INFLUENCE OF THE DOPANT THIOUREA ON FTIR AND UV SPECTRAL ANALYSIS OF PVA-Li2SO4 SOILD POLYMER ELECTROLYTE

A PROJECT REPORT

Submitted by

K. UMAMAHESWARI

in partial fulfillment for the award of the degree of

MASTER OF SCIENCE IN PHYSICS

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MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI - 627 012

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SRI PARAMAKALYANI COLLEGE
ALWARKURICHI-627412

BONAFIDE CERTIFICATE

This is to certify that the project entitled **‘‘Influence of the dopant thiourea on FTIR and UV spectral analysis of PVA-Li2SO4 soild polymer electolyte’’** is a record of original work done by K. UMAMAHESHWARI under the guidance and supervision of **DR. A. ANNALAKSHMI MSc., M.Phil., Ph.D.** in partial fulfilment for the award of **Degree of Master Science** in Physics at the Department of Physics, Sri Paramakalyani College, Alwarkurichi, during the period of 2023-2024.

DR. S. MEENAKSHI SUNDAR	**DR. A. ANNALAKSHMI**
MSc., M.Phil., Ph.D.	**MSc., M.Phil., Ph.D.**
(HOD)	**(SUPERVISOR)**

Submitted for the project viva-voice Examination held on 03.05.2024.

External Examiner	**Internal Examiner**

1)

2)

DECLARATION

I hereby declare that the investigation reported in this dissertation entitled**“INFLUENCE OF THE DOPANT THIOUREA ON FTIR AND UV SPECTRAL ANALYSIS OF PVA-Li2SO4 SOILD POLYMER ELECTROLYTE”** is submitted to the Manonmaniam Sundaranar University, Tirunelveli in partial fulfilment of the requirement for the award of the degree of Master of Science in Physics is a record of original work carried out by me at Sri Paramakalyani College, Alwarkurichi under the supervision of **Dr. A. ANNALAKSHMI, M.Sc. M.Phil., Ph.D**., Assistant Professor of Physics, Sri Paramakalyani College, Alwarkurichi. I also declare that the context of this work has not formed the basis of any Degree, Diploma or similar type of any University or Institution.

Name	Reg.no	Signature
K. UMAMAHESWARI	**20221232521124**	

Place: Alwarkurichi

Date:03.05.2024

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ABSTRACT

The polymer Polyvinyl alcohol (PVA) doped with Lithium Sulphate and Thiourea (CH_4N_2S) salt membranes were prepared by solution cast technique. The prepared polymer films are characterized by FTIR and the complexion of polymer electrolyte films has been confirmed via FTIR studies. The linear optical parameters such as transmission, refractive index, extinction coefficient, reflectance and energy gap for the composition of Soild Polymer Electrolytes (SPE) based on polymer PVA and Li2SO4 and PVA-Li2SO4 doped with CH4N2S were studied using UV-visible spectroscopy.

Key words : PVA, Li2SO4,CH_4N_2S,Solution casting method, FTIR, UV, Solid Polymer electrolyte film, transmittance, refractive index, optical extinction coefficient.

CONTENTS

CHAPTER – I:

CHAPTER – II:

CHAPTER – III:

CHAPTER – IV: RESULTS AND DISCUSSION

LIST OF FIGURES

INTRODUCTION

1.1 POLYMER

Ongoing research in polymer science focusing on new synthesis methods, properties enhancement, applications as Innovations in polymer processing techniques, including injection molding, extrusion, additive manufacturing (3D printing) and controlled/living polymerization methods like atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization. Polymer from variety of materials and existing in the market as molded article which are playing an important role in our day to day life. They are used in rubber as elastomers, plastic, resins, adhesives, paints varnishes, propeller shafts, electrical equipment, aircrafts, automobile parts, electrical ins Polymers play a crucial role in biomedical applications such as tissue engineering, drug delivery, medical devices, and regenerative medicine. Current research focuses on developing biocompatible and bioresorbable polymers with tailored properties to meet the specific requirements of medical applications, including controlled release of therapeutic agents and promoting tissue regeneration. Current research aims to optimize the dispersion of nanoparticles within polymer matrices and understand their effects on the overall material.

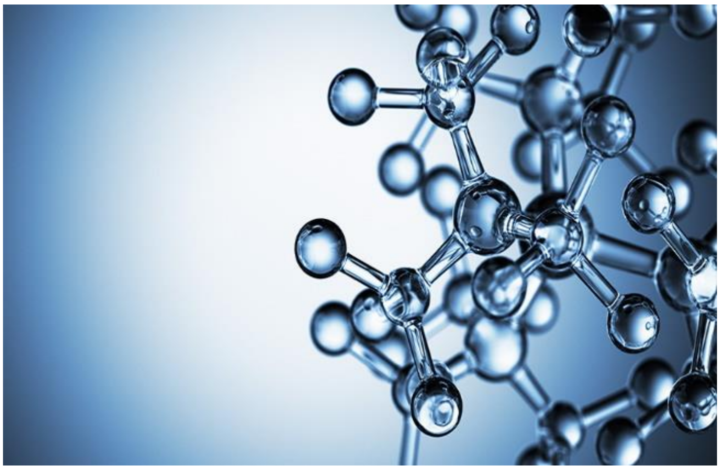


Fig 1.1 Polymer

1.2 POLYMER ELECTROLYTE

A polymer with an ionic type of charge transport is known as polymer electrolytes. Polymer electrolytes have the properties of both polymers and electrolytes. They are typically solid-state electrolytes consists of a polymer matrix, such as polyethylene oxide (PEO), and a salt that dissociates into ions, providing conductivity. These materials have gained significant attention in recent years due to their potential applications in various fields, including energy storage devices like lithium-ion batteries and supercapacitors. polymer electrolytes are solid at room temperature, which offers several advantages, including improved safety and stability. Polymer electrolytes can be tailored to be compatible with various electrode materials, making them versatile for use in different types of batteries and electrochemical cells. Polymer electrolytes are finding applications in lithium-ion batteries, solid-state lithium batteries, fuel cells, electrochromic devices, sensors, and more. Their versatility and unique properties make them promising candidates for next-generation energy storage and conversion technology properties.

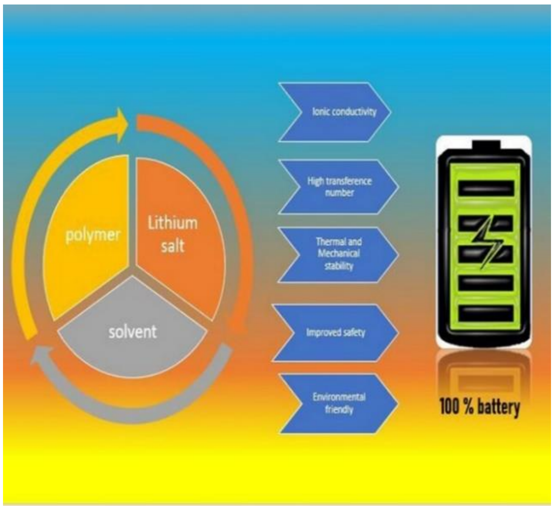


fig 1.2 Polymer electrolytes

Properties

- Transparency
- Solvent-free
- Light Weight
- Flexible
- High ionic conductivity
- Easy processability
- Wide electrochemical
- Good reliability

Advantages

- Prevent leakage
- No internal shorting
- No production of harmful gases
- Eliminate the use of Corrosive solvent
- Low cost
- Non-toxicity

- Provides easy path of ion motion

Applications

- Solid state batteries
- Solar cells
- Fuel cells
- Dye-sensitized solar cells
- Electro capacitors
- Actuators
- Thermoelectric generators
- Electric vehicles
- Thin credit cards
- Mobile cellular
- Laptop computers
-

1.3Classification of Polymer Electrolytes

We have classified the Polymer electrolytes based on their sources and origins, meaning that there are two types of Polymer electrolytes. (a) Natural and (b) Synthetic. Some Natural Bio- polymer electrolytes that are widely used in research are chitosan, starch, and cellulose materials. Bio-polymer electrolytes can also be categorized into five different types based on their physical state and composition: (a) gel biopolymer electrolytes, (b) hydro gel biopolymer electrolytes, (c) solid biopolymer electrolytes, (d) blend biopolymer electrolytes and (e) composite polymer electrolytes.

The applications of biopolymers earlier were focused on three areas: medical, agricultural, and consumer goods packaging. The storage, production, and distribution of energy are among the main concerns of modern industry and society. Space development, the creation of new types of memory, and new computer architecture along with biomedical devices and micro sensors are all areas that could benefit from the development of solid-state ionic conductors .

1.3.1 Natural polymers

Natural polymers are polymers produced by living organisms. The main advantage of these polymers is biodegradable, recyclable, and display natural biogeochemical cycle. Natural polymers have many advantages over synthetic polymers because of many reasons including their natural resources, being inexpensive, and having the capability of modifying chemically. Proteins, starch, and cellulose these are the examples of natural polymer.

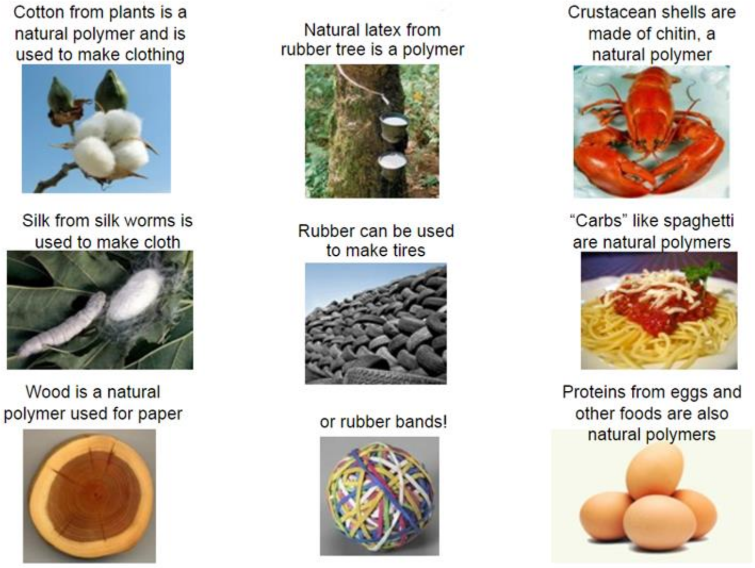


Fig 1.3 Natural polymer

1.3.2 Synthetic polymers

Synthetic polymers are polymers made from human and not existing in nature. When these synthetic products are made from natural building blocks, they are called Bio (derived) – polymers. Most of the synthetic polymers are hard to degrade naturally by biological processes. Polyethylene, Polylactic acid, Polypropylene, and Polyhydroxy Butyrate these are some examples of synthetic polymers.

Polyethylene (PE): Used in plastic bags, bottles, and toys.
Polypropylene (PP): Commonly used in packaging, textiles, and automotive parts.
Polyvinyl chloride (PVC): Used in pipes, window frames, and electrical insulation.
Polystyrene (PS): Used in packaging materials, disposable cutlery, and insulation.
Polyester (PE): Used in clothing, upholstery, and bottles.
Nylon: Used in textiles, carpets, and ropes.

Fig 1.4 synthetic polymer

1.3.3 Gel polymer electrolytes (GPE)

Gel polymer electrolytes are prepared by incorporating huge amount of organic liquid solvent or liquid plasticizer. Most energy gels are made of quick-digesting carbohydrate source, often in the form of maltodextrin, sucrose, fructose, or glucose. Somehow have high ionic conductivity of 10−3 S/cm at room temperature. The gel system framed by means of physical cross-connecting is called an entangled network. (GPEs) are applied onto electrochemical devices such as dye–sensitized solar cells, electrical super-capacitors, actuators, light– emitting electrochemical cells and ion batteries.

1.3.4 SOLID POLYMER ELECTROLYTE

solid polymer electrolyte (SPE) is defined as a solvent -free solution in a polymer host material that conducts ions through the polymer chains. compared to ISEs, SPEs are much easier to process, generally by solution casting, making them greatly compatible with large-scale manufacturing processes. SPEs comprising polymer matrices and Li salts exhibit good flexibility, superior processability and compatibility with electrodes. SPEs have advantages of improved safety, higher mechanical strength & potentially higher energy density. They are used in various electrochemical devices such as batteries, fuel cells and super capacitors.

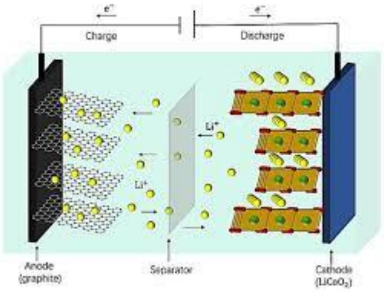


Fig:1.5 Electrolyte cell

Composite Polymer Electrolyte

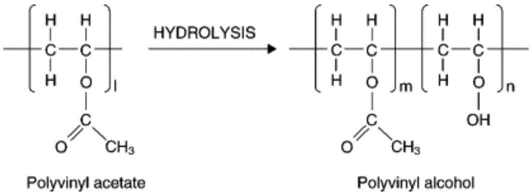
Composite polymer electrolytes (CPEs) are advanced materials used in various electrochemical devices, including lithium-ion batteries, fuel cells, and supercapacitors. These materials combine the properties of a polymer matrix with inorganic or organic fillers to enhance the overall performance and safety of the electrolyte. Research and development in the field of composite polymer electrolytes are ongoing to overcome these challenges and further improve the performance and reliability of electrochemical devices.

Blend Polymer Electrolyte

(BPE) is a type of solid-state electrolyte that combines two or more different polymers to achieve a synergistic effect and improve the overall performance of the electrolyte. Five distinct techniques are utilized for the preparation of polymer blends: melt mixing, solution blending, latex mixing, partial block or graft copolymerization, and preparation of interpenetrating polymer networks (IPN). BPEs can be employed in various electrochemical devices such as fuel cells, sensors, and actuators

1.4Polyvinyl Alcohol (PVA)

Polyvinyl alcohol (PVOH, PVA, or PVAl) is a water-soluble synthetic polymer. It has the idealized formula $[CH_2CH(OH)]_n$. It is used in papermaking, textile warp sizing, as a thickener and emulsion stabilizer in polyvinyl acetate (PVAc) adhesive formulations, in a variety of coatings, and 3D printing.



Polyvinyl alcohol (PVA) is a vinyl polymer joined by only carbon–carbon linkages. The linkage is the same as those of typical plastics such as polyethylene, polypropylene, and polystyrene, and of water-soluble polymers such as polyacrylamide and polyacrylic acid. Among the vinyl polymers produced industrially, PVA is the only one known to be mineralized by micro-organisms. PVA is water soluble and biodegradable; hence it is used to make water-soluble and biodegradable carriers, which may be useful in the manufacture of delivery systems for chemicals such as fertilizers, pesticides, and herbicides.

Polyvinyl alcohol (PVOH) is a water-soluble polymer and its solubility greatly depends on the hydrolysed percentage, i.e., percentage of hydrolysis of polyvinyl acetate. PVOH is fully biodegradable. PVOH is produced by no less than 20 companies worldwide; the renowned producers are Kuraray, Denka, Sekisui, Syntheses and many more. The water-soluble characteristic of PVOH makes it extensively used as a binder, emulsifier and thickening agent for a wide range of products such as paper, remoisten able adhesives, textile finish, paper surface treatment as well as cosmetics, food and pharmaceutical products. For packaging purposes, PVOH is suitable for food, drugs and cosmetics, since it has outstanding barrier properties to gases such as oxygen, nitrogen and carbon dioxide.

Fig 1.6 Polyvinyl Alcohol PVA resin

1.4.1 PROPERTIES OF POLYVINYL ALCOHOL(PVA)

1) PVA is highly soluble in water, forming a clear and viscous solution.

2) PVA can be cast into thin films, which are flexible, transparent, and have good tensile strength.
3) These solutions have high viscosity, which can be adjusted by changing the degree of polymerization or by blending with other polymers or plasticizers.

1.4.2 USES

- PVA is used in a variety of medical applications because of its biocompatibility, low tendency for protein adhesion, and low toxicity.
- Specific uses include cartilage replacements, contact lenses as a thickener in ointments and lotions, and as a binder in tablets. Medically it may also use as the embolic agent in a Uterine Fibroid Embolectomy (UFE).
- It is possible to create drug-loaded tablets with modified drug-release characteristics where PVA is used as a binder substance.
- Polyvinyl alcohol is used as an aid in **suspension polymerizations.** Its largest application in China is its use as a protective colloid to make PVA dispersions.
- In Japan its major use is the production of **Vinylene** fibre. This fibre is also manufactured in **North Korea** for self-sufficiency reasons, because no oil is required to produce it. Another application is photographic film.
- PVA-based polymers are used widely in additive manufacturing (i.e) 3D printed oral dosage forms demonstrate great potential in the pharmaceutical industry.

1.5 LITHIUM SULPHATE

(*Lithium sulphate* is a white inorganic salt with the formula Li_2SO_4. It is the lithium salt of sulfuric acid.Lithium sulfate is used **to treat bipolar disorder** (lithium pharmacology). Lithium sulfate is researched as a potential component of ion conducting glasses. Transparent conducting film is a highly investigated topic as they are used in applications such as solar panels and the potential for a new class of battery

Fig 1.7 Lithium sulphate

Physical properties

Lithium sulphate is soluble in water, though it does not follow the usual trend of increasing solubility of most salts with temperature. To the contrary, its solubility in water decreases with increasing temperature, as its dissolution is an exothermic process. This relatively unusual property, also called retrograde solubility, is shared with few inorganic compounds, such as calcium hydroxide (portlandite, an important mineral phase of hydrated cement paste), the calcium sulphate and lanthanoid sulphate whose dissolution reactions are also exothermic. The retrograde solubility is common for gases dissolution in water, but less frequently encountered for the dissolution of solids. Calcium carbonate also exhibits a retrograde solubility, but it also depends on the behaviour of CO_2 dissolution in the calcium-carbonate equilibria.

Lithium is used for bipolar disorder.

Lithium sulphate is researched as a potential component of ion conducting glasses. Transparent conducting film is a highly investigated topic as they are used in applications such as solar panels and the potential for a new class of battery. In these applications, it is important to have a high lithium content; the more commonly known binary lithium borate ($Li_2O \cdot B_2O_3$) is difficult to obtain with high lithium concentrations and difficult to keep as it is hygroscopic. With the addition of lithium sulphate into the system, an easily produced, stable, high lithium concentration glass is able to be formed. Most of the current transparent ionic conducting films are made of organic plastics, and it would be ideal if an inexpensive stable inorganic glass could be developed

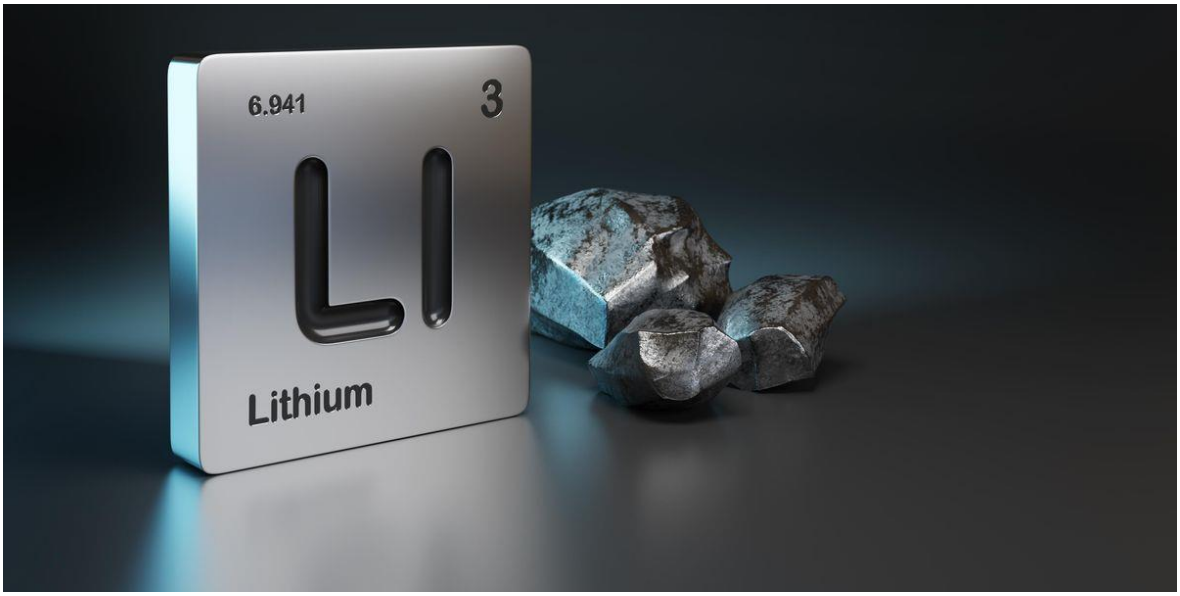


Fig 1.8 Lithium

Lithium-ion Batteries: Lithium sulphate is a key precursor in the production of lithium-ion batteries, which are used in numerous electronic devices, including smartphones, laptops, tablets, and electric vehicles. It serves as a source of lithium for the cathode material in these batteries.

1.**Ceramics Industry**: Lithium sulphate is used in the ceramics industry as a flux, which helps lower the melting point of materials during the firing process. It improves the strength and durability of ceramic products.

2.**Chemical Synthesis**: It is utilized as a catalyst or reagent in certain chemical reactions, particularly in organic synthesis.

3.Pharmaceuticals: While lithium carbonate is more commonly used in the treatment of bipolar disorder, lithium sulphate may also have pharmaceutical applications, though these are less common.

4.**Research and Development**: Lithium sulphate is sometimes used in research and development laboratories for various experimental purposes, particularly in studies related to battery technology and electrochemistry.

5.**Drying Agent**: It can be used as a drying agent for certain organic solvents due to its hygroscopic nature, which means it readily absorbs moisture from the surroundings.

Chapter 2

2.1 Literature Review

[1]**Ihsan Ullah, Abdur Rab, Abdur Rahim, Muhammad Tariq, Ayaz Hassan, Tawfik.A.Saleh, jehangeer khan and Hizb Ullah Khan** et al have studied encompasses the evaluation of mechanical, and electrical properties of PVA-MWCNT-based thin film composites (TFC) in the presence of Li_2SO_4. The PVA-MWCNT-based TFC is obtained using solvent casting technique while the characterization is carried out through thermogravimetric analysis (TGA), Fourier transform infrared (FTIR), X-ray diffractometry (XRD), and scanning electron microscopy (SEM) techniques. Tensile testing techniques is used for measuring mechanical properties such as elasticity, tensile strength, elongation, hardness and fracture toughness of the PVA-MWCNT-based TFC. The dielectric constant, dielectric loss and dielectric tangent loss properties of the PVA-MWCNT-based TFC also enhanced with the increase in lithium salts.

[2]Siyeon Lee, Heejin Koo, Hong Suk Kang, Keun-Hwan Oh, Kwan Woo Nam et al have investigated the Lithium-ion batteries (LIBs) have become indispensable energy-storage devices for various applications, ranging from portable electronics to electric vehicles and renewable energy systems. In this review paper, various binder options that can align with the evolving landscape of environmentally friendly and sustainable battery production, considering the current emphasis on battery performance enhancement

[3] Randhir Singh, Chandra Charu Tripathi have reported the synthesis of colloidal graphene via electrochemical exfoliation of graphite in Li_2SO_4 aqueous solution. In this electrochemical exfoliation method, high quality graphene was prepared within short time of 1.5 hr. This electrochemical exfoliation mechanism suggests that SO_4^{2-} and H_2O are intercalated into graphite sheets and as a result single and few-layer graphene sheets are produced with SO_2 and O_2 gases. The electrochemically exfoliated colloidal graphene was stable in NMP solvent for more than 2 weeks. The colloidal graphene was used for preparing the conducting graphene electrodes by brush painting on A4 paper for flexible supercapacitor applications. Our method exhibits potential for large-scale synthesis of good-quality graphene and its applications in flexible energy storage devices such as supercapacitors.

[4] Gulfam Nasar, Mohammad Saleem Khan, Uzma Khalil et al have prepared the Polymer composites are among the most rapidly growing research fields in material science. Polymer composites are adding a great deal of material that is more durable and useful as compared to the conventional material. Properties of composite materials greatly depend on the nature, proportion and compatibility of the components of the composite materials. In this paper we have conducted an analysis of the XRD study of polymer composites of Poly (vinyl alcohol) with inorganic salts such as sodium sulphate and lithium sulphate

[5]Riza Asmaa Saari, Ryota Maeno, Warinda Marujiwat, Muhammad Shahrulnizam Nasri, Kazuazki Matsumura Yamaguchi et al investigated the effect of lithium sulphate (Li2SO4) on the structure and properties of poly (vinyl alcohol) (PVA) fibres obtained by wet-spinning was studied. The tensile modulus and strength of a PVA fibre were greatly enhanced irrespective of the post-spinning hot-stretching process. The high degree of molecular orientation arose from the reduction in the crystalline and hydrogen bonding between PVA chains in the solution resulting from the addition of Li2SO4, which was revealed by the rheological properties of aqueous solutions. The LiBr was removed from the fibre during the spinning process in the coagulation bath, and during the washing process. This ensures strong hydrogen bonding in the fibres, and results in excellent mechanical properties.

[6]Rachna Mishra a, N. Baskaran b, P.A. Ramakrishnan b, K.J. Rao et al have prepared the thin film of lithium salt containing polymer composites were prepared from LiI, Li_2SO_4 and Li_3PO_4 PEO, PVA and PEO-PVA (50:50) blends by solution casting method, for various salt concentration (10, 15, 20 mole%). The conductivity and dielectric measurements were carried out on these films as a function of frequency at various temperatures. The highest conductivity was observed in LiI-polymer composites. The variation of conductivity with salt concentration has been explained on the basis of percolation path. In the case of Li_2SO_4 and Li_3PO_4 composites, the variation of conductivity with salt composition is found to depend more on the nature of coordination of Li^+ ions in the composites rather than the mole % of salt itself. AC conductivity and dielectric relaxation behaviour of these composites were also studied and the results are discussed.

[7]G. Hirankumar, N. Mehta et al investigated to date high ionic conducting polymer electrolytes are of great interest because of their potential applications in various electrochemical devices such as batteries, fuel cells, solar cells and super capacitors etc., as electrolytes. Ion conduction through polymer electrolytes can occur mostly in amorphous environment exists above their glass transition temperature (Tg). In order to improve ionic conductivity, many approaches such as addition of plasticizer, blending of polymers, nanocomposite have been employed. This paper reviews the influence of different plasticizers/additives on the ion transport mechanism of Poly (vinyl alcohol) (PVA)-LiClO 4 polymer electrolytes since poly vinyl alcohol is a semi crystalline, synthetic biodegradable polymer and lithium perchlorate is one of the most moisture resistant lithium salts. This review also reveals the relation between dynamical disorder in polymer electrolyte with ionic conductivity.

[8]Siti Rohana Majid, Rebar T.Abdulwahid, Mohd F.Z.Kadir, and Ranjdar M.Abdullah et al have prepared the Plasticized lithium-ion-based-conducting polymer blend electrolytes based on poly (vinyl alcohol) (PVA)chitosan (CS) polymer was prepared using a solution cast technique. The conductivity of the polymer electrolyte system was found to be 8.457×10^{-4} S/cm, a critical factor for electrochemical device applications. It is indicated that the number density (n), diffusion coefficient (D), and mobility (μ) of ions are increased with the concentration of glycerol. High values of dielectric constant and dielectric loss were observed at low frequency region. A correlation was found between the dielectric constant and DC conductivity. The achieved transference number of ions (t_{ion}) and electrons (t_e) for the highest conducting plasticized sample were determined to be 0.989 and 0.011, respectively. The electrochemical stability for the highest conducting sample was 1.94 V, indicated by linear sweep voltammetry (LSV). The cyclic voltammetry (CV) response displayed no redox reaction peaks through its entire potential range. Through the constructing electric double-layer capacitor, the energy storage capacity of the highest conducting sample was investigated. All decisive parameters of the EDLC were determined. At the first cycle, the specific capacitance, internal resistance, energy density, and power density were found to be 130 F/g, 80 Ω, 14.5 Weight/kg, and 1100 W/kg, respectively.

[9]Xing Zhang, Liangilang Wang, Jing Peng, Pengfei Cao, Xiaosheng Cai, Jiuqiang Li,Maolin Zhai et al prepared A novel high-performance flexible gel polymer electrolyte (FGPE) for supercapacitors is prepared by a freeze-drying method. In the presence of 1-butyl-3-methylimidazolium chloride (BMIMCl) ionic liquid, Li_2SO_4 can easily be added into poly (vinyl alcohol) (PVA) aqueous solution over a large concentration range. The ionic conductivity and charge–discharge behaviours of the resultant FGPE are not affected by bending up to 180°. The flexible supercapacitor device shows only a small capacitance loss of 18% after 1000 cycles of 135° bending.

[10]K.Sundaramahalingam, M.Muthuvinayagam, N.Nallamuthu, D.Vanitha and M.Vahini et al investigated the Lithium ion conducting solid polymer blend electrolytes (SPBE) are prepared using the host polymers poly [vinyl alcohol] (PVA), poly [vinyl pyrrolidone] (PVP) and the lithium acetate. The complexation between the polymers and salt is confirmed by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).The dielectric and loss tangent analysis is also carried out for prepared polymer electrolyte and the higher-conductivity sample at different temperatures. The transference numbers of polymer electrolytes are calculated by Wagner’s polarizing technique and also confirmed by Bruce–Vincent technique.

[11]Y.S. Zhu, X.J. Wang Y.Y.Hou, X.W. Gao, L.L. Liu, Y.P.Wu, M. Shimizu et al have prepared a novel single-ion conducting polymer electrolyte, lithium polyvinyl alcohol oxalate borate (LiPVAOB), from the reaction of poly(vinyl alcohol) (PVA) with different molar ratio of boric acid, oxalic acid and lithium carbonate was prepared. The prepared materials were characterized by Fourier transformation infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetry (TG), differential thermal analysis (DTA), electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry. Ionic conductivity of these polymer electrolytes from adding an assistant (about 20 wt.% propylene carbonate) is dependent on molar ratio of the reactants and can up to 6.11×10^{-6} S cm^{-1} at ambient temperature. Their electrochemical window can be stable up to 7 V (*vs*. Li^+/Li), which is of great attraction for high voltage lithium ion batteries with high energy density.

Chapter III

EXPERIMENTAL METHODS AND CHARACTERIZATION TECHNIQUES

METHODS AND METHODOLOGY

3.1. Materials and methods:

Polyvinyl alcohol (PVA), Sodium nitrate (Li2SO4), and Thiourea (CH4N2S) are used as raw materials. (PVA-Li2SO4-CH4N2S), (PVA-Li2SO4), (PVA-CH4N2S) composite films were prepared by using solution casting method. (PVA) was used as the polymer, (Li2SO4/CH4N2S) as the doping salts and double distilled water as a solvent.

3.2 Solution casting Method

Polymer electrolyte films are generally obtained by simple casting procedure. The solution casting method is a popular technique used to prepare thin films of polymers, composites, and other materials. This method is mainly carried out using magnetic stirrer.

Figure 1.8: Magnetic stirrer

It is widely employed in various industries, including electronics, biomedical, and coatings, among other methods.

Synthesis of the solution casting method is prepared by the following process,

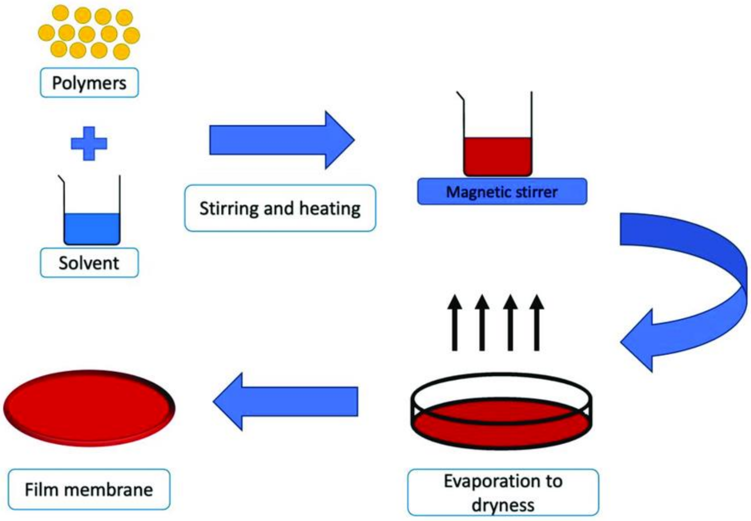


Figure 1. 9 Schematic diagram of solution casting method

3.2.1 Preparation of synthetic polymer electrolyte (PVA-Li2SO4)

(Figure 2.0: **Preparation of PVA-Li2SO4)**

/

Synthetic polymer (PVA –Li2SO4) salt complex Membrane was prepared by solution casting technique using Double Distilled water (20 ml) as a solvent. The composition is (PVA-70 M.wt.%: Li2SO4 - 30 M. wt.%).

Appropriate quantity of PVA was dissolved in double distilled water and stirred in a magnetic stirrer continuously until the solution became transparent. Then the corresponding amount of Li2SO4 was dissolved in the solution of PVA.

This mixture was stirred continuously for 3-4 hours to obtain a homogeneous mixture. Then poured it into polypropylene petri dishes and slowly dried at room temperature for 48 hours. The obtained blend polymer film is detached from dishes for further studies.

Figure 2.1: PVA-Li2SO4

3.2.2 Preparation of (PVA-Li2SO4) doped with CH4N2S.

Biodegradable polymer electrolyte based on the composition of (PVA-Li2SO4) with dopant (CH4N2S) were synthesized by solution Casting technique using Double Distilled water (50 ml) as a solvent.

The polymer-salt complex membrane (PVA-Li2SO4-CH4N2S) have been prepared by dissolving 2 g of polyvinyl alcohol (PVA) and 20 mg of sodium nitrate (Li2SO4) in 50 ml of Double distilled water under vigorous stirring in a magnetic stirrer at 60℃ for 2 h. Afterward, a gelatinous, clear solution appeared, and under vigorous stirring, 10 mg of Thiourea (CH4N2S) were added into the (PVA-Li2SO4) mixed solution. This mixture was stirred continuously for 3 – 4 hours to obtain a homogeneous solution. The obtained solution was casted in Polypropylene dishes and slowly dried at room temperature for 4 days. Finally, the Transparent, free-standing film was obtained.

Figure 2.2(PVA-Li2SO4-CH4N2S)

3.3 Characterization Technique

- **FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR)**
- **ULTRA VIOLET-VISIBLE SPECTROCOPY (UV-vis)**

3.3.1 FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR stands for FOURIER TRANSFORM INFRARED SPECTROSCOPY. It's a powerful analytical technique used to identify and characterize chemical compounds based on their absorption of infrared radiation. it is an efficient tool to study the local structural changes in polymer samples through frequency shifts, changes in band shapes and intensities.

Figure 2.4: FTIR instrument Photograph

PRINCIPLE OF FTIR SPECTROMETER

The basic principle of IR spectroscopy is the excitation of polar bonds of molecules by absorption of IR region of the electromagnetic spectrum. Absorption occurs primarily between the atoms of hydrogen, carbon, oxygen and nitrogen (for example, C-H, C-O, C=C). It causes molecular vibrations with a life time of the order of nano to micro second after excitation.

The frequency at which atoms are excited and start to vibrate depends on the type of vibrating atoms, bond strength and structure of the molecules.

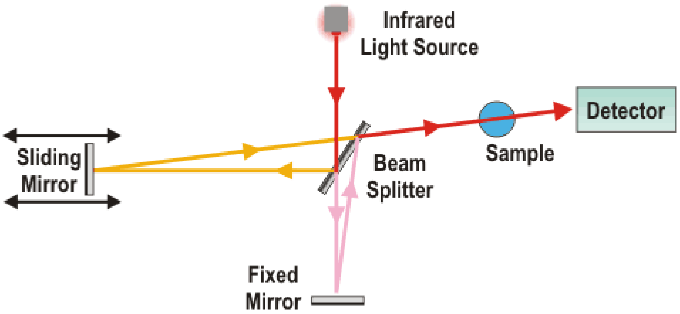


Figure2.5: principle of FTIR

FTIR Spectrometer secures and digitizes the interferogram, plays out the FT capacity and yields the range. Utilizations of the strategy spread the entire range from simple material identification to the dissemination of materials to their interactions. The main parts of the FTIR Spectrometer are as follows

1.source

A source of continuous radiation over the region of interest is used. The radiation source is usually made up of ceramic filaments operating at about 1500k with temperature stabilization. The ratio of the two spectra, one obtained with the radiation emitted by the source and the other with the radiation of the source after passing through the sample, gives the desired result.

2. Interferometer

An interferometer uses a beam splitter that splits the infrared beam into two optical beams. The two beams reflect off of their particular mirrors and are recombined when they get together at the beam splitter. The recombined signal outcomes from the "interfacing" with one another therefore, the subsequent signal is called interferogram, which has each infrared recurrence "encased" into it.

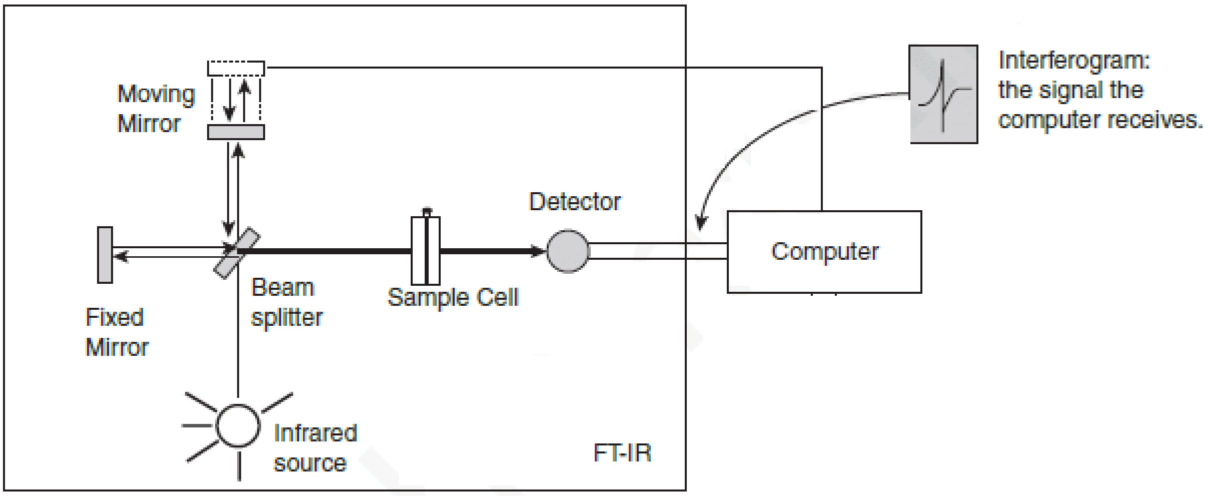


Figure 2.6 : Instrumentation of FTIR

3. Sample

As infrared spectroscopy has been used for the characterization of solid, liquid or gas samples. The sample must be transparent to IR. In FTIR analysis, IR radiation is passed through the sample where partial absorption and transmission of IR radiation takes place. The resultant spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample

♦Solid sample

Solid run in solution, Solid films, Mull techniques, Pellet techniques.

♦Liquid sample

Liquid Samples are poured into rectangular cells of NaCl, KBr, or ThBr and their IR Spectra are obtained directly.

♦Gas samples

The Gas sample cell is like the cell for fluid samples .The cells are bigger; for the most part they are about 10cm long, however they might be up to 1m long. Different reflections can be utilized to make the compelling wavelength as long as 40m, so constituents of the gas can be resolved.

4. Detectors

The detector converts the beam into photons, which are then translated into measurable electric signals that the computer can read. some examples of common detectors are Room temperature DLATGS is a regular analysis tool, Cooled liquid nitrogen is employed in sensitive applications, Si-photodiodes are employed in near-IR and visible infrared applications, Silicon far-infrared bolometers. The detector in the instrument measures the amount of energy at each frequency which has passed through the sample. This results a spectrum which is a plot of intensity versus frequency. The IR region is commonly divided into three regions as follows:

(a) Near infrared region 14000 – 4000 cm-1
(b) Mid infrared region 4000 – 200 cm-1
(c) Far infrared region 200 – 10 cm-1

5.Computation and recording

In FTIR spectrometers, high speed, large memory capacity micro computers are used to accumulate a large number of scans and to convert the interferogram into a plot of absorption against wavenumber and this is recorded in the form of spectrum by the recorder. The spectra supports in identifying the nature of bonding and different functional groups present in a sample by monitoring the vibrational energy levels of the molecules, which are essentially the fingerprint of different molecules. In addition, the intensity of the peaks in the spectrum is a direct indication of the amount of materials present. Hence the complex formation between the polymer and the salt can be confirmed by using FTIR spectrum.

In the present investigation, the complex formation of biopolymer with different concentrations of ionic salt dopant has been identified using Thermofisher, USA, model Nicolet iS10 spectrometer, by passing IR light through the sample in the frequency ranging from 4000 to 400 cm-1 at room temperature with the spectral resolution of 1 cm-1 in transmittance mode.

3.4.2 APPLICATIONS OF FTIR

FTIR spectroscopy finds widespread applications in various fields, including chemistry, pharmaceuticals, materials science, environmental analysis, and forensics. It is used for high-resolution experiments, trace analysis in raw materials or final products, Reactions on the microsecond time scale, Chromatographic and thermogravimetric sample fraction analysis, It is used to identify reaction components and conduct kinetic studies on reactions, It is used for compound identification by matching the spectra of an unknown substance with a reference spectrum (fingerprinting), monitor chemical reactions, assess sample purity, and investigate molecular structure.

3.5 ULTRA VIOLET-VISIBLE SPECTROCOPY (UV-vis)

UV-Visible spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or blank sample. This property is influenced by the sample composition, potentially providing information on what is in the sample and at what concentration.

Light has a certain amount of energy which is inversely proportional to its wavelength. Thus, shorter wavelengths of light carry more energy and longer wavelengths carry less energy. A specific amount of energy is needed to promote electrons in a substance to a higher energy state which we can detect as absorption. Electrons in different bonding environments in a substance require a different specific amount of energy to promote the electrons to a higher energy state. This is why the absorption of light occurs for different wavelengths in different substances. Humans are able to see a spectrum of visible light, from approximately 380 nm, which we see as violet, to 780 nm, which we see as red. UV light has wavelengths shorter than that of visible light to approximately 100 nm. Therefore, light can be described by its wavelength, which can be useful in UV-Visible spectroscopy to analyze or identify different substances by locating the specific wavelengths corresponding to maximum absorbance.

Instrumentation of UV-Visible spectroscopy

Light source:

As a light-based technique, a steady source able to emit light across a wide range of wavelengths is essential. A single xenon lamp is commonly used as a high intensity light source for both UV and visible ranges. Xenon lamps are, however, associated with higher costs and are less stable in comparison to tungsten and halogen lamps.

For instruments employing two lamps, a tungsten or halogen lamp is commonly used for visible light, whilst a deuterium lamp is the common source of UV light. As two different light sources are needed to scan both the UV and visible wavelengths, the light source in the instrument must switch during measurement. In practice, this switchover typically occurs during the scan between 300 and 350 nm where the light emission is similar from both light sources and the transition can be made more smoothly.

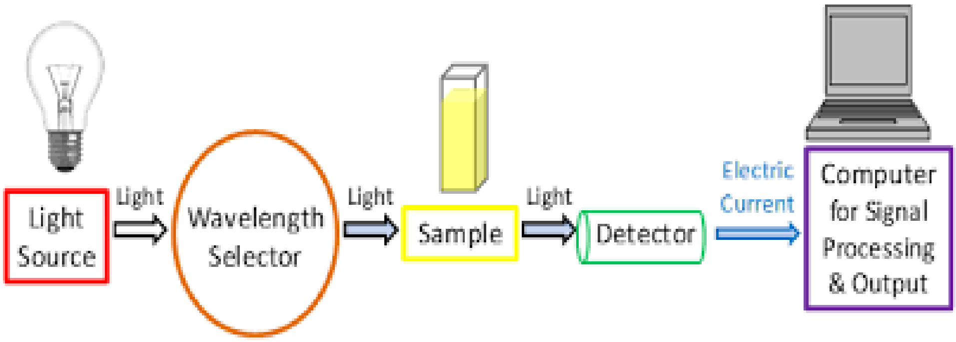


Figure 2.7 : **schematic diagram of the main components in UV-visible spectrometer**

Wavelength Selection:

In the next step, certain wavelengths of light suited to the sample type and analysis for detection must be selected for sample examination from the broad wavelengths emitted by the light source. Available methods for this include:

Monochromators:

A monochromator separates light into a narrow band of wavelengths. It is most often based on diffraction gratings that can be rotated to choose incoming and reflected angles to select the desired wavelength of light. The diffraction grating's groove frequency is often measured as the number of grooves per mm. A higher groove frequency provides a better optical resolution but a narrower usable wavelength range. A lower groove frequency provides a larger usable wavelength range but a worse optical resolution. 300 to 2000 grooves per mm is usable for UV-Visible spectroscopy purposes but a minimum of 1200 grooves per mm is typical. The quality of the spectroscopic measurements is sensitive to physical imperfections in the diffraction grating and in the optical setup. Therefore, ruled diffraction gratings tend to have more defects than blazed holographic diffraction gratings. Blazed holographic diffraction gratings tend to provide significantly better-quality measurements

Sample Analysis:

Whichever wavelength selector is used in the spectrophotometer, the light then passes through a sample. For all analyses, measuring a reference sample, often referred to as the "blank sample", such as a cuvette filled with a similar solvent used to prepare the sample, is imperative. If an aqueous buffered solution containing the sample is used for measurements, then the aqueous buffered solution without the substance of interest is used as the reference. When examining bacterial cultures, the sterile culture media would be used as the reference. The reference sample signal is then later used automatically by the instrument to help to obtain the true absorbance values of the analytes. It is important to be aware of the materials and conditions used in UV-Visible spectroscopy experiments. For example, most plastic cuvettes are inappropriate for UV absorption studies because plastic generally absorbs UV light. Glass can act as a filter, often absorbing the majority of UVC (100-280 nm) and UVB (280-315 nm) but allowing some UVA (315-400 nm) to pass through. Therefore, quartz sample holders are required for UV examination because quartz is transparent to the majority of UV light. Air may also be thought of as a filter because wavelengths of light shorter than about 200 nm are absorbed by molecular oxygen in the air. A special and more expensive setup is required for measurements with wavelengths shorter than 200 nm, usually involving an optical system filled with pure argon gas. Cuvette-free systems are also available that enable the analysis of very small sample volumes, for example in DNA or RNA analyses.

Detection:

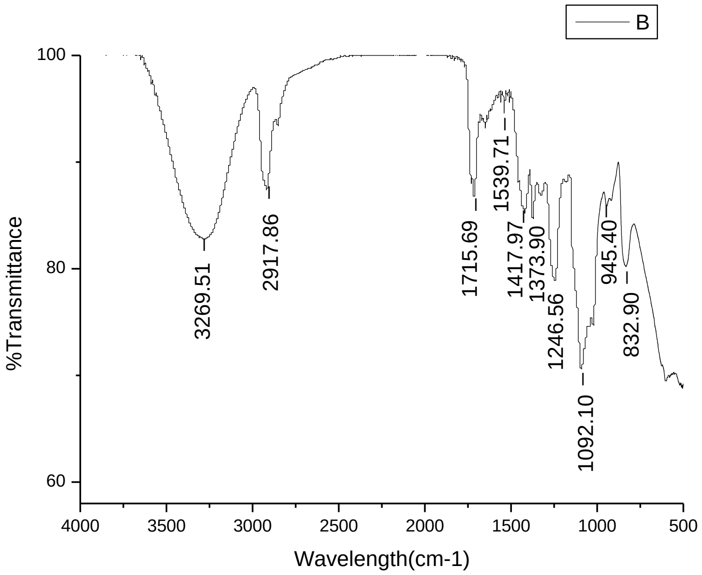
After the light has passed through the sample, a detector is used to convert the light into a readable electronic signal. Generally, detectors are based on photoelectric coatings or semiconductors. A photoelectric coating ejects negatively charged electrons when exposed to light. When electrons are ejected, an electric current proportional to the light intensity is generated. A photomultiplier tube (PMT) is one of the more common detectors used in UV-Visible spectroscopy. A PMT is based on the photoelectric effect to initially eject electrons upon exposure to light, followed by sequential multiplication of the ejected electrons to generate a larger electric current. PMT detectors are especially useful for detecting very low levels of light. When semiconductors are exposed to light, an electric current proportional to the light intensity can pass through. More specifically, photodiodes sand charge-coupled devices (CCDs) are two of the most common detectors based on semiconductor technology. After the electric current is generated from whichever detector was used, the signal is then recognized and output to a computer or screen.

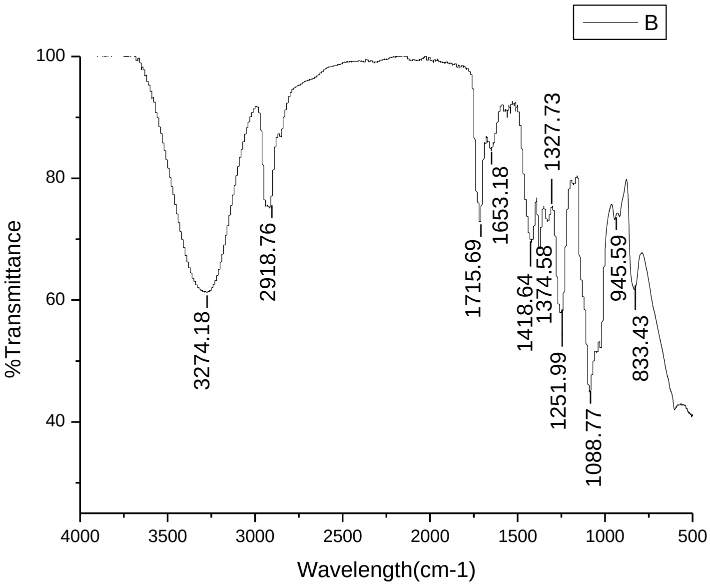
APPLICATIONS OF UV-VISIBLE SPECTROSCOPY

- UV spectroscopy is extensively used in pharmaceutical analysis for drug quantification, purity testing, and stability studies.
- UV spectroscopy is used for protein and nucleic acid analysis, such as determining protein concentration or DNA purity.
- In clinical laboratories, UV spectroscopy is used for analyzing blood components, detecting biomarkers, and monitoring disease progression.

CHAPTER 4

4.1 FTIR ANALYSIS





FTIR is an effective and essential characterization that determines the chemical compositions, chemical interaction and it also follows the variation in functional group during reaction. The FTIR spectrum of PVA-Li2SO4 and PVA-CH$_4$N$_2$S-Li2SO4are shown. The IR spectra observed the broad peaks at 3275,2918,1716,1247 and 1087 cm-1 for PVA-Li2SO4 composition and at 3269,2917,1715,1246 and 1092 cm-1for PVA- CH$_4$N$_2$S-Li2SO4 composition indicates O-H Stretching.

A small peak at 830 and few peaks are also found between 400-515 cm^{-}1.

S.no	Wavenumber (cm1) PVA-Li2SO4	Wavenumber(cm1) PVA-CH4N2S-Li2SO4	Band
1	3269	3274	O-H Stretching
2	2917	2918	C-H Stretching
3	1715	1653	C=O Stretching
4	1539	1539	C-O Stretching
5	1373	1327	O-H Bending
6	1246	1250	CH2 Bending
7	1092	1088	C-O Stretching
8	945	945	C-H Bending
9	830	833	C=C Bending

The broad peak around 3276 cm^{-}1 indicates stretching of hydroxyl groups (O-H), and peaks at 2918 cm^{-}1 is due to C-H stretching vibration is asymmetric. The peaks observed at 1716,1374,1247, and 830 cm-1 were observed for all spectra with some shifts due to the doping with Na+1 corresponding to out-of-phase stretching (of vinyl acetate group of PVA) and plane deformation respectively.

4.2 UV-visible spectral Analysis

UV Analysis for Polyvinyl alcohol (PVA), sodium nitrate, and Thiourea would likely focus on determining their UV absorbance spectra and possibly quantifying their concentrations. Each compound exhibited characteristic absorption patterns at specific wavelengths. The optical parameters such as extinction coefficient, Reflectance, refractive index, and optical conductivity were studied. The Tauc plot is drawn between photon energy h$\vartheta\ and\ (\alpha hv)$^2.

4.2.1 UV Analysis of PVA-Li2SO4and PVA-CH$_4$N$_2$S-Li2SO4

Transmission spectra for PVA-Li2SO4 and PVA-CH$_4$N$_2$S-Li2SO4 are calculated in the wavelength range (200 nm–1200 nm) because of the concentrations. It is detected that PVA-CH$_4$N$_2$S-Li2SO4 have a high transmission than PVA-Li2SO4 due to the dopant concentrations. A small transmission is noticed at about 293 nm. Optical transmission is occured at a low level due to its low optical transmission for PVA

70%: 30% Li2SO4concentration. The photon energy is perfectly observed by the films then it transmits a very low amount of energy.

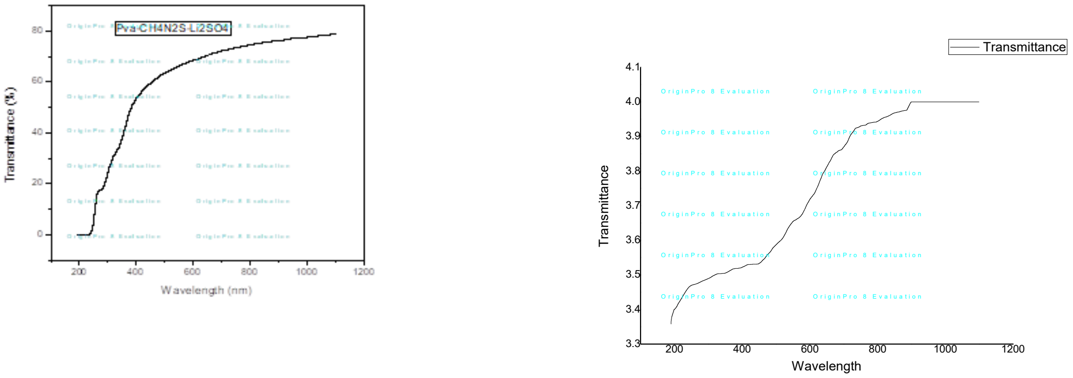


Figure 2.9 : The graph is drawn for the compositions of (PVA-Li2SO4 and PVA-CH_4N_2S-Li2SO4) between hv(eV) and Transmittance(%)

The transmittance 'T' is the ratio of two terms such as power radiant transmission (P) by sample material and power of radiant incidence ($P0$).

$$\text{But, } P = P0\mathrm{T}$$

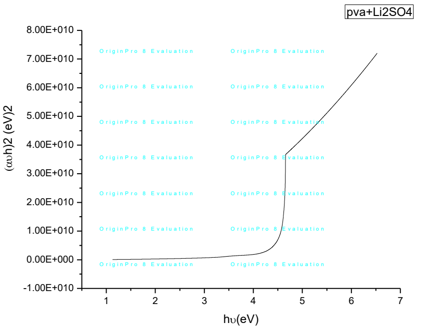
$$T = e\alpha t$$

Where 'α' is an optical coefficient of absorption and 't' is the thickness of the sample material, optical transmission can be calculated. The optical parameters such as as extinction coefficient, refractive index, optical conductivity, and Tauc plot were plotted.

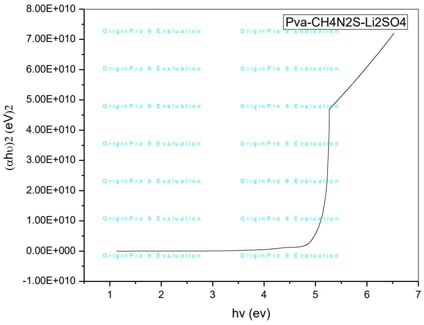
a. The graphs are plotted between h$\vartheta(eV)$ and (αhv)^2

   R = 1 - (T + A)

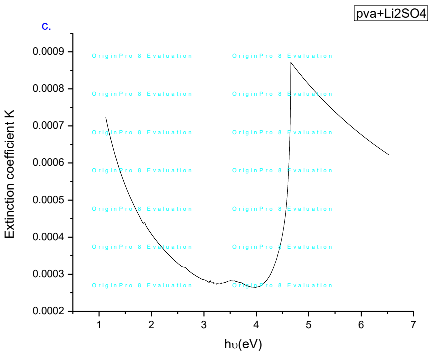
Where 'T' is an optical transmittance The energy bandgap is determined from the graph of $(\alpha h\upsilon)^2$ vs. (hυ) photon energy. Here $(\alpha hv)2$ vs. photon energy 'hv' generates the direct bandgap value. The graphs are plotted for h$\vartheta(eV)$ and ReflectanceThe optical reflectance can produce a refractive index and many optical parameters. The reflectance of the film is calculated from a given relation.



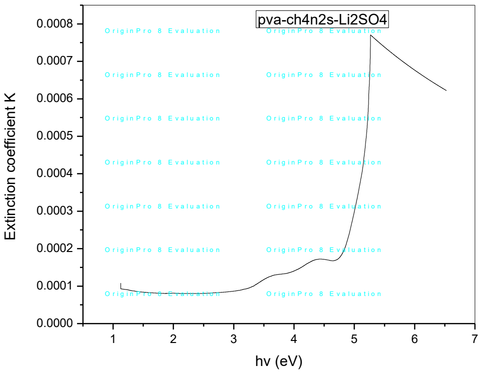
a.



b. Graph is plot between h$\vartheta(eV)$ and extinction coefficient K



b.

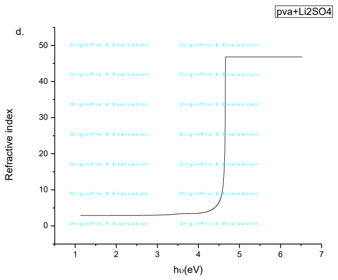


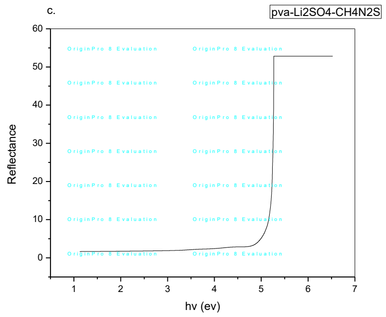
The extinction coefficient is represented as an imaginary component of the optical refractive index. Optical properties of optical extinction coefficient and optical refractive index can produce an optical constant of the material. The variation of the excitation coefficient with wavelength shows such interaction between medium and photon energy. The small fraction of electromagnetic energy (Light energy) loss is known as coefficient extinction Specific optoelectronics applications relate to this refractive index, atomic structure, electrical properties, and electronic bond structure.

$$K = \frac{\alpha\lambda}{4\pi}$$

Here ‘λ’ represents wavelength, ‘α’ is coefficient absorption. With the help of this excitation, the coefficient can calculate real, imaginary, and complex parts.

c.The graph is plotted for h$\vartheta(eV)$ and Refractive index





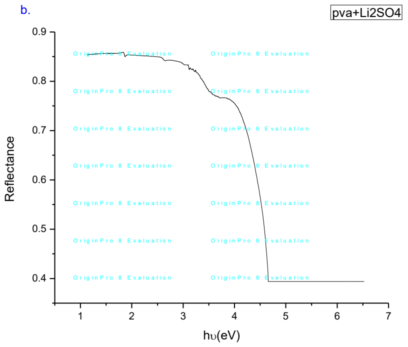
Optical properties of optical extinction coefficient and optical refractive index can produce an optical constant of the material.15 Specific optoelectronics applications relate to this refractive index, atomic structure, electrical properties, and electronic bond structure. The reflectance in terms of optical refractive index is given by

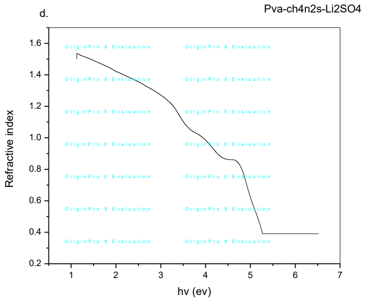
$$R = \frac{(n-1)^2 + K^2}{(n+1)^{2} + K^2}$$

And

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}$$

Here optical reflectance is ‘R’, ‘K’ is a coefficient of extinction, ‘n’ is the refractive index of the sample. The refractive index of an optical material indicates electronic and molecular polarization of the electromagnetic field of light. These plots showing the change in the refractive index. The refractive index nearly minor and constant for all samples up to 4 eV, it can increase by increasing photon energy. Then after again they become constant. Normally by increasing doping concentration, the refractive index is also changed by changing the dopant concentration to the polymer. Finally, the optical refractive index is high for 70%PVA: 30% Li2SO4.





CHAPTER –V

CONCLUSION

The ionic conductive polymer electrolytes are composed of polymer and organic or inorganic salts. The polymeric property of polymer electrolyte gives it advantages over liquid electrolytes. The polymer PVA-Li2So4 and PVA-CH4N2S-Li2SO4 salt membrabes were prepared by solution cast technique. The chemical composition of polymer electrolytes was investigated on the basis of FTIR spectrum. The linear optical parameters such as transmission, refractive index, extinction coefficient, reflectance and energy gap for the composition of Soild Polymer Electrolytes (SPE) based on polymer PVA and Li2SO4 and PVA-Li2SO4 doped with CH4N2S were studied using UV-visible spectroscopy

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