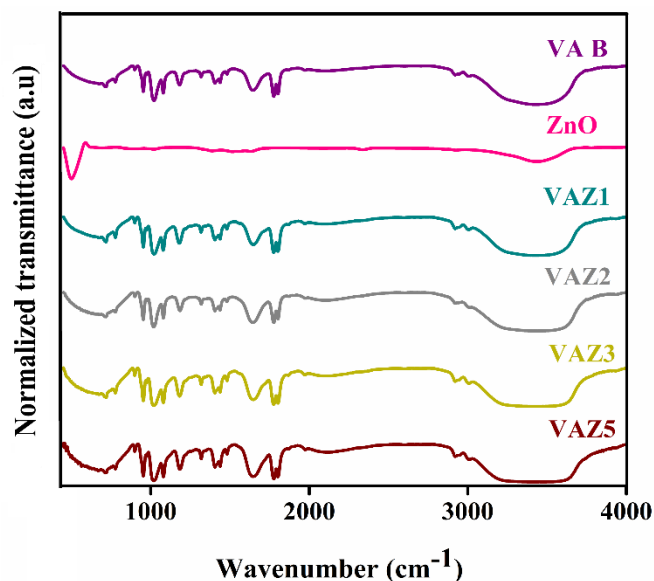


Figure 4.9: FT-IR spectra of VA B, ZnO and different weight % of ZnO incorporated VA B

The IR spectra of ZnO shows a sharp peak at 498cm^{-1} , which corresponds to Zn-O stretching frequency⁴⁴. A sharp peak at 3436cm^{-1} corresponds to the vibration of $-\text{OH}$ group from the moisture adsorbed to the surface of ZnO molecule. A broadening

observed at around 3436cm^{-1} corresponds to the extensive –OH stretching between the polymeric network structure and the surface hydroxyl group of ZnO. A comparison of the spectra observed for VA B, ZnO and ZnO incorporated PVA gel electrolyte, eliminates any complex formation between ZnO and the polymer chain⁴⁵.

4.4.2 Electrochemical impedance analysis

The conductivity and transport behavior of the ions in the filler incorporated gel electrolyte was studied using Electrochemical Impedance Spectroscopy (EIS) and the same has been compared with filler free electrolyte. The measurements were taken under dark condition and so the magnitude of impedance depends strongly on the total conductivity of the electrolyte. The results show that the conductivity increases with increase in concentration of the filler concentration. Polyvinyl alcohol is semi-crystalline in nature. In most of the polymers both crystalline and amorphous phase coexist. These crystalline phase hampers the segmental motion of the polymer chains. The added fillers interact with the crystalline phase and increases the amorphous region by altering the polymer chain reorganization. The greater free volume thus developed within the polymer enhances the ionic conductivity of the whole system⁴⁶. Also these fillers helps in the complete dissociation of the salt by forming an ion-inorganic oxide complex via a Lewis acid-base interaction of the fillers with the ionic species. Thus a conducting pathway is formed for the migration of the ionic species and thus enhances the overall ionic conductivity of the polymeric system^{47,48}.

Expected conduction mechanism in filler incorporated PVA gel electrolyte

Addition of nanofillers to the polymer gel electrolyte enhances the ionic conductivity of the system. The same Grotthius charge exchange mechanism contribute to the conduction by building a proper transport channel for the redox couple. Figure 4.10 shows the general schematic of the expected electron transfer mechanism in filler incorporated polymer gel electrolyte.

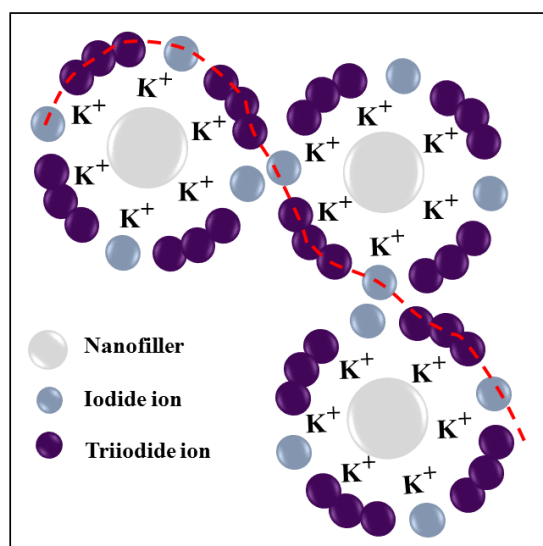


Figure 4.10: Expected electron transfer mechanism in nanocomposite polymer gel electrolyte

The ionic conductivity of the electrolyte depends upon all the ionic species present in the electrolyte other than the I^- , I_3^- and the polyiodides. In the absence of these fillers the cations will get adsorbed on the photoanode TiO_2 film. In filler incorporated polymer gel electrolyte the cations present in the electrolyte get adsorbed on the surface of the uniformly dispersed filler and align the anionic redox couple by electrostatic force, forming an electron transport pathway to facilitate the charge-exchange mechanism⁴⁹.

4.4.2.1 EIS of TiO_2 incorporated PVA gel electrolyte

The EIS measurement was carried out by sandwiching the polymer gel electrolyte in between two electrodeposited Pt electrodes. EIS of polymer gel electrolyte with different weight percentage of TiO_2 was shown in figure 4.11. The charge transport in PVA gel electrolyte is effectively facilitated by adding fillers. The smaller semi-circle in the high frequency region represents the charge transfer resistance at the Pt counter electrode– electrolyte interface and is represented by R_1 . R_2 is the resistance towards the diffusion of the ionic species within the electrolyte⁵⁰. The fitted data obtained from the Nyquist plot is given in table 4.1. With the addition of fillers the R_1 and R_2 values decreased initially (VAT 1 and VAT2) and then increases (VAT3 and VAT5). The lowest R_1 and R_2 value and the highest conductivity was obtained for VAT2. It is presumed here that, at this concentration of fillers a well-defined continuous transport pathway is developed by the alignment of the fillers and thereby increase the volume of the amorphous region. R_1 and R_2 values are interdependent to each other. A decrease in R_1 value shows the enhanced catalytic activity of the Pt surface for the reduction of the triiodide ion. Similarly with the introduction of fillers the warburg impedance also decreases which shows the faster diffusion of the ionic species within the electrolyte. Thus the rate of diffusion of the triiodide ions towards the counter surface, its reduction and the removal of the oxidized species formed at the surface of the counter get enhanced and can be well related to the decrease in R_1 and R_2 values. Beyond 2wt% of TiO_2 added, the R_1 and R_2 value increases and the conductivity decreases.

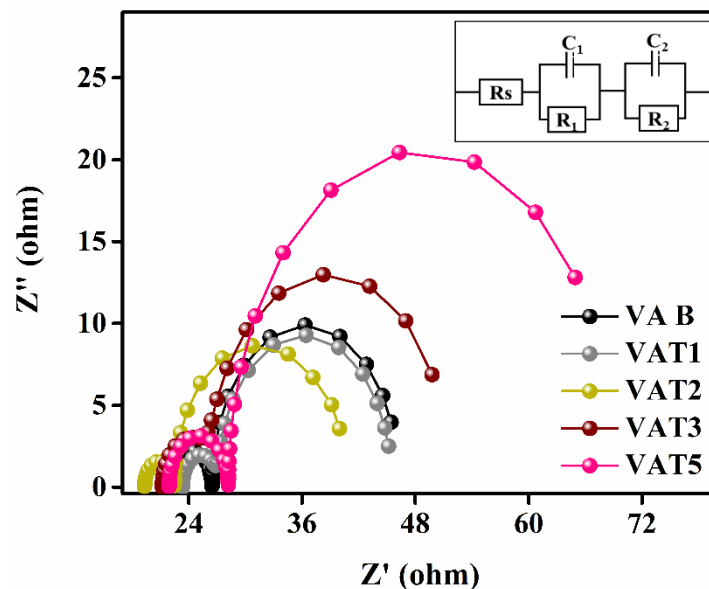


Figure 4.11: Nyquist plot of different weight percentage of TiO_2 incorporated gel electrolyte

Table 4.1: The Nyquist plot data and the conductivity measured for filler free and different weight percentage of TiO_2 incorporated gel electrolyte

Filler content	R_1 (Ω)	R_2 (Ω)	σ (mho cm^{-1}) * 10^{-4}
VA B	4.50	18.93	8.45
VAT1	3.58	18.53	8.63
VAT2	3.11	17.71	9.03
VAT3	4.49	24.03	6.65
VAT5	6.42	36.63	4.36

4.4.2.2 EIS of ZnO incorporated PVA gel electrolyte

EIS of polymer gel electrolyte with different weight percentage of ZnO was done and the Nyquist plot of ZnO incorporated PVA gel electrolyte is shown in figure 4.12 and the parameters obtained from the plot is listed in table 4.2.

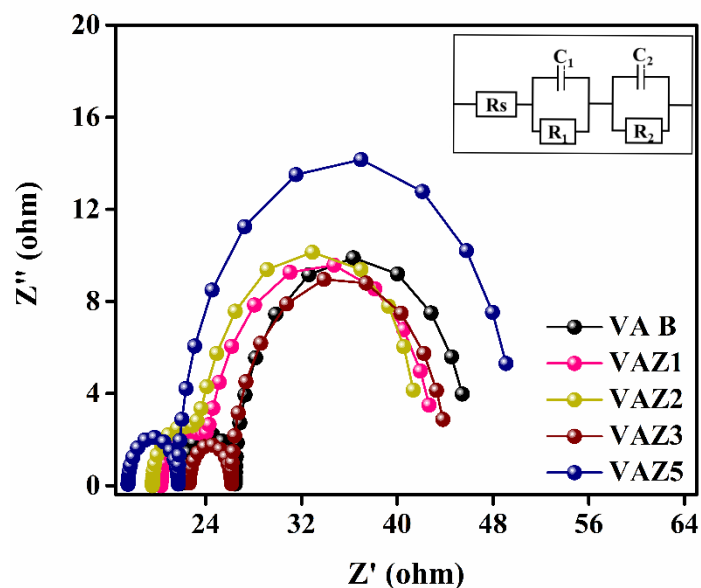


Figure 4.12: Nyquist plot of different weight percentage of ZnO incorporated gel electrolyte

Table 4.2: The Nyquist plot data and the conductivity measured for filler free and different weight percentage of ZnO incorporated gel electrolyte

Filler content	R_1 (Ω)	R_2 (Ω)	σ (mho cm^{-1}) $\times 10^{-4}$
VA B	4.50	18.93	8.45
VAZ1	3.80	18.61	8.59
VAZ2	3.60	18.13	8.82
VAZ3	3.48	17.86	8.95
VAZ5	4.20	27.30	5.96

The same trend in performance was repeated when different weight percentage of ZnO was added as filler. R_1 and R_2 values decreases and the conductivity increases with increase in filler content up to VAZ3. Further increasing the concentration of the filler, the conductivity decreased with higher R_1 and R_2 value.

Increasing the filler concentration (both TiO_2 and ZnO) cannot further improve the conductivity, confirming that the ionic conductivity/transport is suppressed by the excess filler present within the electrolyte. On increasing the concentration, there is a chance for agglomeration of these fillers rather than forming the ionic transport channel resulting in the formation of an electrically inert component. These filler clusters reduces the free volume, immobilize the polymer chains and also hinders the physical diffusion of the ionic species responsible for the conductivity^{7,8, 14}.

4.4.3 Linear sweep voltammetric analysis

The LSV of the best performing samples (VAT2 and VAZ3) and samples with maximum weight percentage of filler (VAT5 and VAZ5) were taken and compared with polymer gel electrolyte without filler.

4.4.3.1 LSV of TiO_2 incorporated PVA gel electrolyte

The limiting current density obtained for the filler free VA B is 25.73mAcm^{-2} . With the introduction of 2wt% of TiO_2 the limiting current density get enhanced to 31.02mAcm^{-2} . This enhancement can be explained by the ion-exchange mechanism with the formation of an electron transport pathway discussed in section 4.4.2. Figure 4.13 shows the linear sweep voltammogram of VA B and TiO_2 incorporated gel

electrolyte. The limiting current density and the triiodide diffusion coefficient calculated is listed in table 4.3.

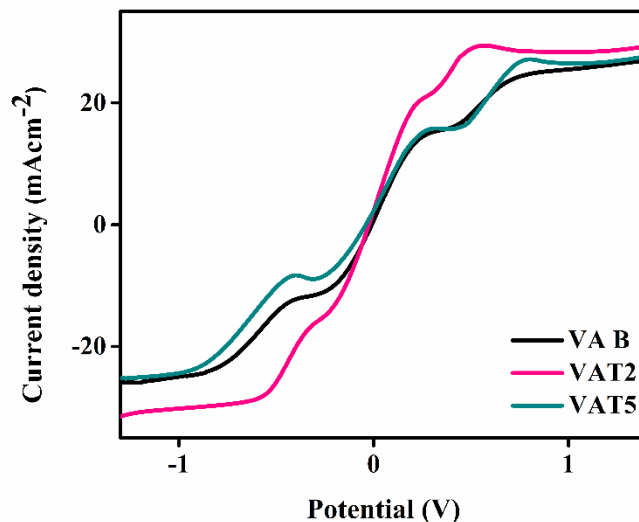


Figure 4.13: LSV of VA B and different weight % of TiO_2 incorporated PVA gel electrolyte

Table 4.3: Limiting current density and the triiodide diffusion coefficient calculated for VA B, VAT2 and VAT5

Electrolyte	$J_{lim} \text{ (mAcm}^{-2}\text{)}$	$\text{DI}_3^- \text{ (cm}^2\text{S}^{-1}\text{)} * 10^{-5}$
VA B	25.73	8.88
VAT2	31.02	10.71
VAT5	25.14	8.68

The added nanoparticles helps in reducing the interaction between the polymeric chains and thereby the local crystallization in polymer gel electrolyte. This decrease in crystallinity of the filler incorporated gel electrolyte is inferred to be the major factor for their higher ionic conductivity when compared to filler free bare system. Further increasing the concentration of the filler content in the polymer gel electrolyte has got adverse effect on its performance and the current density value get

lowered to 25.14 mAcm^{-2} for 5wt% of TiO_2 .

4.4.3.2 LSV of ZnO incorporated PVA gel electrolyte

Figure 4.14 shows LSV of VA B and different weight % of ZnO incorporated PVA gel electrolyte. The limiting current density is obtained from the plot and the triiodide diffusion coefficient calculated is listed in table 4.4.

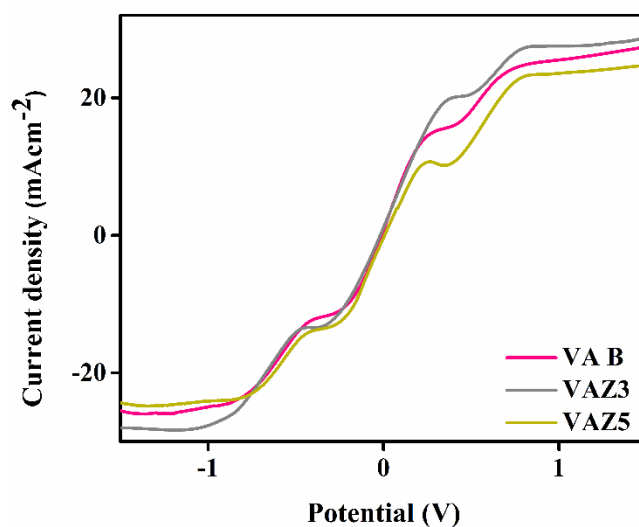


Figure 4.14: LSV of VA B and different weight % of ZnO incorporated PVA gel electrolyte

Table 4.4: Limiting current density and the triiodide diffusion coefficient calculated for VA B, VAZ3 and VAZ5

Electrolyte	$J_{lim} \text{ (mAcm}^{-2}\text{)}$	$\text{DI}_3^- \text{ (cm}^2\text{S}^{-1}) * 10^{-5}$
VA B	25.73	8.88
VAZ3	28.12	9.71
VAZ5	24.68	8.52

The results show that the diffusion coefficient first increases with increase in filler content and then starts decreasing. The diffusion coefficient calculated for 3wt%

ZnO and 5wt% ZnO is 28.12 mAcm^{-2} and 24.68 mAcm^{-2} respectively. With increase in filler content for both TiO_2 and ZnO, clustering or agglomeration of the nanoparticle takes place creating a tortuous pathway for the ion diffusion. Also the solvent holding capacity of the polymer matrix get adversely affected in presence of excess of filler content.

4.4.4 Thermogravimetric analysis

For both VA B and filler incorporated polymer gel electrolyte, two reaction stages are observed over the temperature range. During the first stage, dehydration and de-polymerization occurs and end up with conjugated polyene sequences. Gasification is prominent in the second stage via an intramolecular cyclization of the polyene residues⁵¹. Figure 4.15 and figure 4.16 shows the TGA curves of TiO_2 incorporated and ZnO incorporated PVA gel electrolyte. Thermal stability of polymer gel electrolyte get enhanced when nanofillers are introduced. All the composition shows one main weight loss region but a slight variation in temperature can be observed with respect to the added additives. This shows the improvement in stability of the filler incorporated polymer gel electrolyte. The enhancement in stability suggests a successful incorporation of the fillers into polymer matrix⁵². The fillers are found to be homogeneously embedded in the PVA matrix. Most of the polymers undergo complete pyrolysis before reaching 600°C while the semiconductor oxide fillers remain stable over 600°C . On increasing the weight percentage of the filler the temperature of weight loss region increases⁵².

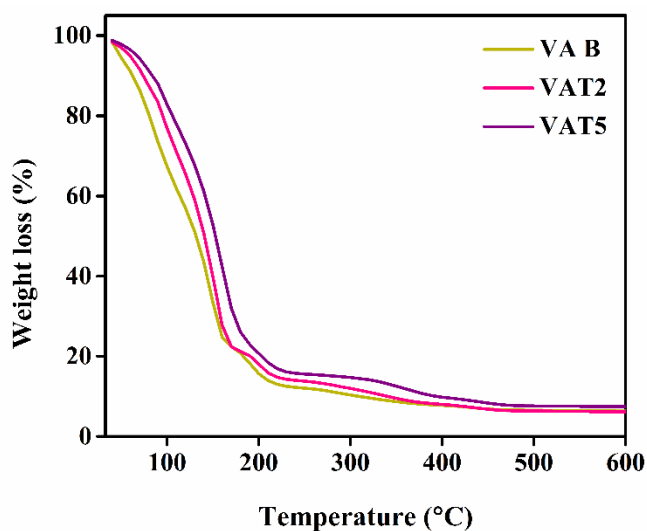


Figure 4.15: TGA of pure powder VA B and TiO₂ incorporated PVA gel electrolyte

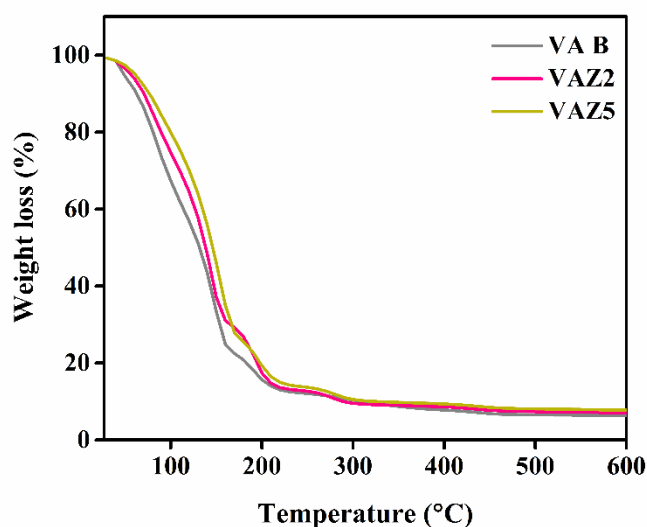


Figure 4.16: TGA of pure powder VA B and ZnO incorporated PVA gel electrolyte

The shifting of curves to higher temperature as compared to filler free system indicates some interaction between the filler and the polymeric chain that lead to their mutual stabilization. As a result the segmental mobility and molecular mobility of the PVA chains get reduced. The reduced mobility of the polymer chain suppress the chain transfer reaction and slow down the degradation process leading the decomposition to

a higher temperature. The increase in the weight percentage of fillers increases the viscosity and stiffen the polymer gel electrolyte which is disadvantageous to the penetration of the electrolyte and easy transport of the ionic species between the electrodes.

4.4.5 Time dependent stability study

Syneresis was a natural process taking place in gel electrolyte systems upon long storage time. A time dependent stability study of the filler incorporated PVA gel electrolyte (VAT2 and VAZ3) was done by performing EIS. For that, dummy cells were prepared by sandwiching the polymer gel electrolyte in between Pt coated FTO substrate. The R_1 value shows the charge transfer resistance at the counter electrode-electrolyte interface and the R_2 value shows the resistance induced to the diffusion of the ionic species within the electrolyte. Figure 4.17 and 4.18 shows the EIS spectra of VAT2 and VAZ3 taken over a period of one month. The data obtained from the plot is listed in table 4.5 and 4.6 respectively.

A conductivity of $9.03 \times 10^{-4} \text{ mho cm}^{-1}$ and $8.95 \times 10^{-4} \text{ mho cm}^{-1}$ was shown by VAT2 and VAZ3 during the first day of synthesis. The rate of decay of the efficiency increased with increasing testing time for all the samples. Second reading was taken after five days of synthesis and a higher R_1 and R_2 value was observed. This is mainly due to syneresis which results in the loss of liquid electrolyte trapped within the network of the polymer matrix. As a result of this, the concentration of the ionic species decreases and offers a greater resistance for the reduction triiodide ion at the surface of the counter electrode. This may also disturb the easy diffusion of the ionic

species within the electrolyte. Poor wetting of the electrode surface and proper dispersion of the filler particles within the electrolytic network get disturbed with the loss of liquid electrolyte.

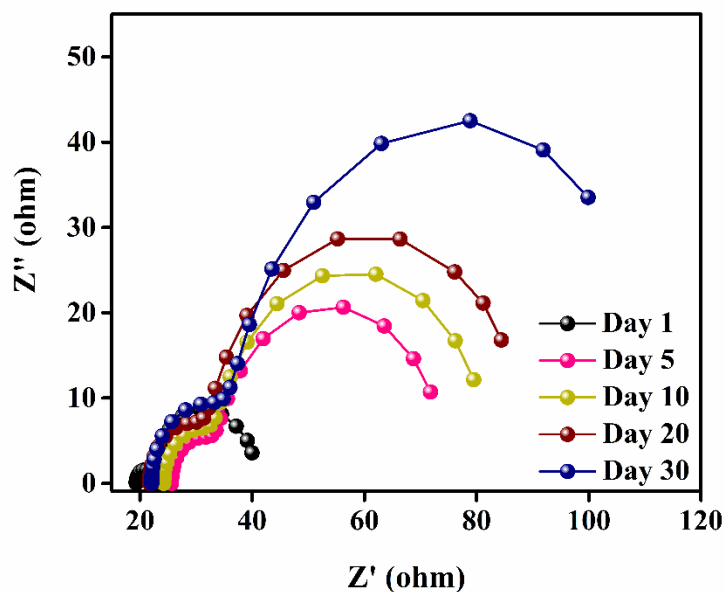


Figure 4.17: EIS spectra of VAT2 taken over a period of one month

Table 4.5: Nyquist plot data and the conductivity measured for VAT2 taken over a period of one month

Filler content	R_1 (Ω)	R_2 (Ω)	σ (mho cm^{-1}) * 10^{-4}
Day 1	3.11	17.71	9.03
Day 5	7.24	38.85	4.12
Day 10	8.31	46.97	3.40
Day 20	9.33	53.24	3.00
Day 30	13.04	64.94	2.46

Both VAT2 and VAZ3 show the loss of liquid electrolyte due to syneresis but at different extent. VAT2 was found to be more susceptible to syneresis and a sudden drop in performance was observed compared to VAZ3. The percentage loss of liquid electrolyte was found to be high in the presence of TiO_2 filler. This can be explained on the basis of the size of the filler added. The TiO_2 nanoparticle added is smaller in size when compared to the synthesized ZnO. For smaller size the particle density will be high and that facilitates a blocking effect due to the closeness of the filler grains⁷. This reduces the cohesive force that hold the polymeric chains along with the liquid electrolyte in the three dimensional network and make the long polymer chains more immobilized, leading to the decrease in conductivity.

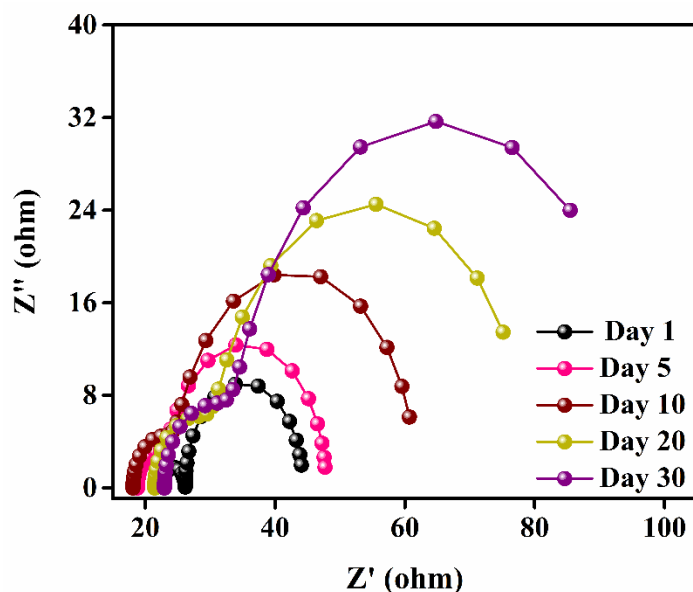


Figure 4.18: EIS spectra of VAZ3 taken over a period of one month

Table 4.6: Nyquist plot data and the conductivity measured for VAZ3 taken over a period of one month

Filler content	R_1 (Ω)	R_2 (Ω)	σ (mho cm^{-1}) * 10^{-4}
Day 1	3.53	17.86	8.90
Day 5	4.09	24.79	6.45
Day 10	6.09	36.38	4.39
Day 20	8.96	44.88	3.56
Day 30	10.58	51.95	3.07

The stability of filler incorporated polymer gel electrolyte was compared with that of filler free VA B and is shown in figure 4.19.

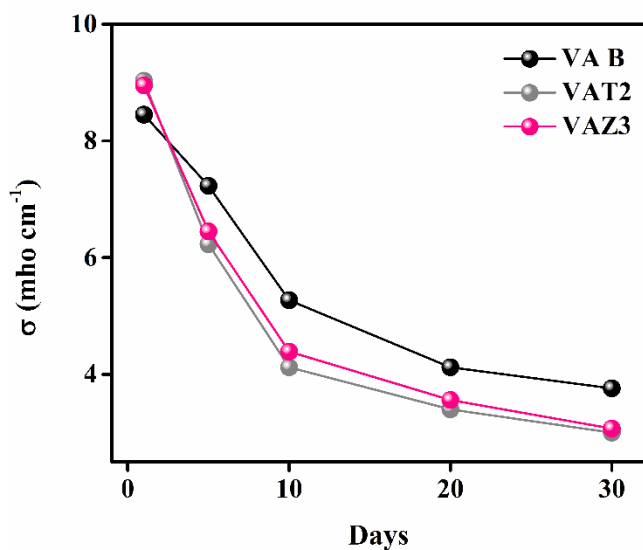


Figure 4.19: Comparison of time dependent stability study of VAT2 and VAZ3 with filler free VA B

The comparative study shows that the best performance was given by all the three electrolytes during the first day of experiment. Filler incorporated electrolytes give higher conductivity than the filler free VA B on the first day of synthesis. All the

three samples were found to be stable during first few days. After five days of synthesis, all the three samples started to show syneresis. But the extent of syneresis was found to be different and the liquid electrolyte loss was in the order VAT2>VAZ3>VA B. i.e., this shows that the electrolyte holding capacity of the polymer matrix is degrading fast in the presence of fillers. Throughout the period of study, better stability was shown by the filler free VA B and the order is VA B>VAZ3>VAT2.

4.5 Application

QSDSSC was fabricated with filler incorporated gel electrolyte to study their influence in enhancing the device performance. The components of the device and the fabrication procedure is given in section 3.7.1 of chapter 3. Figure 4.20 and figure 4.21 shows the photocurrent density-voltage plot of QSDSSC's with polymer gel electrolyte containing different weight percentage of TiO_2 and ZnO fillers. Upon adding fillers (both ZnO and TiO_2) into VA B an enhancement in cell performance was observed.

4.5.1 J-V curve of TiO_2 incorporated PVA gel electrolyte

The photovoltaic parameters obtained from figures 4.20 is tabulated in table 4.7. The parameters J_{sc} and V_{oc} are greatly influenced by the concentration of TiO_2 in VA B. J-V curve shows that an increase in filler concentration initially increases the current density but after VAT2, i.e. at higher concentrations of the filler, the J_{sc} value decreases. V_{oc} shows a steady increase in liner with the filler concentration in the electrolyte. This can be explained on the basis of agglomeration of the fillers.

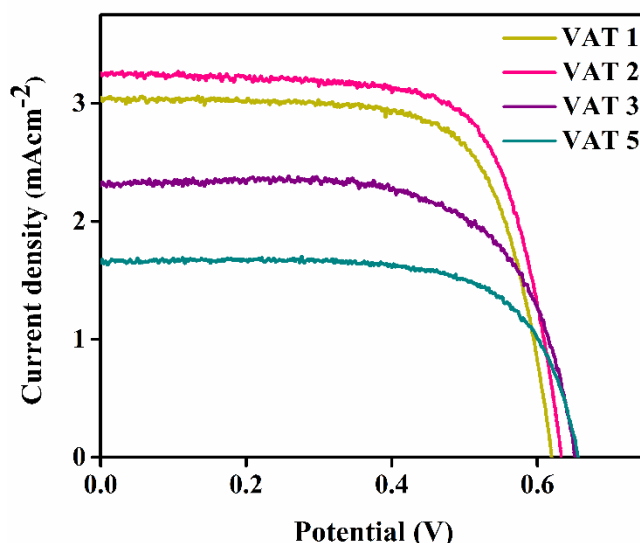


Figure 4.20: Current density-voltage plot of TiO_2 incorporated PVA gel electrolytes

Table 4.7: Photovoltaic parameters obtained from current density-voltage plot of TiO_2 incorporated PVA gel electrolytes.

Electrolyte	J_{sc} (mAcm^{-2})	V_{oc} (V)	FF (%)	Eff (%)
VAT1	3.04	0.62	71.7	1.35
VAT2	3.28	0.63	71.3	1.48
VAT3	2.27	0.65	71.0	1.05
VAT5	1.63	0.66	72.3	0.77

When present in excess, the fillers may build an inactive blockage in the electrolyte which slows down the diffusion of the ionic species in the electrolyte. As a result, the reduction of triiodide ion at the counter electrode surface and the fast regeneration of the dye gets decelerated. Thus the rate of electron injection to the TiO_2 conduction band decreases which lowers the J_{sc} of the device. With increase in filler content an increase in V_{oc} is also observed. Usually a shift in the conduction band of TiO_2 and an increase in density of electrons in TiO_2 conduction band gives rise to an

increase in V_{oc} . In PVA gel electrolyte an interaction between the hydroxyl group of PVA and conduction band of TiO_2 (photoanode) is possible. So when fillers are added the PVA hydroxyl group interact with the filler TiO_2 . With increase in filler content the interaction of PVA hydroxyl group with the photoanode decreases causing an upward shift of the TiO_2 conduction band resulting in an increase in V_{oc} .

4.5.2 J-V curve of ZnO incorporated PVA gel electrolyte

The photovoltaic parameters obtained from figures 4.21 is tabulated in table 4.8. Similar behavior is shown by QSDSSC with ZnO incorporated gel electrolyte. A maximum J_{sc} was observed for VAZ3 with a current density value of 3.09 mA/cm^2 . V_{oc} also increases with concentration of the filler in electrolyte. Agglomeration of the fillers at higher concentration may contribute nonlinearity to current density.

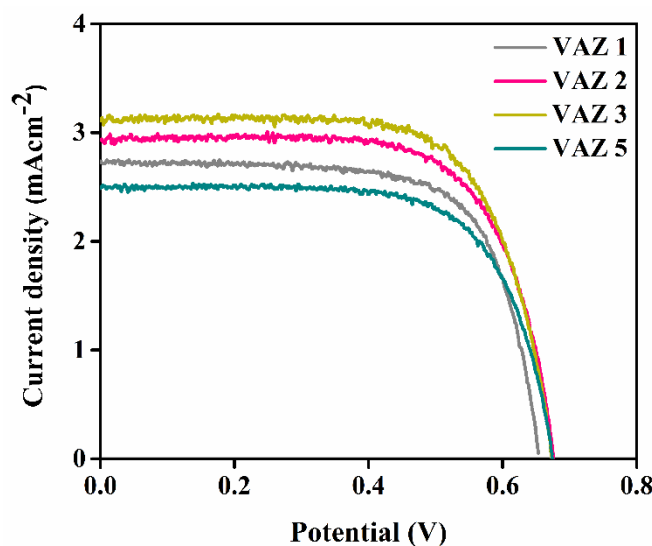


Figure 4.21: Current density-voltage plot of ZnO incorporated PVA gel electrolyte

Table 4.8: Photovoltaic parameters obtained from current density-voltage plot of ZnO incorporated PVA gel electrolytes

Electrolyte	J_{sc} (mAcm ⁻²)	V_{oc} (V)	FF (%)	Eff (%)
VAZ1	2.76	0.65	72	1.29
VAZ2	2.86	0.67	71.3	1.37
VAZ3	3.09	0.67	72.3	1.51
VAZ5	2.45	0.68	72.3	1.20

A significant enhancement in cell performance was observed when 2wt% TiO₂ and 3wt% ZnO was introduced. The efficiency of the cell increases to 1.48 % and 1.51% for TiO₂ and ZnO incorporated systems respectively. Further increasing the concentration of the filler slightly decreases the efficiency of the cell.

The power conversion efficiency of QSDSSC's are dependent on the ionic conductivity of the polymer gel electrolyte. The addition of fillers to the polymer gel electrolyte enhances the conductivity of the system by building a proper transport channel for the ionic diffusion. Up to an optimum concentration of these fillers the diffusion coefficient and the ionic conductivity of the system was found to increase. On further increasing the wt% of these fillers above the optimum concentration a decrease in performance was observed. With increase in filler content, the proper dispersion of fillers forming the transport channel is disturbed resulting in cluster formation. As a result resistance is induced to the diffusion of I⁻/I₃⁻ redox couple between the photoanode - counter electrode. The total kinetics of the cell reaction get disturbed and the availability of I⁻ ion for the fast regeneration of the dye molecule at

the photoanode/electrolyte interface and the reduction of the triiodide ion at the surface of the Pt counter electrode takes place at a lower rate. Hence a decrease in cell performance was observed on higher weight percentage of fillers. The results are consistent with the data obtained for the diffusion coefficient and the ionic conductivity measured for the gel electrolyte.

4.5.3 Comparison of the photovoltaic parameters of VA B and the best performing filler incorporated gel electrolyte (VAT2 and VAZ3)

VAT2 and VAZ3 was the optimized electrolyte composition and their photovoltaic performance was compared with the filler free system (VA B). The current density-voltage graph is shown in figure 4.22 (a). The photovoltaic parameters obtained from the J-V plots are listed in table 4.9.

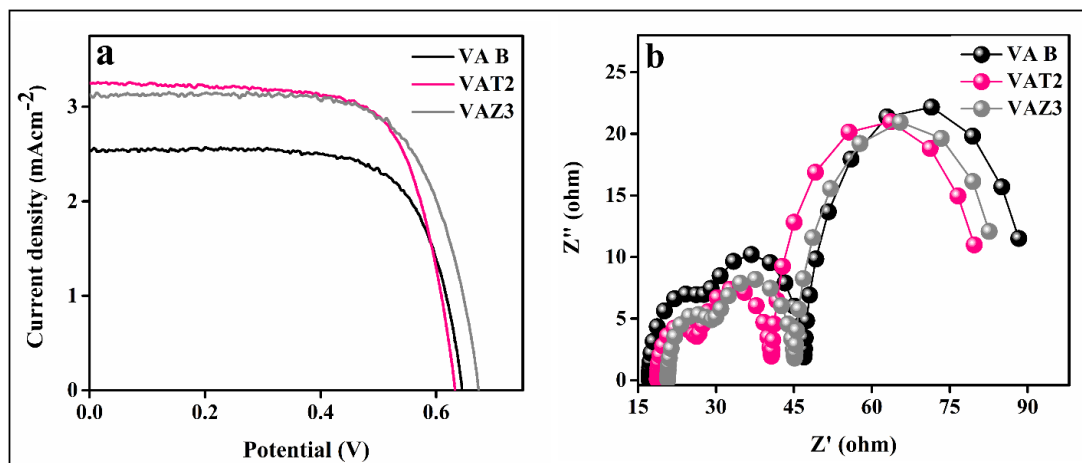


Figure 4.22: Current density-voltage plot (a) and the Nyquist plot (b) of VA B, VAT2 and VAZ3

Table 4.9: Current density – voltage data of VA B, VAT2 and VAZ3

Electrolyte	J_{sc} (mAcm ⁻²)	V_{oc} (V)	FF (%)	Eff (%)
VA B	2.54	0.64	73.0	1.19
VAT2	3.28	0.63	71.3	1.48
VAZ3	3.09	0.67	72.3	1.51

Table 4.10: Nyquist plot data of VA B, VAT2 and VAZ3

Electrolyte	R_s (ohm)	R_1 (ohm)	R_2 (ohm)	R_3 (ohm)
VA B	17.02	10.5	19.26	43.06
VAT2	18.73	7.63	14.32	41.53
VAZ3	20.85	8.32	16.05	37.48

The current density, J_{sc} is greatly influenced by the addition of these fillers which helps in improving the overall performance of the cell. For both VAT and VAZ an enhancement in J_{sc} was observed and this can be explained on the basis of improved conductivity of the polymer gel electrolyte upon filler addition. When comparing VAT2 and VAZ3, VAZ3 has got lower current density and a higher V_{oc} . The higher V_{oc} exhibited by VAZ3 can be attributed to the shifting of the conduction band edge of TiO₂ photoelectrode. As a result, energy gap between the CB of TiO₂ and LUMO of the photoexcited dye decreases, and that lowers the driving force for the injection of electrons to the CB of TiO₂ by the dye⁵³.

The interfacial charge transfer resistance of these QSDSSC's were analyzed by taking EIS measurements. Nyquist plot, to show the charge transfer resistances at

different interfaces of QSDSSC with electrolyte having optimum fillers TiO_2 , ZnO , and without filler is shown in figure 4.22 (b). The EIS parameters are listed in figure 4.10. The first semicircle corresponds to the charge transfer resistance at the Pt counter/electrolyte interface (R_1). The second semicircle is related to the recombination reaction taking place at the photoanode/dye/electrolyte interface (R_2) and R_3 corresponds to the Warburg impedance⁵⁴. R_s is the sheet resistance.

The R_1 value decreases significantly when the fillers (TiO_2 and ZnO) are introduced to the polymer gel electrolyte. The decrease in R_1 value is due to the adsorption of the fillers on to the Pt surface, thereby extracting electrons from the counter electrode for the fast reduction of the triiodide ion. A similar observation was reported by Ching-Lun Chen et. al., when TiO_2 was added to poly(acrylonitrile-co-vinyl acetate)⁵⁵. The R_2 value was found to decrease with the addition of fillers. Lower R_2 value suggests a greater recombination taking place at the photoanode-dye-electrolyte interface. When compared to the filler free system, a fast transport of the ionic species within the electrolyte is taking place in the presence of these fillers. So the ease of accessibility of the I^- ion at the surface of the photoanode increases and hence there is a greater chance for back recombination than VA B. The R_3 value was found to decrease in the presence of filler content. This lower R_3 value is mainly attributed to the enlargement of the amorphous region in the polymer gel electrolyte by the addition of filler developing a transfer channel for the easy transport of the electrolytic species.

The photovoltaic performance of QSDSSC with filler incorporated gel electrolyte (VAT2 and VAZ3) has got a power conversion efficiency higher than that of a DSSC with liquid electrolyte. A comparison on the performance of QSDSSC with filler free gel electrolyte (VA B) and DSSC with liquid electrolyte shows comparable efficiency. The efficiency values thus obtained is 1.19 and 1.44 for QSDSSC (VAB) and DSSC respectively under 1 sun illumination. Thus the problems confronted by using liquid electrolyte can be solved in all respect by replacing liquid electrolyte with polymer gel electrolyte and further enhancement in performance can be achieved by modifying the polymer gel electrolyte with addition of inorganic fillers.

4.6 Conclusion

The present study clearly shows the influence of inorganic fillers in enhancing the properties of PVA based polymer gel electrolyte. Filler incorporated VA B was synthesized with different weight percentage of TiO_2 and ZnO nanoparticles. Characterizations were done on the synthesized gel electrolytes to study the effect of fillers. FT-IR studies performed on the gel electrolyte show a peak broadening in the range 400 to 1000 cm^{-1} and at around 3500 cm^{-1} , indicating the interaction of semiconductor oxide fillers with the polymer matrix in the polymer gel electrolyte. TGA studies performed on the gel electrolyte shows an increase in thermal stability for filler incorporated gel electrolyte. Dummy cells were fabricated to study the conductivity measurement like EIS and LSV of the gel electrolyte. With increase in filler content the conductivity and apparent diffusion coefficient of the gel electrolyte increases. An optimized composition of filler incorporated gel electrolyte (VAT2 and

VAZ3) provided the most effective pathway for the redox species to move in the electrolyte thus exhibiting anionic conductivity of $9.03 \times 10^{-4} \text{ mho cm}^{-1}$ and $8.95 \times 10^{-4} \text{ mho cm}^{-1}$ respectively. A time dependent stability study of VAT2 and VAZ3 gel electrolytes were performed to check the extent of syneresis and was compared with that of the VA B. The rate of decay increased with increasing testing time for all the samples. However an average performance was maintained by filler free VA B throughout study.

QSDSSC's were fabricated with all the four weight percentage of VAT and VAZ and their photovoltaic characteristics were measured. The photovoltaic performance increases initially with filler content then observed a drop in the performance by showing low J_{sc} value. This is same for both fillers, indicating an optimum filler concentration for the enhanced performance QSDSSC. Highest efficiency was shown by filler incorporated PVA gel electrolyte with 2wt% of TiO_2 and 3wt% of ZnO and the results are in good agreement with the conductivity measurements done. Filler incorporated QSDSSC's achieved a better photovoltaic performance than the corresponding DSSC performance.

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5

SYNTHESIS, CHARACTERIZATION
AND APPLICATION OF FILLER
INCORPORATED PMMA GEL
ELECTROLYTE

5. SYNTHESIS, CHARACTERIZATION AND APPLICATION OF FILLER INCORPORATED PMMA GEL ELECTROLYTE

5.1 Synthesis of filler incorporated PMMA gel electrolyte

Materials

- *Potassium Iodide*
- *Iodine*
- *Propylene carbonate*
- *Filler (ZnO / TiO₂)*
- *Polymethyl methacrylate*

Method

Liquid electrolyte was first prepared by adding 0.3 M KI and 0.03 M I₂ to PC. Required amount of filler was added (1wt%, 2wt%, 3wt% and 5wt%) to the above mixture and stirred. To the solution mixture, 0.2 g of PMMA was added and stirring was continued for another 15 minutes for the uniform distribution. The temperature of the system was raised to 70°C with stirring till the polymer get completely dissolved in the organic mixture. The result was a uniform highly viscous molten solution which on keeping for overnight set to give a “*honey thick*” filler incorporated PMMA polymer gel electrolyte. The samples are named as MAT1, MAT2, MAT3 and MAT5 for 1,2,3,and 5 wt % TiO₂ incorporated PGE and MAZ1, MAZ2, MAZ3 and MAZ5 for 1,2,3,and 5 wt % ZnO incorporated PGE. Figure 5.1 and 5.2 shows the photographs of MA B and gel electrolyte with different weight percentage of TiO₂ and ZnO.

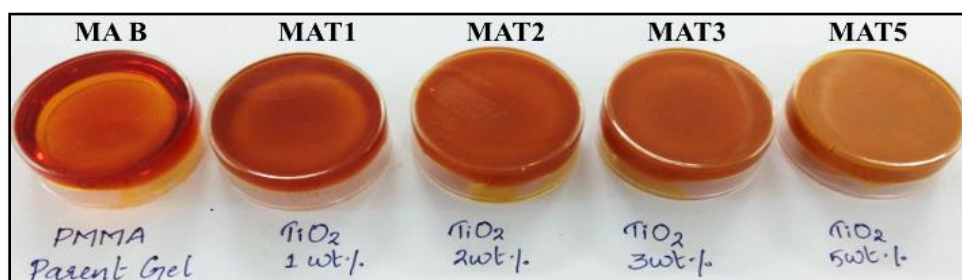


Figure 5.1: Photograph of PMMA parent gel (MA B) and different weight percentage of TiO₂ incorporated PMMA gel electrolyte

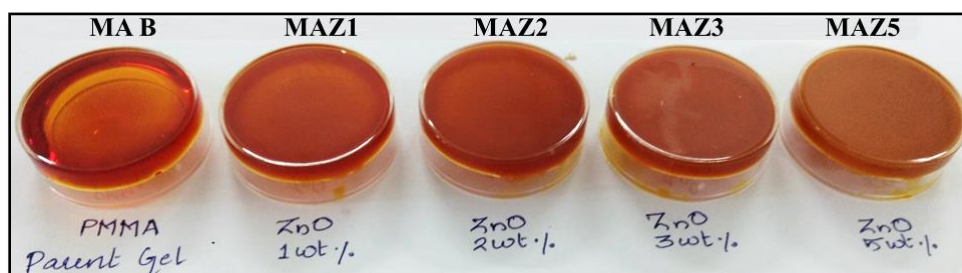


Figure 5.2: Photograph of PMMA parent gel (MA B) and different weight percentage of ZnO incorporated PMMA gel electrolyte

5.2 Characterization of filler incorporated PMMA gel electrolyte

The structural, thermal and conductivity properties of the filler incorporated PMMA gel electrolytes are studied by performing characterizations like FT-IR, EIS, LSV and TGA. The results obtained are compared with the parent electrolyte without filler and the results are discussed below in detail.

5.2.1 Fourier transform infrared analysis

FT-IR spectral analysis was carried out to study the chemical affinity of PMMA segments towards the surface of the oxide filler particles. A shift in the peak position, developments of new peaks, changes in peak intensity, development of

shoulders in the existing peaks etc gives information about the interaction of the added fillers with the polymer chains^{1,2}.

5.2.1.1 FT-IR of TiO₂ incorporated PMMA gel electrolyte

The FT-IR spectra of PMMA gel electrolyte, TiO₂ and different weight percentage of TiO₂ (1, 2, 3 and 5wt%) incorporated PMMA gel electrolytes are shown in figure 5.3.

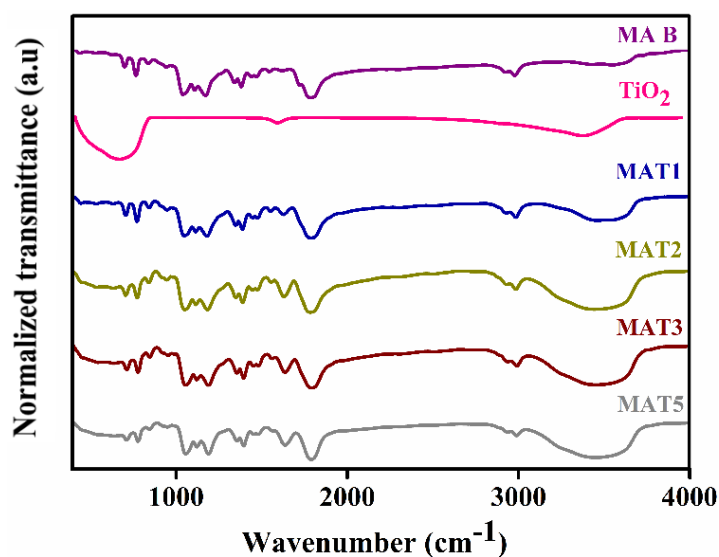


Figure 5.3: FT-IR spectra of MA B, TiO₂ and different weight % of TiO₂ incorporated MA B

In the FT-IR spectrum of TiO₂, a broad absorption peak is observed in the range 400–800 cm⁻¹ which is the characteristic absorption of Ti–O vibration. In the TiO₂ incorporated PMMA gel electrolytes, with increase in concentration of TiO₂ a broadened dip can be observed at this range. In the filler free system (MA B) no such dip was observed. Also at around 3500 to 3600 cm⁻¹ a broadened peak is observed and this broadening increases with increase in the TiO₂ wt%. This shows the presence and interaction of the TiO₂ in the gel electrolyte. The hydroxyl group present on the TiO₂

surface can get anchored with the carbonyl groups of the PMMA chains through weak hydrogen bonding interaction. A similar observation was found in the studies made by Xiangfu Meng et.al³.

5.2.1.2 FT-IR of ZnO incorporated PMMA gel electrolyte

The FT-IR spectra of pure PMMA gel electrolyte, ZnO and different weight percentage of ZnO incorporated PMMA gel electrolytes are shown in figure 5.4.

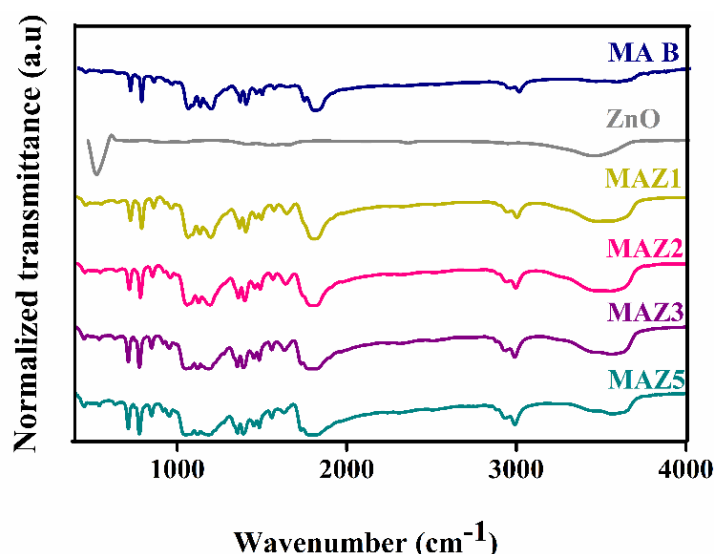


Figure 5.4: FT-IR spectra of MA B, ZnO and different weight % of ZnO incorporated MA B

The IR spectra of ZnO shows a sharp peak at around 498 cm^{-1} , which corresponds to Zn-O stretching frequency⁴. The presence of ZnO in the polymer gel electrolyte was identified as a small bend in the 400 to 500 cm^{-1} region in MAZ 1 to 5. It was observed that the stretching frequency at 1789 cm^{-1} corresponding to CO group has shown a broadening effect on adding ZnO. Hydrogen bonding interaction between the surface -OH group of the filler and the carbonyl group of PMMA could be the reason for this peak broadening. Also there is a broadened peak in the range

3500 to 3600 cm^{-1} observed for all ZnO incorporated PMMA gel electrolytes. This confirms the interaction between the ZnO and the polymeric matrix^{5,6}.

5.2.2 Electrochemical impedance analysis

The ionic conductivity of the polymer gel electrolyte was studied by performing the EIS of gel electrolyte. The spectra of different weight percentage of filler incorporated PMMA gel electrolytes were taken by fabricating dummy cells. Detailed discussion on the dummy cell fabrication is given in section 3.3.1 of chapter 3. The measurements were taken under dark condition. PMMA is amorphous in nature owing to the presence of bulky side groups attached to the polymer backbone. Studies show that the ionic conductivity of PMMA polymer gel electrolyte remains very close to that of liquid electrolytes⁷. So the addition of fillers definitely will improve the performance of MA B. R_1 shows the resistance at the Pt electrode – electrolyte interface and R_2 shows the warburg impedance⁸. The conductivity of the electrolytes were calculated as per equation 2 in Chapter 3.

5.2.2.1 EIS of TiO_2 incorporated PMMA gel electrolyte

EIS of polymer gel electrolyte with different weight percentage of TiO_2 is shown in figure 5.5 with the fitted equivalent circuit in the inset. R_s , R_1 , R_2 are respectively the sheet resistance, counter electrode-electrolyte interface resistance and warburg diffusion resistance of the electrolyte. EIS parameters obtained from the Nyquist plot and the conductivity calculated are listed in table 5.1.

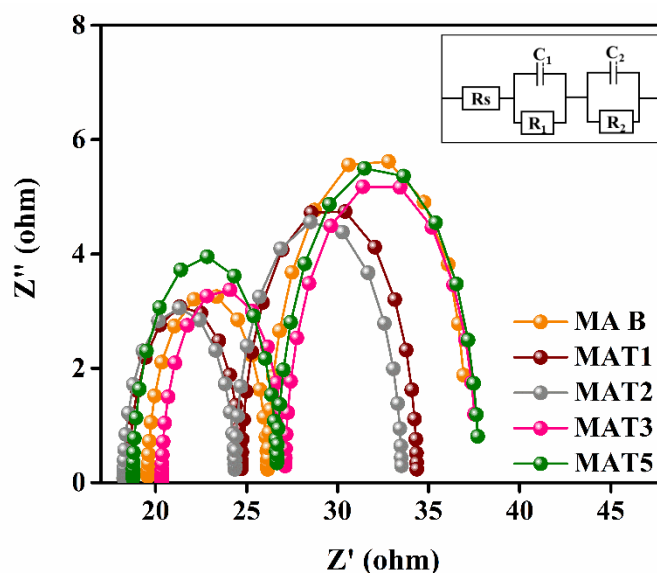


Figure 5.5: Nyquist plot of PMMA gel electrolytes with different weight percentage of TiO_2 incorporation

Table 5.1: EIS parameters and the calculated conductivity of filler free and different weight percentage of TiO_2 incorporated PMMA gel electrolytes

Filler content	R_1 (Ω)	R_2 (Ω)	σ (mho cm^{-1}) * 10^{-4}
MA B	6.57	10.67	14.99
MAT1	6.20	9.64	16.59
MAT2	6.11	9.12	17.54
MAT3	6.84	10.43	15.38
MAT5	7.93	10.75	14.88

The result shows an enhancement in conductivity with the introduction of fillers. Both R_1 and R_2 decreases with the addition of fillers. A decrease in R_1 value shows the fast reduction of triiodide ion at the counter surface and a decrease in R_2 value shows the easy transport of the ionic species within the electrolyte. This is

because a definite transport pathway is built within the electrolyte by these fillers for the transport of the ionic species⁹. Highest conductivity of $17.54 \times 10^{-4} \text{ mho cm}^{-1}$ is shown by MAT2. On further increasing the concentration of TiO_2 the R_1 and R_2 value increased resulting in a decreased ionic conductivity.

5.2.2.2 EIS of ZnO incorporated PMMA gel electrolyte

EIS of polymer gel electrolyte with different weight percentage of ZnO is shown in figure 5.6. The fitted data obtained from the Nyquist plot and the ionic conductivity calculated is given in table 5.2.

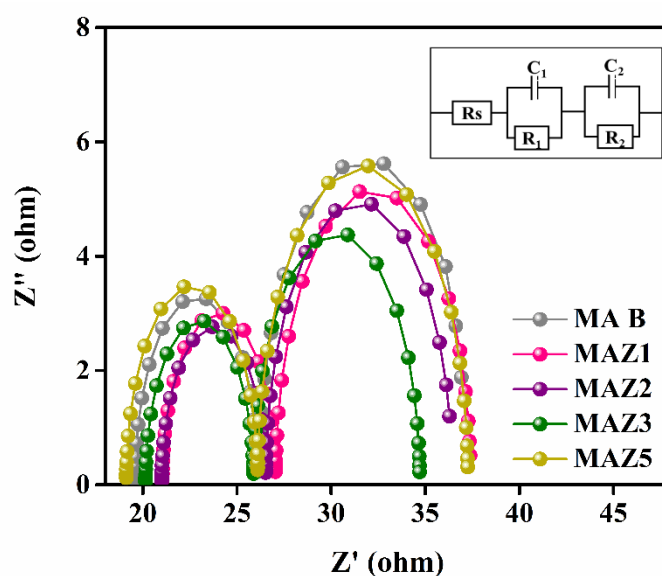


Figure 5.6: Nyquist plot of different weight percentage of ZnO incorporated PMMA gel electrolyte

Same trend in performance as discussed above for TiO_2 incorporated gel electrolytes is observed when different weight percentage of ZnO was added as filler. An increase in performance was initially observed with the introduction of fillers and

Table 5.2: The Nyquist plot data and the conductivity measured for filler free and different weight percentage of ZnO incorporated PMMA gel electrolyte

Filler content	$R_1 (\Omega)$	$R_2 (\Omega)$	$\sigma (\text{mho cm}^{-1}) * 10^{-4}$
MA B	6.57	11.98	13.35
MAZ1	6.03	10.19	15.71
MAZ2	5.52	9.75	16.39
MAZ3	5.73	8.69	18.41
MAZ5	6.98	10.35	15.45

on increasing the weight percentage, after an optimum concentration the performance begins to decline. Here, the best performance was shown by MAZ3 (3wt % ZnO) with a conductivity value of $18.41 \times 10^{-4} \text{ mho cm}^{-1}$. Beyond this concentration a decrease in ionic conductivity was observed by showing an increase in R_1 and R_2 value.

The increase in conductivity of the filler incorporated PMMA polymer gel electrolyte can be explained on the basis of a transport channel developed by these fillers and is well explained in section 4.4.2. of chapter 4. Generally, addition of fillers increases the amorphous region of the polymer gel electrolyte¹⁰. Adding fillers to the already amorphous PMMA gel electrolyte helps the electrolyte to behave more like a liquid. The viscosity of the electrolyte decreases and the ionic species experience very less resistance to their diffusion within the electrolyte between the electrodes. On increasing the concentration of the filler, the viscosity of the electrolyte increases. At higher filler concentration the flow of the electrolyte is restricted and stiffening of the honey thick polymer gel electrolyte resulted with consistency. This suggests a

restriction in mobility of the polymer chains in the presence of excess of filler that may agglomerate or form clusters and restricts the charge transport.

5.2.3 Linear sweep voltammetric analysis

The I_3^- diffusion coefficient was calculated by running the LSV of the samples, those exhibited best performance in the EIS measurement. To confirm the trend in conductivity, LSV of the samples with highest weight percentage of filler was also carried out.

5.2.3.1 LSV of TiO_2 incorporated PMMA gel electrolyte

Figure 5.7 shows the linear sweep voltammogram of symmetric dummy cell employing MA B and TiO_2 incorporated PMMA gel electrolytes (2wt% and 5wt%). The platform of the limiting current density determines the diffusion of charge carriers. The limiting current obtained from figure 5.7 and the triiodide diffusion coefficient calculated is listed in table 5.3. The limiting current density obtained for the filler free MA B is 11.32 mAcm^{-2} . With the introduction of 2wt% of TiO_2 the limiting current density get enhanced to 12.13 mAcm^{-2} . 5wt% of TiO_2 in MA B decreased the value to 10.39 mAcm^{-2} . An increase in performance followed by a decrease as obtained from the EIS measurement is repeated here.

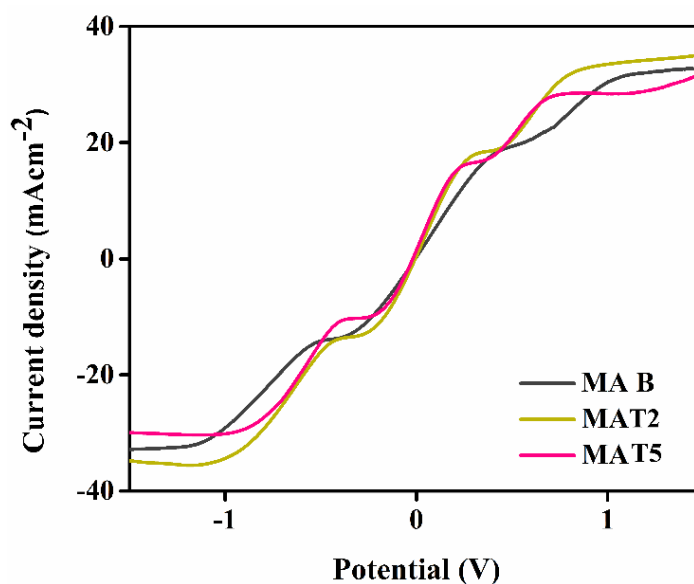


Figure 5.7: LSV of MA B, 2 and 5wt% of TiO₂ incorporated PMMA gel electrolyte

Table 5.3: Limiting current density and the apparent diffusion coefficient calculated for filler free MA B and TiO₂ incorporated PMMA gel electrolyte

Filler content	J_{lim} (mAcm ⁻²)	DI_3^- (cm ² S ⁻¹) * 10 ⁻⁵
MA B	32.78	11.32
MAT2	35.12	12.13
MAT5	30.09	10.39

5.2.3.2 LSV of ZnO incorporated PMMA gel electrolyte

LSV plots of filler free PMMA gel electrolyte (MA B) and ZnO incorporated PMMA gel electrolyte are shown in figure 5.8. The limiting current density is obtained from the plot and the I_3^- diffusion coefficient calculated is listed in table 5.4. With the introduction of 3wt % ZnO the limiting current density increased to 13.45 mAcm⁻². With the introduction of 5wt% ZnO, the limiting current density decreased to 12.6 mAcm⁻². The initial increase in performance and a decrease on further increase in

concentration of the filler above the optimum concentration is due to the formation of a transport pathway by these fillers that facilitate the easy transport of these ionic species in the former situation. In the latter case agglomeration of fillers takes place developing a blockage for the ionic transport.

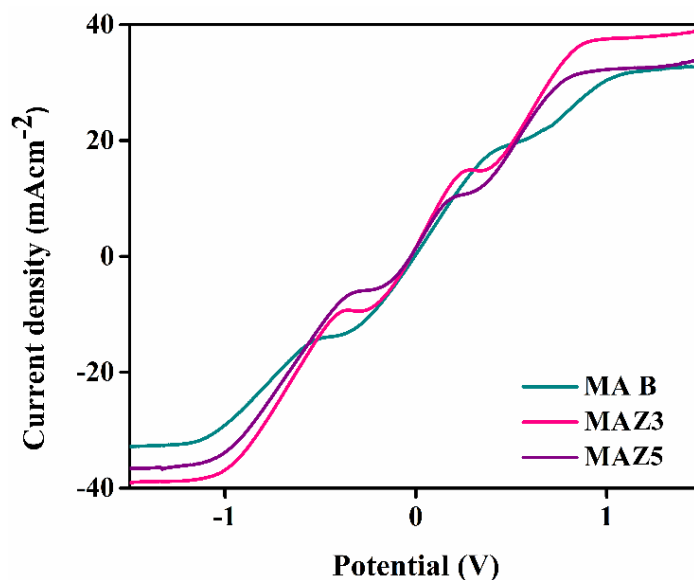


Figure 5.8: LSV of MA B, 3 and 5wt % of ZnO incorporated PMMA gel electrolyte

Table 5.4: Limiting current density and the apparent diffusion coefficient of filler free MA B and ZnO incorporated PMMA calculated

Filler content	J_{lim} (mAcm ⁻²)	DI_3^- (cm ² S ⁻¹) * 10 ⁻⁵
MA B	32.78	11.32
MAZ3	38.94	13.45
MAZ5	36.60	12.60

5.2.4 Thermogravimetric analysis

TGA of the pure PMMA (MA B) and PMMA incorporated with TiO_2 and ZnO under nitrogen atmosphere were performed with the aim to investigate the thermal stabilities of the polymer gel electrolytes. All the curves show similar degradation trend. Three main steps take place during the thermal degradation of PMMA in nitrogen atmosphere. The first step corresponds to the initial scission of weak head-to-head bonds. Second step is attributed to the decomposition of PMMA chain and the third step is related to the random scission of the polymer chains. The properties of the polymer composites containing inorganic spherical particles depend on many factors, such as the size and dispersion of the particles, the interaction between the particles and the polymer chains, and the properties of the polymer matrix and the particles.

Figure 5.9 shows the thermal degradation of TiO_2 incorporated PMMA gel electrolyte. With the introduction of TiO_2 filler, at each step a shift in the curve is observed towards the higher temperature region. This shift shows an interaction between the added TiO_2 and the PMMA network and also a better dispersion of TiO_2 in PMMA matrix. As the content of TiO_2 increases in the PMMA polymer; the matrix get more stiffened and the polymer gel electrolyte became more thermally stable¹¹. Studies shows that electron transfer takes place between the free radicals formed during the scission of the polymer chain to the TiO_2 fillers. A quenching of free radicals by the added TiO_2 filler takes place resulting in retarding of the thermal degradation^{3,12}.

For both filler incorporated systems show a higher decomposition temperature compared to pure PMMA gel electrolyte (MA B). With increase in concentration of the added filler, the thermal decomposition temperature increases.

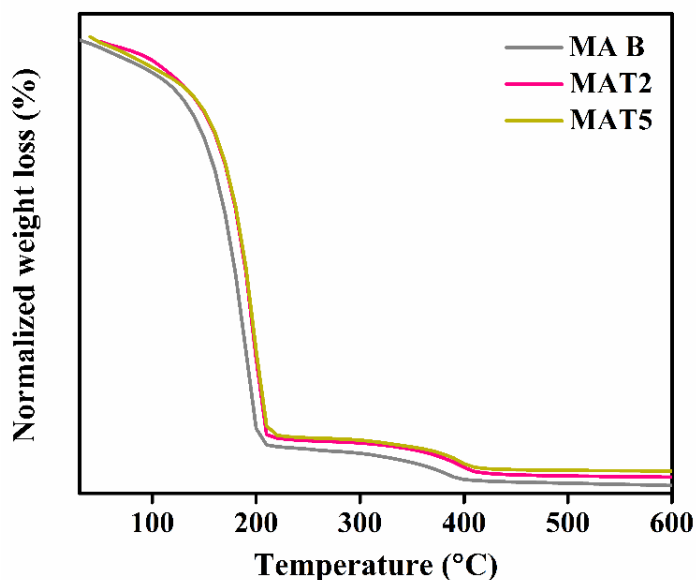


Figure 5.9: TGA of pure powder MA B and TiO₂ incorporated PMMA gel electrolyte

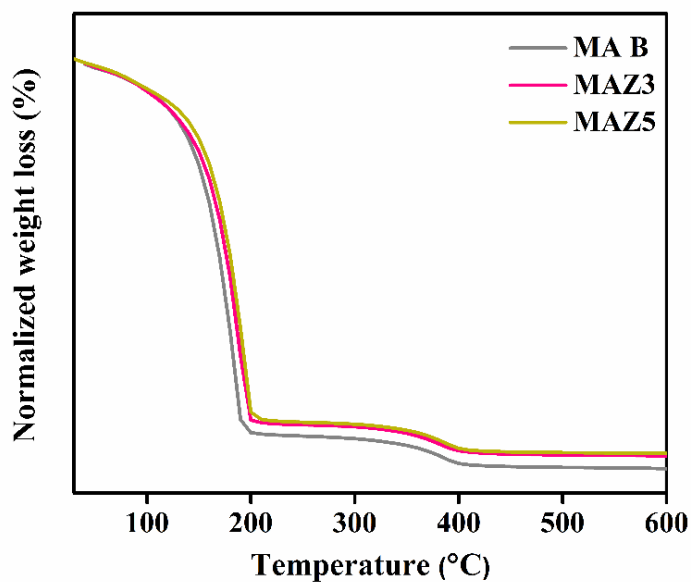


Figure 5.10: TGA of pure powder MA B and ZnO incorporated PMMA gel electrolyte

The TGA curves for pure PMMA, and that for PMMA mixed with 3 and 5wt% ZnO samples are shown in Figure 5.10. From the curve it is clear that the pure PMMA (MA B) lost weight before the ZnO incorporated gel electrolyte decomposes. It could be concluded that the good dispersion of ZnO nanoparticles in PMMA had improved the thermal properties of the nanocomposites obtained and the improvement depends on the amounts of nanoparticles added¹³. A similar observation of electron transfer and quenching of the free radicals¹⁴ was observed by Haase *et al*¹⁵ in his work to improve the thermal stability of the filler incorporated system.

5.2.5 Time dependent stability study

A time dependent stability study of the best performing filler incorporated PMMA gel electrolyte (MAT2 and MAZ3) was done by performing EIS. For that dummy cells were prepared by sandwiching the polymer gel electrolyte in between Pt coated FTO substrate. The R_1 value represents the electron transfer resistance at the Pt electrode-electrolyte interface and R_2 represents the resistance encountered by the ionic species within the electrolyte. Figure 5.11 and 5.12 shows the EIS spectra of MAT2 and MAZ3 taken over a period of one month. The R_1 and R_2 values obtained from the plot and the conductivity calculated are listed in table 5.5 and 5.6 respectively.

A conductivity of $17.60 \times 10^{-4} \text{ mho cm}^{-1}$ and $18.41 \times 10^{-4} \text{ mho cm}^{-1}$ was shown by MAT2 and MAZ3 on the first day of the electrolyte. The performance of the gel did not change obviously during the first few days of the experiment and as time passes the performance gradually degraded. Second characterization was done on the fifth day of electrolyte synthesis. A very slight decrease in conductivity was observed with

little increase in R_1 and R_2 values. The susceptibility of PMMA gel electrolyte towards syneresis were almost nil during the first few days of characterization and a notable hike in R_1 and R_2 was observed after 5th day. After 5th day the conductivity of the polymer gel electrolyte decreased steeply for filler incorporated systems. 69.47% and 70.28% decay in performance was observed respectively for ZnO and TiO₂ incorporated polymer gel electrolyte after one month of synthesis. Syneresis was not prominently observed in the case of filler incorporated PMMA gel electrolyte even after one month of synthesis.

On introducing fillers the liquid electrolyte retention ability of the polymer matrix remain unchanged. But the activity was found decreased. Since there is no loss of liquid electrolyte and no visible changes or degradation to the polymer matrix, the only chance for the deterioration in performance may be due to the unavailability of the ionic species responsible for the conduction process. i.e., the degradation of the ionic species on long storage or the formation of some other products may be the reason. It has been observed that the redox couple is prone to photo-degradation. One of the main reason for the low performance and stability is due to the degradation of the electrolyte properties due to absorption of light¹⁵. The iodine present in the electrolyte is bleached by the absorption of light and the electrolyte becomes inactive. The bleaching of the electrolyte may be due to the side reaction of the photo-generated holes at the surface of the TiO₂ surface^{16,17}. Also there is a chance for the formation of IO₃⁻ in presence of moisture. When exposed to ambient atmospheric condition for a long time, the atmospheric moisture can get captured by the iodide ion resulting in its

oxidation and forms iodate instead of triiodide¹⁸. Thus the concentration of the triiodide ion get decreased. Also the iodate formed cannot be reduced at the counter electrode. On keeping for long time, the chances of sublimation of iodine present in the equilibrium mixture high. As a result the concentration of the ionic species get changed and the equilibrium get disturbed.

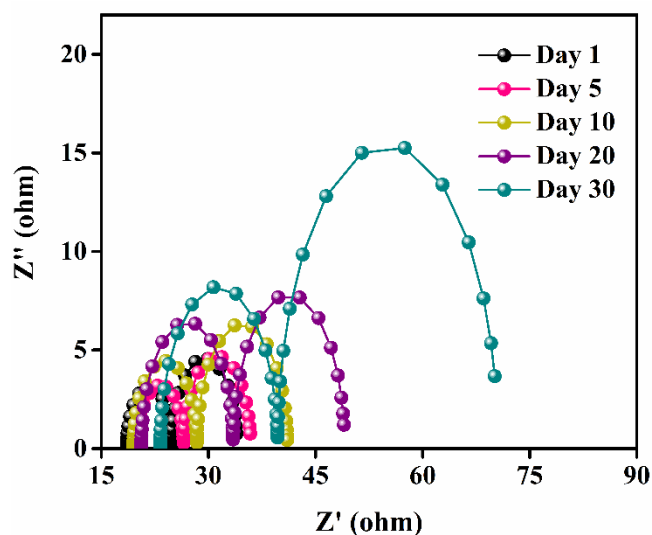


Figure 5.11: EIS spectra of MAT2 taken over a period of one month

Table 5.5: Nyquist plot data and the conductivity measured for MAT2 taken over a period of one month

Days	$R_1 (\Omega)$	$R_2 (\Omega)$	$\sigma (\text{mho cm}^{-1}) * 10^{-4}$
Day 1	6.31	9.09	17.60
Day 5	6.54	9.28	17.24
Day 10	9.00	12.60	12.69
Day 20	12.85	15.51	10.31
Day 30	16.46	30.56	5.23

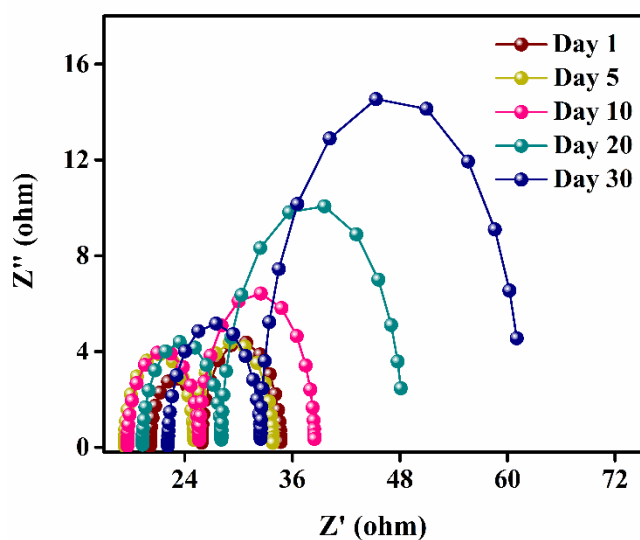


Figure 5.12: EIS spectra of MAZ3 taken over a period of one month

Table 5.6: Nyquist plot data and the conductivity measured for MAZ3 taken over a period of one month

Days	$R_1 (\Omega)$	$R_2 (\Omega)$	$\sigma (\text{mho cm}^{-1}) * 10^{-4}$
Day 1	5.73	8.69	18.41
Day 5	7.62	8.76	18.26
Day 10	7.84	10.5	15.23
Day 20	8.85	19.97	8.01
Day 30	10.38	28.48	5.62

The performance of the filler incorporated polymer gel electrolyte was compared with that of filler free MA B and is shown in figure 5.13. The filler incorporated gel electrolytes show best performance in the first few days and the performance got declined after 5th day of synthesis. The rate of decay of the efficiency increased with increase in testing time for these samples. Filler free MA B shows a

stable performance throughout the period under observation without much compromise in its conductivity. Even after one month 84.19% efficiency in performance was maintained by the filler free MA B. The deterioration in performance of filler incorporated PMMA gel electrolyte cannot be explained on the basis of syneresis because no trace of liquid electrolyte loss was observed during the period of study. MAZ3 and MAT2 remained completely stable throughout the experimental time. Thus the problem of syneresis while using gel electrolyte was completely solved by using PMMA matrix. Here, the time dependent performance decay of filler incorporated gel electrolytes is due to the photo-bleaching of iodine species by the oxide filler surface.

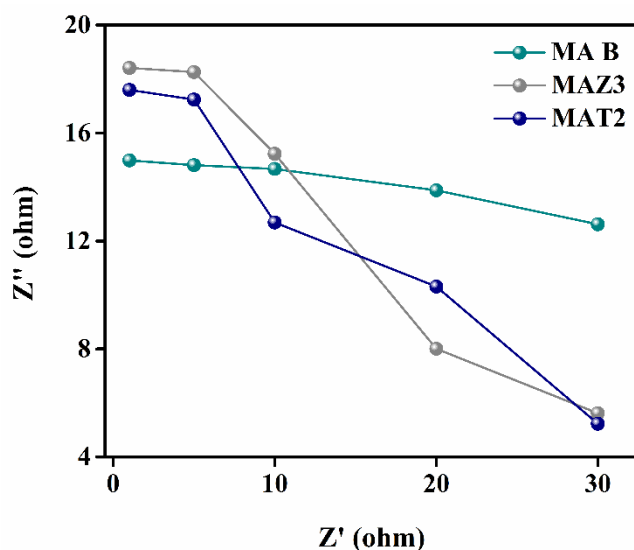


Figure 5.13: Comparison of time dependent stability study of MAT2 and MAZ3 with filler free MA B

5.3 Application

The performance of the filler incorporated polymer gel electrolyte in solar cells can be studied by fabricating QSDSSC. All filler incorporated PMMA gel electrolytes were applied to study the trend in their performance with respect to percentage of filler. The photovoltaic performance of the cell is recorded under 1 Sun illumination (100 mW cm^{-2}).

5.3.1 J-V curve of TiO_2 incorporated PMMA gel electrolyte

Figure 5.14 shows the photocurrent density – voltage curve of cells with different weight percentage of TiO_2 incorporated PMMA gel electrolyte. The cell parameters obtained are given in table 5.7. The result shows that an enhancement in performance was observed with the addition of TiO_2 . The photovoltaic parameter J_{sc} was greatly influenced by the addition of TiO_2 . Here the enhancement in efficiency of QSDSSC solely depend on the J_{sc} . This can be explained on the basis of fast injection of the electrons to the conduction band of TiO_2 and the reduced recombination at the surface of photoanode. With the addition of filler an electron transport pathway is developed for the smooth diffusion of the ionic species. Thus a fast regeneration of dye ground state takes place with the easy diffusion of the iodide ions. Also the recombination loss at the photoanode – electrolyte interface can be reduced. i.e., after the reduction of the oxidized dye, the triiodide ion formed get easily transported away from the surface by this transport channel. So the availability of triiodide ion to get recombined with the photo-injected electron is also getting reduced. The highest efficiency of 2.34% was obtained for MAT2 with a short circuit current density of 6.08

mAcm^{-2} . Further increasing the concentration of the filler lowers the cell performance.

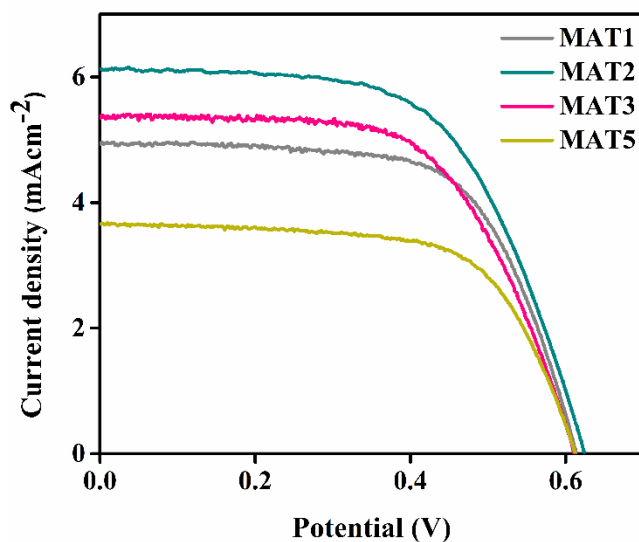


Figure 5.14: Current density-voltage plot of TiO_2 incorporated PMMA gel electrolyte

Table 5.7: Photovoltaic parameters obtained from current density-voltage plot of TiO_2 incorporated PMMA gel electrolytes

Electrolyte	J_{sc} (mAcm^{-2})	V_{oc} (V)	FF (%)	Eff (%)
MAT1	4.92	0.61	66.3	2.00
MAT2	6.08	0.62	62.8	2.34
MAT3	5.3	0.61	63.0	2.04
MAT5	3.66	0.61	65.7	1.48

5.3.2 J-V curve of ZnO incorporated PMMA gel electrolyte

QSDSSC was fabricated with four different weight percentage of ZnO and the current density-voltage plots are shown in figure 5.15. The photovoltaic parameters obtained from the plot are listed in table 5.8. The trend remains the same for both the fillers. The performance of the cell increases with increase in filler concentration up

to an optimum concentration and then the performance of the device started to decline. The optimum efficiency was exhibited when MAZ3 was applied. A short circuit current density of 6.05 mAcm^{-2} and an efficiency of 2.38 % was obtained for MAZ3.

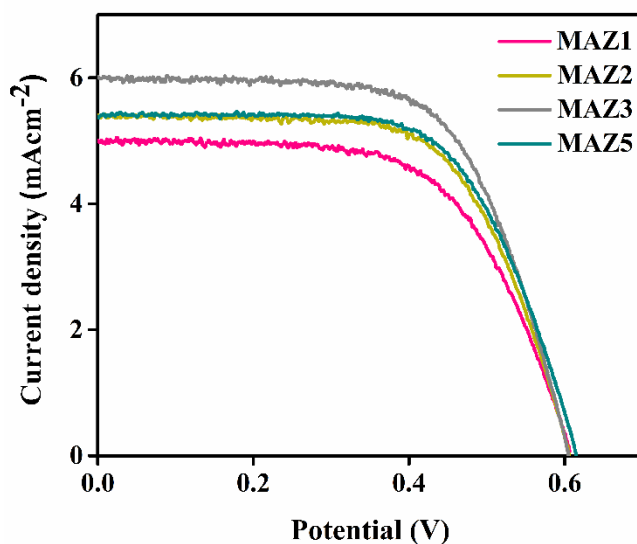


Figure 5.15: Current density-voltage plot of ZnO incorporated PMMA gel electrolyte

Table 5.8: Photovoltaic parameters obtained from current density-voltage plot of ZnO incorporated PMMA gel electrolytes

Electrolyte	$J_{sc} \text{ (mAcm}^{-2}\text{)}$	$V_{oc} \text{ (V)}$	FF (%)	Eff (%)
MAZ1	4.98	0.61	64	1.92
MAZ2	5.42	0.61	65	2.13
MAZ3	6.05	0.61	65	2.38
MAZ5	5.32	0.62	66	2.19

5.3.3 Comparison of the photovoltaic parameters of MA B and best performing filler incorporated gel electrolyte (MAT2 and MAZ3):

From the J-V plots of MAT and MAZ, the best performance was shown by MAT2 and MAZ3 and was shown in figure 5.16 (a). Their performance was compared with MA B. For both systems, enhancement in cell performance was observed with hike in current density value and this was well discussed in section 5.3.1 of this chapter. The data was listed in table 5.9.

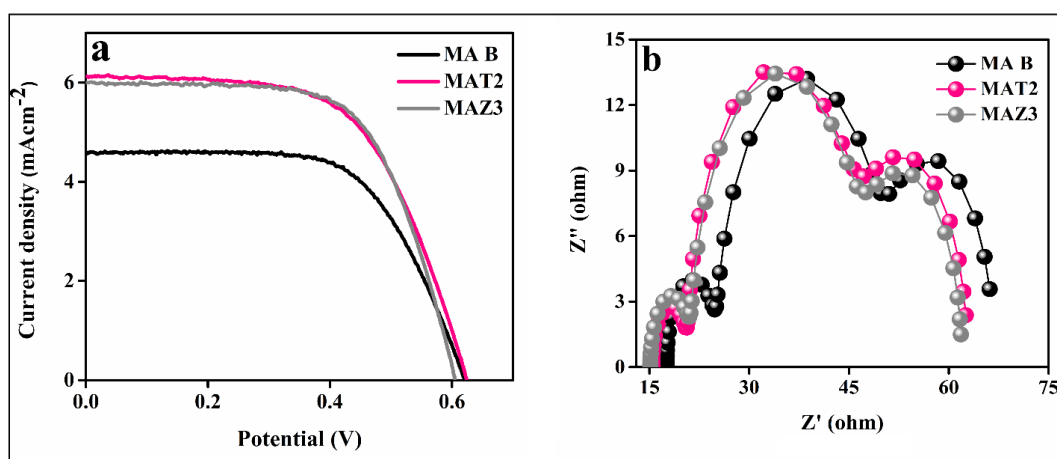


Figure 5.16: Current density-voltage plot (a) and the Nyquist plot (b) of MA B, MAT2 and MAZ3

Table 5.9: Photovoltaic parameters obtained from current density-voltage plot of MA B, MAT2 and MAZ3

Electrolyte	J_{sc} (mAcm^{-2})	V_{oc} (V)	FF (%)	Eff (%)
MA B	4.58	0.62	64	1.84
MAT2	6.08	0.62	63	2.34
MAZ3	6.05	0.61	65	2.38

Table 5.10: EIS data of MA B, MAT2 and MAZ3 from Nyquist plot

Electrolyte	R_s (ohm)	R_1 (ohm)	R_2 (ohm)	R_3 (ohm)
MA B	17.48	7.94	25.15	16.57
MAT2	15.50	5.14	26.48	15.41
MAZ3	15.31	5.84	26.12	14.88

To study about the resistance stemming out at each interface of the cell, EIS was recorded and is represented by Nyquist plot as shown in figure 5.16 (b) and the fitted data is listed in table 5.10. Nyquist plot of MAT2 and MAZ3 was recorded and was compared with that of MA B. The addition of filler does not significantly affect the R_2 value of the QSDSSC's. However the situation is different for the charge transfer resistance at the Pt counter/electrolyte interface R_1 and the Warburg impedance of the electrolyte R_3 . The R_1 value, which represents the electron transfer resistance at the counter – electrolyte interface, greatly decreases with the incorporation of fillers. This decrease in R_1 value increases the rate of reduction of the I_3^- ion and creation of I^- ions in the electrolyte. The fillers added in the electrolyte align to give an effective pathway for the easy transport of I^- and I_3^- between the electrodes. The lower R_1 value also suggests an effective collection of the photo-injected electron at the transparent back contact. i.e., most of the electrolyte injected into the TiO_2 conduction band is transported to the external circuit without any loss.

The resistance at the photoanode-electrolyte interface is given by the R_2 value. The R_2 value has no great influence on adding fillers. i.e., for both filler free and filler incorporated system, the recombination taking place at the phototanode-electrolyte

interface remains almost same. R_3 reflects the warburg impedance of the electrolyte and was found to decrease for filler incorporated system. This shows an easy transport of the ionic species within the electrolyte between the electrodes. The low viscous nature of the gel electrolyte formed by PMMA and the fast transport of the I^- and I_3^- ion from the vicinity of the counter electrode and the photoanode surface is responsible for this comparatively lower value of R_3 . As a result of the fast transport of these ionic species the R_3 value decreases. The lower R_1 and R_3 values accounts for the better performance of the filler incorporated system than the filler free electrolytes based QSDSSC's.

The photovoltaic performance of filler incorporated electrolyte in QSDSSC has got the power conversion efficiency resembles those of DSSC with corresponding liquid electrolyte. Specifically, the photovoltaic performance of MAT2 and MAZ3 based electrolytes gave better performance efficiency. The J_{sc} - V_{oc} curve of QSDSSC with MA B shows J_{sc} of 4.58 mAcm^{-2} , V_{oc} of 0.62 V, FF of 63.7% and Eff of 1.84. DSSC with corresponding liquid electrolyte (LE) has shown a J_{sc} of 5.47 mAcm^{-2} , V_{oc} of 0.61 V, with FF 61.2% and an efficiency of 1.92 % at 1sun intensity. Thus the problems confronted by using liquid electrolyte can be solved in all respect by modifying the polymer gel electrolyte by adding suitable fillers.

5.4 Conclusion

Filler incorporated PMMA based gel electrolytes were synthesized with different weight percentage of TiO_2 and ZnO . Electrolyte characterization results shows the influence of inorganic fillers in enhancing the properties of PMMA based polymer gel electrolyte. FT-IR studies performed on the gel electrolyte shows a slight dip in the range 400 to 1000 cm^{-1} range which shows the presence of semiconductor oxide fillers in the polymer gel electrolyte. TGA studies performed on the gel electrolyte shows an increase in thermal stability for filler incorporated gel electrolyte. Conductivity measurement studies like EIS and LSV shows an increase in conductivity and apparent diffusion coefficient of the electrolyte initially and shows a decline at higher filler concentration.

MAT2 and MAZ3 are the optimum concentrations that provide the most effective pathway for the redox species to move in the electrolyte thus exhibiting an ionic conductivity of $17.60 \times 10^{-4}\text{ mho cm}^{-1}$ and $18.41 \times 10^{-4}\text{ mho cm}^{-1}$ respectively. Further increase in filler content decreases the electrolyte performance. The problem of syneresis shown by the gel electrolyte was studied by performing a stability study for a period of one month. A time dependent EIS study of the best performing compositions - MAT2 and MAZ3 were performed by measuring the total conductivity of the system and was compared with the results obtained for MA B. The comparison shows an increase in rate of decay of the electrolyte performance with time for filler incorporated systems. But throughout the period under observation a highly stable performance was exhibited by the filler free MA B without much compromise in its

conductivity. Even after one month 84.19% efficiency in performance was maintained by the filler free MA B. So PMMA was proven to be a promising matrix to immobilize the liquid electrolyte for electrochromic devices.

QSDSSC's were fabricated with all the four weight percentage of MAT and MAZ and their photovoltaic characteristics were measured. With increase in filler content the photovoltaic performance of the cell also increases. A better performance and highest efficiency was shown by filler incorporated PMMA gel electrolyte with 2wt% of TiO_2 and 3wt% of ZnO . The results obtained is consistent with the EIS and LSV results. The parameter J_{sc} is greatly influenced by the ionic conductivity of the polymer gel electrolyte. An enhancement in cell performance with the filler content was solely due to a hike in their J_{sc} value. V_{oc} and FF of the device was not much affected by the incorporation of these fillers. EIS data obtained for the cell well support the result obtained. Also the photovoltaic performance of MAT2 and MAZ3 has got J_{sc} value and efficiency that is higher than the value obtained for corresponding DSSC.

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6

CONCLUSION AND FUTURE OUTLOOK

6. CONCLUSION AND FUTURE OUTLOOK

The problem of electrolyte leakage and volatilization observed in conventional electrochromic devices can be solved to a great extent by replacing the liquid electrolyte by quasi solid state electrolyte or gel electrolyte. Polyvinyl alcohol and polymethyl methacrylate are the two polymer matrix chosen for the synthesis of quasi solid state electrolyte. Polyvinyl alcohol is the least explored matrix and polymethyl methacrylate is the highly explored polymer in preparing the gel electrolyte for electrochromic applications. An attempt was made to study and compare the properties of PVA and PMMA based gel electrolyte and its performance in a solar cell assembly. Amount of the polymer in the proposed gel electrolyte was optimized to immobilize the liquid electrolyte to obtain a stable gel electrolyte. PVA gave a pudding thick and PMMA resulted in a honey thick gel electrolyte. The functional group present and the bulkiness of the group in the polymer chain plays an important role in deciding the nature of the electrolyte consistency.

Characterization of the gel electrolytes were carried out using tools like FT-IR, TGA, LSV and EIS to get information on the thermal and conducting properties. Further, property improvement was incorporated by adding different weight percentage of semiconducting oxide fillers, such as TiO_2 and ZnO , in to the gel composition. The filler incorporated gel electrolyte shows better thermal stability and conductivity. An optimum concentration of the filler was fixed by trial and error analysis. A time dependent stability study of the electrolyte with and without filler was

done for a period of 30 days. Finally the application study was done by fabricating QSDSSC utilizing these electrolytes and their performance was compared with the corresponding liquid electrolytes.

The storage of the polymer gel electrolyte and all the studies were performed under ambient conditions. Structural identification of the formed gel electrolyte was studied by taking the FT-IR of the samples. The ion transport behavior in the polymer gel electrolyte was studied by measuring the total ionic conductivity and the diffusion coefficient from EIS and LSV measurements. The thermal stability of the electrolytes can be understood from TGA analysis. The results shows that all polymer host loss mechanical strength on plasticizing. The dispersion and interaction of the filler with the polymer matrix was obtained from FTIR and TGA results.

Among the two polymers used, a better performance was given by PMMA based polymer gel electrolyte. The ionic conductivities of the PVA and PMMA based polymer gel electrolyte were $14.99 \times 10^{-4} \text{ mho cm}^{-1}$ and $8.45 \times 10^{-4} \text{ mho cm}^{-1}$ respectively. Time dependent stability study shows that PVA polymer gel electrolyte was more prone to syneresis effect. PMMA polymer gel electrolyte shows least syneresis and a better stability in ambient temperature. So gel electrolyte formed by PMMA matrix can be considered as gel with stable framework and that formed by PVA matrix can be considered as gel with metastable framework. Application study also replicates the same trend in performance.

DSSC and QSDSSC were fabricated utilizing these electrolytes for their photovoltaic studies under at 1Sun illumination and compared their performances. The

results show that the parameters V_{oc} and FF were not affected by the electrolyte gelation process. Only the J_{sc} is affected by the introduction of polymer into the liquid electrolyte. The current voltage parameters obtained for QSDSSC with VA B are comparable with DSSC with corresponding liquid electrolyte. The current voltage parameters obtained for QSDSSC includes a J_{sc} of 2.54 mAcm^{-2} , V_{oc} of 0.64 V, FF of 73 %, Eff of 1.19 %, while for DSSC with corresponding LE has got a J_{sc} value of 3.05 mAcm^{-2} , V_{oc} of 0.65 V, FF of 73 %, Eff of 1.44 %. With PMMA based gel electrolyte (MA B) QSDSSC shows a J_{sc} of 4.58 mAcm^{-2} , V_{oc} of 0.62 V, FF of 63.7 %, Eff of 1.84 %, while the corresponding LE has got J_{sc} of 5.47 mAcm^{-2} , V_{oc} of 0.61 V, FF of 61.2 %, Eff. of 1.92 % at 1sun intensity.

The lower performance of QSDSSC can be greatly connected with the decrease in J_{sc} of the device. The decrease in J_{sc} can be explained on the basis of decrease in diffusion coefficient and decrease in total ionic conductivity of the gel electrolyte. On gelation a three dimensional network is built in the electrolyte which offers a resistance to the easy diffusion of the ionic species. Also the high viscous nature of the polymer gel electrolyte results in poor wetting of the electrolyte on to the photo-anode and counter surface. As a result, fast regeneration of the dye ground state and the reduction of the triiodide ion at the counter electrode by collecting the electrons from the external circuit get delayed.

To enhance the physical and chemical properties of the polymer gel electrolyte, commercial TiO_2 and ZnO was incorporated as fillers. ZnO synthesized via a simple co-precipitation method was characterized using XRD, SEM, EDAX etc. Optical

properties were studied from absorption spectrum of the sample and the bandgap is elucidated from the Tauc plot as 3.16 eV. Gel electrolytes with different weight percentage of the fillers were added to get the optimum performance in a solar cell structure.

The interaction of the fillers with polymer backbone was understood from the corresponding IR spectra and the ionic conductivity of the filler incorporated gel electrolyte was obtained from the EIS measurement. The performance of filler incorporated gel electrolyte is compared with that of filler free system. Filler modified gel electrolyte shows performance enhancement in the device. Here, the added fillers align themselves in such a way to build a channel within the polymer matrix for the transport of ionic species between the electrodes. The results show that an optimum concentration of 2wt% TiO_2 and 3wt% ZnO (for PVA and PMMA) provided the most effective pathway for the redox species to move within the electrolyte to exhibit a comparatively higher ionic conductivity. The triiodide limiting current density of the best performing composition was carried out by running the linear sweep voltammetry from which the diffusion coefficient of the triiodide ion was studied. The improvement in thermal stability of the polymer matrix on adding the fillers was studied by performing the thermogravimetric analysis. The enhancement was mainly due to the proper dispersion and the interaction of the filler with the polymer matrix. A time dependent stability study of the best performing electrolyte combinations were done for a period of one month and was compared with the corresponding filler free system. In all the cases, the best performance was shown by the filler incorporated system only.

For PVA and PMMA based polymer gel electrolytes, with time a degradation in performance was observed for both filler incorporated and filler free systems. 55.50 % loss in performance was observed for VA B (filler free). The degradation was found high in VAT2 and VAZ3 and the loss is found to be 72.75% and 65.50% respectively. But, PMMA based MA B (without filler) shows only 15.81% degradation for the said period. Filler incorporated PMMA shows 70.28% and 69.47% loss for MAT2 and MAZ3 respectively. Throughout the period of study a highly stable performance was exhibited by MA B, hence PMMA can be considered as a promising polymer matrix to detain liquid electrolyte for all electrochromic applications.

The photovoltaic measurements of the filler incorporated polymer gel electrolyte was done. With the addition of fillers an enhancement in cell performance was observed. On increasing the filler content, the efficiency of the QSDSSC also increases. The best cell performance was shown by 2wt% of TiO_2 and 3wt% of ZnO for both PVA and PMMA. This efficiency enhancement was mainly due to the hike in the J_{sc} value. The current density of VA B is 2.54 mAcm^{-2} . On incorporating TiO_2 and ZnO , the J_{sc} value got enhanced to 3.28 mAcm^{-2} and 3.09 mAcm^{-2} respectively. Similarly the current density of MA B is 4.58 mAcm^{-2} . On incorporating TiO_2 and ZnO , the J_{sc} value got enhanced to 6.08 mAcm^{-2} and 6.05 mAcm^{-2} respectively. The enhancement in performance of the device by introducing filler was mainly due to the enhancement in ionic conductivity and the data was highly in consistent with EIS results of the gel electrolytes.

The QSDSSC results are compared with the corresponding DSSC and their efficiency was comparatively higher. This suggests that, by immobilizing the liquid electrolyte by adding a polymer with a suitable filler of optimum concentration can solve the major problems confronted by using the liquid electrolyte. Thus these polymer gel electrolytes can be considered as a promising future generation electrolyte material for electrochromic devices.

Further enhancement in performance of the polymer gel electrolyte can be done by optimizing the size and morphology of the fillers. Attempting different types of fillers like other oxides, conducting polymers etc., can also influence the performance of the polymer gel electrolyte. Also solvents have a great influence on the formation of the polymer network structure, electrolyte viscosity and conductivity property. So by introducing different solvents the property of the polymer gel electrolyte can be enhanced.

PUBLICATIONS



Synthesis and electrochemical characterization of physically cross-linked gel electrolyte for QSDSSC application

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ABSTRACT

Use of liquid electrolyte in dye sensitized solar cells (DSSC) causes a serious challenge in terms of long-term stability. Quasi-solid-state electrolyte solves this problem to a great extent. In this work a physically cross-linked polyvinyl alcohol (PVA) based quasi-solid-state or gel electrolyte (GE), incorporated with KI/I₂ was synthesized using ethylene carbonate (EC) as plasticizer. Thermal analysis, linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) of gel electrolyte were done. Quasi-solid-state dye (N719) sensitized solar cell (QSDSSC) was fabricated with this gel electrolyte and the current-voltage characteristics and electrochemical impedance were tested under irradiance of AM 1.5 (100 mW cm⁻²). Cell performance was compared with liquid electrolyte based DSSC, where the liquid electrolyte contains KI/I₂ in DMSO/EC mixture without any fillers or additives. Efficiency values of 4.4% and 3.4% were obtained respectively for liquid electrolyte based DSSC and QSDSSC. The effect of plasticizer and the polymeric network gives a comparable performance of QSDSSC. A time-dependent stability of the gel in QSDSSC was studied and the performance was found to be better than that of liquid based DSSC.

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1. Introduction

Polymer gel electrolytes are quasi-solid in which liquid electrolyte is trapped within the entangled network of the polymer matrix [1–3]. Gel electrolytes are a very promising substitute for liquid electrolyte in dye sensitized solar cells (DSSC). Its superior properties like non-propensity to leakage, long term stability and its ability to switch between the quasi-solid and viscous state, inspired people around the world to do intense research and development in the field of quasi-solid-state DSSC (QSDSSC) [4,5]. It comprises of a polymer backbone, a plasticizer and a liquid electrolyte. The polymers provide mechanical strength to the electrolyte by increasing the viscosity, whereas, the plasticizers lower the brittleness of the polymer [6,7].

Electrolytes play a key role in converting solar energy into electricity in DSSC. The long-term stability of the device strongly depends on the electrolyte component. The electrolyte usually employed in DSSC contains iodine and its salt that institute a redox shuttle to revive the dye ground state and a suitable solvent which act as the medium for charge transportation between the counter electrode and photoanode [7,8]. The highest efficiency reported so far in DSSC with liquid electrolyte is 13% [5]. Liquid electrolytes are widely used for DSSC fabrication because of its ease of preparation, high conductivity, low viscosity, good interfacial wetting between the electrode-electrolyte and resultant high conversion efficiency [7–9]. The practical impediments

like, leakage and volatilization of the solvent, corrosion of Pt counter electrode, desorption of attached dye etc. prevent the long term stability of the cell while using liquid electrolyte [2,3,10,11]. To solve this problem, solid-state electrolytes are introduced. The poor mobility of the charge carriers and less interfacial contact between the electrode-electrolyte in solid-state electrolyte due to the lack of solvent deteriorate its application in DSSC [2,7]. Search for a better substitute led to the development and progress of quasi-solid-state electrolyte or gel electrolyte. The first attempt to use gel electrolyte in QSDSSC was done by Cao et al. using a mixture of poly(acrylonitrile), ethylene carbonate, propylene carbonate, acetonitrile and NaI [8]. The performance was poor because of its lower ionic conductivity than that of liquid electrolyte [9]. Many of the problems faced while using liquid electrolyte can be overcome to a great extent by the introduction of gel electrolyte. These gel electrolytes exist in quasi-solid-state at room temperature and as viscous liquid at higher temperature. It has got both the properties of solid and liquid electrolytes like stability, good adhesion and high ionic conductivity [10,12]. This makes the gel electrolyte unique and a better alternative to liquid electrolyte. A recent study by Ramesh et al. reports the use of ionic liquid incorporated rice starch based gel electrolyte in DSSC for a conversion efficiency of 2% [13]. Reports also show the application of gel electrolyte in electrical double layer capacitor [14].

In the current study, polyvinyl alcohol was taken as the gelator for liquid electrolyte. A mixture of solvents like dimethyl sulfoxide (DMSO) and ethylene carbonate (EC) were chosen as the medium for ionic transport which meets almost 80% requirement for a suitable solvent to be used in DSSC [7]. In polymer gel electrolyte, EC has got the

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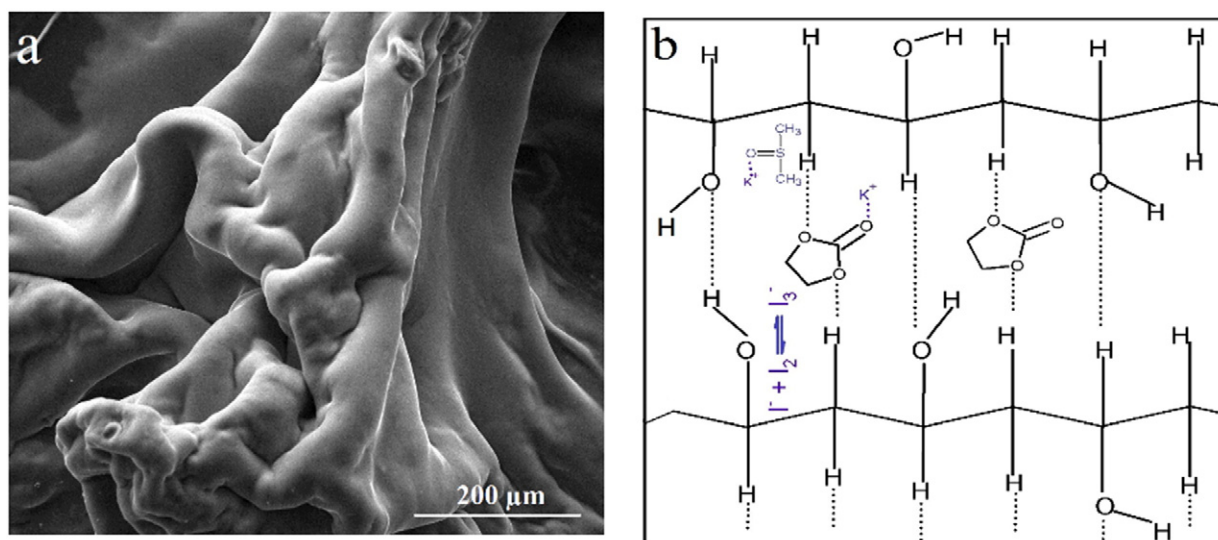


Fig. 1. SEM image (a) and 3-D network structure of polymer gel electrolyte (b).

role of solvent and plasticizer which holds the polymer chain segments together resulting in the formation of a network structure [4,7,10]. The gelation process prevents leakage and volatilization of liquid electrolyte and extends its stability and durability. In this part of study, synthesis and characterization of gel electrolyte is done. The impact of three dimensional network structure and effect of plasticizer on the kinetics of electron transfer at TiO_2 -electrolyte interface and Pt-electrolyte interface is also studied. The gel stability study and stability of QSDSSC are also done.

2. Experimental

2.1. Materials

Fluorine doped tin oxide (FTO-7 Ω/cm^2), N719 ($\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$) – 95%, ethylene carbonate (EC-98%), hexachloroplatinic acid (H_2PtCl_6), potassium iodide (KI) (bio ultra, 99.5%), polyvinyl alcohol (PVA, 99% hydrolyzed) were from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) and iodine (I_2) were from MERCK.

2.2. Gel electrolyte synthesis

Liquid electrolyte was prepared by dissolving 0.5 M KI and 0.03 M I_2 in 13 mL of DMSO/EC mixture and stirred until the salt was completely

dissolved to obtain a homogenous solution. To this electrolyte 1.25 g of PVA was added and heated at 100 °C and stirred till the polymer was completely dissolved in the organic solvent. This resulted in the formation of a highly viscous solution. The temperature was lowered and stirring continued till the system cooled down to ambient condition. The solution was then kept overnight for complete polymerization to obtain PVA based gel electrolyte.

2.3. DSSC assembly

Transparent conducting oxides are usually taken as substrate material for photoanode and platinum coated FTO as counter electrode in DSSC. TiO_2 paste was made in ethanol with Triton X-100 as a binder material. This TiO_2 paste was spread on the FTO substrate by using a glass rod. The film was then air dried and sintered at 450 °C for 30 min to remove the organic contents present and to get a continuous network of TiO_2 particles. The FTO/ TiO_2 electrode was then loaded with the photosensitizer by dipping in a solution of N719 dye overnight. The photoanode was then rinsed with ethanol and dried. Pt deposited FTO was used as the counter electrode [8,15]. Cell assembly was completed

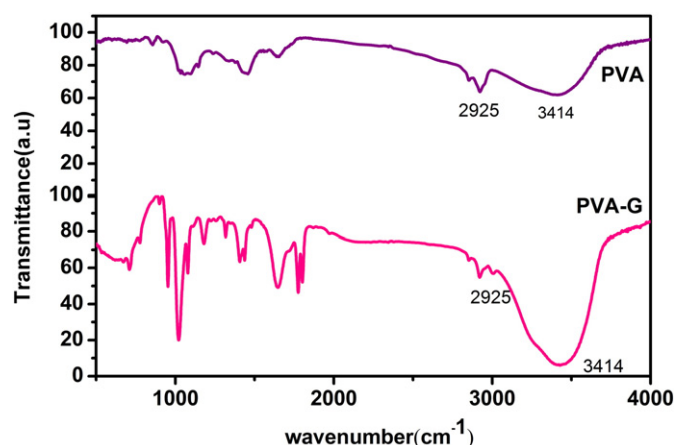


Fig. 2. FT-IR spectra of pure PVA and PVA gel (PVA-G).

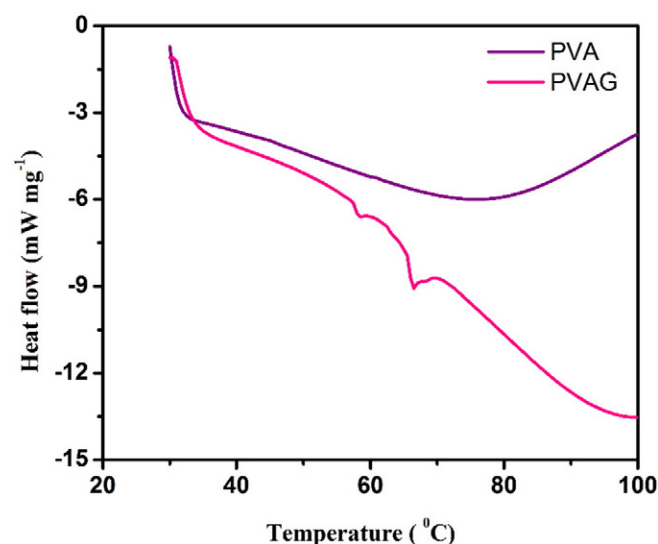


Fig. 3. DSC curves of pure PVA and PVA gel electrolyte.

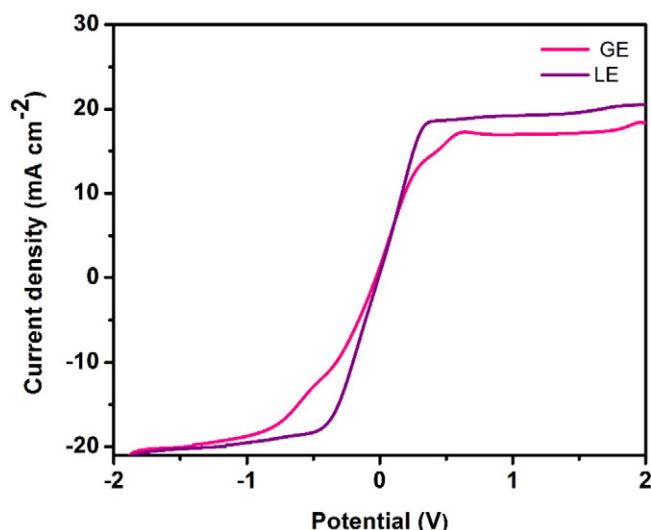


Fig. 4. Linear sweep voltammograms of symmetrical cells with liquid (LE) and gel electrolyte (GE) with an active surface area of 0.25 cm^2 . Scan rate: 100 mV s^{-1} .

by sandwiching the polymer gel electrolyte in between the two electrodes. The active area of the cell was fixed as 0.25 cm^2 .

2.4. Measurements

The morphology and chemical structure of the gel were examined with field emission scanning electron microscope (FEI-QUANTA-FEG 250), operating at 30 kV and FT-IR (Spectrum Two PerkinElmer). Electrochemical impedance spectroscopy and cyclic voltammetry measurements were carried out on Bio-Logic SAS SP-150 potentiostat at room temperature by sandwiching the electrolyte between two symmetrical Pt coated FTO substrates with an electrode area of 0.25 cm^2 . Glass transition temperature of the gel was obtained from differential scanning calorimetry using Mettler Toledo DSC 822e. The current-voltage measurements for the cells were done with Bio-Logic SAS SP-150 using Sciencetech SF 150B solar simulator as the light source with 100 mW cm^{-2} light output, AM 1.5 illumination.

Table 1

Parameters obtained by fitting the EI spectra for liquid and gel electrolyte.

Sample	$R_1 (\Omega)$	$R_2 (\Omega)$	$R_3 (\Omega)$	$\sigma (\text{ohm cm}^{-1})$
Liquid electrolyte	21.36	13.53	7.72	20.73
Gel electrolyte	23.18	35.04	24.82	6.45

3. Results and discussion

3.1. Structure and morphology of gel electrolyte

Polymer gel electrolyte has got a 3-dimensional network structure with liquid electrolyte trapped within. During gel formation a weak intermolecular force of attractions established between polymer-polymer and polymer-plasticizer-polymer gives rise to the formation of a thermoplastic polymer gel electrolyte [7,10]. The space created in between the network structure holds the liquid electrolyte. The plasticizer used improves the flexibility and the segmental mobility of the polymer which adds to the conductivity of the electrolyte [6,7]. In QSDSSC, at the photoanode-electrolyte interface, a weak physical interaction is established between the negatively charged TiO_2 film and the polymeric chain. Thus a hindrance is ingrained at the photoanode-electrolyte interface. This reduces the back recombination occurring at the $\text{TiO}_2/\text{electrolyte}$ interface. The SEM image of the polymer gel electrolyte and its expected network structure is given in Fig. 1(a) and (b). The network structure formed during gelation is confirmed from the FT-IR analysis of pure PVA and PVA gel electrolyte. Fig. 2 shows the FT-IR spectra of pure PVA and PVA gel (PVA-G). The peak centered at 3414 cm^{-1} in PVA corresponds to intermolecular hydrogen bonding due to polymer association. This peak is found intense in PVA-G due to the extensive physical cross-linking formed during gelation. The peak at 2924 cm^{-1} is assigned to the C—H stretching vibration mode of PVA. But its intensity gets lowered in PVA-G. This is due to the non-availability of free C—H group in the gel due to its participation in forming network structure. Peaks at 1649 cm^{-1} corresponds to C=C stretching of vinyl group and 1096 cm^{-1} corresponds to C—O stretching of alcohol for pure PVA. Towards lower wavenumber in PVA-G, few more peaks are observed which correspond to other electrolyte components present in the gel. The peak at 1780 cm^{-1} is assigned to C=O stretching and 1077, 1180 and 1319 cm^{-1} peaks correspond to the C—O stretching of ethylene carbonate.

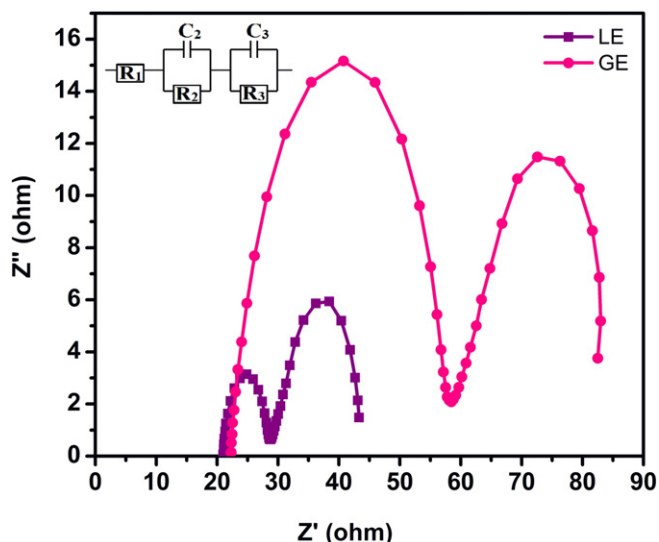


Fig. 5. Nyquist plots of the symmetrical cell with liquid (LE) and gel (GE) electrolyte.

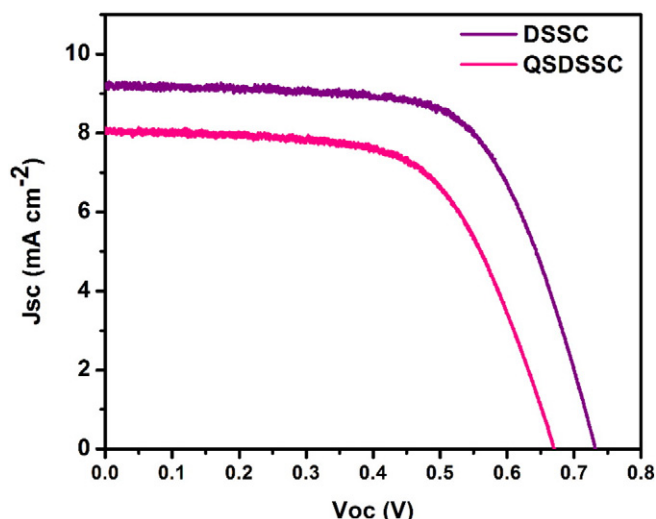


Fig. 6. Photocurrent density–voltage curves of the DSSC and QSDSSC.

Table 2
Photovoltaic parameters of DSSC and QSDSSC.

Sample	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	η (%)
DSSC	9.20	0.73	65.9	4.4
QSDSSC	7.98	0.68	62.2	3.4

3.2. Differential scanning calorimetry (DSC)

Thermal transition of the polymer gel electrolyte has been studied using differential scanning calorimetry. Fig. 3 shows the DSC curves of pure PVA and PVA gel electrolyte. The glass transition temperature (T_g) of pure PVA is 70.03 °C and PVA gel is 64.9 °C. This decrease in T_g value for gel electrolyte is imputed to the plasticizer present in it [6,7]. These plasticizers reduce the cohesive force of attraction between the polymeric backbones by establishing a poor attractive force between the chain segments. This helps in improving the segmental mobility of the polymeric chain [6,7]. The chain motion or rearrangement of the polymer matrix virtually contributes to the ion transport in polymer gel electrolyte [16,17]. A reduction in the crystalline content and increase in the segmental mobility results in an increased ion dissociation, which allows greater number of charge carriers for ionic transport enhancing the overall conductivity [7,16].

3.3. Electrochemical measurement

The charge transport behavior in the electrolyte has been measured by scanning the diffusion limiting current density using linear sweep voltammetry with a scan rate of 100 mV s⁻¹. Studies have been carried out by fabricating symmetrical cells, in which the electrolyte is injected/sandwiched between two Pt electrodes with a fixed area (0.25 cm²). The cell structure is FTO/Pt/electrolyte/Pt/FTO [18]. Fig. 4 shows the linear sweep voltammogram of liquid and polymer gel electrolyte (LE and GE). The sigmoid representation indicates the redox reaction occurring at the Pt surface, i.e. $3I^- \leftrightarrow I_3^- + 2e^-$. The diffusion limiting current is measured using Eq. (1) [18,19].

$$I_{\text{limiting}} = \frac{2nFD_{\text{app}}C}{d} \quad (1)$$

Where n is the number of electrons required for the reduction reaction, F is the Faraday's constant, C is the concentration of triiodide ions, D_{app} is the apparent diffusion coefficient and d is the electrolyte

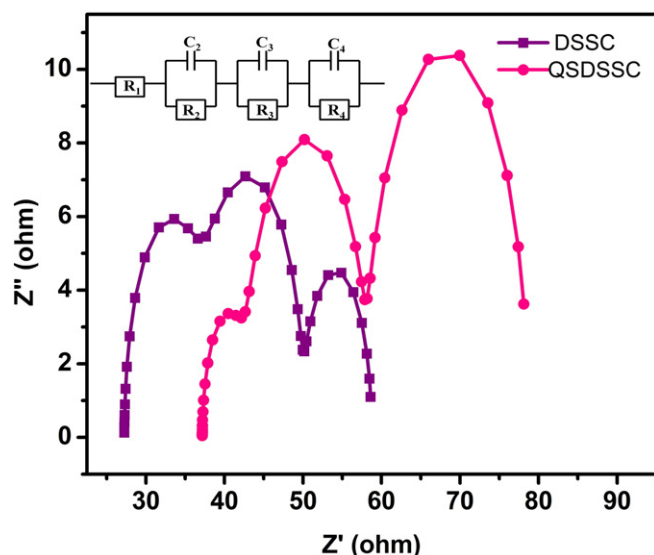


Fig. 7. Nyquist plot for DSSC and QSDSSC.

Table 3
Fitted impedance parameters for DSSC and QSDSSC.

Sample	R_1 (Ω)	R_2 (Ω)	R_3 (Ω)	R_4 (Ω)	τ_e (ms)
Liquid electrolyte	27.26	8.73	12.67	10.1	1.13
Gel electrolyte	37.23	5.52	15.34	20.7	2.55

thickness. The limiting current density values of 18.35 mA cm⁻² and 20.54 mA cm⁻² are obtained for gel and liquid electrolyte respectively. The apparent diffusion coefficients thus calculated for the liquid and gel electrolytes are 0.71×10^{-8} S⁻¹ cm² and 0.63×10^{-8} S⁻¹ cm². The restriction inflicted by the polymeric network structure to the motion of the triiodide ions corresponds to the lower diffusion coefficient value for the gel electrolyte. The result accounts well with the lower short-circuit current density (J_{sc}) of the DSSC with the polymer gel electrolyte.

3.4. EIS measurement

Electrochemical impedance measurement of the symmetrical cell has been done with Bio-Logic SP-150. The Nyquist plot gives the resistance offered by each interface to the electron transfer and is given in Fig. 5. The equivalent circuit for fitting the curve of the impedance spectra is shown in the inset of Fig. 5. Both the cells with liquid and gel electrolytes have well defined semi-circles starting from the high frequency region. The sheet resistance is represented as R_1 which arises due to the TCO contact resistance and electron transfer at TCO-TiO₂ interface. R_2 is the charge transfer resistance at the Pt-electrolyte interface and R_3 is the impedance due to Warburg diffusion. The data obtained by fitting the curve is given in Table 1. Both R_2 and R_3 values of the gel electrolyte are higher than that of liquid electrolyte. This is due to the restricted diffusion of triiodide ions towards the counter surface. The sluggish electron transfer at the Pt-electrolyte interface corresponds to the poor catalytic activity of the counter for the redox reaction [$I_3^- \leftrightarrow I^-$] taking place at its surface [20,21]. The conductivity (σ) of the gel electrolyte is calculated using Eq. (2) [11,22].

$$\sigma = \frac{L}{R_b A} \quad (2)$$

Where L is the thickness of the film, R_b is the bulk resistance/Warburg diffusion resistance of the electrolyte and A is the area of the sample (0.25 cm²). The conductivity of liquid electrolyte is found to be three times higher than the polymer gel electrolyte. But this difference does

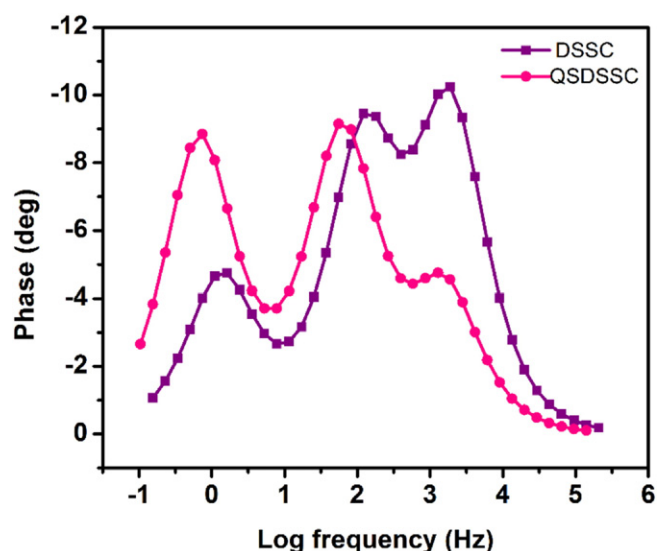


Fig. 8. Bode plot of DSSC and QSDSSC.

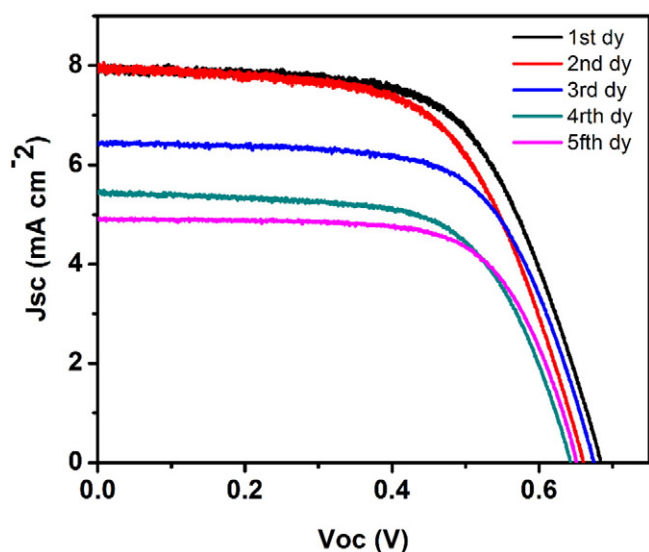


Fig. 9. Gel stability study: I-V curves of QSDSSC recorded at regular intervals.

not give any exciting result when coming to cell performance which once again reinforces the limitation of liquid electrolyte for its application in DSSC and hence the necessity of gel electrolyte.

3.5. Photovoltaic measurements of the cell

The photovoltaic performance of the cell has been done under 1 Sun illumination (100 mW cm^{-2}). Fig. 6 shows the I-V curve of cells with both liquid and gel electrolytes. The cell parameters obtained are given in Table 2. The DSSC and QSDSSC exhibit an overall power conversion efficiency of 4.4 and 3.4% respectively. The lower cell parameter values for QSDSSC is due to the restriction offered by the polymeric network to the transfer and transport reactions within the electrolyte and also the poor wetting of the photoanode in comparison to DSSC. This disturbs the overall kinetics of the cell reactions. High efficiency can be achieved through fast electron transport and slow back recombination. However, the comparable performance of QSDSSC can be attributed to the presence of plasticizer and the cage like 3-D structure of polymer matrix in the gel electrolyte. The result is further supported by the electrochemical impedance study.

Electrochemical impedance measurement of the cell has been done at open circuit condition to understand the changes occurring during electron transfer and transport at the interface when the electrolyte changed from liquid to gel. Nyquist plot has three semi-circles corresponding to the resistance generated at each interface of the cell and is given in Fig. 7 with the corresponding equivalent circuit in the inset. The data obtained by fitting the curve is given in Table 3. The high frequency response corresponds to the resistance at Pt-electrolyte interface (R_2), the middle frequency response corresponds to the resistance at the TiO_2 -dye-electrolyte interface (R_3), the low frequency response corresponds to the impedance arising from the diffusion of I_3^- (R_4) [19,22–24] and R_1 gives the sheet resistance. The low charge transfer resistance at the Pt-electrolyte interface (R_2) of QSDSSC can be attributed

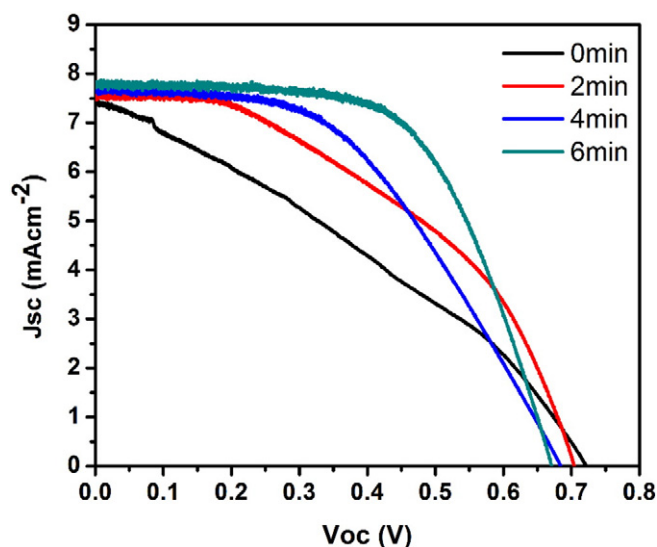


Fig. 10. I-V curves of QSDSSC on prolonged exposure to light and showing the effect of temperature on its performance.

to the increased contact time of the electrolyte on the electrode surface compared to that in the case of DSSC with liquid electrolyte. In the latter case there is increased probability for liquid electrolyte loss due to leakage and evaporation, factors which will be minimized in the QSDSSC with gel electrolyte. High impedance in the R_3 region of QSDSSC shows a restriction to the electron flow at the photoanode-electrolyte interface caused by the hindrance developed due to the interaction of TiO_2 and the polymer matrix. The back recombination is thus minimized. All the photo-generated electrons can be injected to the external circuit and is made available at the Pt counter. The R_4 value of QSDSSC manifest the restricted I^-/I_3^- flux in the electrolyte and this is due to the complex network structure of the matrix. However the positive recombination resistance (R_3) equilibrates the negative ion diffusion (R_4) within the electrolyte, which helps QSDSSC to perform equally well.

The electron life time is obtained from bode plot (Fig. 8) by the equation $\tau_e = 1/2\pi f_{\text{max}}$, where, f_{max} is the maximum frequency of the central arc [19,22,25,26] and is given in Table 3. The life time of electron in the case of QSDSSC is higher than liquid based DSSC. The higher electron life time suggests reduced electron back recombination due to the presence of polymeric network structure that hinders the direct contact between the photoanode material and the ionic species in the electrolyte [23].

3.6. Stability study

Gel stability and cell stability studies have been done at regular intervals. For carrying out gel stability study, fresh anode and counters were prepared each day and the gel electrolyte being sandwiched was the one synthesized on the first day. I-V measurements are done and the results are shown in the Fig. 9. The best performance is on the first day and gradually all the parameters are seen decreasing. This may be due to the solvent transudation upon storage in open condition which negatively affects the performance of the cell. The photovoltaic parameters are given in Table 4. Usually, performance of QSDSSC improves upon prolonged exposure to light. Fig. 10 shows the I-V curves of a single QSDSSC recorded at intervals on prolonged exposure to light. The first few curves are found malformed and later on attain their characteristic shape. On continuous illumination the temperature of the polymer system increases adding more kinetic energy to the individual molecules. At the initial state the segmental motion or the internal Brownian movement gets activated and at higher temperature the molecular motion or external Brownian motion comes into play. When both the movements are activated, the individual polymer chain starts moving i.e. at this stage the polymer gel gets converted to a highly viscous liquid

Table 4
Gel stability study of QSDSSC recorded at regular intervals.

Days	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	η (%)
Day 1	7.98	0.68	62.2	3.4
Day 2	7.73	0.676	61.9	3.23
Day 3	6.44	0.67	65.5	2.84
Day 4	5.42	0.64	64.9	2.27
Day 5	4.91	0.65	68.4	2.18

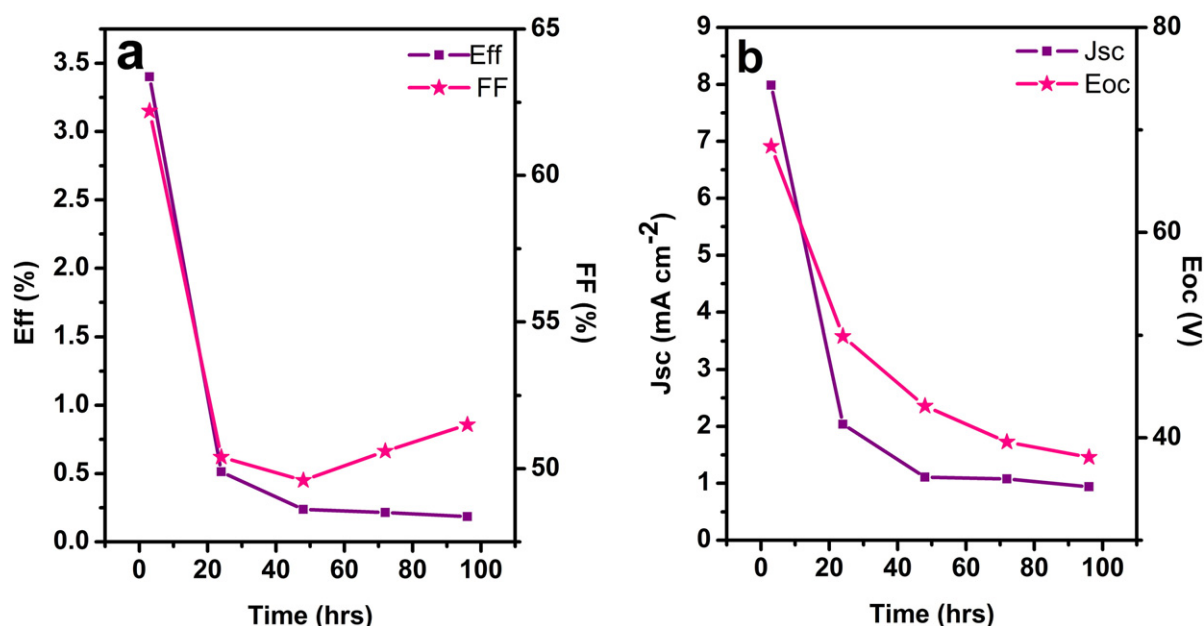


Fig. 11. Cell parameters (a) efficiency and fill factor (b) short-circuit current density and open-circuit potential recorded at regular intervals for a single cell.

[10]. Gel electrolyte alone has the characteristic of transforming from quasi-solid to viscous state on continuous exposure to light. This aids in the more effective wetting of the photoanode surface and performs like a conventional DSSC. Here, the thermal instability of the gel electrolyte helps for its sustainable performance and the transition of gel polymer electrolyte from the rubbery form to visco-fluid state is evident from the I-V curve.

Cell stability study has been done by taking the I-V measurements on a single cell at regular intervals without replacing the anode, counter and electrolyte. After 24 h of first measurement all the parameters declined steeply. This is because the cell stability study is done on a non-sealed cell. Hence, a conclusion on cell stability is difficult with current result. Here, the fast decay in cell parameters can be attributed to the corrosion of the Pt counter, degradation of the photoanode, exudation of solvent etc. Since the problem of leakage and volatilization exist this sort of study is not possible for liquid electrolyte based DSSC without sealing. Fig. 11 shows the plot of cell parameters of efficiency, fill factor, short-circuit current density and open circuit potential as a function of time.

4. Conclusion

Electrolytes play a vital role in enhancing the efficiency of DSSC. In this part of work, QSDSSC is fabricated by a simple method using PVA based gel electrolyte and the cell performance is studied. The results have been compared with conventional liquid electrolyte based DSSC. Conventional DSSC has an overall efficiency of 4.4% while QSDSSC has 3.4%. The dual nature of ethylene carbonate, both as solvent and plasticizer, and the polymeric network structure of gel electrolyte improve the recombination resistance at the TiO_2 -electrolyte interface. The negative effect of network structure on ionic diffusion can be equilibrated by the improvement in recombination resistance and thereby add to the fine performance of QSDSSC. The studies and results have scope for improving the long term stability of gel electrolyte for DSSC application and promise gel electrolyte as a better alternative to the liquid electrolyte.

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Application of gel electrolyte in dye sensitized solar cells

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The volatility of liquid electrolytes has been a major problem for their application in dye-sensitized solar cells (DSSC). In this study, liquid electrolyte was replaced by polymer based gel electrolyte. Polyvinyl alcohol is chosen as the polymeric matrix to gelate the liquid electrolyte with iodide-triiodide redox couple and suitable organic solvent. The amorphous nature and the physical cross linking formed between polymer-polymer and polymer-solvent is analyzed from XRD and FT-IR. Cell was fabricated and characterization was done. I-V and EIS measurements of the cell was taken. Easy fabrication and its advantages over liquid electrolyte makes gel electrolyte a promising alternative for liquid electrolyte.

Keywords: dye sensitized solar cells, quasi solid state dye sensitized solar cells, gel electrolyte.

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1. Introduction

DSSC have received great attention owing to their low production costs and high efficiencies [1,2]. The certified record efficiency of DSSC is 12–13 %. A DSSC consists of a photo anode, a semiconductor film coated on a transparent conducting oxide layer, which is dye sensitized, a counter electrode, usually FTO coated with a catalytic material and electrolyte which includes a redox couple usually I^-/I_3^- system and a suitable solvent. In DSSC, the electrolyte is the medium for charge transportation between the two electrodes and acts as a source for dye regeneration [3]. The long term stability of the device strongly depends on the electrolyte component [4]. The highest efficiency reported in DSSC was by employing liquid electrolyte. But there are some practical impediments when using this liquid electrolyte like leakage while sealing and volatilization of the solvent, desorption and photo-degradation of the attached dye, corrosion of the counter electrode etc., which prevent DSSC's from further application and commercialization [4,5]. So, as an alternative to liquid electrolyte, solid state electrolytes and quasi solid state electrolytes (gel electrolytes) were introduced. Though solid state electrolytes seem to be an ideal material for DSSC, the efficiency was not up to expectations [6]. This might be due to poor interfacial contact and poor charge carrier mobility. When coming to gel electrolyte, all the problems related to liquid and solid state electrolyte can be resolved. It remains as quasi solid at room temperature and as a highly viscous liquid at high temperatures. Thus, a gel electrolyte possesses both the cohesive property of solid as well as diffusive transport property of liquid [7]. In the present work a polymer-based gel electrolyte is synthesized and its behavior in the performance of dye sensitized solar cell is studied by using two different photoanode materials – TiO_2 and ZnO .

2. Experimental

2.1. Materials

Fluorine doped tin oxide (FTO-7 Ω /Sq.), N719 ($Ru(dcbpy)_2(NCS)_2$) -95%, Hexachloroplatinic acid (H_2PtCl_6), Potassium iodide (KI) (bio ultra, 99.5 %), Polyvinyl alcohol (PVA, 99 % hydrolyzed) were purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) and Iodine (I_2) is supplied by MERCK.

2.2. Gel electrolyte synthesis

Polyvinyl alcohol is used as the polymeric matrix. Gel electrolyte is prepared by adding adequate amount of polymer, KI and I_2 to dimethyl sulfoxide. The resulting mixture is heated to 2 hrs and stirred continuously to obtain the gel.

2.3. Assembling of quasi solid state dye sensitized solar cell

The nanocrystalline TiO_2 photo anode was fabricated by doctor blading TiO_2 paste on FTO substrate. The film was air dried and sintered at 450°C for 30 mins. The sintered sample was then cooled to room temperature and was dipped in the dye solution for 24 hrs. The dye loaded sample was then air dried and sealed. The counter electrode was made by electrodepositing Pt on FTO surface. The two electrodes were then kept face to face with gel electrolyte in between to obtain a sandwich structure and is then clamped tightly.

3. Results and discussion

3.1. Gel characterization

Figure 1 shows the FT-IR of pure PVA and PVA based gel electrolyte. The presence of broad band at 3416 cm^{-1} shows the inter-molecular hydrogen bonding. In PVA-G, the intensity of the band was found to increase, and this is because of extensive hydrogen bonding between the polymeric chains due to its complete expansion. The band at 2914 cm^{-1} shows the $-\text{CH}-$ stretching vibration. The band at 1654 cm^{-1} is for terminal vinyl group. Bands at 1783 cm^{-1} and 1806 cm^{-1} correspond to the ester group present. The 1315 cm^{-1} and 1434 cm^{-1} bands correspond to S-O stretching, while those at 1024 cm^{-1} , 1083 cm^{-1} , 1186 cm^{-1} show the C-O vibration of PVA.

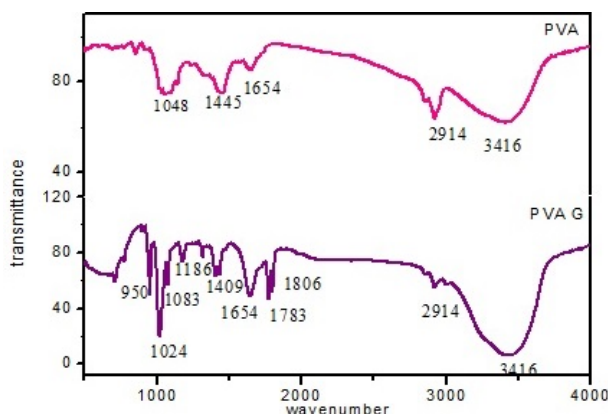


FIG. 1. FT-IR spectra of pure PVA and PVA gel electrolyte

The XRD spectra of gel electrolyte, pure PVA, KI, and I_2 are shown in figure 2. Diffraction peak at $2\theta - 40.76$ is ascribed to pure PVA. Diffraction peak at $2\theta - 21.67, 30.80, 54.98$ and $24.62, 25.07, 29.04$ is for pure KI and I_2 respectively, shows the crystalline nature of the ionic salt. An amorphous peak is observed for polymer gel electrolyte, which shows the complete dissolution of the ionic salt and also increased liquid electrolyte uptake by the matrix.

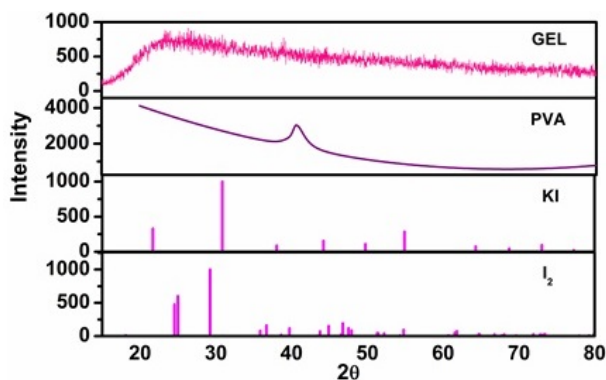


FIG. 2. XRD of pure I_2 , KI, PVA and polymer gel electrolyte

3.2. Cell characterization

The current-voltage characteristics and Nyquist plot of the DSSCs based on polymer gel electrolyte were performed with two different photoanode semiconductor materials-TiO₂ and ZnO. The table below summarizes the best values of their photovoltaic parameters.

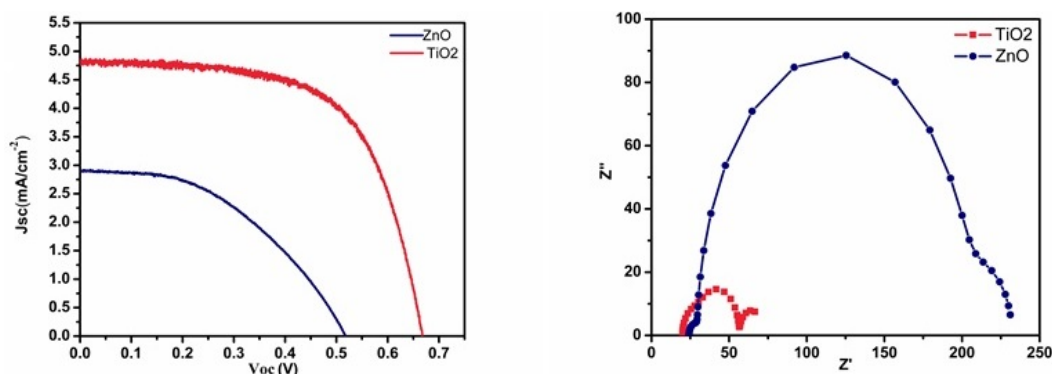


FIG. 3. (a) Jsc-Voc curve, (b) nyquist plot of the cell

TABLE 1. Photovoltaic parameters of TiO₂ and ZnO based DSCs with gel electrolyte

Photoanode material	Jsc(mA/cm ²)	Voc(V)	FF(%)	Eff(%)
TiO ₂	1.21	0.67	63.6	2.05
ZnO	0.723	0.517	45.8	0.684

The obtained efficiencies are 2.05 and 0.68 % respectively for TiO₂ and ZnO based DSSC with PVA gel electrolyte. Here, the pure PVA based gel electrolyte of KI/I₂ in DMSO/EC mixture without ionic liquid and any additives or fillers is used. An enhancement in the efficiency is anticipated with ionic liquid and other additives in the gel electrolyte and more studies in this direction are ongoing to enhance the efficiency. The efficiency values are low compared to perovskite-based DSSC. Perovskites give better efficiency and absorption coefficient as a sensitizer along with conventional electrolytes. However, focus of current work is on the synthesis of gel electrolyte, a better substitute for liquid electrolytes, and its application in electrochemical cells.

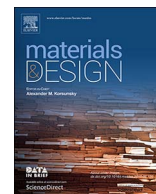
The charge transfer or transport behavior of the cell was measured by utilizing electrochemical impedance spectroscopy. The three semicircle from left to right gives the electrochemical behavior at the Pt counter electrode, TiO₂/dye/electrolyte interface and Warburg diffusion. The resistance offered at each interface when using ZnO as photoanode is very high when compared to the cell fabricated with TiO₂ as the photoanode. This confirms the lower performance of the ZnO-based quasi solid state dye sensitized solar cell.

4. Conclusion

PVA based polymer gel electrolyte was synthesized. DSSC were fabricated with two different photoanode materials to study the performance of the cell. Photovoltaic studies show that the gel works well with TiO₂-based solar cell, displaying an overall efficiency of 2.05 %.

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Anchoring of polymeric precursor on oxygen deficient ZnO nanotubes: A chelation assisted combined nucleation-growth-dissolution synthesis strategy

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ABSTRACT

A template-free method has been adopted to synthesize predominantly oxygen deficient and morphologically tuned zinc oxide nanotubes. A relatively simple sol-gel route was chosen for the same using zinc acetate dihydrate and beta-aminoethylamine as precursors and the feasibility of the photocatalytic activity of the nanotubes was analyzed comprehensively. Etching of the nanotubes was fine-tuned effortlessly by changing the ratio of precursor concentration during synthesis. Here, polymeric precursor plays multiple roles and controls the shape and roughness of the formed nanotubes by serving as a co-ordination assisted precipitation, dissolution, etching and reducing agent. Nonpolar, chelating bi-dentate polymeric precursor anchors both heterogeneous nucleation and dissolution controlled growth in single stretch. Oxygen deficient ZnO nanotubes with varying surface properties were obtained from zinc to beta-aminoethylamine ratio of 2:1, 1:2 and 1:1 (21ZE, 12ZE, 11ZE). Structure, morphology and optical properties of the ZnO nanotubes were systematically examined. Nanotubes with etched surface showed better photocatalytic activity in methylene blue degradation compared to those with non-etched surface. ZnO nanotubes synthesized from equimolar concentration of the precursors (11ZE) showed stable photocurrent in chronoamperometric study with more than 60 percentage degradation of methylene blue within 90 min.

1. Introduction

Research in improving the photocatalytic activity of zinc oxide, either by doping or making nanocomposites [1] has been occupying the centre stage for quite a long time. In recent times, studies tend to focus on novel applications of ZnO in solar cell [2], biological labeling [3], LED [4] and in varistors [5] etc., due to its economically viable production methods and eco-friendly nature. Another area that has gained fresh momentum is that of application of pure ZnO nanomaterials as photocatalyst [6]. Abdullah et al. report that powdered pure ZnO is better for the degradation of broad range of pollutants than its composite with Ag₂O [7]. A plethora of morphological variants of ZnO nanomaterials such as, nanoflowers [8], nanosheets [9], nanorods [10], nanospheres [11], nanoplates [12], nanowires [13] and nanoflakes [14] etc. are being extensively explored as photocatalyst in recent times. However, nanotubes have carved a niche for themselves as their favourable energy band alignments for efficient trapping of solar energy leads to high photocurrent and photocatalytic activity [15]. Acharyya et al. report that among different morphology of ZnO nanomaterials, nanotubes with better carrier transport have an advantage over other

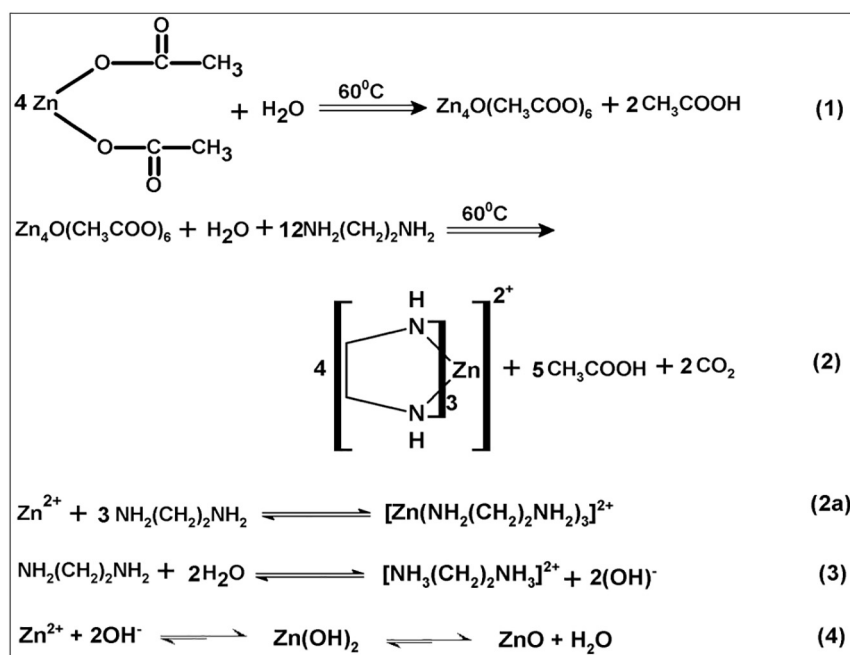
morphologies [16].

A host of comprehensive studies have been conducted on the electrochemical synthesis of ZnO nanotubes [15,16] to establish the advantage of short time production, but the use of conducting substrate is the flipside of this process. Most of the reports show templated synthesis of nanorods prior to the synthesis of etched nanotubes [17]. However, expensive templates and multiple steps involved in their removal make those methods more difficult. Hence, template-free sol-gel synthesis with minimal usage of cost effective precursors with one-step surface etched nanotube formation commencing from nucleation without the assistance of other reagents is of prime significance [18]. In such cases one precursor can play multiple roles during the formation by eliminating multiple steps and other byproducts during synthesis.

The photocatalytic activity of ZnO finds wider application in the recycling of polluted water, a major public health challenge across the globe [7,9–11]. Textile industry contributes enormously to the pollutants by way of harmful dyes like Rhodamine B [9], methylene blue [11] etc. Radical changes are possible in the field of textile dye degradation process with nano zinc oxide photocatalysts due to the small quantity needed for broad range of degradation [19]. It is found

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Scheme 1. Proposed mechanism of the sol-gel synthesis of ZnO nanotubes.

that these toxic, refractory, carcinogenic and non-biodegradable textile dyes can be completely decomposed into CO_2 , water and mineral acids under room temperature and atmospheric pressure by ZnO nanotubes.

Here, an attempt is made to explore the photocatalytic activities of zinc oxide nanotubes for the degradation of methylene blue (MB), a textile dye. For this, ZnO nanotubes have been prepared in an easier and economical way through sol-gel approach using zinc acetate dihydrate and beta-aminoethylamine (edamine) with water as the medium for synthesis. A slight manipulation in the concentration of the polymeric precursor in reaction medium results in gaining ZnO nanotubes with varying degrees of surface roughness. A template-free single step sol-gel method, which has not been reported previously, is used for the synthesis of ZnO nanotubes in powder form in water medium. The formation mechanism illustrates that precipitation, coordination, dissolution and etching happen in a single stretch within 6 h at mild and constant temperature. A systematic study on the effect of edamine in the surface etching of ZnO nanotubes and the role of etched surface in the degradation of methylene blue dye is discussed in detail in this paper. Previous report by Wang et al., on dye degradation by ZnO nano sheets gives only 9.4% degradation [20]. Chang carried out MB degradation under UV light by ZnO/ZnS nanocable and nanotube arrays and got a rate constant (k) value of 0.025 min^{-1} within 2.30 h [21]. Chang et al. report, 11% MB degradation under visible light by pure ZnO and maximum 71% degradation by Ag-ZnO-RGO composite within 2 h exposure [22]. Here, the synthesized surface etched nanotubes give 66% dye degradation under visible light within 1.30 h with a k value of 0.012 min^{-1} . The photocatalytic activity of ZnO nanotubes with their varying degrees of surface roughness is correlated by employing photocurrent generation and dye degradation studies.

2. Experimental

Detailed description of the chemicals, reagents, apparatus and instruments used for the experiment and analysis is given in Supporting information.

2.1. Synthesis of ZnO nanotubes

ZnO nanotubes with varying surface roughness were synthesized by changing the molar ratio of zinc acetate and edamine gradually to

1:0.5, 1:1 and 1:2. For the synthesis of ZnO nanotubes with equimolar ratio (1:1), 0.015 M zinc acetate solution was prepared in double distilled water and kept in a water bath at 60°C . 0.015 M edamine was injected to this solution with micro pipette and the beaker was kept for 6 h of aging at the same temperature. The white powder formed was washed thrice in water and extracted with the help of a high speed centrifuge at 12000 rpm for 10 min. The precipitate thus synthesized with equimolar concentration of precursors was named as 11ZE. The same procedure was repeated with changed molar concentrations of the precursors for the preparation of two more samples named 21ZE and 12ZE respectively for 1:0.5 and 1:2 ratio of zinc acetate to edamine. The synthesized samples were sintered at 400°C for 1 h and stored for further characterizations.

2.2. Chronoamperometric analysis

Chronoamperometric analyses were done to study the photoactivity of 11ZE, 12ZE and 21ZE by measuring the photocurrent density. Photocurrent was measured under 1 sun illumination (100 mW/cm^2) using a solar simulator interfaced with Biologic SP-150 potentiostat instrument. A three electrode system was used with Ag/AgCl as reference electrode, Pt wire as counter electrode, evenly distributed ZnO film (with a fixed area of 0.25 cm^2) on FTO as working electrode and 0.1 M Na_2SO_4 as electrolyte. Chronoamperograms were recorded after ten cycles of periodic illuminations with intervals of 60 s.

2.3. Photocatalysis of methylene blue

Photocatalytic activity of the three samples was studied by checking the degradation of a textile dye, methylene blue, in aqueous solution. A weighed amount of 0.05 g of each sample was taken in a beaker. 50 mL methylene blue solution in distilled water (0.002 wt%) was added to the beaker containing ZnO nanotubes and was stirred in dark for 30 min. Then, the beaker was placed under solar simulator with stirring continuing. At 15 min of periodic intervals of exposure, small volumes of the solution mixture were taken to study the dye degradation by recording the absorption spectra.

3. Results and discussions

3.1. Nucleation and growth of ZnO nanotubes

Sol gel synthesis involves hydrolysis of precursors and here, when zinc acetate dissolves in water, the resultant temporary complex (step (1) of Scheme 1) retains a solution pH of 5 [23]. On addition of alkaline precursor, edamine, to the medium pH shoots up suddenly to 7.5/6.5/5.5 for 12ZE, 11ZE and 21ZE respectively. As nucleation is the first stage of nanoparticles synthesis, this increase in pH lead to immediate Zn^{2+} precipitation followed by the formation of Zn^{2+} - edamine complex (step 2 of Scheme 1) [24]. At the same time edamine also gets hydrolysed and paves the way for ample formation of hydroxyl ions (step 3 of Scheme 1). The Zn^{2+} from step (2) and OH^- from step (3) combine to form $\text{Zn}(\text{OH})_2$ which lead to the formation of ZnO nuclei. In the case of 12ZE, increase in pH helps to increase the nucleation excessively because of the higher edamine concentration. Here growth starts only after completion of the heterogeneous nucleation [25] as pH of the solution spirals down from 7.5 to 5 in the final stage of the synthesis. Fast consumption of nutrients and inhibition of further growth leads to uncertain crystal growth in 12ZE. At low edamine concentration (21ZE), the reversible reaction (step (3) in Scheme 1) predominates and reduces the availability of OH^- in the solution. Here, the pH of the solution observed as 5.5 after addition of edamine and this pH gets maintained throughout the process without fluctuations. This facilitates the occurrence of heterogeneous nucleation, growth and dissolution process simultaneously. Here, water and acetate helps to accelerate the growth process [23,26] to compensate the shortage of edamine and zinc oxide is formed directly from the complex $\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$ without undergoing co-ordination with edamine, i.e. in such cases steps (2) and (3) of Scheme 1 takes place scarcely. The precursor concentration was optimized in 11ZE, for the synthesis of surface etched ZnO nanotubes for efficient photocatalysis. In the case of 11ZE, the initial pH drops from 6.5 to 5.5 in the early stages of the growth process and the SEM images at this point reveals

that no tubular structure was attained (Fig. 1(d)). Surface etched nanotube formation takes place by the dissolution and etching along with growth process at a stable solution pH of 5.5 [27].

Wurtzite ZnO crystal structure is formed by the alternate stacking of Zn^{2+} and O^{2-} enriched polar surfaces. Zn^{2+} polar surfaces {0001} are of two types; O-atom terminated and Zn-atom terminated. The growth occurs along oxygen atom terminated zinc polar surfaces; as the double layer formed from solution contain fewer number of OH^- . Here, the fewer number of OH^- can be attributed to the oxygen atom termination in zinc polar surface which occurs through hydroxyl groups. When pH reaches 5.5, the unstable O^{2-} rich polar surfaces undergo dissolution [28] at a comparatively faster pace. Nonpolar surfaces {1010} in presence of edamine become relatively stable because these {1010} planes are covered by nonpolar chains of edamine. The dissolution of oxygen rich polar surfaces is inferred from the PL spectra by the presence of emission peaks due to oxygen vacancies along with band edge emission and no peak due to zinc vacancies are detected. From our experimental observation it was found that the pH 5.5 trigger the formation of nanotubes with chelation assisted combined growth-dissolution-etching mechanism. The schematic illustration of the synthesis procedure adopted for the nanotube formation is shown in Scheme 2.

The multitasking characteristics of edamine during ZnO nanotube synthesis and optimization of its concentration for efficient photocatalyst are evident from the points listed. (1) The presence of edamine rapidly brings up the alkalinity of the precursor solution to facilitate nucleation by precipitating Zn^{2+} cations. (2) The bi-dentate chelating effect helps to control the supersaturation for the nucleation and growth of ZnO nanotubes. (3) Capping property of edamine helps to hinder agglomeration of nanocrystals and assist anisotropic growth. (4) A particular concentration level of edamine promotes etching of nanotubes along with growth of particles. (5) Edamine also plays a role in concentration dependent selective dissolution of polar planes to accelerate ZnO nanotube formation.

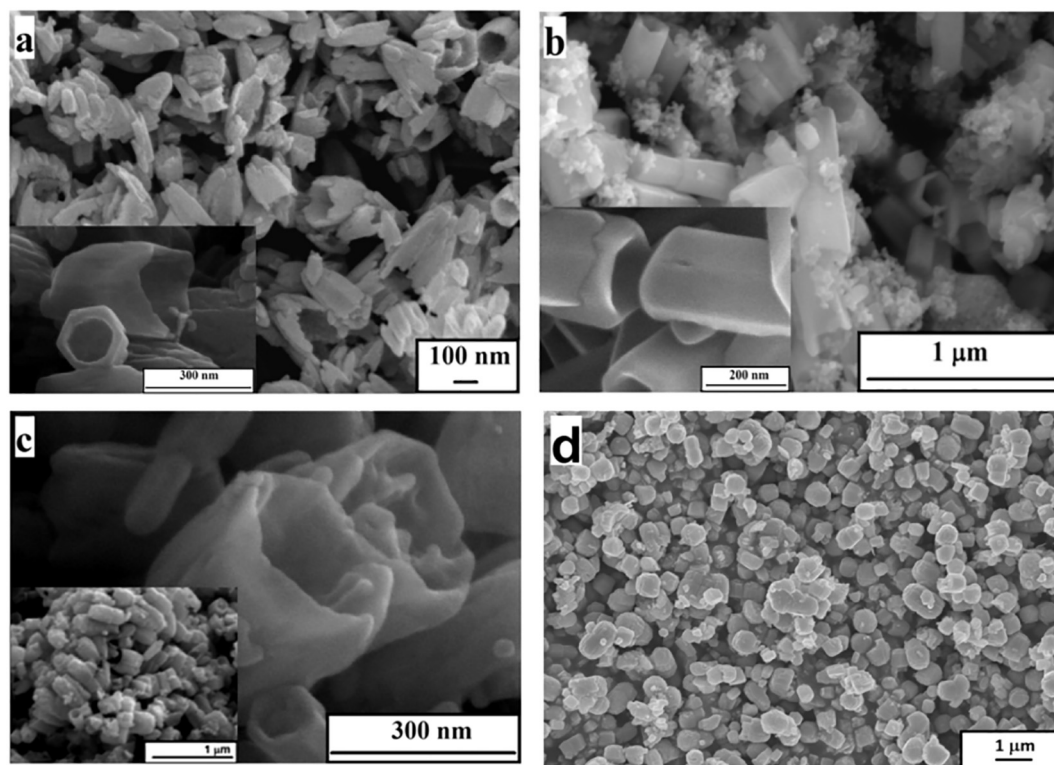
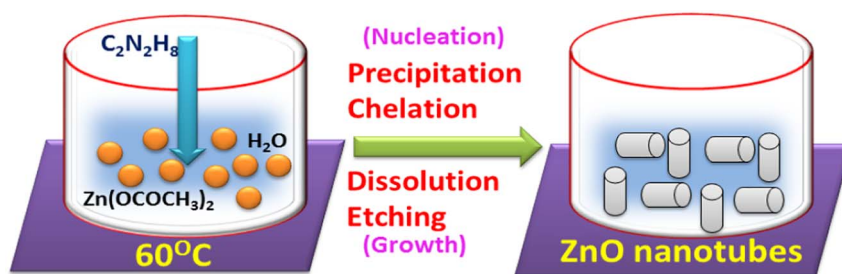


Fig. 1. SEM images of calcined (a) 12ZE, (b) 21ZE, (c) 11ZE (d) 11ZE at the time of pH change.



Scheme 2. Schematic diagram of the synthesis procedure of ZnO nanotubes.

3.2. Morphology and structural properties

From SEM analysis it is evident that the edamine concentration has a significant role in the shape, size and surface roughness of the formed nanotubes. The SEM micrographs of 12ZE, 21ZE, and 11ZE show nanotube morphology with different tube size and surface roughness as seen in Fig. 1(a–c).

Edamine concentration increases gradually from 21ZE, 11ZE and 12ZE. 21ZE shows slightly elongated nanotubes with smooth surface with hexagonal edge, but for 11ZE, the tube surface becomes etched due to the increased concentration of edamine and loses definite edge shape. Further increase on the concentration of edamine leads to the destruction of nanotube structure and uncertain particle dimension for 12ZE samples. It is presumed here that, the presence of edamine in the reaction medium acts as an etching agent and gradually destroys ZnO nanotubes with increased concentration. The formation of nanoparticles along with the nanotubes seen in the case of 21ZE (Fig. 1(b)) may be an outcome of lesser concentration of edamine, which in turn results in the formation of zinc oxides directly from the complex $Zn_4O(CH_3COO)_6$ without undergoing co-ordination with edamine [23]. Fig. 1(d) shows the SEM image of the 11ZE at the initial stage when the pH dropped from 6.5 to 5.5. At this phase, the tubular structure is absent.

The crystal structure is characterized by X-Ray powder diffraction (XRD) as shown in Fig. 2. XRD is taken for ZnO, before and after calcination to confirm the purity and crystal structure of the prepared nanoparticles. Sample before calcination (BC-11ZE) do not undergo any phase changes but shows extra peaks (marked by * in Fig. 2). After calcination, all impurity peaks disappeared and the purity of the ZnO samples is ensured. The data is compared with JCPDS File No: 89-0510 to confirm the anisotropic growth of wurtzite ZnO with hexagonal geometry [22]. The maximum intense peak is observed at a 2θ value of 36.4° (101) and other peaks are at 31.8° (100), 34.6° (002), 47.6° (102), 56.6° (110), 63° (103) and 68° (112) for all three samples. From the XRD pattern the crystallite size is calculated using Scherrer equation [23] and is found to be 15.41, 20.94 and 28.03 nm for 11ZE, 12ZE and 21ZE respectively. The dislocation density of three samples is calculated [29] and it is higher for 11ZE (Table T1 in Supporting information (SI)). The elemental composition of the sample is confirmed from EDAX

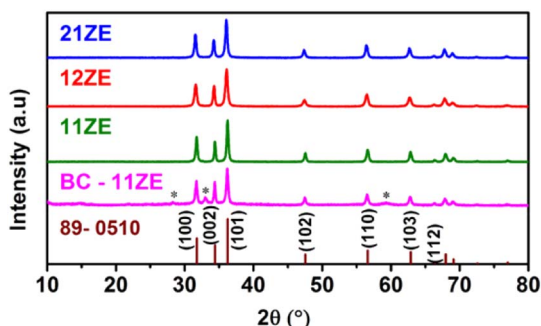


Fig. 2. XRD of ZnO samples before and after calcination compared with standard JCPDS.

analysis and a representative graph for the 11ZE is given as Fig. S1 in SI. The result of the EDAX spectra indicates zinc atom richness in the zinc oxide crystals which points to oxygen deficiency present in the sample [30].

3.3. Optical properties

Absorption spectra of samples have been taken before and after calcination and the spectra are shown in Fig. S2 in SI. All samples show almost similar absorption in both cases with a band edge absorption around 369 nm. The bandgap of samples before and after calcination is determined by means of Tauc plot and is found to be ~ 3.3 and 3.1 eV respectively. This narrowing of bandgap after calcination may be due to self-doping arises in the crystal lattice [31] or increased oxygen deficiency [32]. The corresponding Tauc plot is given in SI as Fig. S3.

Emission behaviour of the calcined ZnO nanostructures has been checked by recording the photoluminescence spectrum at room temperature. All the samples are excited at 340 nm and the resultant band edge emission is observed around 400 nm as shown in Fig. 3. The emissions, observed at 420, 485 and 528 nm are due to defect emissions from the ZnO nanocrystals [33].

The blue emission observed at 420 nm can be assigned to the transition between the conduction/valence bands and trap states near the valence or conduction band [34]. The emission at 485 nm may arise due to oxygen vacancy (V_o) or singly ionised oxygen vacancy (V_o^-) in ZnO lattice or interface [35]. The green emission observed at 528 nm can be attributed to the transition of electrons from the conduction band to the defect state due to the oxygen vacancies [33–36].

Raman spectra of the samples have been taken with a laser wavelength of 532 nm and are shown in Fig. 4. The major peaks are observed at 99, 195, 331, 437, and 580 cm^{-1} . The peaks at 99 (E_2 low) and 437 cm^{-1} (E_2 high) are characteristic of Wurtzite ZnO structure [37] and the strong and high intense E_2 mode indicates good crystallinity of the samples. Peaks at 144 and 195 cm^{-1} are attributed to lattice vibrations and TO (Transverse and Optical) overtone respectively [38]. The vibrational mode at 256 cm^{-1} corresponds to laser plasma lines [39].

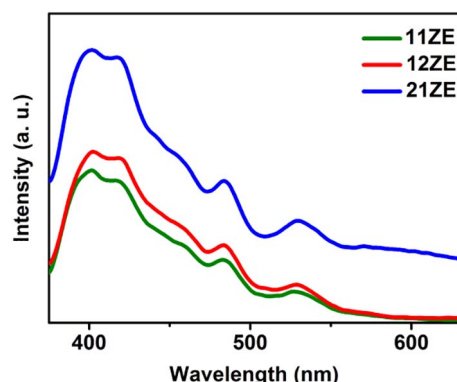


Fig. 3. Photoluminescence spectra of 11ZE, 12ZE, 21ZE.

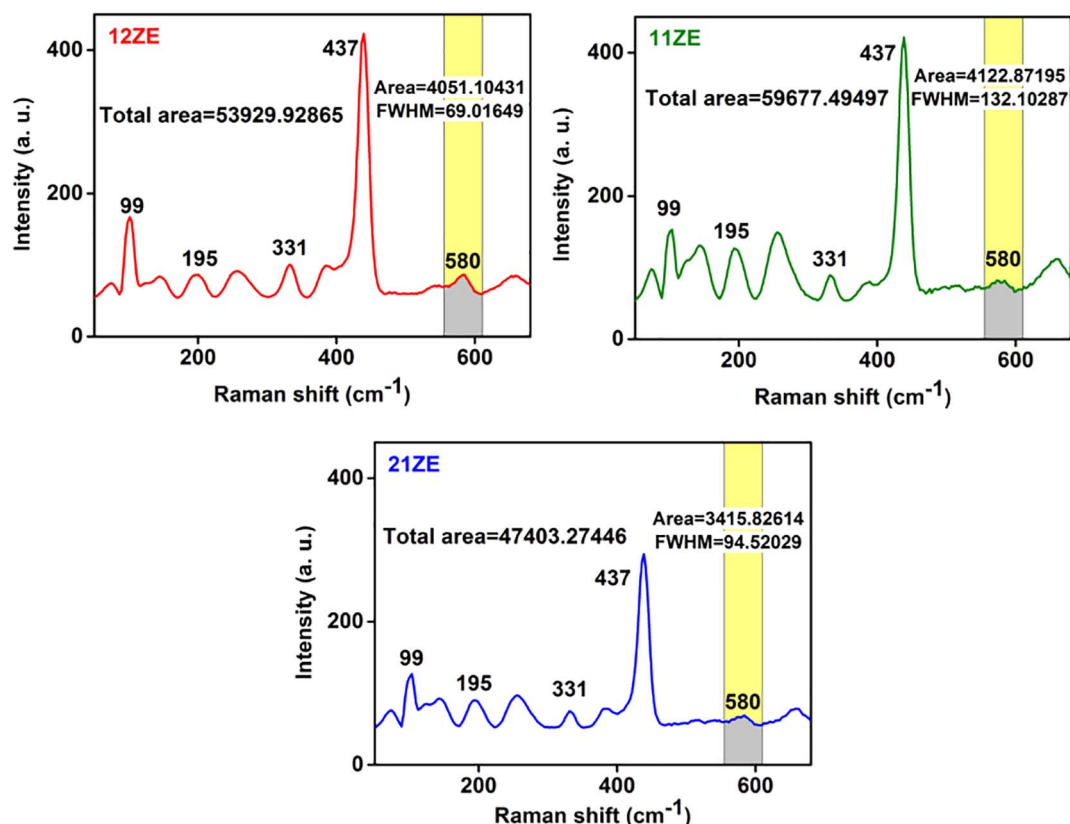


Fig. 4. Raman spectra of 12ZE, 11ZE and 21ZE.

The peak at 331 cm^{-1} corresponds to phonon scattering peak overlap of E_2 (high) and E_2 (low) and the one observed at 660 cm^{-1} represents an intrinsic mode of ZnO (TO + LO). The peak at 560 cm^{-1} is assigned to zinc deficiencies [37,40] which is absent in all three samples. The peak at 580 cm^{-1} is assigned to oxygen vacancy which is integrated for each sample to get the area for comparison. The obtained area ratio of this peak for 12ZE, 11ZE and 21ZE is 1.19:1.21:1. Further a comparison on total area of the peaks among the three samples has been done and the obtained ratio is 1.14:1.26:1 for 12ZE, 11ZE and 21ZE.

3.4. Photoactivity study

Photoactivity of ZnO nanostructures has been studied by using chronoamperometry under illumination and the corresponding time dependent current behaviour is shown in Fig. 5.

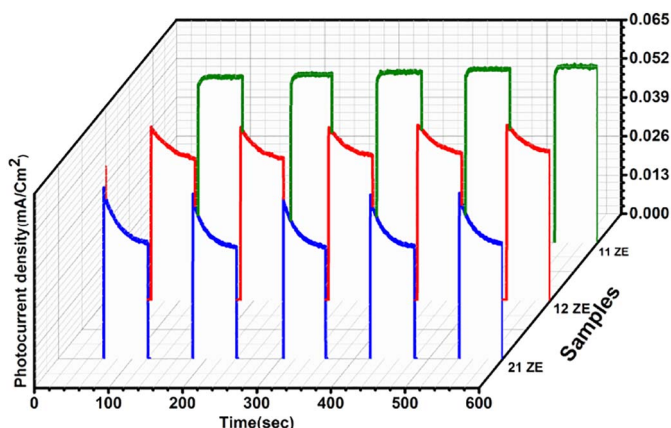


Fig. 5. Chronoamperogram of 11ZE, 12ZE and 21ZE.

Photoconductivity being surface related, the ZnO samples with different surface roughness show different photocurrents. When ZnO is illuminated, the excitons generated are proportional to the photocurrent generated from the sample [41,42]. The stability and degradation of photocurrent are different for the three samples and 11ZE is found to be more stable (0.056 mA/cm^2) with minimum rate of photocurrent degradation. It is presumed here that, more oxygen species from the electrolyte is chemisorbed on the etched surface of 11ZE and converted to superoxides (O_2^-) by accepting the excited electrons (reaction 1). Photocurrent is contributed by the electrons generated as a result of oxygen desorption by the reaction of holes with the superoxides (reaction 2) [43].



The stable photocurrent observed for 11ZE can be attributed to the increased defect states arise from the etched surface. These defect states due to oxygen increases the carrier lifetime and prevent recombination resulting in a steady photocurrent formation by desorption of chemisorbed oxygen on the surface of the ZnO nanotube. For 12ZE and 21ZE, under illumination, initially photocurrent attains a maximum value then slowly decays to a steady state [44]. It is presumed here that both the chemisorbed oxygen and oxygen related defects are less for these two samples, showing photocurrent decay. The photocurrent stability after many cycles of illumination denotes the photocatalytic stability of the sample maintained by means of continuous charge transport at the electrode-electrolyte interface [45].

3.5. Photocatalytic performance

Photocatalytic activity of the ZnO nanostructures with tuned morphology and surface has been tested for textile dye (methylene blue) degradation. During photocatalysis, the degradation process is

activated by the excitons generated by ZnO and the degradation rate of dye is influenced by the exciton recombination rate [46]. Being a direct bandgap semiconductor, radiative recombination occurs faster for ZnO. However, the defect density controls the exciton recombination behaviour by triggering Shockley-Read-Hall (SRH) recombination [47]. The oxygen related defect states are capable of controlling the photocatalytic degradation of organic dyes [46].

In the process of dye degradation the excitons generated in ZnO on illumination produce highly reactive hydroxyl free radicals ($\text{OH}^\bullet$) and superoxide species (O_2^-) by reacting with water present in the MB solution. These hydroxyl free radicals and superoxides decompose methylene blue to CO_2 , H_2O and volatile organic compounds (VOC), leading to decolourisation of the dye solution. The mechanism of dye degradation is shown as Scheme S3 in SI. To eradicate any error due to initial adsorption of methylene blue on the surface of zinc oxide samples, the mixture was stirred in dark for 30 min before being placed under light source to establish adsorption-desorption equilibrium. It is presumed here that, 11ZE having etched surface adsorb more methylene blue than the other two samples to establish adsorption-desorption equilibrium. This is further supported by the dye loading study conducted on ZnO nanostructures with methylene blue under dark condition and the details are given in SI as S5. The BET surface area results obtained for 21ZE, 11ZE and 12ZE (Fig. S6 in SI) show negligibly small difference in surface area hence not correlated with the photocatalytic activity. Many studies have demonstrated that photocatalytic activity depends on many factors such as, excitonic recombination rate, dye adsorption ability, surface defects and surface area of the photocatalyst [15,22]. A report by Yuyu Bu and Zhuoyuan Chen, explains that, the adsorptive capacity of nanomaterials is independent on specific surface area obtained from BET measurements [48]. Photocatalysis indicates slow excitonic recombination and high adsorption which contributes to better efficiency (S3 in SI).

A time dependent concentration study of the dye in the presence of 11ZE, 12ZE and 21ZE is done under illumination and is graphically represented in Fig. 6(a). The heat dispersed due to illumination is considered to be insignificant as it doesn't play any role in photocatalysis [49].

Methylene blue is found to be photostable in the absence of photocatalyst [50] and the degradation of methylene blue in presence of ZnO follows a pseudo first order kinetics with rate constant $k = 1/t \ln (C_0 / C)$ [46], where, C_0 is the initial and C the final concentration of the dye. The degradation rates of methylene blue in the presence of ZnO nanostructures are depicted in Fig. 6(b). The chemisorbed oxygen on the surface of ZnO nanostructure has a significant role in the regeneration mechanism of hydroxyl and superoxide species for the degradation of dye and the same can be represented as follows [51].



Among the three oxygen deficient zinc oxide samples, surface etched 11ZE shows better degradation efficiency towards methylene blue [46]. Here, the photocatalytic degradation rate is influenced by the rate of formation of superoxides and hydroxyl free radicals that correlate with the exciton lifetime. Recombination of excitons eliminates the formation of superoxides and hydroxyl free radicals and thus affects the photocatalytic reaction rate. PL data (Fig. 3) support this argument by showing high intense band edge emission for 21ZE indicating high recombination rate of photogenerated carriers, leading to low photocatalytic activity [37]. The less band edge recombination in 11ZE and 12ZE is undoubtedly due to the presence of oxygen vacancies (which is evident from Raman spectra (Fig. 4)). The maximum photocatalytic efficiency obtained for 11ZE reveals the combined activity of oxygen vacancies and high dye adsorption on etched surface. The oxygen defect density in ZnO nanostructures is sensitive to synthesis parameters such as pH, precursor concentration, temperature, reaction time and stirring procedure [52,53]. In the present study, three morphologically tuned nanostructures are prepared under fixed temperature, reaction time and stirring procedure. Hence, it is assumed that the precursor concentration alone controls the morphology and oxygen vacancy of zinc oxide samples.

4. Conclusion

Oxygen deficient morphologically tuned ZnO nanostructures with varying photocatalytic activities were obtained by changing the concentration of polymeric precursor in the reaction medium. One dimensional ZnO with three different samples were obtained by changing the zinc to beta-Aminoethylamine ratio of 2:1, 1:2 and 1:1 (21ZE, 12ZE and 11ZE). Photocatalytic activity of these ZnO nanostructures shows that 11ZE gives stable photocurrent behaviour with better photocatalytic performance with more than 60 percentage degradation of methylene blue. Performances of these three ZnO nanostructures on methylene blue degradation were correlated with the surface chemisorbed oxygen, oxygen related defect density, adsorbed dye and slow excitonic recombinations. Among the three samples 11ZE surface accommodates more chemisorbed oxygen and shows stable photocurrent in chronoamperometrical observations. High exciton life time, oxygen vacancies and dye adsorption capability contribute high photocatalytic activity of 11ZE. All these factors indirectly affect the photocatalytic degradation of methylene blue by producing more superoxides and hydroxyl free radicals under illumination.

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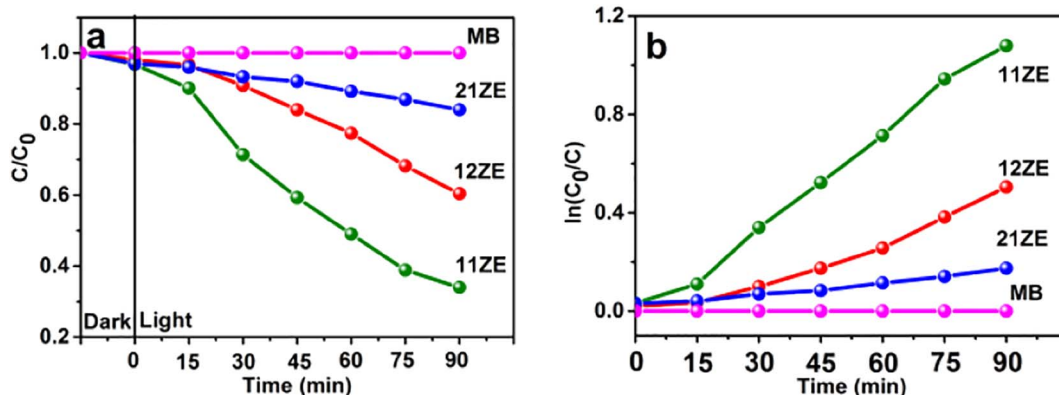


Fig. 6. (a) Photocatalytic MB degradation efficiency of zinc oxide samples and (b) photodegradation rate of MB.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.matdes.2017.05.090>.

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Natural dyes from red amaranth leaves as light-harvesting pigments for dye-sensitized solar cells



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ABSTRACT

This study reports red amaranth as a source of two natural dyes to be used as low cost sensitizers for wide bandgap semiconductors in dye sensitized solar cells. The two dyes were identified as Chlorophyll and Betalain from their characteristic absorption spectra. The photo electrochemical properties of dye sensitized solar cells using natural pigments containing Chlorophyll and Betalain was investigated in this work. The results indicate that the Chlorophyll dye shows a maximum photocurrent density of 1.3 mA/cm² with an energy conversion efficiency (η) of 0.53%. The Betalain dye showed a photocurrent density of 0.87 mA/cm² with energy conversion efficiency (η) of 0.23%. The better performance of chlorophyll dye as sensitizer for dye sensitized solar cells was supported by electrochemical impedance spectroscopy and bode plot measurements.

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1. Introduction

Dye sensitized solar cells (DSSC) provides a technically and commercially viable alternative concept to the conventional solar cell technologies since first reported by O Regan and Grätzel [1]. In DSSC a wide bandgap oxide semiconductor acts as a photoanode which accepts electrons from the photoexcited dye/sensitizer. The dye molecule is regenerated by the redox system which itself is regenerated at the counter electrode by the electrons passing through the load. Titanium dioxide is the most successful photoanode material due to its low cost, non-toxic nature, high stability and its photoelectrical properties are strongly dependent on shape, size and dimensionality [2–4]. Hence the efficiency of DSSC can be improved by increasing absorption of photons by a photo sensitizer/dye to a large extent [5]. The ideal sensitizer for a solar cell converting standard Air Mass (AM1.5) should absorb all light below a threshold wavelength of about 920 nm. In addition, it must have strong adsorption to the semiconductor metal oxide surface, efficient electron injection onto the conduction band of metal oxide, must be rapidly regenerated to avoid recombination process and be fairly stable. The best photovoltaic performance both in terms of conversational yield and stability has been achieved by the poly-pyridyl complex of Ruthenium [6].

However the use of expensive Ruthenium complexes extracted from scarce natural resources provides ample space for researchers to experiment with natural pigments as sensitizing dyes for conversion of solar energy to electrical energy. The natural dyes have an added advantage of being in abundant supply, environment friendly and relatively cheap methods of preparation [7]. These pigments are extracted from fruit, leaves, flowers and roots of plants. A plant pigment is a type of coloured chemical substance produced by plants which absorb visible radiation between 380–780 nm. The major types of plant pigments classified according to colour are chlorophylls, anthocyanins, betalains and carotenoids. Chlorophylls absorb red and blue light from sunlight and hence appear green. The chlorophyll molecules (C₅₅H₇₀MgN₄O₆) are large in size. They are not soluble in aqueous solution that fills the plant cells, but attached to disc like structures called chloroplasts inside cells. Chlorophyll is an attractive candidate for being photosensitizer and efficiencies above 4% have been reported [8–10]. The photoelectric conversion efficiencies of DSSC with chlorophyll dye as sensitizer extracted from spinach [11] and pomegranate leaves [12] are 0.49 and 0.59% respectively.

Anthocyanins are coloured water soluble natural pigments have been which are widely used as photosensitizers in DSSC [13,14]. Betalains are a class of red–violet (betacyanins) and yellow (betaxanthins) pigments that are present in plants of caryophyllales. The common major sources of betalains are plants of amaranthaceae, red beet, bougainvillea, cactacea [14]. Carotenoids are another class of yellow and yellow orange pigments used as photosensitizers in DSSC [15]. There have been studies comparing

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efficiencies of anthocyanins, betalains and chlorophyll extracted from different plants [16–21]. This investigation reports extraction of betalain and chlorophyll from a single leaf which has been rarely reported. Water and ethanol used as solvents for a single dye in previous reports [18,20] have extracted different dyes in this work. The previous report on red amaranth as natural sensitizer in DSSC by J. Uddin et al. [22] have separated the various components using chromatography but the efficiencies reported are low and the individual coloured pigments were not classified. In this paper two natural dyes namely chlorophyll and betalain from leaves of red amaranth were used as photosensitizers for DSSC. The extracted dyes were characterized by UV–vis absorption spectra and their structures confirmed through FTIR spectra. Finally the photo-electrochemical properties of the DSSC using these extract as sensitizers was investigated in this work.

2. Materials and methods

The dye used in this work has been extracted from red amaranth (*Amaranthus tricolor* L.), a plant found abundantly in India belonging to Amaranthaceae. The leaves are reddish purple in colour and widely used as a vegetable. Titanium dioxide nanoparticles (TiO_2), Fluorine doped tin oxide (FTO- $7\Omega/\text{cm}^2$), hexachloroplatinic acid (H_2PtCl_6) and potassium iodide (KI) (99.5%), were from Sigma-Aldrich and iodine (I_2) from MERCK.

2.1. Fabrication of DSSC

The leaves of red amaranth (Fig. 1a) was washed and cleaned, cut into small pieces prior to extraction. The dye was extracted by adding the leaves to the respective solvent and heated with stirring at 60°C for 15 min. The resulting solution was filtered using syringe filter ($0.2\ \mu\text{m}$) and stored at 4°C for further experiments. The dye was extracted using two solvents namely DI water and ethanol (Fig. 1b). The dyes extracted showed different colours namely red-violet with distilled water and green with ethanol showing the presence of two different pigments.

FTO conductive glass plates (resistance $7\Omega/\text{square cm}$) were first cleaned with soap solution and rinsed with de-ionized water and acetone for 10 min in an ultrasonic bath. The TiO_2 paste was prepared by blending commercial TiO_2 powder (anatase, 25 nm) with ethanol and one drop of TritonX –100. The resultant paste was deposited on the FTO glass plate using doctor blading technique. The TiO_2 deposited FTO glass plates were calcined at 450°C for 30 min in a muffle furnace. On cooling, the area confinement of 0.25 cm^2 was done and dyes were attached to TiO_2 surface by dipping the electrodes in dye solution for 24 h. The

photoelectrodes were taken from dye solution, rinsed with methanol to remove impurities and air dried for further use. The counter electrode was prepared by electrodepositing 4 mM hexachloroplatinic acid (H_2PtCl_6) with a scan rate of 20 mV/s for four cycles. The electrolyte was prepared by mixing 0.6 M 4-butyl methyl imidazolium iodide (BMII), 0.04 M Iodine (I_2), 0.1 M lithium iodide (LiI), 0.1 M guanidium thiocyanate (GuSCN) and 0.5 M tertiary butyl pyridine in acetonitrile. The TiO_2 electrode and electrodeposited Pt counter electrode were assembled to form a solar cell by sandwiching the redox electrolyte using binder clips.

3. Optical and electric measurements

The UV–vis spectrophotometer was used to measure the nature of absorbance of the dye in the visible range of the solar spectrum. Fourier transform infrared spectra (FTIR) of dye extracts and dye adsorbed TiO_2 films were measured using PerkinElmer FTIR spectrometer in the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$. For measuring the performance of the dye as sensitizer in DSSC, I–V characteristics were done using solar simulator (Sciencetech) under 1 sun illumination ($100\text{ mW}/\text{cm}^2$). The electrochemical impedance spectroscopic measurements were carried out using computer controlled electrochemical interface (SP150, Biologic) in the frequency range 1 mHz to 10 MHz under illumination of $100\text{ mW}/\text{cm}^2$.

4. Results and discussions

4.1. Absorption spectra

Dyes extracted using different solvents show different absorption peaks in the UV–vis absorption spectra. The difference in the absorption spectra is due to the presence of different photosynthetic pigments in the leaves of red amaranth in the visible spectrum ($400\text{--}700\text{ nm}$). From Fig. 2(a) the absorption peaks of the dye in ethanol can be seen at a wavelength of 415, 438 and 664 nm, for distilled water a single peak located at 536 nm was observed. The absorption peak observed in the wavelength range of $400\text{--}440$ and 660 nm indicate the presence of chlorophyll pigment whereas peak around 536 nm attributes to betalain pigment [23–27]. The ethanol based extraction of chlorophyll showed better and broader absorption in the visible range of the electromagnetic spectrum.

Fig. 2(b) shows the absorption spectrum of dyes extracted from red amaranth and loaded onto the surface of TiO_2 . The enhancement of absorbance and presence of peaks with dye loading shows the anchoring and chemical interaction of the dye molecules to the TiO_2 photoanode. The figure indicates that the chlorophyll dye

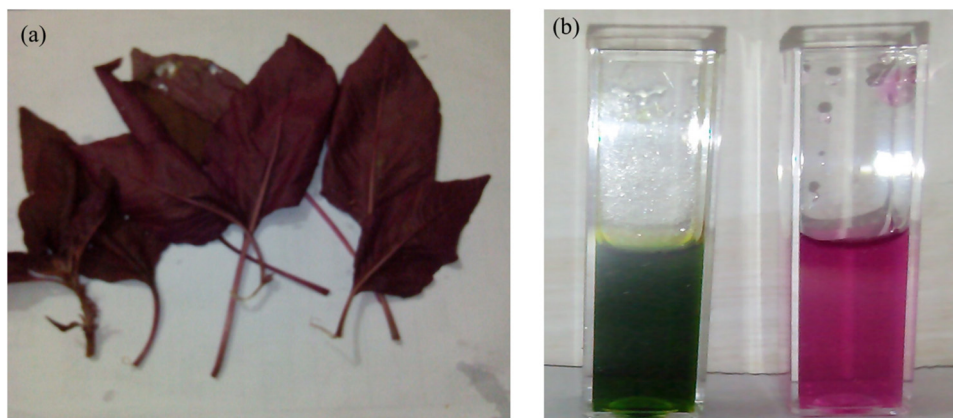


Fig. 1. (a) Red amaranth leaves (b) Extract of red amaranth in ethanol (green) and water (red-violet). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

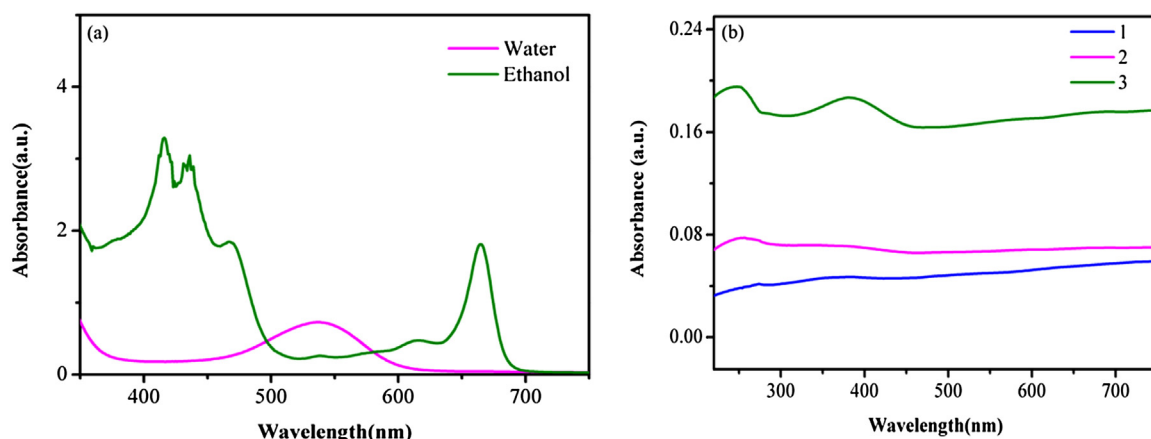


Fig. 2. (a) UV-vis absorption spectra of dyes extracted from red amaranth leaves (b) The absorption spectra of (1) bare TiO_2 (2) TiO_2 -betalain dye (3) TiO_2 -chlorophyll dye.

extracted with ethanol has adsorbed better on the surface of TiO_2 photoanode compared to betalain dye extracted with distilled water.

4.2. FTIR studies of dye and dye adsorbed TiO_2

The molecular structure of chlorophyll and betalain is shown in Fig. 3. The structure of the isolated dyes was confirmed by its FTIR spectra (Fig. 4). The chlorophyll dye exhibits OH group stretching vibrations at 3438 cm^{-1} , C—H vibrations of CH_3 and CH_2 groups at 2904 cm^{-1} and 2848 cm^{-1} , C=O stretching vibrations at 1644 cm^{-1} , C—O vibrations at 1045 cm^{-1} . The betalain dye exhibits OH and NH stretching vibrations indicating H bonding at 3423 cm^{-1} , CH stretching vibrations at 2930 cm^{-1} and 2835 cm^{-1} due to CH groups, C=N stretching vibrations at 2362 cm^{-1} , C=O stretching vibrations at 1638 cm^{-1} , C—N—C bending vibrations at 1375 cm^{-1} , C—O stretching vibrations 1057 cm^{-1} , C—H bending vibrations at 591 cm^{-1} .

The adsorption of dyes onto the surface of TiO_2 was studied by comparing FTIR of bare TiO_2 , dye and dye adsorbed TiO_2 (Fig. 4). The bare TiO_2 has peaks at 720 cm^{-1} corresponding to O—Ti—O bonding in anatase titania and peaks at 1637 cm^{-1} and 3429 cm^{-1} corresponding to hydroxyl groups [28]. The peak broadening of dye

adsorbed TiO_2 around 1014 cm^{-1} and 720 cm^{-1} indicates attachment of the dyes onto TiO_2 surface. Confirmation of peaks corresponding to dyes on dye adsorbed TiO_2 show the suitability of these dyes as photo sensitizers for DSSC.

4.3. Photoelectrical parameters of DSSC

The J-V (current density-voltage) curves were obtained from natural dye sensitized DSSC and are shown in Fig. 5. The cell parameters obtained are tabulated and shown in Table 1. Chlorophyll dye (ethanol extracted) sensitized cell had an open circuit voltage of 0.582 V and short circuit current density of 1.31 mA/cm^2 compared to 0.486 V and 0.87 mA/cm^2 of betalain dye (water extracted). Chlorophyll based natural dye showed better efficiency of 0.53% and fill factor of 69.7% compared to 0.23% and 53.4% of betalain based dye. This could be due to the stronger and broader absorbance of the chlorophyll dye in the visible region and its better attachment on to TiO_2 surface.

4.4. Electrochemical impedance spectra of DSSC

The steady state I-V characteristics of DSSC provide the information about the performance parameters of the cell namely

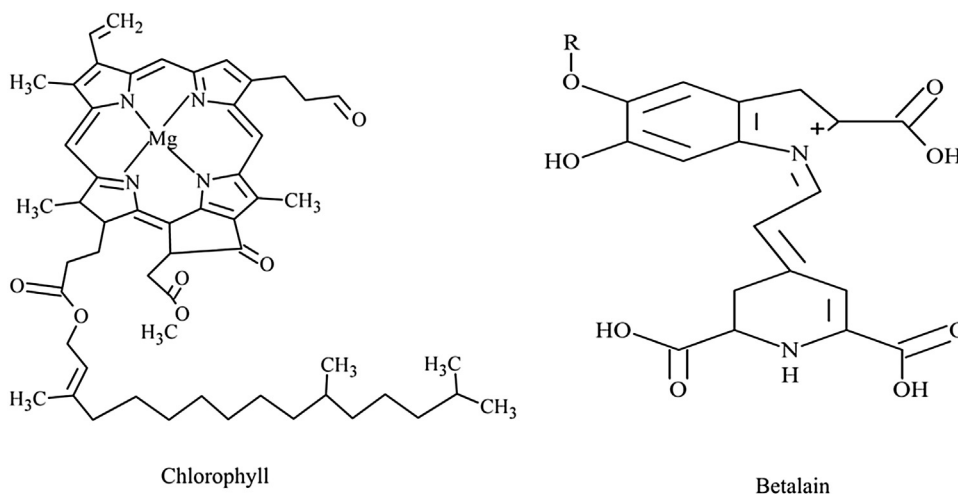


Fig. 3. Structure of Chlorophyll and Betalain.

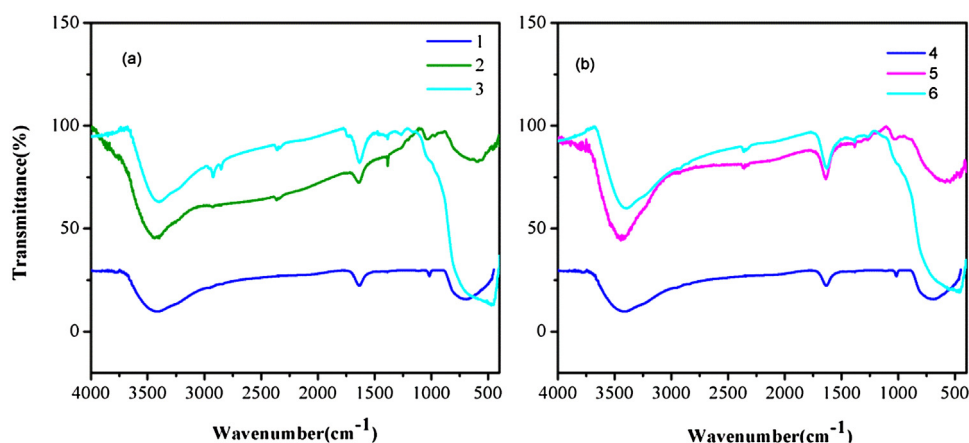


Fig. 4. (a) The FTIR spectra of (1) bare TiO₂ (2) chlorophyll dye (3) TiO₂-chlorophyll dye and (b) the FTIR spectra of (4) bare TiO₂ (5) betalain dye (6) TiO₂-betalain dye.

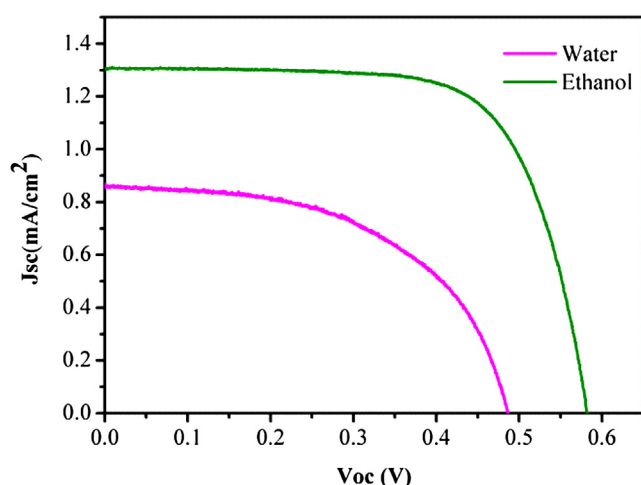


Fig. 5. Current-voltage characteristics of natural dye sensitized DSSC.

J_{sc} (short circuit current), V_{oc} (open circuit voltage), FF (fill factor) and η (efficiency) but are unable to explain the individual processes behind it. EIS (electrochemical impedance spectroscopy) is a dynamic technique which has the ability to separate various

Table 1

Cell parameters of DSSC.

Solvent	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	η (%)
Water	0.87	0.486	53.4	0.23
Ethanol	1.31	0.582	69.7	0.53

complex processes occurring at the various interfaces of the DSSC [29]. This method is employed to study the kinetics of electrochemical and photoelectrochemical processes in DSSC by measuring the current response to ac voltage as a function of frequency.

The Nyquist plot shown in Fig. 6a features three semicircles that are in order of decreasing frequency corresponding to counter electrode-electrolyte interface resistance (R_1), the electron transfer at the oxide/electrolyte interface (R_2) and Warburg resistance related to diffusion of redox couple (R_3). R_s is the sheet resistance of the FTO substrate. The first two semicircles correspond to high frequency and middle frequency regions and last semicircle corresponds to low frequency region. The impedance of each interface is plotted after fitting the EIS data with software in terms of an equivalent circuit. EIS parameters are listed in Table 2.

The R_1 , R_2 and R_3 values are different for the different dyes which could be due to the difference in binding between the dye molecules and TiO₂. A higher value of R_2 in both dyes indicates lower probability of back recombination of electrons which is a

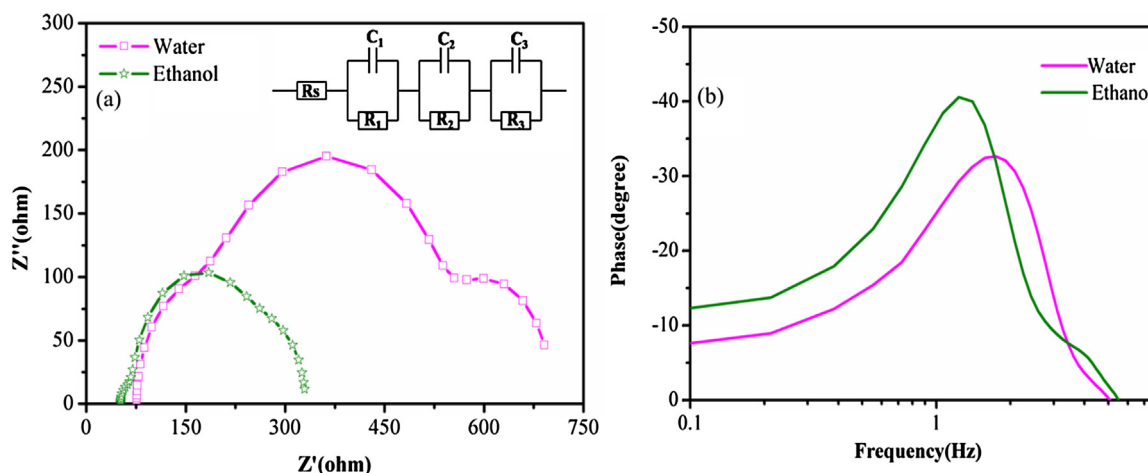


Fig. 6. (a) Electrochemical impedance spectra and (b) Bode phase plot of DSSC sensitized with natural dyes extracted with water (betalain) and ethanol (chlorophyll).

Table 2
EIS parameters of DSSC.

Solvent	$R_1(\Omega)$	$R_2(\Omega)$	$R_3(\Omega)$
Water	83	391	136
Ethanol	26	228	33

decisive factor in determining cell efficiency. The high value of R_1 and R_3 can cause a decrease in J_{sc} leading to lesser efficiency in the case of natural dye betalain extracted from water. The Impedance curves (Fig. 6a) obtained was in agreement with the efficiencies obtained from the I–V curves (Fig. 5). Fig. 6b shows the bode phase plot of the cell sensitized with dye extracted with water and ethanol in the range low frequency of 0.1–10 Hz corresponding to effective lifetimes of electrons on the surface of TiO_2 photoanode. The peak frequencies obtained from the graph are inversely proportional to lifetimes of electrons [30,31]. The peak frequency of dye extracted from ethanol is 1.26 Hz and that of water extracted dye is 1.70 Hz. This leads to better electron lifetime of ethanol extracted chlorophyll dye compared to water extracted betalain dye leading to better efficiency of DSSC. The bode plot results are in agreement with the I–V experimental data.

4.5. Stability studies

In spite of their numerous advantages, DSSC faces stability problem which is a vital parameter in solar cells. In this work we have compared the efficiency of solar cells after two hours of their assembly as shown in Fig. 7 and Table 3.

The DSSC assembled using chlorophyll dyes extracted from ethanol and betalain dyes extracted from water show poor stability after two hours. The fast degradation could be due to a highly volatile electrolyte which can quench the dye and corrode the counter electrode. Improving attachment of the dyes onto TiO_2 by introducing carboxyl groups and the use of solid/gel electrolyte can also address the problem to a great extent.

5. Conclusions

This study reports the extraction of two different coloured dyes from the red amaranth leaf as photosensitizers for DSSC. The investigations conducted indicate that the dyes extracted using water and ethanol are respectively betalain and chlorophyll. The chlorophyll dye showed a better efficiency of 0.53% with a fill factor of 69.7% compared to betalain dye with an efficiency of 0.23% and a

Table 3
Stability study of DSSC for two hour time.

Solvent	Time (hrs.)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
Water	0	0.870	0.486	53.4	0.230
	2	0.026	0.170	32.9	0.001
Ethanol	0	1.310	0.582	69.7	0.530
	2	0.033	0.411	32.5	0.004

fill factor of 53.4%. The V_{oc} of 0.582 V of chlorophyll dye is comparable to the V_{oc} of high efficiency chlorophyll dyes reported in literature. The sensitization of TiO_2 surface can be improved by replacing alkyl groups by carboxylic groups in chlorophyll dye. Similarly the V_{oc} of betalain dye of 0.486 V is also comparable to betalain sensitized DSSC reported in literature. The acidification of water extract could lead to better extraction and hence better efficiency of the betalain dye. Though both natural dyes exhibit good photosensitizing properties, efficiencies can be further improved by optimizing parameters like dye extraction, dye loading time, photoanode, pretreatment etc. Further stability needs to be improved and alternate sources of extraction needs to be explored for the large scale commercial production of natural dyes. Overall the leaf of red amaranth shows great promise as a potential source of natural dyes in future.

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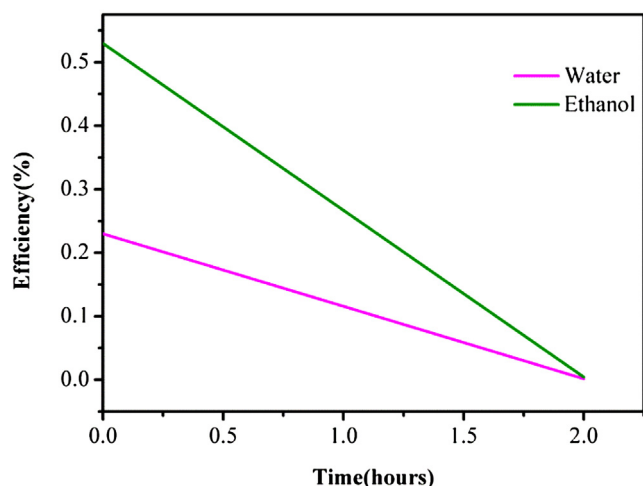


Fig. 7. Stability curve based on efficiency of DSSC after 2 h.

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