BIODEGRADABLE GUAR GUM-PECTIN BLEND ELECTROLYTE FOR SODIUM-ION BATTERIES

K PRAVEENA
REG NO: 20PCH013

Thesis submitted to

Avinashilingam Institute for Home Science and Higher Education for Women

Coimbatore - 641043

In partial fulfilment of the requirements for the Degree of Master of Science in Chemistry

May – 2022

Certificate

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Signature of Head of the Department

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"Wear gratitude like a cloak, and it will feed every corner of your life."

- ***Rumi***

It is with the choice of blessings and the divine grace of LORD ALMIGHTY that any human endeavour is achieved.

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Content

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Abbreviations

Abbreviation	Expansion	Abbreviation	Expansion
NaI	Sodium Iodide	SPE	Solid Polymer Electrolyte
GG	Guar Gum	GPE	Gel Polymer Electrolyte
DSSC	Die Synthesized Solar Cell	SPI	Solid Permeable Interface
$NaClO_4$	Sodium perchlorate	SIB	Sodium-ion battery
$NaNO_3$	Sodium nitrate	ZIB	Zinc Ion Battery
NaTf	Sodium triflate	PC	Polyethylene carbonate
$NaCH_3COO$	Sodium acetate	EC	Ethylene carbonate
NaSCN	Sodium thiocyanate	SN	Succino nitrile
$NaCF_3SO_3$	Sodium trifluoro methane sulfonate	EG	Ethylene Glycol
LiTFSI	Lithium bis (trifluoromethanesulphonyl) imide	XPS	X-ray Photoelectron Spectroscopy
NH_4NO_3	Ammonium nitrate	PVA	Polyvinyl Alcohol

SA	Sodium Alginate	PVDF	Polyvinylidene fluoride
FTIR	Fourier transforms infrared	HFP	Hexa fluoro propylene
XRD	X-ray diffraction	MC	Methyl cellulose
DSC	Differential scanning calorimetry	NH_4I	Ammonium Iodide
LSV	Linear Sweep Voltammetry	NH_4Br	Ammonium bromide
CV	Cyclic Voltammetry	NH_4Cl	Ammonium Chloride
TG/DTA	Thermal Gravimetric/Differential Thermal Analysis	PEO	Polyethylene oxide
SEM	Scanning Electron Microscopy	PVP	Polyvinyl pyrrolidone
TEM	Transmission electron microscope	GO	Graphene Oxide
XANES	X-ray adsorption near-edge spectroscopy	PNC	Polymer Nano Composite
EIS	Electrochemical Impedance Spectroscopy	PVC	Polyvinyl chloride

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Introduction

CHAPTER-I

INTRODUCTION

A *thermal storage device* is a renewable energy source of one or more electrochemical cells with external access to electrical power devices such as mobile phones, flashlights, and electric vehicles. Once a power source provides electricity, the positive terminal is the Cathode, and the negative terminal is known as the Anode. Electrons transfer through an intrinsic electrical circuit to a positive terminal from the negative terminal. A redox reaction occurs when a battery is exposed to an external power supply, converting high-energy substances to lower-energy materials. The electricity in the external circuit is due to the difference in free energy. Historically, devices made up of multiple cells are termed "battery; however, the term refers to devices of a single cell. Batteries can be classified into primary and secondary batteries. Primary batteries are also known as primary cells or non-rechargeable batteries.

These classes of batteries are batteries where the redox reactions proceed in only one direction. Primary batteries are used until their energy is depleted, at which point they are discarded, because their chemical reactions are customarily irreversible; they are not rechargeable. When the supply of reactants is depleted, the power supply ceases to produce current and becomes useless. Primary batteries are typically inexpensive, light in mass, tiny, and very easy to use with no or little preservation. Most of the primary batteries used for residential purposes are single cells in a cylindrical configuration. Primary batteries are used in radios, torchlights, transistors, watches, calculators, hearing aids, etc., (**figure: 1).**

Figure: 1 Examples for Primary Batteries

Secondary batteries are also known as secondary cells or rechargeable batteries. This battery can be rechargeable after passing a current through the electrodes in the opposite direction i.e., from the negative terminal to the positive terminal. Their chemical reactions can be changed by passing an electric current through the cell, representing initial chemical reactants, allowing them to be refuelled and reused multiple times. Secondary batteries have a lower energy density than primary batteries, despite multiple advantages such as high battery capacity, simple discharge lines, high discharge rate, and low-temperature performance. Secondary batteries are used in automobiles, telephone exchange, power stations, supplying current to railways, etc.,**(figure: 2)**

Figure: 2 Examples for secondary batteries

EXAMPLES FOR BATTERIES

Primary batteries

- ❖ Alkaline manganese battery
- ❖ Mercury-cadmium battery
- ❖ Zinc chloride battery
- ❖ Silver-zinc battery
- ❖ Zinc-carbon battery

Secondary batteries

- ❖ Lead storage battery
- ❖ Nickel-Cadmium battery
- ❖ Lithium-ion battery
- ❖ Mercuric Oxide battery
- ❖ Aluminium air battery
- ❖ Silver-hydrogen battery

ELECTRODES IN BATTERY

An electrode is an electrical conductor used to connect with a non-metallic part of a circuit. Electrodes are an essential part of the batteries and consist of various materials depending on the type of battery.

Anode and Cathode:

- The **Anode** is the negative or oxidizing electrode that releases electrons to the external circuit and oxidizes during an electrochemical reaction.

- The **Cathode** is the positive or reducing electrode that acquires electrons from the external circuit and reduced during the electrochemical reaction.

Electrolyte in Battery

In batteries, the electrolyte is the compound that enables electric current to pass between the Anode and the Cathode. Electrolytes can be either fluids or solids. Electrolytes are typically soluble salts, acids, and bases. Current flows through an electrolyte within the atoms or molecules that transfer charge due to electron addition or subtraction. Electrons enter and leave the electrical connections to affect chemical changes at the electrodes, resulting in the formation of the earth's atmosphere of these ions around them. Ions with opposite charges then gravitate toward one another. An anode contains ionic compounds with excess electrons, passing electrons to Cathode (oxidation). At the same moment simultaneously, cations in the Cathode are with an electron deficit, so they gain electrons from the Anode (reduction). As a result, electrical charge flows in both directions through the electrolyte. Most electrolytes are liquid; these will not always present as a separate pool of liquid from the electrodes.

LIQUID ELECTROLYTE

Liquid electrolyte means a liquid phase electrolytic solution comprising at least one salt dissolved in one liquid non-aqueous polar solvent. Furthermore, bi-phase electrolyte systems in which a liquid electrolyte coexists with a gel electrolyte in an electrode or the separator are considered Liquid Electrolytes and not Gel Electrolytes. Liquid electrolytes have several essential characteristics, including ease of processing, high electrical conductivity, low viscosity, and strong interfacial wettability between electrolytes and electrodes, resulting in high energy conversion for DSSCs. Today, polymer electrolytes are the most used transport medium for Die Synthesized Solar Cells (DSSCs), with a 13 % efficiency for traditional DSSCs. Liquid electrolytes used in DSSCs must be chemically and physically stable, have a low viscosity to reduce charge transport transit resistance, and be a better solvent for redox couple components. A liquid electrolyte comprises three major components: a solvent, an ionic conductor, and compounds.

SOLID ELECTROLYTE:

The solid electrolyte has high flexibility, the ability to initiate electrode-electrolyte contact quickly, and simple process ability. Polymer electrolytes are made up of a salt that has been diluted in a polymer matrix to produce an ion-conducting compound. Solid polymeric electrolytes are a promising option for liquid electrolytes. Because they are lighter, have no internal shorting, no electrolyte leakage, produce quasi side reactions at the electrode surface, are mechanically stable, and are very flexible for packaging. While polymers are functionalized with host dopants such as inorganic/organic acids/salts, their systemic and electrical properties change noticeably. However, the polymer must have specific properties, such as an amorphous structure, oxygen molecules, a poor glass transition temperature, electrochemical and geometrical stability, mechanical resistance, and the ability to form relatively thin films or pellets. It is preferable to achieve high order electrical conductivity by incorporating plasticizers or ionic liquids into the polymer matrix, such as polyethylene carbonate (PC), ethylene carbonate (EC), and Succino nitrile (SN). The following criteria can be used as a 'thumb rule' for selecting polymer and salt. Polymers should have a poor glass transition temperature (Tg) to ensure complexation for their flexible core component. The polar groups responsible for cation complexation are more concentrated as much as possible.

HISTORY OF BATTERIES

The word battery comes from the Old French word Baterie. The meaning of Batarie is the action of beating, which relates to a group of cannons in battle. To store energy using energy storage systems, scientists in the 1700s coined the term "battery," which referred to a collection of interconnected electrochemical cells. Types of batteries and year of invention is mention in the **Table 1**

Ewald Georg Von Kleist - The Leyden Jar is a static electricity storage device invented by Ewald Georg Von Kleist (1745). The Leyden jar is a device for storing electrical currents found by accident. The jar was charged by contacting the exposed end of the wire with a friction device that generated static electricity. Metal foil sheets are being used to coat the inlet and outlet surfaces of insulating jars to increase their capacity to hold charges. A lightning rod, also known as a lightning conductor, is a metal rod or conductor put on the top of a building. An electrical current is connected to the base through a cable to protect the structure against lightning strikes. "Voltaic Pile" was created in the year 1800. According to Luigi Galvani, a frog's leg twitches when connected by arcs formed of iron and brass, discovered in the 1780s. Galvani believed that the twitching began in the tissue of the leg, implying that animals generate electricity. Later in the 1790s, Volta constructed a contemporary battery by stacking zinc and silver discs in pairs to form a "pile." The first device for creating continuous current, hence the name "voltaic pile," was the first device for supplying constant current.

Table 1: Types of Batteries and Year of Invention

Types of batteries	Year of invention
Voltaic cell	1800
Daniel cell	1836
Fuel cell	1839
Lead Acid Battery	1859
Leclanche carbon-zinc cell	1866
Ni-Cd Battery	1899
Ni-Fe Battery	1902
Nickel Zinc	1932
Parthian Battery	1936
Alkaline-Manganese battery	1949
Rechargeable alkaline	1950
Nickel hydrogen	1977
Alkaline Battery	1960
Li-air Battery	1976
Nickel Hydrogen Battery	1977
Ni-metal Hydride Battery	1990
Li-ion Battery	1996

Sodium-ion battery

In terms of electrochemical performance, sodium-ion batteries are comparable to lithium-ion batteries, and they are expected to be a promising substitute for energy storage. Because sodium ranks sixth (2.75 percent) in the crust, the high raw material abundance and low cost of sodium-ion batteries have piqued the interest of researchers in recent years. At high voltage, the interface between cathodes and electrolyte solution undergoes side oxidation reactions and becomes intrinsically unstable in sodium-ion batteries. Side oxidation reactions degrade the electrolyte solution's chemical structures and the cathodic active materials, resulting in harmful by-products and significant capacity fade. A solid permeable interface (SPI) can passivate the cathode surface and prevent oxidation reactions. As a result, forming solid permeable films is essential in advanced energy storage for sodium-ion batteries. Extensive research was conducted to create SPI films in suitable ionic liquids and urea at high concentrations by adding electrolyte salts, solvents, and additives.

Because of the abundance of sodium resources, rechargeable sodium-ion batteries (SIBs) based on solid polymer electrolytes (SPE) are regarded as one of the most promising candidates for next-generation large-scale high energy and high-safety energy storage applications. SPEs are an excellent candidate as an electrolyte due to their low cost, simplicity of preparation, versatility, compatibility, excellent adhesion with the electrode, and ability to withstand volume changes at the electrode/electrolyte functionality, mostly during charge/discharge mechanism due to its excellent mechanical solidity.

Pectin

Pectin is a polysaccharide of esterified D-galacturonic acid in an alpha-(1-4) chain. In the natural product, the acid groups throughout the chain are esterified with methoxy groups, free hydroxyl groups, and acetyl groups may also be present. The galacturonic acid main chain has an infrequent rhamnose group, disrupting helix formation. Because pectin obtained from plants and fruits is biodegradable and renewable, the researchers focused on using it as the polymer electrolyte. It is non-toxic and soluble in water. An oxygen atom seeks to build a coordination link with cations of more hydroxyl groups. Pectin has a special place among available polysaccharides due to its biodegradable and non-toxic nature.

Guar gum

The synthesis of Guar-gum based polymer electrolytes improves conducting nature. This type of electrolyte possesses low cost, easy fabrication, high efficiency, and biodegradable. It is a natural non-ionic polysaccharide extracted from guar beans. It is composed of (1-4)-D mannopyranosyl units with D- galactopyranosyl units. Guar gum, also called "guaran". According to application, the guar seeds are mechanically dehusked, hydrated, milled, and screened. It produced as a free-flowing, off-white powder.

Sodium Salt

Sodium salts such as Sodium nitrate ($NaNO_3$) **(M. Vahini *et al.*, 2019)**, Sodium iodide (NaI) (**Devesh Chandra Bharati *et al.*, 2020), (Vidhya Selvanathan *et al.*, 2018), (Noriah Abdul Rahman *et al.*, 2021), (R. H. Y. Subban *et al.*, 1996), (Syakirah Shahrudin *et al.*, 2016), (Aziz M. Abdullah *et al.*, 2021), (Devesh Chandra Bharati *et al.*, 2021), (A.H. Ahmad *et al.*, 2017),** Sodium trifluoro methane sulfonate ($NaCF_3SO_3$) **(K. B. Md Isa *et al.*, 2017)**, Sodium acetate ($NaCH_3COO$) **(M.S.A. Rani *et al.*, 2020)**, Sodium thiocyanate (NaSCN) **(M. Infanta Diana *et al.*, 2021)**, Sodium triflate (NaTf) **(Jingwei Wang *et al.*, 2019)**, **(Ahmad**

S.F.M. Asnawi *et al.,* 2021), Sodium perchlorate ($NaClO_4$) **(K. Vignarooban *et al.,* 2017)**, **(Supriya K Shetty *et al.,* 2021)** are used to prepare electrodes. Their excellent charge delocalization is favourable to ionic dissociation in a solvating polymer, with good chemical, electrochemical, and thermal stabilities. "Plasticizing" effect decreases the host polymer's crystallinity and higher ionic mobility**.**

OBJECTIVES

- To prepare composite electrolyte using Pectin and Guar Gum with Sodium salt.
- To find the nature of interaction of Na ions with the polymer.
- To measure the thermal stability and morphology.
- To determine ionic conductivity of the prepared electrolytes to establishes its efficiency of the electrochemical performance.
- To determine the transport number of the prepare electrolyte.

Review of literature

CHAPTER-II

REVIEW OF LITERATURE

To find the research gap review of the previous research work has been made. This review work is also useful to establish a theoretical framework for the topic area, define key terms, definitions, and terminology, identify studies, models, case studies, etc., supporting the topic, and define the area of study, i.e., the research topic.

2.1 PREPARATION OF BIOPOLYMER-BASED ELECTROLYTE

In recent decades bio-based polymer electrolyte grabs much attention from researchers to find alternatives to petrochemical-based polymers to reduce environmental effects. These bio-based polymers have a wide range of possible applications, from everyday applications to high-end advanced applications also minimize the depletion and sustainability difficulties of traditional polymers. As a result, this article examines the latest trends and breakthroughs in bio-based polymers for the manufacture of polymer electrolytes used in electrochemical devices. A variety of bio-based polymers are discussed with an emphasis on the source, general synthesis methods, and the features of the polymer electrolyte system, particularly ionic conductivity. Some major applications of bio-based polymer electrolytes are discussed. This review examines the past studies and prospects of these materials in the polymer electrolyte field (***Marwah et al., 2020)***

Yumei Wang et al., (2019) have discussed the all-solid-state sodium-ion battery which is considered the next-generation battery to replace the existing commercialized lithium-ion battery, due to the benefits of abundant sodium supplies, low cost, and excellent safety. The solid-state electrolyte is one of the most important components in a sodium-ion battery, because of its superior operating safety, design simplicity as well as a sufficiently high room-temperature ionic conductivity. This paper provides a comprehensive review of recent progress in sodium-ion battery solid-state electrolyte materials, including inorganic ceramic/glass-ceramic, organic polymer, and ceramic-polymer composite electrolytes, and also compared ionic conductivity in different solid electrolyte materials. The advancement of solid-state electrolytes points to a promising future: all-solid-state sodium-ion batteries might be utilized to power electric vehicles, portable electronic gadgets, and large-scale grid support.

The impact of SEI dissolution is investigated through a series of studies on carbonaceous anodes. The findings show that the SEI layer in sodium-ion cells is inferior to that in lithium-ion cells in terms of self-discharge; sodium cells lose capacity at a much faster rate than lithium cells when stored in sonicated and litigated states, respectively, for long periods with no external current or potential. In addition, synchrotron-based hard x-ray photoelectron spectroscopy observations show that the dissolution of considerable portions of the sodium-based SEI is a major contributor leading to greater self-discharge. In addition, the effect of fluoroethylene carbonate (FEC) electrolyte additive on self-discharge was investigated by ***Ronnie Mogensen et al., (2016)***

2.2 PREPARATION OF BLENDED BIOPOLYMER ELECTROLYTE

Ahmad S.F.M. Asnawi et al., (2021) have discussed the solid polymer electrolyte incorporating of blended the Chitosan and Dextran polymers, Sodium Triflate salt used as doping salt. The polymer electrolyte prepared by the solution casting technique. The blend electrolyte was characterized by FT-IR, FESEM, XRD, Impedance analyses, Transference

Number Measurement and Linear Sweep Voltammetry. The highest ionic conductivity of the electrolyte was observed as 6.10×10^{-5} S cm^{-1} at room temperature.

Pritam et al., (2019) have explained the solid polymer electrolyte consisting of polyethylene oxide and polyvinyl pyrrolidone polymers for blended, sodium nitrate salt used as doping salt for ion-conducting species, and solid polymer electrolyte prepared by the solution casting method. The ionic conductivity of the solid polymer electrolyte for PEO and PVP was observed as 2.90×10^{-4} $Scm^{-}.^{1}$at 100°C and 2.90×10^{-4} Scm^{-1} at room temperature. The structural and microstructural changes have been analyzed through XRD and FESEM analysis.

Shujahadeen et al., (2021) have reported a solution casting method to prepare plasticized polyvinyl alcohol (PVA) and methylcellulose (MC) - ammonium iodide (NH_4I) electrolyte at room temperature. The maximum ionic conductivity of 3.21×10^{-3} S/cm was obtained. It has shown that the number density, mobility, and diffusion coefficient of ions are enhanced by increasing the glycerol. Several electric and electrochemical properties of the electrolyte impedance, dielectric properties, transference numbers, potential window, energy density, specific capacitance (Cs), and power density were determined and applicable to utilization in energy storage devices.

A. Rosdi et al., (2016) have established the gel polymer electrolytes (GPEs) samples consisting of polyvinylidene fluoride-co-Hexa fluoro propylene (PVDF-HFP), ethylene carbonate (EC), and propylene carbonate (PC) with different concentrations of Magnesium triflate salt Mg $(CF_3SO_3)_2$ were prepared by using the solution casting technique. The ionic conductivity of the GPEs was studied by using A.c impedance spectroscopy and the sample containing 20 wt% salt exhibited the highest conductivity of 5.11×10^{-3} S cm^{-1}. The ionic transport number of the

GPEs shows that the samples contain ionic species as main charge carriers while the cationic transport number for the highest conducting sample was found to be 0.27. The electrochemical properties of the GPEs were studied using Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV). The GPEs showed high electrochemical stability ~3.5V (versus Mg2+/Mg), where the highest conducting sample exhibited the highest stability.

R. Shilpa and R. Saratha, (2020) have discussed Pectin- Guar Gum- LiTFSI coalesce polymer electrolytes prepared through solution casting techniques. The phase identification of the blend Pectin- GG and the blend polymer complex has been confirmed by XRD analysis. Conductance spectra results of the blend polymer electrolytes exhibited the conductivity of 1.59×10^{-4} S cm^{-1} at room temperature, being applicable as an electrolyte. The improvement in the conductivity of the prepared electrolyte with an increase in the amorphous phase suggests that the polymeric blend (SPE) was suitable for Li-ion batteries. The results demonstrate that the solid polymer electrolyte systems were eligible for next-generation high energy density all-solid-state lithium-ion batteries.

Dure N. Iqbal et al., (2020) have prepared the chitosan/polyvinyl alcohol /guar gum (CS/PVA/GG) blends. This synthesis was carried out using different combinations of CS and GG while keeping PVA constant by casting solution method. The effect of formaldehyde as a crosslinking agent was also evaluated. The blends were characterized by scanning electron microscopy (SEM), Fourier Transform Infra-red (FTIR), and X-ray powder diffraction (XRD). Additionally, the swelling ratio along with antimicrobial activity was also studied. SEM exhibited the phenomenon that surface morphology was mostly affected by blend ratios and cross-linker. The XRD shows the crystalline structure of blends. It is also used an antimicrobial activity against *P. multocida, S. aureus, E. coli, and B. subtilis* bacterial agents.

Shujahadeen B. Aziz et al., (2020) have studied the plasticized films of polyvinyl alcohol (PVA): chitosan (CS) based electrolyte impregnated with ammonium thiocyanate (NH_4SCN) were prepared by using a solution-casting technique. The structural features of the electrolyte films were investigated through the X-ray diffraction (XRD) pattern. The electrical impedance spectroscopy (EIS) portrays the improvement of ionic conductivity from 10^{-5} S/cm to 10^{-3} S/cm upon the addition of a plasticizer. The electrolytes incorporated with 28 wt.% and 42 wt.% of glycerol were observed to be a mainly ionic conductor as the ionic transference number measurement (TNM) was found to be 0.97 and 0.989.

Potato starch (PS)-methylcellulose (MC) blend solid biopolymer electrolytes added with ammonium nitrate (NH_4NO_3) and glycerol as plasticizer are made by ***M. H. Hamsan et al., (2017)*** via the solution cast technique. Fourier transforms infrared (FTIR) spectroscopy indicates that NH_4NO_3 has interacted with the polymer blend host. The addition of 40wt% glycerol in the highest conducting plasticizer, the free electrolyte has improved the conductivity to the order of $(1.26 \pm 0.1) \times 10^{-3}$ S cm^{-1}. The thermal stability of the electrolytes is identified by thermogravimetric analysis (TGA). A result from X-ray diffraction (XRD) analysis shows that the electrolyte with maximum conductivity value has the lowest degree of crystallinity. Differential scanning calorimetry (DSC) analysis reveals that the highest conducting plasticized electrolyte possesses the lowest glass transition temperature of−27.5 °C.

V. Aravindan et al., (2009) have prepared the blend polymer electrolytes of polyvinylidene fluoride-co-Hexa fluoro propylene- poly ethyl methacrylate by using a solution casting method. Diethyl carbonate and ethylene carbonate were used as plasticizers, Nano sized Sb_2O_3 as filler and sodium trifluoromethanesulfonate ($NaCF_3SO_3$) was used as an ionic conducting source.

The ionic conductivity of the CPE polymer electrolyte was studied by using AC impedance spectroscopy and the sample containing 10 wt% Sb_2O_3 exhibited the highest ionic conductivity was 0.569 mS cm^{-1} at room temperature. Molecular interactions of the constitutions were analyzed by FTIR spectroscopy.

Polymer blend electrolytes based on Polyethylene oxide (PEO) and polyvinyl pyrrolidone (PVP), complexed with NaIO4 salt and Graphene oxide (GO) are investigated by ***H K Koduru et al., (2016)*** by solution cast technique. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were employed to study the influence of ion–polymer interactions on the microstructural properties of blend electrolytes. Measurements of electrical conductivity of the blend polymer complexes have been performed by using complex impedance spectroscopy in the frequency range 1 Hz - 1 MHz and within the temperature range 303 K – 343 K

An intercalated blend of polymer nanocomposite (PNC) films based on a blend of Polyethylene oxide and polyvinyl chloride (PEO– PVC), LiPF6 as salt, and modified montmorillonite (MMMT) as nano clay was prepared by ***Anil Arya, A. L. Sharma (2019)*** via solution cast method. The highest ionic conductivity values were obtained as 8.2×10^{-5} S cm^{-1} at room temperature to 1.01×10^{-3} S cm^{-1} at 100 °C was exhibited by 5wt% MMMT based PNC. The intercalated PNC shows thermal stability up to 300 °C, a high ion transference number 1, and a broad voltage stability window of 5 V.

2.3 PREPARATION OF GUAR GUM BIOPOLYMER-BASED ELECTROLYTE

Zu-Wei Yin et al., (2020) have highlighted the recent application of high-capacity Li-rich cathode materials hindered by capacity fading and voltage decay because it could be effectively overcome by using water-soluble guar gum (GG) binder instead of traditional polyvinylidene fluoride (PVDF). However, the specific role of the GG binder is not clear yet, though the GG binder can significantly improve the electrochemical performance of the Li-rich cathode. To understand the effect of GG binder on the morphology, microstructure of electrode and electrode/electrolyte interfaces, ex-situ scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray adsorption near-edge spectroscopy (XANES), in-situ electrochemical impedance spectroscopy (EIS) were applied to comparatively study the charge-discharge processes of $Li_{1.2}$ $Ni_{0.2}$ $Mn_{0.6}$ O_2 cathode when using GG and PVDF as binders.

The Guar gum (GG)–lithium bis (trifluoromethanesulphonyl) imide (LiTFSI)-glycerol-based solid biopolymer electrolyte was investigated by ***M Abirami et al., (2020)*** via solution casting technique and characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), 3D-laser profilometry and AC impedance studies. The amorphous nature and complexation have been revealed by XRD and FTIR. TGA revealed that the thermal stability of polymer electrolytes is stable up to 260°C. The average roughness was measured using 3D-laser profilometry. The ionic conductivity of the electrolyte was studied using impedance analysis. The highest ionic conductivity of 2.041×10^{-3} S cm^{-1} has been achieved for the film containing 60 wt% GG–40 wt. % LiTFSI.

Ahalya Gunasekaran et al., (2020) have investigated a Guar Gum-based biopolymer (GG), a characteristic non-ionic polysaccharide extracted from guar beans, which was utilized in this work as a cost-effective polymer gel electrolyte for the fabrication of dye-sensitized solar cells (DSSC). A redox electrolyte is prepared by stirring Guar Gum biopolymer with a known amount of LiI/I2, 4- tert-butylpyrdine, 1-methyl-3-propylimidazolium iodide, and polyethylene glycol for 24 hrs. The polymer gel electrolyte was carefully characterized through Fourier transform infrared spectra, UV–visible spectrum, Field- emission scanning electron microscopy, and Differential Scanning Calorimetry. This polymer gel electrolyte used in dye-sensitized solar cells was fabricated by sandwiching metal-free organic MK-2 dye coated TiO_2 photoanode and Pt counter electrode as a photocathode. The photoelectrochemical characterization of the fabricated device shows maximum power conversion efficiency of 4.96% instead of 2.13% obtained with the liquid electrolyte without Guar Gum. The electrolyte containing Guar Gum polymer gel shows ionic conductivity (σ) of 1.46 S cm^{-1} while the liquid electrolyte show 2.44 S cm^{-1}

Yuan Huang et al., (2019) have fabricated flexible zinc ion batteries (ZIBs) as alternative portable energy storage technology for wearable or flexible electronics due to their low cost and high safety performance. The development of stable solid-state electrolytes with high ionic conductivity is key to the practical application of ZIBs. Herein, we construct a high rate performance and long cycling life quasi-solid-state ZIB using guar gum biopolymer electrolyte. As a result, the ionic conductivity of 1.07×10^{-2} S cm^{-1} at room temperature, and delivered a high specific capacity of 308.2 mAh g^{-1} at 0.3 A g^{-1}, fast charging, and discharging capability (131.6 mAh g^{-1} at 6.0 A g^{-1}). The elastic guar gum electrolyte can effectively suppress the formation of zinc dendrites during cycling, leading to remarkable cyclability and high bending durability.

Jiawei Wang et al., (2021) have reported blending guar gum (GG) and sodium alginate (SA). The zinc-ion batteries with GG/SA hydrogel electrolytes showed a superior electrochemical performance (354.9 mAh g^{-1} at 0.15A g^{-1}, 137.0 mAh g^{-1} at 6 A g^{-1} and capacity retention of 91.52% over 1000 cycles) than the zinc-ion batteries with the pure GG hydrogel electrolyte In addition of ethylene glycol (EG) into GG/SA to form GG/SA/EG anti-freeze hydrogel to extend the application range of GG/SA hydrogels into the sub-zero temperature region Below -20 °C, the GG/SA/EG hydrogel maintains a high ionic-conductivity 6.19 mS cm^{-1} and constructed zinc-ion batteries using GG/SA/EG hydrogel electrolyte, showed an excellent low-temperature discharge performance, for a specific capacity of 181.5 mAh g^{-1} at 0.1 A g^{-1}.

Y.N. Sudhakar et al., (2014) have found a supercapacitor based on a biodegradable gel polymer electrolyte (GPE) prepared using guar gum (GG) as the polymer matrix, $LiClO_4$ as the doping salt, and glycerol as the plasticizer. The scanning electron microscopy (SEM) images of the gel polymer showed an unusual tubular array type surface morphology. FTIR, DSC, and TGA results of the GPE indicated good interaction between the components used. The highest ionic conductivity and lowest activation energy values were 2.2×10^{-3} S\cm and 0.18 eV. Dielectric studies revealed ionic behavior and good capacitance with varying frequencies of the GPE system. The fabricated supercapacitor showed a maximum specific capacitance value of 186 F g^{-1} using cyclic voltammetry. Variation of temperature from 273K to 293K was not significantly influenced the capacitance values obtained from AC impedance studies.

The electrochemical performance of lithium nickel manganese cobalt oxide (NMC) electrodes using guar gum was studied by X-ray Photoelectron Spectroscopy (XPS) measurements of pristine electrodes and observed that the binder layer surrounding the active material particles is thin. Lithium-ion cells, utilizing guar gum on both positive and negative electrodes, display a stable discharge capacity of ~110 mAh g^{-1} (based on cathode active material) with high coulombic efficiencies has been investigated by ***Diogo Vieira Carvalho et al., (2018)***

2.4 PECTIN BASED BIOPOLYMER ELECTROLYTE

C. Nithya Priya et al., (2020) have prepared biodegradable polymer blend electrolytes based on Pectin–polyvinyl alcohol (PVA) with a constant amount of sodium nitrate ($NaNO_3$) salt using a solution casting technique. The interaction between polymers and salt was calculated by Fourier transform infrared spectroscopy, and the AC impedance technique is implied to analyse the ionic conductivity of the prepared samples. When synthetic polymer PVA is added with pectin, the ionic conductivity increases. Pectin: PVA: $NaNO_3$ [00.100.04] blend polymer electrolyte shows a higher ionic conductivity of 4.3×10^{-6} S cm^{-1} at room temperature.

P Perumal et al., (2019) studied Solid Biopolymer Electrolyte (SBE) membrane, pectin complexed with dilithium borate prepared by using solution casting technique and characterized by XRD, AC impedance, and LSV techniques. The ion conductivity to a maximum of 1.69×10^{-5} S cm^{-1} for 60 wt % pectin: 40 wt % $Li_2B_4O_7$ composition was attributed to the addition of $Li_2B_4O_7$, which increases the number of conducting ion species. An increase in conductivity with temperature can be correlated with the free volume model. The lowest value of activation energy and an electrochemical stability window of 3.11 V was obtained for the highest ion-conducting sample, indicating that this composition is a promising biopolymer membrane electrolyte in all-solid-state batteries.

Shilpa Rajendran et al., (2021) have explained that solid electrolyte using lithium bis (trifluoromethanesulphonyl) imide (LiTFSI) doped in host Pectin (biopolymer) by solution casting technique. The prepared solid polymer electrolyte was characterized using XRD, FT-IR Spectrophotometer, TG/DTA, and 3D Optical Laser Profilometry techniques. The ionic conductivity was determined using an AC Impedance spectroscopy. The highest ionic conductivities attained for the EC-based electrolyte film is approximately 2.43×10^{-4} S cm^{-1} for 60:35: 5 wt. % of the lithium salt doped.

The polymer electrolytes based on the biopolymer pectin doped with ammonium chloride (NH_4Cl) and ammonium bromide (NH_4Br) were prepared by ***N. Vijaya et al., (2017)*** via solution casting technique. The prepared membranes were characterized using XRD, FTIR, and AC impedance techniques to study their complexation behavior, amorphous nature, and electrical properties. The conductivity of pure pectin membrane has been found to be 9.41×10^{-7} S cm^{-1}. The polymer systems with 30 % NH_4Cl-doped pectin and 40 % NH_4Br-doped pectin have been found to have maximum ionic conductivity of 4.52×10^{-4} and 1.07×10^{-3} S cm^{-1}. The conductivity value has increased by three orders of magnitude compared to pure pectin membrane.

M. Muthukrishnan et al., (2019) have synthesized a polymer electrolyte based on biopolymer pectin with ammonium thiocyanate (NH_4SCN) salt by solution casting technique. Amorphous/crystalline nature of the polymer electrolyte has been studied using X-ray diffraction technique. The complexation between polymer and salt has been confirmed by Fourier transform infrared spectroscopy. A shift in glass transition temperature of the pectin: NH_4SCN electrolytes have been observed from the differential scanning calorimetry thermograms. Ionic conductivity of the electrolytes was measured through impedance spectroscopic technique. The frequency and temperature dependence of ionic conductivity has been studied. The highest conductivity of 1.5×10^{-3} S cm^{-1} was observed for 40 % pectin: 60 % NH4SCN sample.

S. Kiruthika et al., (2020) have prepared polymer electrolyte, pectin with magnesium chloride salt for magnesium battery application. Biopolymer electrolytes of different compositions of pectin with different concentrations of magnesium chloride salt were prepared by solution casting technique. The characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), AC impedance spectroscopy, and linear sweep voltammetry were among the tests performed (LSV). The amorphous/crystalline nature of the material was determined via XRD analysis. FTIR spectroscopy was used to examine the complex formation between the polymer pectin and the magnesium chloride salt. DSC analysis is a thermo-analytical technique for determining the sample's glass transition temperature. The ionic conductivities of the sample were determined using the AC impedance technique. Linear sweep voltammetry was used to assess the electrochemical stability of the polymer electrolyte. Among the polymer electrolytes produced, 30 wt% pectin: 70 wt% MgCl2 offers the highest ionic conductivity of 1.14×10^{-3}S cm^{-1}. The electrochemical stability of the highest conducting sample is 2.05 V.

Lithium-ion conducting solid biopolymer electrolyte based on natural polymer Pectin with Lithium perchlorate ($LiClO_4$) has been prepared by ***P. Perumal et al., (2019)*** via solution casting technique. The prepared polymer electrolytes are characterized using XRD, CV, and AC impedance analysis. From AC impedance analysis, the maximum ionic conductivity was observed in the order of 5.15×10^{-5} Scm-1 at room temperature.

Bai Sun et al., (2018) have fabricated BiFeO3 nanoflakes by composting with organic pectin as an outstanding anode material for rechargeable Na-ion batteries by an improved hydrothermal process for the first time. They found that the $BiFeO_3$/pectin nanoflakes as anode hold long-life and excellent charge-discharge performance with reversible capacity of 450 mAh g^{-1} which can retain 100% capacity after 100 charge-discharge cycles.

2.5 BIOPOLYMER ELECTROLYTE PREPARED USING NaI SALT

BPE films based on Chitosan – Polyethylene glycol (PEG)-NaI have been prepared by ***Devesh Chandra Bharati et al., (2020)*** using solution cast technique. The prepared electrolyte films were subjected to thermal, structure, and conductivity studies using TGA, XRD, ATR-FTIR, and AC impedance spectroscopic techniques. The thermal gravimetric analysis (TGA) reveals that the CS and [CS-PEG]-NaI-based films decompose in multistep. The [CS-PEG]-NaI-based films are thermally stable up to 220.2° C. XRD result shows that CS has semi-crystalline in nature having its characteristic peak appeared at $2\theta \sim 23.1°$. The degree of crystallinity (Xc) decreases with increasing NaI content in CS-PEG based films. ATR-FTIR study confirms the interaction between bio-polymer, CS with PEG and NaI. The sample containing 40wt%NaI shows dc conductivity value of 7.25×10^{-4} Scm^{-1} at 30°C temperature. The values of frequency exponents for BPE films were found to be 0.68 to 0.22.

Quasi-solid bio-electrolytes based on hydroxyethyl cellulose (HEC) and sodium iodide (NaI) in three different polar aprotic solvent systems, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and dimethylacetamide (DMA), were fabricated by ***Vidhya Selvanathan et al., (2018)*** and characterized using FT-IR spectroscopy, XRD, electrochemical impedance spectroscopy (EIS) analysis, Linear sweep voltammetry(LSV). The highest ionic conductivity was recorded upon 70 wt% of NaI in each solvent system, with an overall maximum value of 2.16×10^{-2} S cm^{-1} in DMF.

Noriah Abdul Rahman et al., (2021) have prepared chitosan-NaI electrolyte via a simple solution casting technique. The prepared electrolyte was characterized by FT-IR, XRD analysis, Impedance analysis, Scanning electron microscope, and chronoamperometry analysis. Infrared spectroscopy analysis highlights interactions between chitosan and NaI that weaken the semi-crystalline domains of chitosan and favors the conduction of the redox shuttle ions between cell electrodes. The highest ionic conductivity was obtained for the samples loaded with NaI 30 wt%, with values equal to 1.11×10^{-4}S cm^{-1} at room temperature.

R. H. Y. Subban et al., (1996) have prepared chitosan containing sodium iodide by the Solution cast technique. The electrolyte films were prepared by dissolving 1 g of chitosan in different 100ml of 1% acetic acid solution to which 0.5g, 1.0g, 1.5g, 2.0g, and 2.5 g of sodium iodide were added. The electric conductivity of the films measured at room temperature stops increasing after more than 1.5g of sodium iodide was added. The electrolyte film with the highest electric conductivity of 4.9×10^{-2} mS/cm.

Syakirah Shahrudin et al., (2016) studied biopolymer electrolyte prepared by doping corn starch with sodium iodide (NaI) using the solution casting method. The incorporation of 25% NaI resulted in maximum conductivity of the electrolyte at 1.46×10^{-4} S cm-1. The maximum ionic conductivity of 1.6×10^{-3} S cm^{-1} was obtained with the sample containing 10 wt. % of graphene oxide (GO). The electrolyte system was investigated by deploying electrical impedance spectroscopy (EIS) measurement at temperatures of 298K-373K.

Aziz M. Abdullah et al., (2021) investigated solid polymer blend electrolytes based on polyvinyl alcohol (PVA) and methylcellulose (MC) doped with sodium iodide (NaI). The polymer electrolyte films were prepared via a solution casting technique. The host matrix, is doped with different NaI salt concentrations between 10 and 50 wt. %, utilizes the most amorphous blend compositions (60 wt. % polyvinyl alcohol and 40 wt. % methylcellulose). The structural behavior of the electrolyte films was examined utilizing X-ray diffraction (XRD) and Fourier transformation infrared (FTIR) techniques. The semi crystalline nature of PVA: MC with inserted NaI was derived from the X-ray diffraction studies, while the XRD analysis suggests that the highest ion conductive sample displays the minimum crystalline nature. The highest ionic conductivity of 1.53×10^{-5} S/cm was observed for a sample containing 50 wt% of NaI salt.

Devesh Chandra Bharati et al., (2021) have discussed biopolymer blend electrolytes based on (PVA-CS)-NaI added with different concentrations of (x = 10, 20, 30, 40, 50 in wt. %), respectively, were prepared using solution cast technique. Prepared samples have been characterized using XRD, ATR-FTIR, TGA, and AC impedance spectroscopic techniques. The highest ionic conductivity 1.2×10^{-5} S cm^{-1} was obtained at 30 °C.

Poly (L-leucine) 1, 3–diamino propane (PLLTMEDA) has been chosen as an additive to the binary compound sodium iodide (NaI) and sodium phosphate (Na_3PO_4). A small amount of PLLTMEDA was added to the optimum composition of the binary compound (0.5 NaI–0.5 Na_3PO_4). The maximum electrical conductivity of $(1.12 \pm 0.21) \times 10^{-3}$ S cm^{-1} at room temperature was obtained for 50 wt. % NaI–50 wt. % Na_3PO_4–4 wt. % PLLTMEDA. Fourier transform infrared spectroscopy (FTIR) analysis revealed the band of C=O at 1650 cm–1 experienced a shift, indicating that some interaction had occurred. The ionic transference number was found to be ≈1 for the optimum composition with maximum conductivity which suggests that the sample is ionic. The optimum composition of the sample was used as a solid electrolyte in a solid-state sodium battery. The sodium battery was tested by the discharged characteristic at a current of ≈1.0 μA. The solid-state sodium batteries exhibited a discharge capacity of 173 mAh/g are described by ***A.H. Ahmad et al., (2017)***

2.6 PREPARATION OF ELECTROLYTES USING SODIUM SALTS

Carboxymethyl cellulose (CMC) with sodium acetate and integrated with ionic liquid 1-butyl-3-methylimidazolium chloride, [Bmim] Cl, was investigated by ***Mohd Saiful Asmal Rani et al., (2020).*** The highest ionic conductivity of $(4.54 \pm 1.2) \times 10^{-3}$ S cm^{-1} was obtained at 30 wt. % [Bmim] Cl for the weight of CMC. The prepared electrolyte was characterized by FT-IR, XRD, TGA, and AC impedance studies. Infrared spectroscopic analysis revealed the interaction of the polymer host with the sodium salt and ionic liquid.

K. Vignarooban et al., (2017) have synthesized and characterized poly-acrylonitrile (PAN)-based gel-polymer electrolytes formed with $NaClO_4$ and dissolved in ethylene carbonate (EC) and propylene carbonate (PC). By systematically varying the weight ratios of polymer, salt, and the solvents, they obtained an optimum room temperature ionic conductivity of 4.5 mS cm^{-1} for the composition 11PAN-12$NaClO_4$-40EC-37PC (wt. %).

Sodium-ion conducting poly (vinyl alcohol)-based gel polymer electrolyte membrane is developed by ***Jingwei Wang et al., (2019)*** via plasticizing with an ionic liquid, for the fabrication of electric double-layer capacitors. Sodium triflate is selected as the sodium salt. 1-ethyl-3 methyl imidazolium trifluoro methane sulfonate is employed as the plasticizer. The properties of the electrolyte membranes are analyzed in terms of their crystallinity, morphology, thermal stability, electrochemical stability window, ionic transference number, and ionic conductivity. The composition with poly(vinyl alcohol) - 30% sodium triflate + 10% 1-ethyl-3 methyl imidazolium trifluoromethane sulfonate shows the optimal performances such as good thermal stability up to 150 oC and a wide electrochemical stability window of 4.70 V. It is found that the composition of PVA-30% NaTf + 10% EMITf (P-30-10) exhibits an excellent ionic conductivity of 3.8×10^{-3} S cm^{-1} at room temperature.

Biodegradable solid polymer electrolyte based on NaCMC as polymer matrix doped with $NaClO_4 \cdot H_2O$ has been prepared by ***Supriya K Shetty et al., (2021)*** via solution cast technique. The prepared biopolymer electrolyte was characterized by FTIR, XRD, DSC, and EIS techniques. FTIR analysis exhibited a considerable microstructural modification in NaCMC upon NaClO4·H2O doping invoked through complex formation via Lewis acid-base interaction and hydrogen bond formation between ions and dipoles. The highest ionic conductivity of 1.11×10^{-4} Scm^{-1} was obtained with low crystallinity.

K. B. Md Isa et al., (2017) have prepared sodium ion conducting gel polymer electrolyte (GPE) films consisting of polyvinylidene fluoride-co-hexafluoro propylene (PVdF-HFP) as a polymer host using the solution casting technique. Sodium trifluoro methanesulfonate ($NaCF_3SO_3$) was used as an ionic salt and the mixture of ethylene carbonate (EC) and propylene carbonate (PC) as a plasticizing solvent. Impedance spectroscopy measurements were carried out to determine the ionic conductivity of the GPE films. The sample containing 20 wt. % of $NaCF_3SO_3$ salt exhibits the highest ionic conductivity of 2.50×10^{-3} S cm^{-1} at room temperature.

Pectin-based biopolymer electrolytes have been prepared with different concentrations of sodium nitrate by solution casting technique using distilled water as solvent. The amorphous nature of all the prepared biopolymer electrolytes is confirmed by X-ray diffraction studies. The FTIR studies confirm the complexation between polymer and salt. The maximum ionic conductivity (2.7×10^{-9} S/cm) of pure pectin is enhanced to 4.2×10^{-6} S/cm by doping of $NaNO_3$ salt was determined by ***M. Vahini et al., (2019)***

Biopolymer electrolytes were developed using carboxymethyl cellulose (CMC) with different ratios of sodium acetate ($NaCH_3COO$) via a solution casting technique, and their structural, electrical, and electrochemical behaviors were investigated by FT-IR spectroscopy, Electrochemical impedance spectroscopy, XRD analysis, TGA techniques. The incorporation of 30 wt. % sodium acetate yielded an optimized ionic conductivity of 1.83×10^{-3} S cm^{-1} at room temperature was developed by ***M.S.A. Rani et al., (2020)***

M. Infanta Diana et al., (2021) have fabricated the solid biopolymer electrolyte based on sodium alginate and sodium thiocyanate salt via solution casting techniques. The complex formation between sodium alginate and NaSCN has been confirmed with the help of X-ray diffraction (XRD) analysis and Fourier transform infrared spectroscopy (FTIR) techniques. On increasing NaSCN concentration, the semi-crystalline nature of the sodium alginate gets abated thus elevating the amorphous domain of the electrolyte membrane. The biopolymer host material (30 wt. %) can accommodate large amounts of NaSCN salt (70 wt. %) exhibiting ionic conductivity of 1.22×10^{-2} S cm^{-1}.

Materials and Methodology

CHAPTER-III

MATERIALS AND METHODOLOGY

3.1 Introduction

Renewable sodium-ion batteries have grabbed the curiosity of many in recent years due to their low cost, ease of synthesis, adaptability, compactness, and great adherence to the skin. The materials used and methods adopted in the present study are given in this chapter. In sodium-ion batteries, the interaction between cathodes and electrolyte solution conducts and oxidation processes occurs at high voltage and becomes intrinsically unstable. Oxidation reactions destroy the chemical structures of the electrolyte solution and cathodic active materials, producing hazardous byproducts and considerable capacity loss.

Solid polymer electrolytes (SPE)-based rechargeable sodium-ion battery (SIB) is one of the most promising possibilities for next-generation, large-scale, high-energy, and high-safety energy storage applications. SPEs are a great alternative for use as an electrolyte.

The Blending of polymer is an essential method for preparing polymer electrolytes with strong ionic conductivity and great thermal stability at ambient temperature. Polymer blends are polymer systems that are made up of two or more polymers or copolymers that haven't had a lot of chemical interactions between them. The capacity to combine existing polymers into new materials with specified qualities for desired applications is one of the benefits of polymer blends.

The present research is focused to prepare and characterize a new blend polymer electrolyte based on Pectin-Guar gum doped with Sodium Iodide. The polymer blend of pectin and guar gum has been chosen for use as a polymer electrolyte in sodium-ion batteries in this study.

3.2 Details of materials used in the present research

Pectin

Host polymer	-	Pectin
Molecular formula	-	$C_6H_{10}O_7$
Average molecular weight	-	194.1 kg/mol
State	-	White powder
Solvent	-	Water

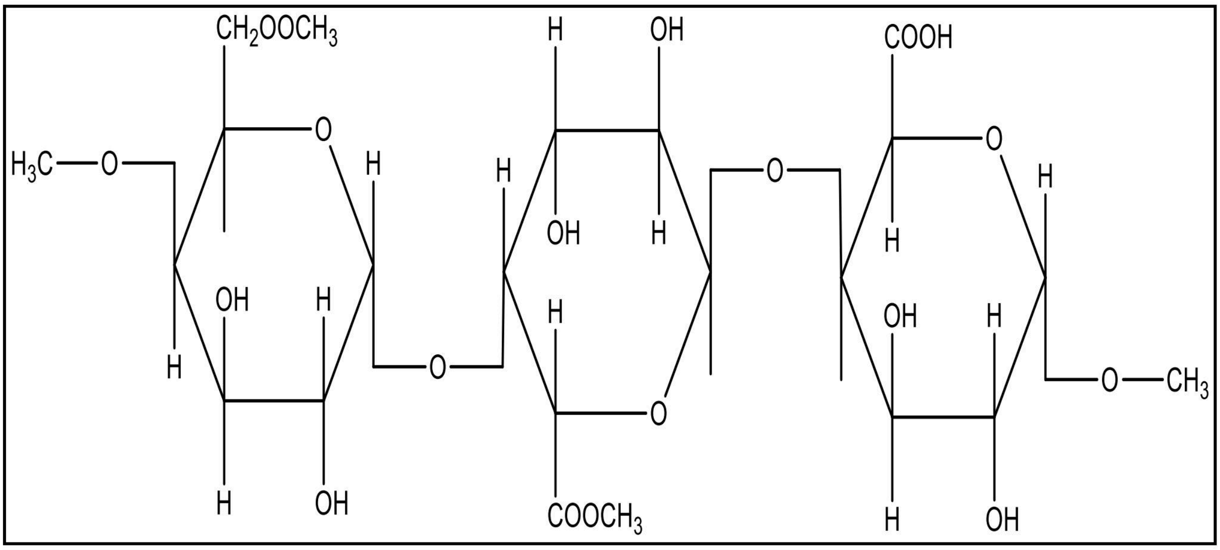

Figure 3: Structure of Pectin

Guar Gum

Host polymer - Guar Gum (GG)

Molecular formula - $C_{18}H_{32}O_{16}$

Average molecular weight - 535.146g/mol

State and appearance - Dirty white colored powder

Solvent - Water

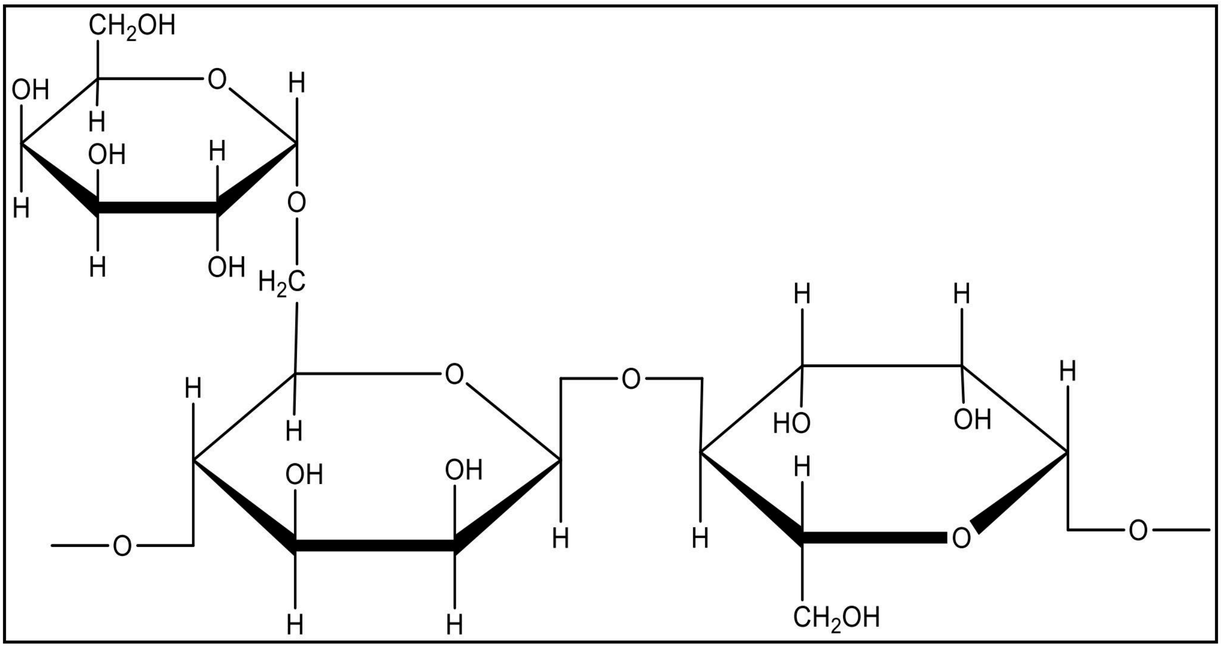

Figure 4: Structure of Guar Gum (GG)

Structure and Properties of the Ionic dopant (Salt)

Ionic dopant - Sodium Iodide (NaI)

Molecular formula - 149.89 g/mol

State and Appearance - White solid, Deliquescent

Solvent - Deionized water

Structure and Properties of Plasticizer

Plasticizer - 1, 2-Dimethoxy ethane

Molecular formula - $C_4H_{10}O_2$

Molecular weight - 90.12 g/mol

State and appearance - Colorless liquid

Solubility in water - Miscible

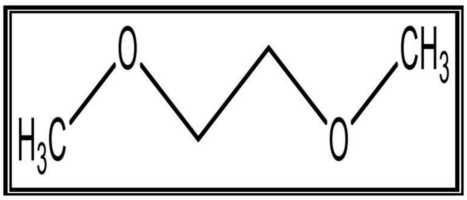

Figure 5: Structure of 1, 2-Dimethoxy ethane

3.3 METHODOLOGY

The blend of polymer Guar Gum and Pectin has been doped with ionic dopant Sodium Iodide to synthesize an ion-conducting polymer electrolyte. The polymer electrolyte has been prepared by adopting the solution casting technique and blending of polymer. The two methods are mostly used, because of their easy preparation with a suitable concentration of blend electrolyte and suitability for mass production. Among the commercially available various methods of electrolyte preparation, the solution casting method is one of the good techniques.

Solution casting method

Polymer electrolytes have been prepared with different compositions of Sodium Iodide (NaI) salt. The concentration of Pectin-Guar Gum and NaI used for the preparation is given below.

- Pectin – 20ml
- Guar Gum – 20ml
- NaI – (0.10 wt%, 0.25 wt%, 0.50 wt%, 0.75 wt %)
- DME (1, 2-Dimethoxy ethane) – 5ml

It has been dissolved separately in deionized water and the solutions were mixed. To obtain a homogeneous mixture, the mixture has been stirred in a magnetic stirrer for about 24 hours. The mixtures were then poured into Petri-dishes and evaporated in a hot-air oven at 40°C for 24 hours **(fig. 6-9)**

Schematic illustration of the preparation of blend polymer electrolyte in the following flow chart

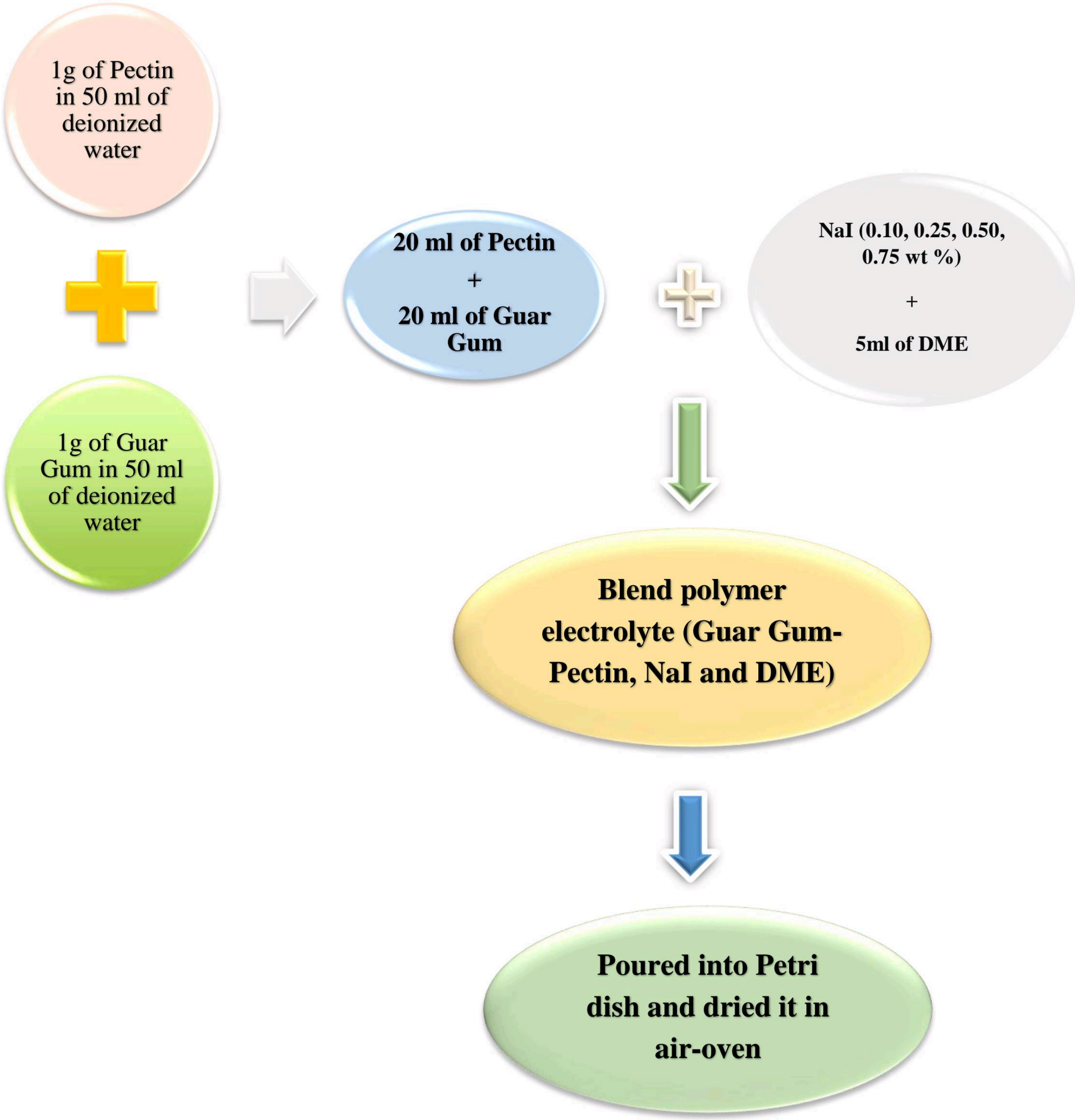

Figure 6: Schematic illustration of preparation of Blend polymer electrolyte

Prepared Electrolyte

Figure 7: Blending of polymer in magnetic stirrer

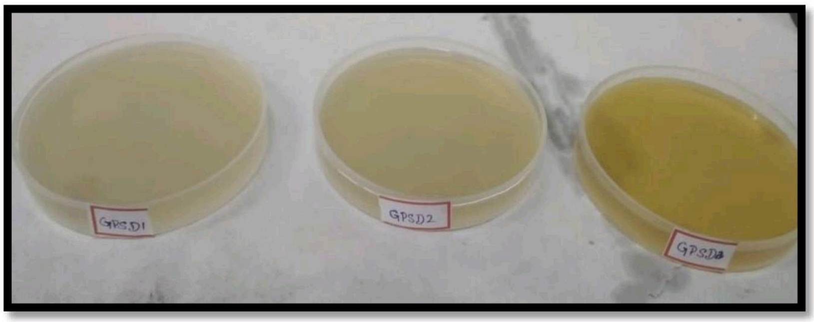

Figure 8: Prepared blend polymer sample-1, sample-2, sample-3, sample 4

Figure 9: Samples were dried in Hot-air oven at 40°C and displayed the dried blend polymer electrolyte film sample-1, sample-2, sample-3, sample -4

3.4 Characterization

The prepared polymer electrolyte is characterized by FT-IR spectroscopy, 3D-Laser optical profilometer, Thermal Gravimetric (TG), and Differential Thermal Analysis (DTA), Impedance Studies, and Transport number measurement by using the Chronoamperometry technique.

The chemical interaction between the blended polymers, the salts, and the functional groups present in the prepared electrolyte and cathode materials was analyzed through Fourier transform infrared (FTIR) spectroscopy (Miracle 10 SHIMADZU) in the frequency range of 400 to 4000 $cm^{-1.}$

The thermal stability of the polymer electrolytes was determined by Thermal Gravimetric/Differential Thermal Analysis (TG/DTA) through the 6300 Model instrument (EXSTAR) to perform thermogravimetric measurements. TGA analysis was performed by gradually raising the temperature (from room temperature to 800°C) of a sample in which the mass of a sample is measured over time as the temperature changes. The mass loss is due to the exposure of the sample to heat at a constant rate which is determined by the fraction of volatile components such as loss of water, loss of solvent, loss of plasticizer, and decarboxylation in the material.

The sample's roughness was determined by 3-D Optical Profilometer (Zeta-20). Profilometry is a technique used to extract topographical data from a surface. Step heights, surface morphology, and surface roughness are obtained from profilometry studies. The electrolyte sample was placed on the grid. The grid is manually adjusted towards the substrate to a safe operating distance. This technique is to direct the light in such a manner that it can detect the surface in three dimensions

Impedance spectroscopy is a technique used to analyze the electrical properties of the electrolyte material and their interfaces using Ametek PARSTAT MC – 1000. **(Figure: 10)** The impedance measurements were done in the frequency range of 1 Hz to 1 MHz at room temperature. The ionic conductivity depends on their mobility and the conducting species. This method is used to establish conductivity, observing the polymer chain participation and carrier generation processes.

To measure the transport number for identifying the conductivity in the polymer electrolyte whether ions or electrons by using the chronoamperometry technique. This equation is used to calculate the transport number.

$$t_{ion} = I_s / I_0$$

Where,

t_{ion} is the transfer of ions

I_0 is the initial current

I_s is the steady-state current

The DC potential of 0.1 V is applied across the cell in the AI electrode/AI electrode configuration and the polarization current is monitored as a function of time. The initial total current has been found to decrease with respect to time due to the depletion of the ionic species in the electrolyte and reaches the constant state in the fully depleted situation. The cell is polarized at the steady-state, and due to the migration of electrons, the current flows across the electrolyte and interfaces

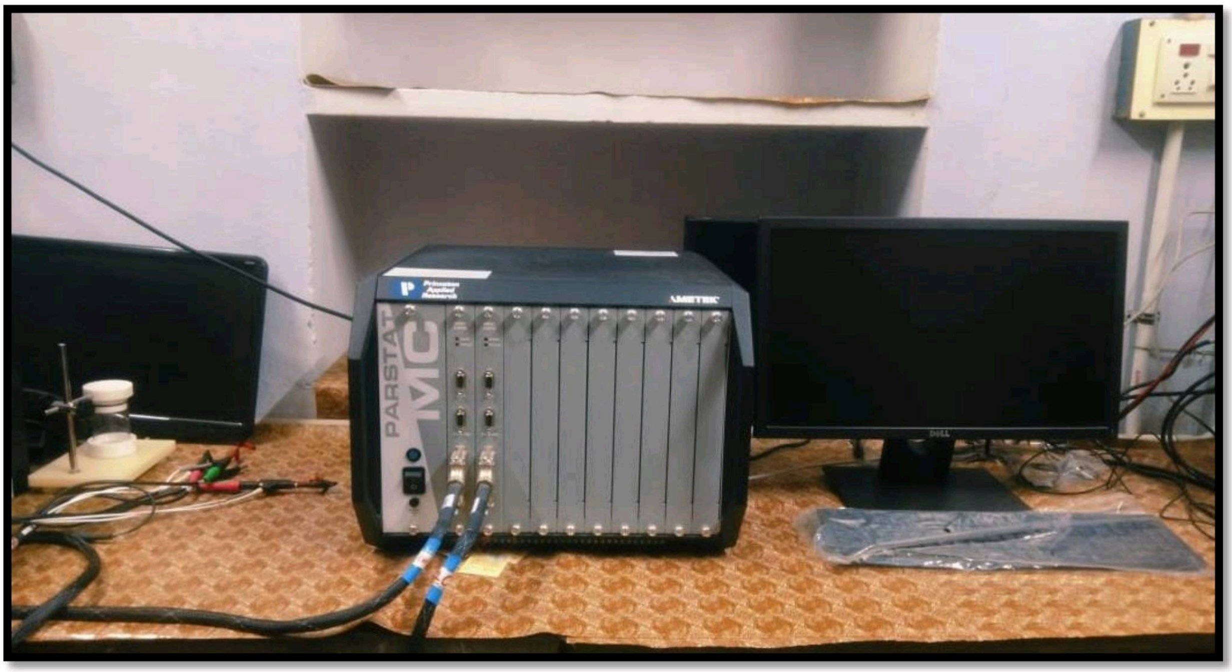

Figure 10: Electrochemical work station

Result and Discussion

CHAPTER-IV

RESULT AND DISCUSSION

4.1 Introduction

The result obtained in the present study or discussed in this chapter. In the present study, Pectin: Guar Gum blend polymer electrolyte have been prepared by Solution casting techniques with different concentrations of NaI (0.10 wt%, 0.25 wt%, 0.50 wt%, 0.75 wt %). The prepared thin film samples are characterized by Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric/Differential Thermal Analysis (TG/DTA), and 3D-Laser Profilometry, AC impedance spectroscopy, Chronoamperometry.

4.2 FT-IR Characterization

FTIR relies on the fact that most molecules absorb light in the region of the electromagnetic spectrum and the absorption corresponds specifically to the bonds present in the molecule. The frequency range is measured as wave numbers typically over the range 4000-600cm^{-1}. FTIR is practically useful for the identification of organic molecular groups and compounds due to the range of functional groups, side chains, and cross-links involved.

Fig 11(a-e) (R. Shilpa and R. Saratha, 2020) shows the FT-IR spectrum of a blend of Guar Gum (20 wt %): Pectin (20 wt %) electrolytes and blend polymer doped with 0.10, 0.25, 0.50, 0.75 wt % concentration of NaI salt

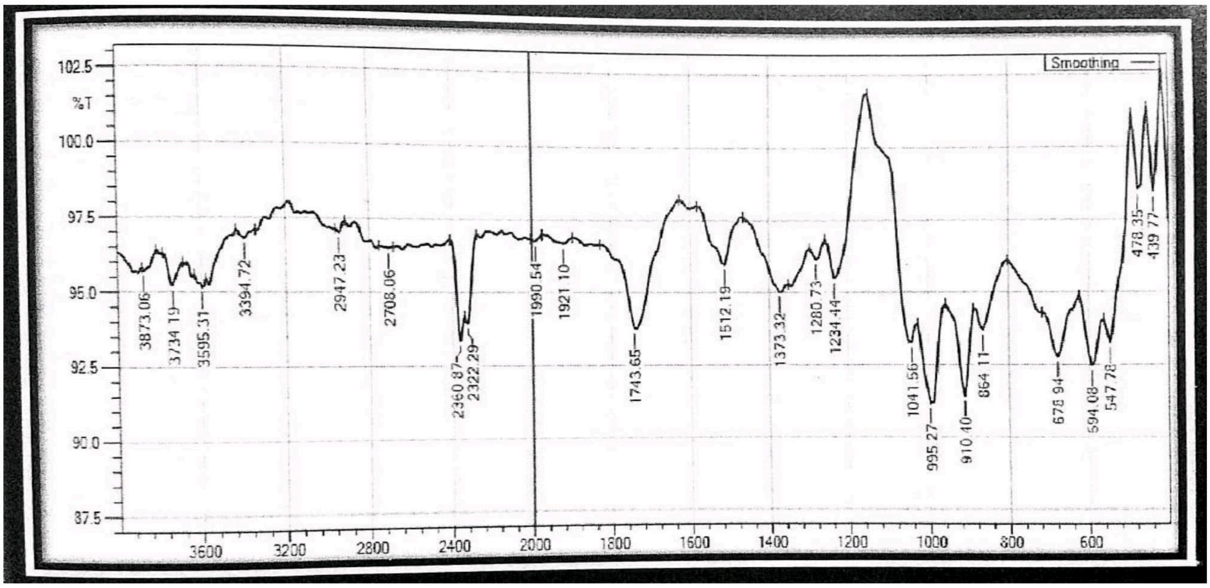

Figure 11a: The observed vibrational frequencies in the FTIR spectra of the Pectin and Guar Gum blend

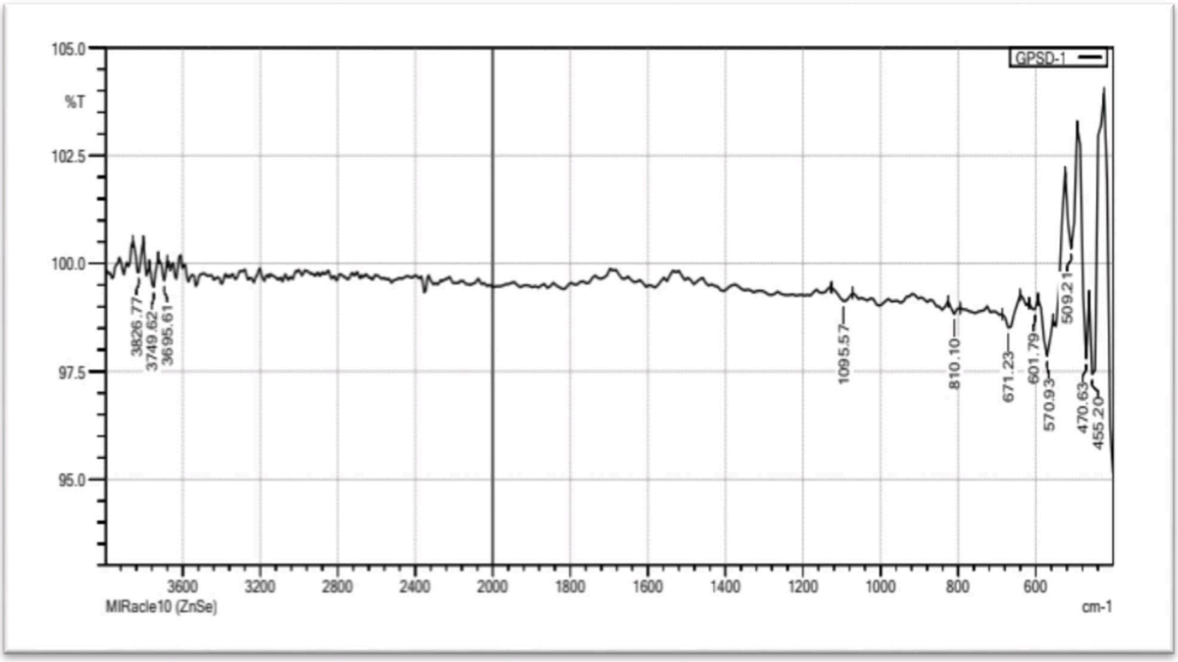

Figure 11b: FTIR spectra of Pectin, Guar Gum, and 0.10 wt% NaI

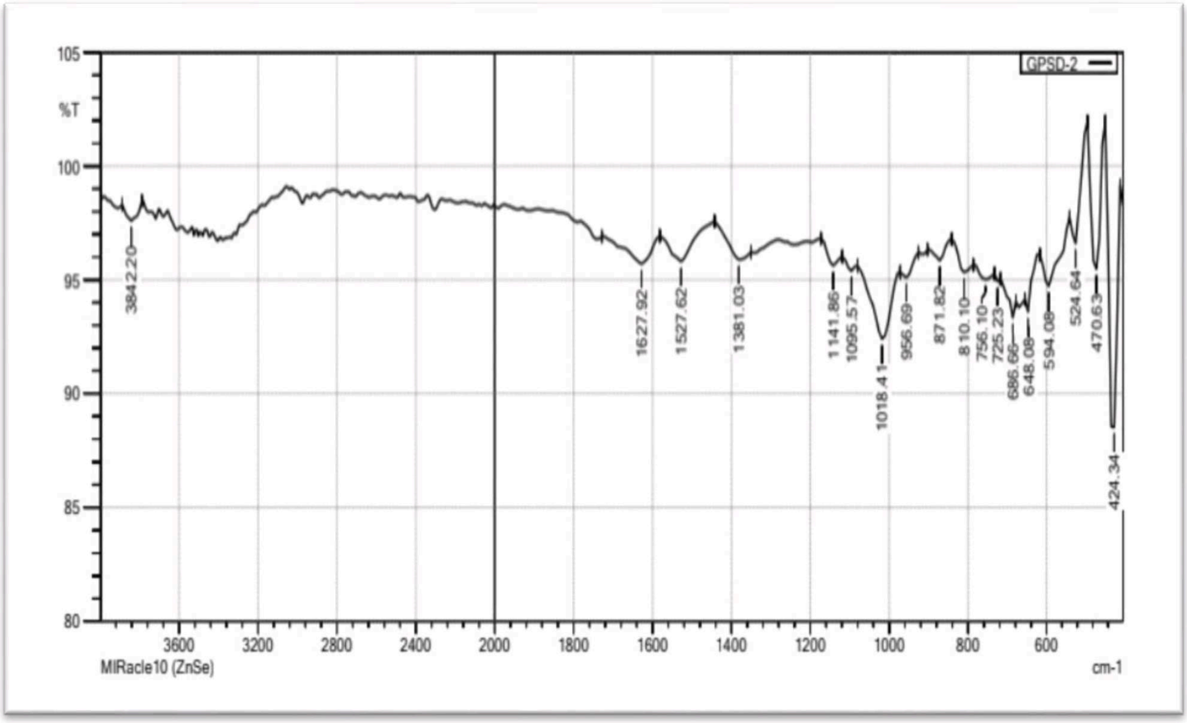

Figure 11c: FTIR spectra of Pectin, Guar Gum, and 0.25 wt% NaI

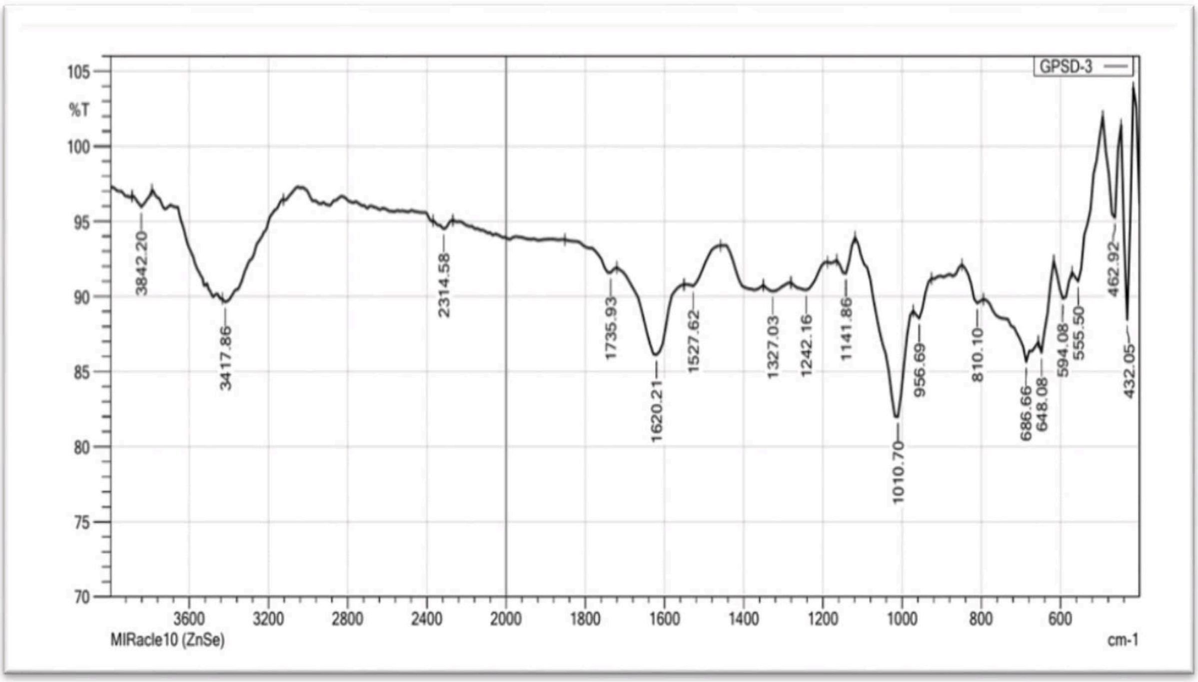

Figure 11d: FTIR spectra of Pectin, Guar Gum, and 0.50 wt% NaI

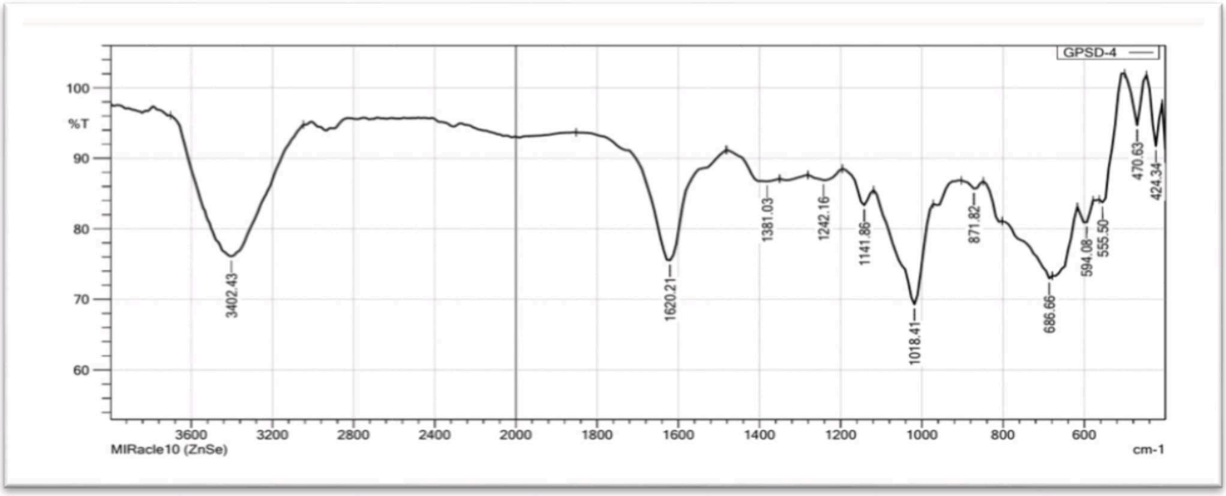

Figure 11e: FTIR spectra of Pectin, Guar Gum, and 0.75 wt% NaI

Table (2): The observed Vibrational frequencies in the FT-IR spectra of Pectin/Guar Gum and NaI blend polymer electrolyte

Wavenumber (cm^{-1})					
Pectin and Guar Gum Blend	**20%Pectin, 20% Guar Gum, 0.10 wt% NaI**	**20%Pectin, 20% Guar Gum, 0.25 wt% NaI**	**20%Pectin, 20% Guar Gum, 0.50 wt% NaI**	**20%Pectin, 20% Guar Gum, 0.75 wt% NaI**	**Characteristic groups**
3394.72	3695.61	-	3417.86	3402.43	OH-stretching vibration
2947.23	-	-	2314.58	-	C-H stretching of CH2 group
1743.65	-	1627.92	1620.21	1620.21	C=O stretching
1512.19	-	1527.62	1527.62	-	Ring stretching
1373.60	-	1381.03	1327.03	1381.03	-OH bending
1157.29	1095.57	1141.86	1141.86	1141.86	C-OH and primary alcoholic CH2OH stretching
1010.70	-	1018.41	1010.70	1018.41	CH2 twisting vibration
786.96	810.10	810.10	810.10	871.82	Galactose and mannose

The vibrational peak of the blend biopolymer (Pectin 20%:Guar Gum 20%) is 3394 cm^{-1} due to O-H stretching vibration which has been shifted to higher wavenumbers at 3695.61, 3417.86, 3402.43 cm^{-1} in the combination of the blend with 0.10wt%, 0.50wt%, 0.75w% of NaI respectively. The vibrational peak at 2924 cm^{-1} was attributed to the C-H stretching of the blend polymer resulting in peak shifting, which is shifted to a greater wave number with decreased intensity in concentration 0.50wt% of NaI salt doped polymer electrolyte (**Table - 2**). It is noticed that the peak at 1743.65 cm^{-1} corresponds to C=O stretching vibration which is shifted to 1627.92, 1620.21, 1620.21 cm^{-1} of 0.25, 0.50, 0.75wt% composition of NaI salt with Pectin-Guar Gum blend. The vibrational peak observed at 1512.19 cm^{-1} for ring stretching in Pectin- Guar Gum blend has been shifted to 1527.62$cm\text{-}^{1}$ in NaI (0.25, 0.50wt%), Pectin-Guar Gum. Blend polymer (Guar Gum: Pectin) and different combinations of NaI (0.25, 0.50, 0.75 wt %) with blend polymer resulted in vibrational peaks at 1373.60, 1381.03, 1327.03, 1381.03 cm^{-1}. The absorption band observed at 1157.29, 1095.57, and 1141.86, 1141.86, 1141.86 cm^{-1} is due to C-OH and primary alcoholic CH_2OH stretching vibrations in blended Pectin: Guar Gum, NaI (0.10, 0.25, 0.50, and 0.75 wt %) doped with blended biopolymer electrolyte. The band at 1010.70, 1018.41, 1010.70, and 1018.86 cm^{-1} resulted in CH_2 twisting vibrations for blend polymer (Guar Gum: Pectin) and different combination of NaI (0.25, 0.50, 0.75 wt %) with blend polymer. The absorbed band at 786.96, 810.10, 810.10, 810.10, and 871.82 cm^{-1} was attributed to galactose and mannose observed in the FTIR spectrum of blend polymer (Guar Gum: Pectin) and different combinations of NaI (0.10, 0.25, 0.50, 0.75 wt%) with blend polymer.

4.3 AC Impedance Spectroscopy Analysis

The typical Cole-Cole plots (Z’ VS Z’’) for the optimized composition of the blend polymer (20% Pectin; 20% Guar Gum) with concentrations (0.50%, 0.75%) are depicted in **figure 12(a)-12(b)**

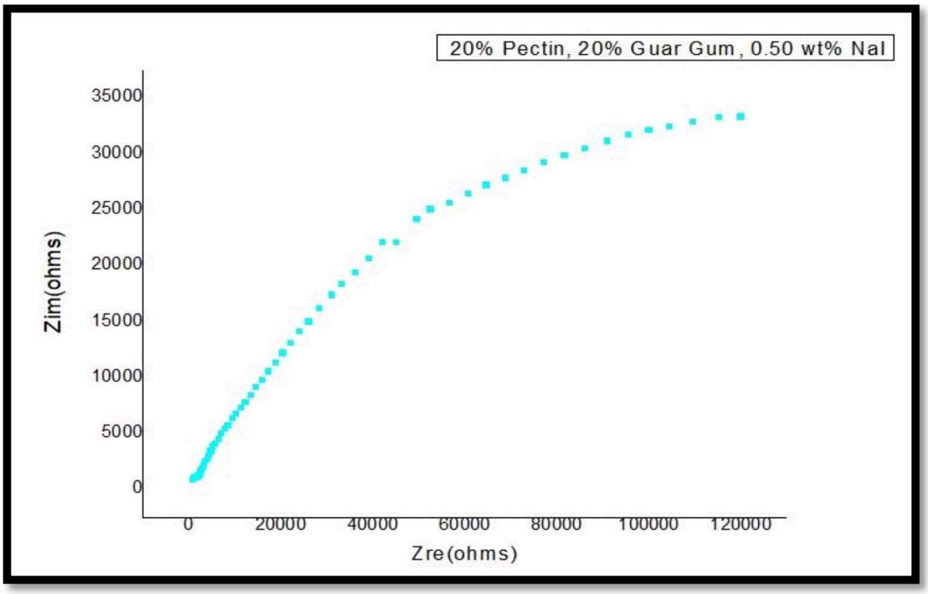

Figure 12(a): AC impedance for Pectin, Guar Gum blend with 0.50 wt% NaI

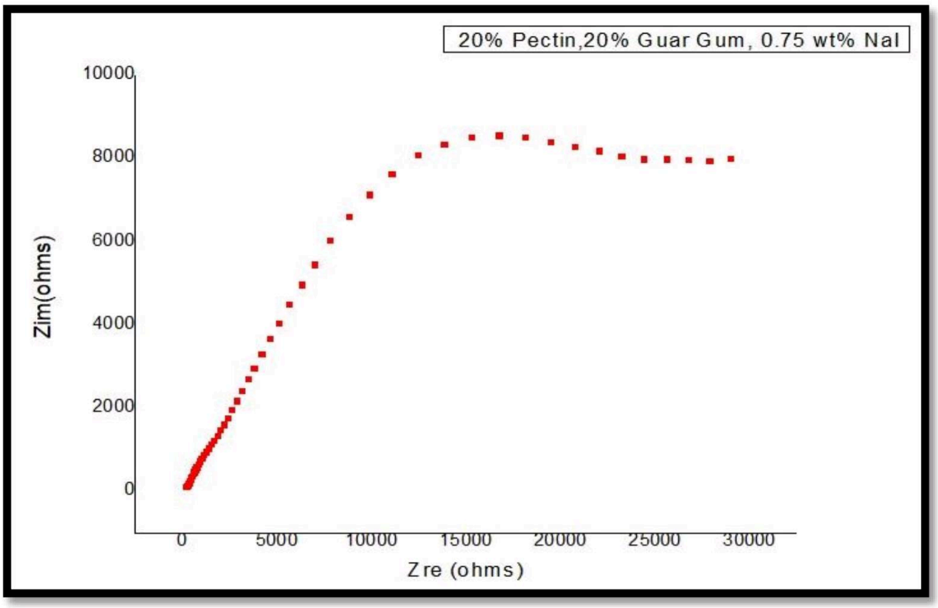

Figure 12(b): AC impedance for Pectin, Guar Gum, and 0.75 wt% NaI

Semi-circles produced due to constant phased element but lower frequency spikes were obtained due to the electrode-electrolyte interface. The occurrence of the resistive component of the polymer electrolyte is the reason for lower frequency spikes. The bulk resistance (R_b) is calculated either from the higher-frequency intercept of the semi-circle or the low-frequency spike on the real axis (Z'). In the present study, bulk resistance is calculated by lower frequency spikes of the real axis. The sample ionic conductivity is calculated by using the below equation,

$$\boldsymbol{\sigma = l \backslash R_b A}$$

Where **σ** is the ionic conductivity,

l is the thickness of the film

A is the effective contact area of the electrode and the blend polymer electrolyte film.

$\mathbf{R_b}$ is the bulk resistance

For the blend polymer electrolyte (20% Pectin and 20% Guar Gum) doped with 0.50 wt% and 0.75wt % NaI at room temperature exhibited ionic conductivity value was 8.54×10^{-2} S cm $^{-1}$ and 1.03×10^{-2} Scm^{-1}.

Table 3: The conductivity values

S.No	**Composition of Pectin: Guar Gum (%)-NaI (wt %)**	**Ionic Conductivity (σ) Scm^{-1}**
1.	20:20:0.50	8.54×10^{-2}
2.	20:20:0.75	1.03×10^{-2}

4.4 Morphology studies

3D-Laser Profilometry Analysis

3D-Laser Profilometry is one of the most recently developed approaches for surface roughness measurements. R_a is a roughness parameter that can be used to analyze surface morphology. It is reported as the R_a value increases, the roughness of the sample surface increases.

The topographical representation of surface features like thickness, roughness, and smoothness for 0.50 wt%, 0.75 wt% compositions of NaI salt doped with blended Pectin and Guar Gum are shown in **figures 13(a)-13(b)**

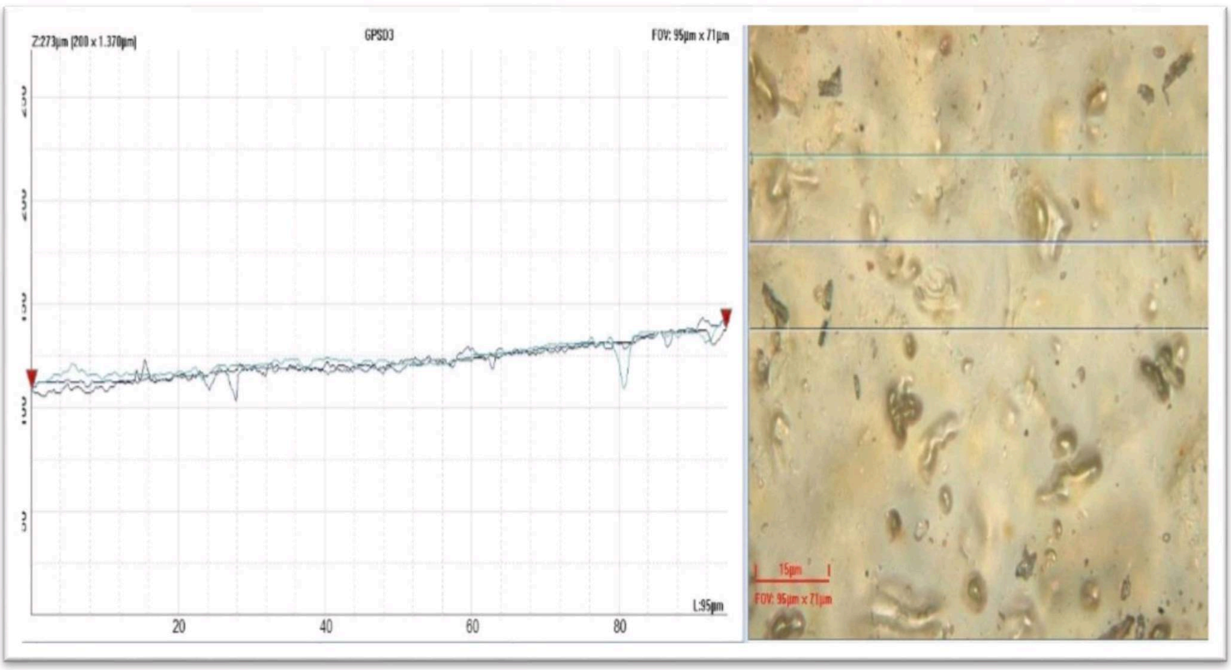

Figure 13 (a) Surface morphology of Pectin, Guar Gum, and 0.50 wt% NaI

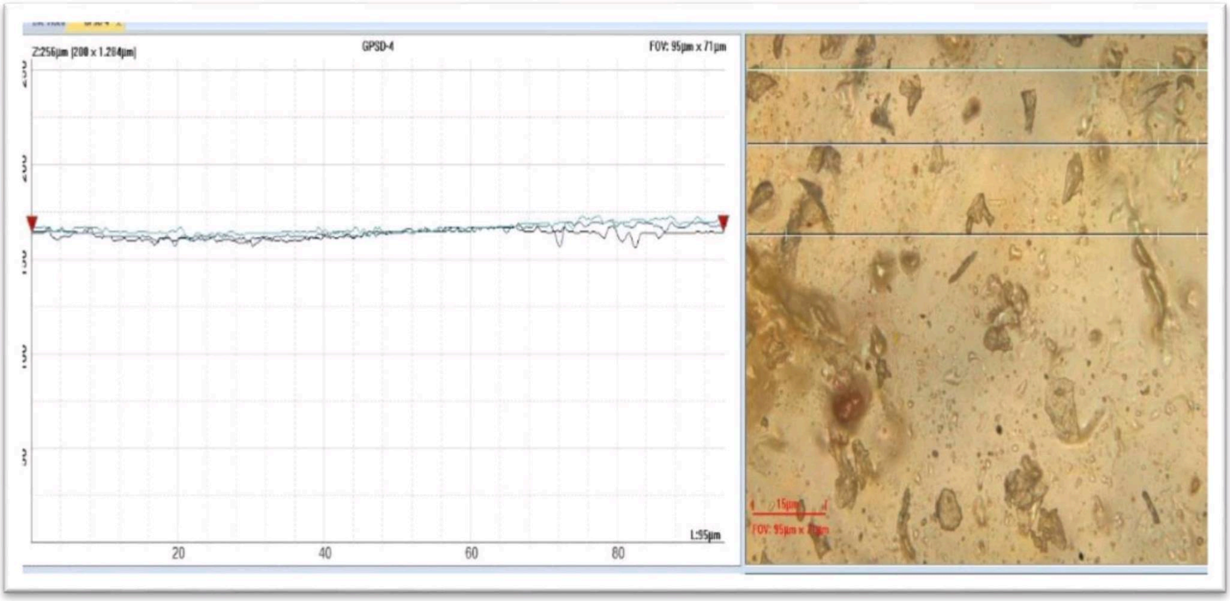

Figure 13(b) Surface morphology of Pectin, Guar Gum, and 0.75 wt% NaI

Zeta 3D images of 0.50 wt% and 0.75 wt% of NaI salt with Pectin, and Guar Gum blended polymer electrolyte are depicted in **figures 14(a – b)**

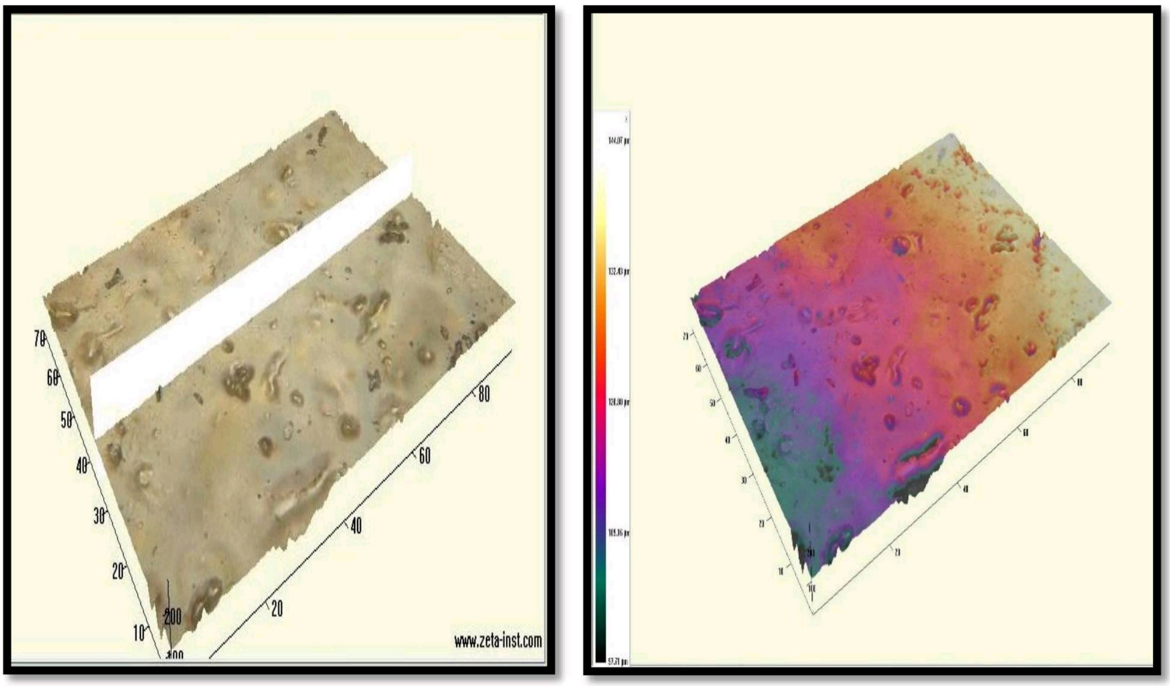

Figure 14a: Roughness of Pectin, Guar Gum, and 0.50 wt% NaI thin films

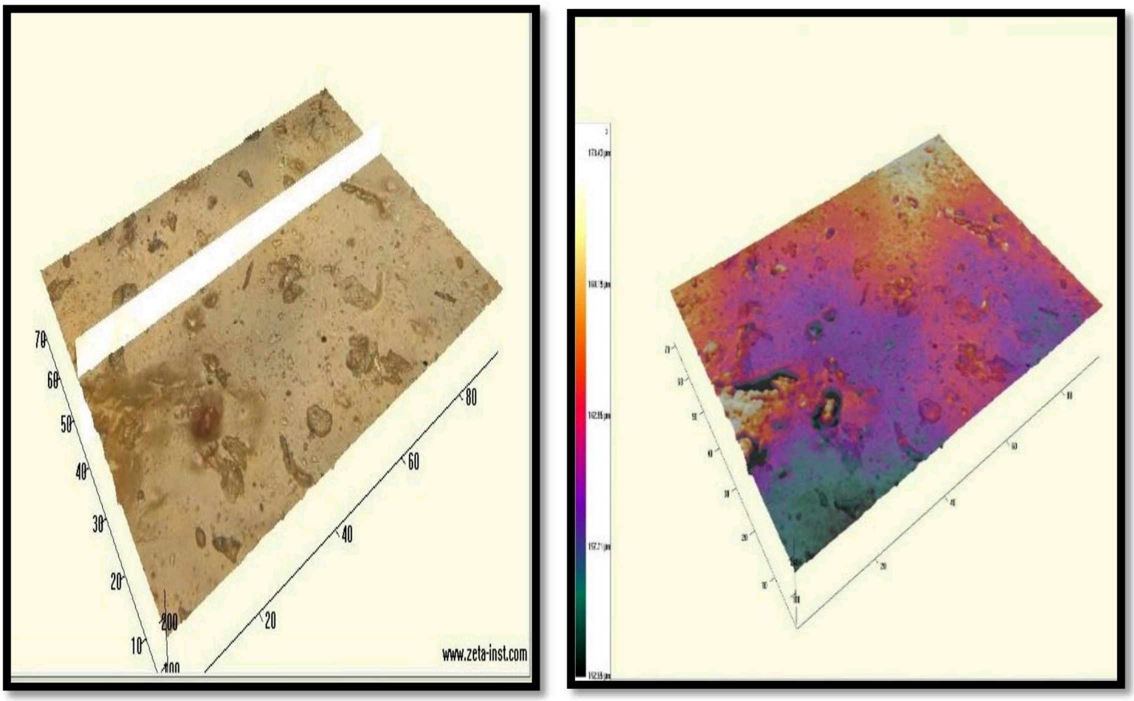

Figure 14b Roughness of Pectin, Guar Gum, and 0.75 wt% NaI thin films

The surface roughness parameters R_a were obtained for different concentrations of blend polymer electrolyte systems. The observed R_a values of Pectin/Guar Gum/NaI blend polymer electrolytes are given in **Table 4**

Table 4: Ra values for Pectin, Guar Gum- NaI blend polymer electrolyte

S.NO	**Concentration Of Pectin, Guar Gum (%) - NaI (wt %)**	**R_a (average roughness %)**
1	20:20:0.50	14.1
2	20:20:0.75	9.18

From table 2 it is clear that the polymer electrolyte thin films, 0.75 wt% showed less R_a value observed as 9.18%, was found to be comparatively smoother than the polymer electrolyte prepared with 0.50 wt% of NaI which possess R_a value in the range of 14.1%.

4.5 Thermogravimetric Analysis

Thermogravimetric analysis is used to find out the thermal stability of the samples. Thermal studies of blend polymer electrolyte films of Pectin, Guar Gum, and NaI were carried out up to 1000 ^{0} C. **Fig 15 (a - b)** showed the TGA patterns for Guar Gum: Pectin 0.50wt% NaI, of Guar Gum: Pectin 0.75wt% NaI respectively.

From the obtained TGA curves, 15% of the blended samples were decomposed up to 120^{0} C due to water loss. NaI being a hydrophilic substance upholds a restored capacity for absorbing water in doped films. 40% mass loss was obtained at 150 ^{0}C – 320 ^{0}C because of the degradation of biopolymer (Guar Gum-Pectin). The electrolyte film decomposition takes place majorly at 140 ^{0} C- 800^{0}C because of the interaction between the NaI salt and biopolymer which exhibited 60-85 % weight loss. The biopolymer electrolytes were thermally stable above 900^{0}C since there is no significant decomposition observed after 900^{0}C.

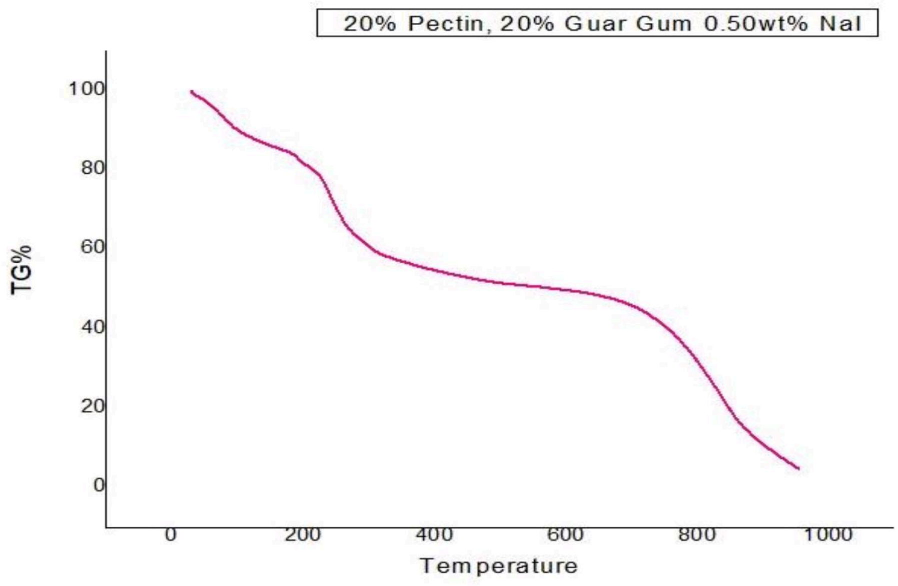

Fig 15 (a) TGA pattern of Guar Gum: Pectin 0.50wt% NaI

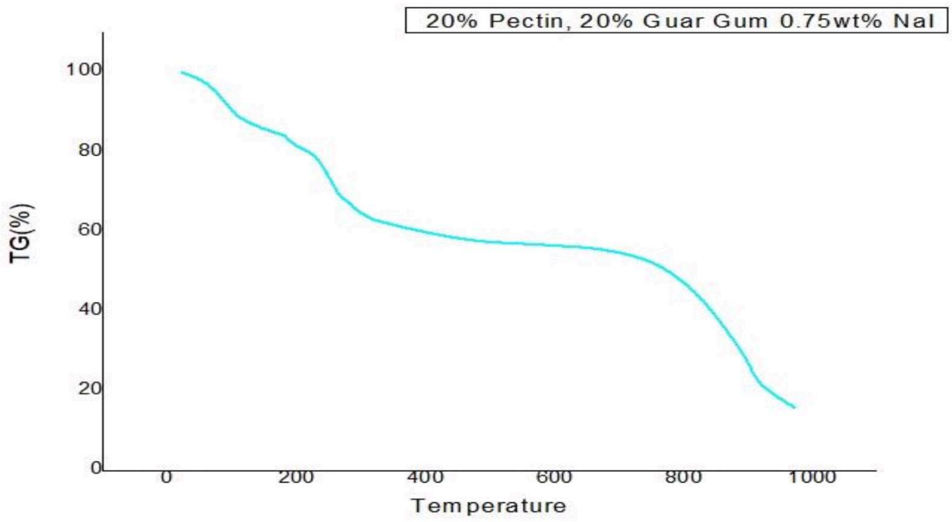

Fig 15 b TGA patterns of Guar Gum: Pectin 0.75wt% NaI

4.6 DTG

The differential thermogravimetric (DTG) method is used to record directly the first derivative of the TGA thermogram by plotting the weight differences per unit time or simply rate of weight loss, as a function of temperature. The rate of thermal decomposition is proportional to the volatilization or mass loss rate. Table 4 Shows decomposition temperature at various stages for combinations of Pectin-Guar Gum- NaI blend polymer electrolytes.

Table-5: Decomposition temperature at various stages for biopolymer electrolytes

Compositions Pectin (%): Guar Gum (%): NaI (wt %)	**Decomposition temperature (^{0} C)**			
	1st Stage	**2nd Stage**	**3rd Stage**	**4th Stage**
20:20:0.50	82	191	240	843
20:20:0.75	92	184	258	896

Figure 16(a-b), represent the DTG patterns of Guar Gum: Pectin (20:20) doped with NaI (0.50, 0.75 wt %). From the DTG curve, we can understand that the decomposition of biopolymer electrolytes takes place at 4 stages which shows the first stage decomposition obtained as 82, 92^0 C, the second stage degradation at $191{,}184^0$C, third stage decomposition observed at 240, 258^0C, fourth stage decomposition obtained as 843, 896^0C for the combination of Pectin-Guar Gum - NaI (0.50,0.75wt%)respectively.

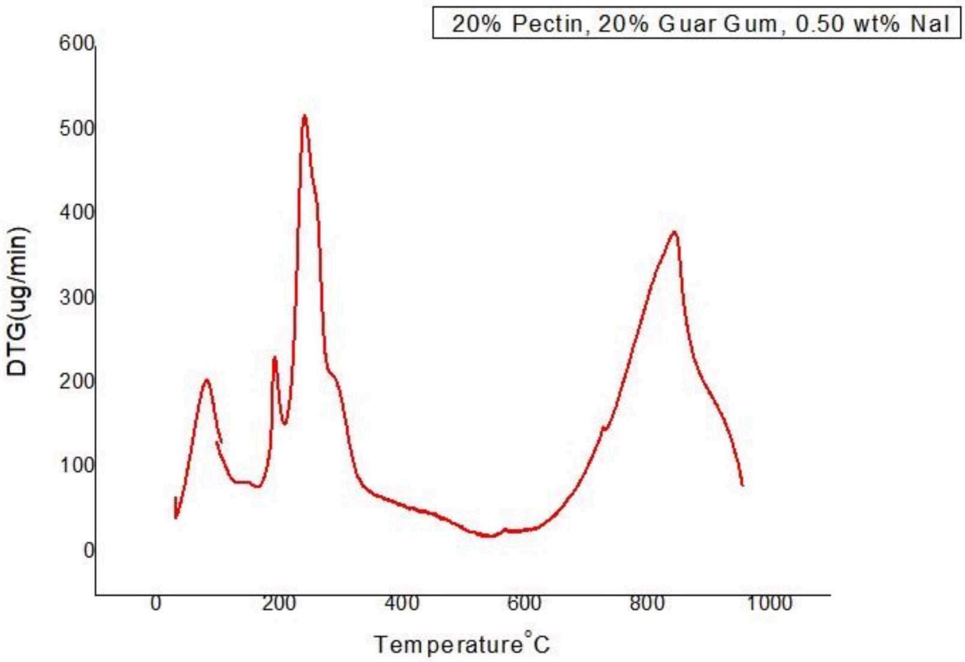

Figure 16(a): DTG patterns of Pectin: Guar Gum, 0.50 wt% NaI

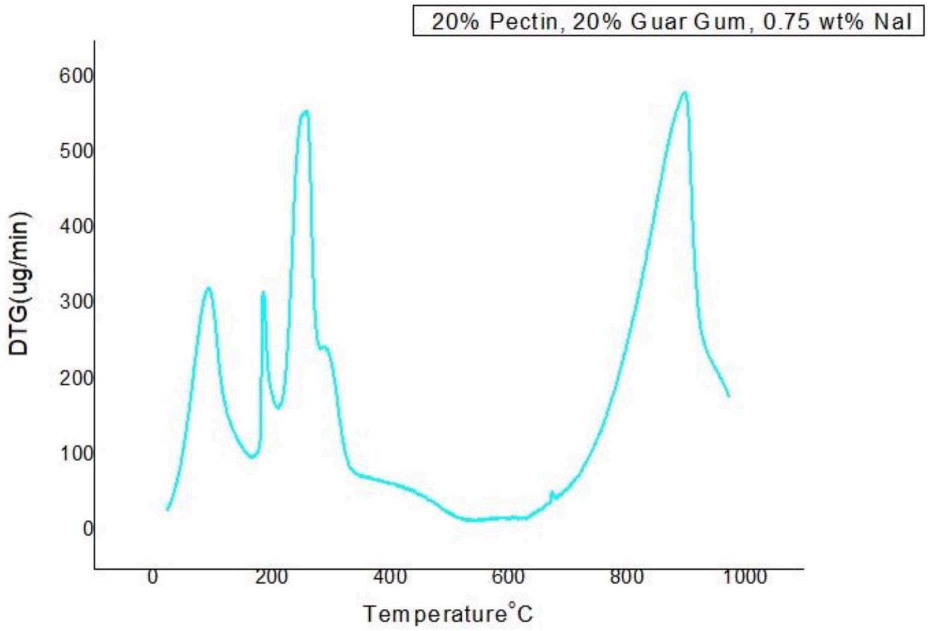

Figure 16(b): DTG patterns of Pectin: Guar Gum, 0.50 wt% NaI

4.7 Transport Number Measurement (TNM)

Chronoamperometry is the best technique to measure the transport number. The conductivity in the polymer electrolyte is given mainly by the conduction of ions and insignificantly by electrons. The Transport Number Measurement has been employed to figure out the main charge carrier at the working voltage of 10mV. **Figure 5** shows the polarization curve of current against time for the two of the most conducting samples of 0.75wt%NaI/Guar Gum/Pectin at ambient temperature (No proper polarization curve was obtained for 0.50wt% which may be due to less number of at lower concentration of NaI). The drop in the initial total current versus time is mainly due to the lessening of the ionic charge carrier species in the electrolyte systems **(Shujahadeen B. Aziz *et al.,* 2020)** Based on the TNM plots, the ions and electrons transference numbers were evaluated using the following equations:

$$\mathbf{t_{ion} = I_i - I_{SS} / I_i}$$

$$t_{el} = I_f / I_i$$

$$t_{ion} = 1 - t_{el}$$

Where t_{ion} is the ion transport,

t_{el} stands for the electron transport,

I_{Is} stands for the initial current which embraces' electrons and ions,

I_{ss} is the steady-state current that holds electron only

The t_{ion} was observed as 0.7587 for the sample 0.75wt%/Guar Gum/Pectin.

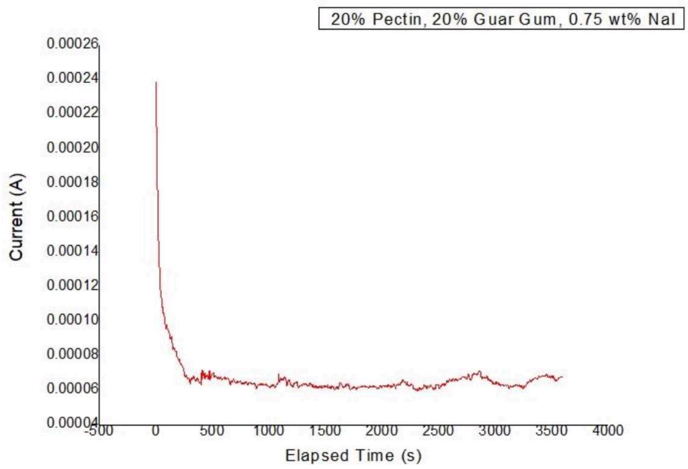

Fig 17- Chronoamperometry for 0.75wt%NaI/Guar Gum/Pectin

Summary and Conclusion

CHAPTER-V

SUMMARY AND CONCLUSION

The important features of the present study on **"Biodegradable Guar Gum-Pectin blend electrolyte for sodium ion batteries"** is summarized below.

- Biopolymer electrolytes of Guar Gum (20%) Pectin (20%) doped with DME (5ml) and NaI (0.10, 0.25, 0.50, and 0.75 wt %) have been prepared by solution casting technique.
- The complex formation of the ionic dopant and host polymer has been confirmed by FT-IR analysis.
- The roughness parameter Ra values of 9.18% for 0.50 wt% and 14.1% for 0.75 wt% were obtained from morphological studies using the 3D Laser Profilometry. The lower Ra value exhibited the smoothness of the blend polymer electrolyte.
- The thermal behavior of blend polymer electrolytes thin films was carried out by TG/DTA analysis and the TG result shows that there is increase in the thermal stability of Pectin-Guar Gum-NaI blend polymer electrolyte systems at higher temperature range.
- From the impedance study it has been found that the highest ionic conductivity of 1.03 x 10^{-2} S cm^{-1} has been obtained for Guar Gum: Pectin: 0.75 wt% NaI blend polymer electrolyte.
- The ion transfer number was found to be 0.7587 for the electrolyte with highest conductivity value 1.03 x 10^{-2} S cm^{-1}.

Recommendation

5.2 Recommendation

Based on the present study **'Biodegradable Guar Gum-Pectin blend electrolyte for Sodium ion Batteries'** the following recommendations are made.

- The present work could be extended by using Pectin/Guar gum/NaI to prepare electrolytes with plasticizer.
- Research work may be carried out with other Sodium salts as the ionic dopant and employ the same Pectin/Guar gum as the host polymer to prepare newer electrolyte with better ionic conductivity
-

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