

**BIO-HOST GUAR GUM COMPLEXED WITH SODIUM
BROMIDE BASED SOLID ELECTROLYTES FOR
SODIUM-ION BATTERIES**

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**Thesis submitted to
Avinashilingam Institute for Home Science and Higher Education
for Women,
Coimbatore- 43.**

**In Partial fulfillment of the requirements for the Degree of
MASTER OF SCIENCE IN CHEMISTRY
May - 2023**

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Rasool
10-5-23
**Signature of the
Supervisor**

Rasool
10-5-23
**Signature of the
Head of the Department**

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Knowledge is in the end based on Acknowledgement.

--Ludwig Wittgenstein

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LIST OF ABBREVIATIONS

S.NO	ABBREVIATIONS	EXPANSION
1	GG	Guar gum
2	PE	Polymer Electrolyte
3	NIB	Sodium-Ion Battery
4	FT-IR	Fourier Transform Infra-Red Spectroscopy
5	TGA	Thermal Gravimetric Analysis
6	EIS	Electrochemical Impedance Spectroscopy
7	CA	Chronoamperometry
8	XRD	X-Ray Diffraction
9	LSV	Linear Sweep Voltammetry
10	ITN	Ionic Transference Number
11	SPE	Solid Polymer Electrolyte
12	GG-NaBr-1,3-DOL	Guar gum- Sodium Bromide- 1,3-Dioxalane
13	GDN	Guar gum-1,3 Dioxalane- Sodium Bromide

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INTRODUCTION

CHAPTER I

INTRODUCTION

1.1 Introduction

The technology for storing energy has been around for nearly 100 years. The future of energy storage has great potential and will continue to evolve with the development of new technologies. Demand increases rapidly with the adoption of researchers into electric vehicles and grid-based energy storage applications.

1.2 Electrochemical Energy Storage Devices

Energy storage devices are devices that can store and release electrical energy when needed. Batteries and other devices with high power or energy densities are the foundation of electrochemical energy storage (electrochemical capacitors). Current and upcoming applications that need high power and energy densities in the same material are becoming more and more necessary. The market for batteries has grown significantly in recent years, making them the most scalable sort of storage available across the network.

1.3 Fundamentals of Battery

A battery is a device that uses an electrochemical oxidation-reduction cycle to directly transfer the chemical energy included in its active components into electrical energy. The procedure is reversed for reloading the battery if the system is rechargeable. This kind of reaction (transfer of chemical energy to electrical energy or vice versa) uses an electrical circuit to transfer electrons between the materials. A high-quality battery needs to be light in weight. An electrolyte reacts with metals in an oxidation-reduction reaction that powers a battery. When two metallic compounds interact with one another in an electrolyte, a process of oxidation or reduction happens depending on the electron affinities of the ions in the electrodes. The pictorial representation of the Battery is shown in **Fig 1**.

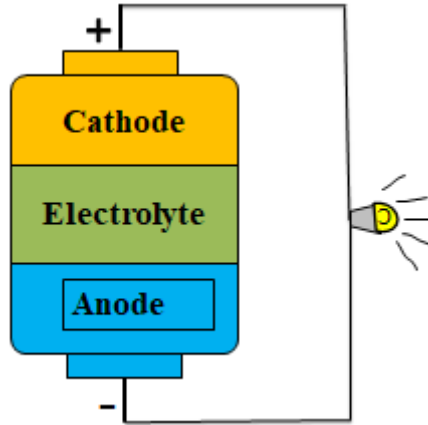


Fig 1: Pictorial representation of Battery

An anode, a cathode, an electrolyte, a separator, and current collectors can all be used to build a battery cell. The separator is enclosed between the anode and cathode, which are located on the opposing ends of the battery. The electrolyte, which transports ions between the anode and cathode, fills the space between them. Sodium ions move from the anode to the cathode of a sodium battery when it is drained. At the anode, the movement of positive ions releases free electrons, which generate a current.

Cathode Material

The proximity of reduction is a cathode. Anions or other substances that can quickly decrease ions constitute cathodes. Transition metal oxides are used as cathode materials most commonly. A rechargeable cathode may repeatedly accept and release ions. The surface area of the cathode, which determines how quickly ions can be absorbed, also determines how much current the battery can produce.

Anode Material

While reduction occurs in the cathode of a battery cell during discharging, oxidation occurs in the anode during charging. The anode can store activated ions in a high energy state; therefore, a good anode can hold ions as densely as possible and in the highest state possible. Metal-oxides, phosphides, as well as other alloys like silicon, tin, and aluminum, are potential anode materials.

Electrolytes

An electrolyte acts as an intermediary for the movement of ions between an anode and a cathode. When the electronics fail, an electrolyte also serves as an insulator. A significant amount of ionic conductivity must be present in the electrolyte. Polymer electrolytes have received recent attention due to their increased stability and high ionic conductivity compared with non-aqueous solvents. Polymer and biopolymer electrolytes are currently used or researched for solar cells, fuel cells, solid-state batteries, supercapacitors, mobile electronic devices, etc [David Linden and Thomas B. Reddy., 2001].

1.4 Operation of a Battery

Charging

A storage or rechargeable cell is recharged by switching the direction of the current flow, which causes oxidation at the positively charged electrode and reduction at the negatively charged electrode. Since the cathode is the electrode where reduction occurs and the anode is the electrode where oxidation occurs, the positive electrode serves as the anode and the negative electrode is the cathode. The charging of the Battery is shown in **Fig 2**.

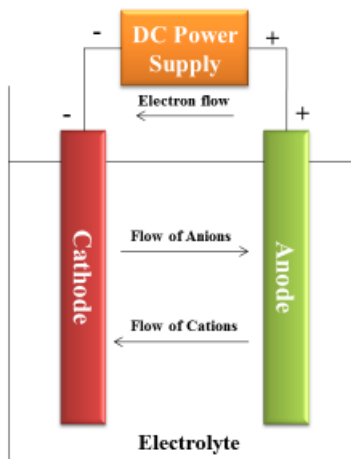


Fig 2: Electrochemical operation of Charge of Battery

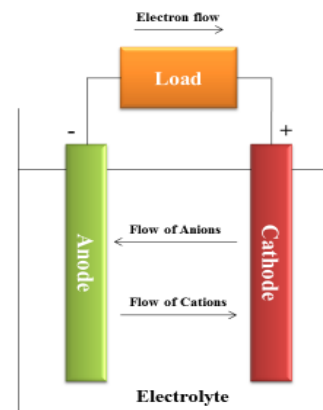


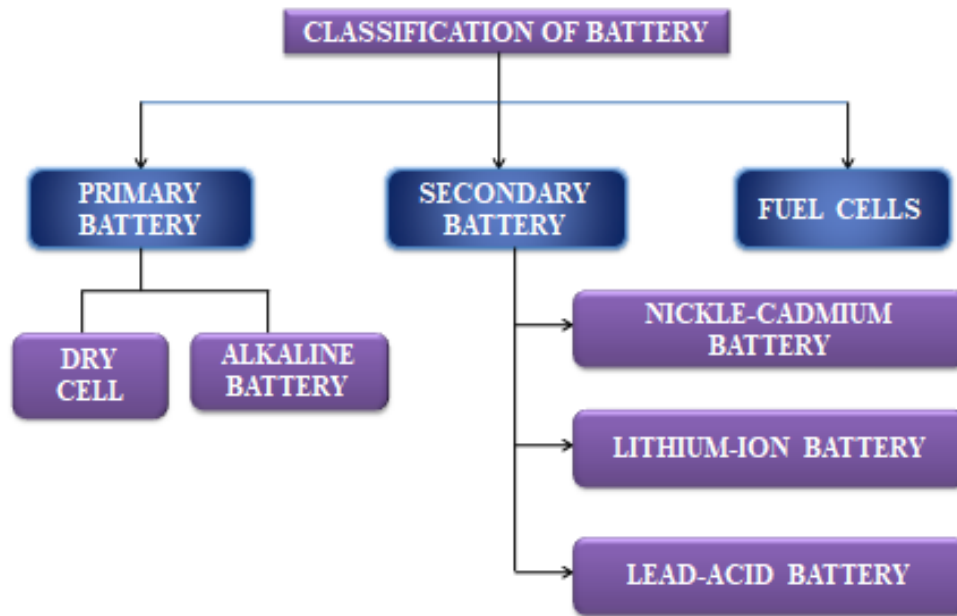
Fig 3: Electrochemical operation of discharge of a Battery [Linden, David, & Reddy, T. B., 2002]

Discharging

When the battery is connected to an external load, electrons move from the oxidizing anode through the load towards the cathode, where they are received and the cathode material is reduced. Anions, or negative ions, and cations, or positive ions, travel to the anode and the cathode respectively, to complete the electric circuit in the electrolyte. **Fig 3** shows the Discharging of the Battery.

1.5 Classification of Battery

Electrochemical batteries and cells can be classified into the primary (non-rechargeable) and secondary (rechargeable) categories based on their ability to be electrically recharged. To distinguish particular constructions or designs within this classification, other classifications are used.



Flowchart 1: Classification of Battery

Primary Batteries

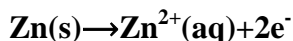
The Primary batteries are disposable because they cannot be recharged.

KINDS OF PRIMARY BATTERIES

- 1) Dry cell
- 2) Alkaline battery

Dry cell or Zinc - Carbon battery

Dry cells are a typical type of primary battery. Batteries built of zinc carbon are used to make dry cells. Zinc can function as a negative electrode or as a container. An ammonium chloride, carbon powder, manganese (IV) oxide, zinc chloride, and a little amount of water paste surround a carbon rod that serves as the positive electrode. The typical oxidation of zinc can be used to depict the anode reaction:

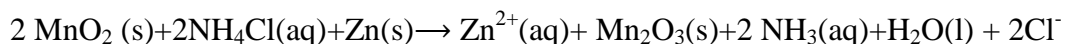


$$E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.7618 \text{ V}$$

The reaction with the cathode is more complicated, in part because there are several reactions. The sequence of reactions that take place at the cathode is approximately

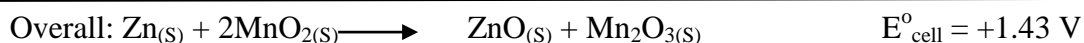
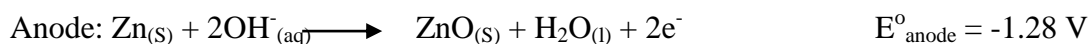


The overall reaction for the zinc-carbon battery can be represented as



Alkaline battery

In the 1950s, alkaline batteries were developed to solve some of the performance problems with zinc-carbon dry cells. They are produced as precise alternatives to zinc-carbon dry cells. These batteries use alkaline electrolytes, frequently potassium hydroxide, as their name suggests. The reactions are



An alkaline battery may generate three to five times as much energy as a zinc-carbon dry cell of the same size. Since alkaline batteries tend to leak potassium hydroxide, it is also advisable to remove them from any equipment that will be stored for an extended period. The majority of alkaline batteries cannot be recharged, while some of them can. When alkaline batteries are attempted to be recharged, it is normal for them to crack and spill potassium hydroxide electrolytes. The development of alkaline batteries served as a direct replacement for zinc-carbon (dry cell) batteries.

Secondary batteries

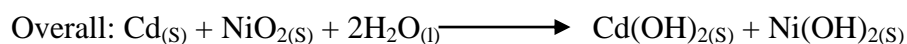
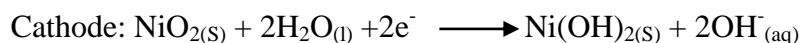
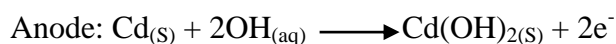
Secondary batteries can be recharged. Cell phones, electronic tablets, and autos all use these kinds of batteries.

Types of Secondary batteries

1. Nickel-Cadmium battery
2. Lithium-ion battery
3. Lead-acid battery

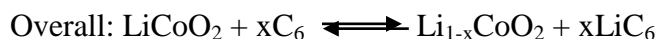
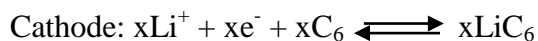
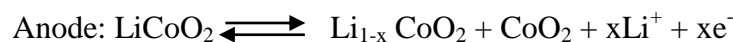
Nickle-Cadmium Battery

Nickle-cadmium batteries have a nickel-plated cathode, a cadmium-plated anode, and an electrolyte of potassium hydroxide. The divider prevents the positive and negative plates from shorting, which are rolled together and placed into the case. The NiCd cell can deliver much more current due to this "jelly-roll" construction than an alkaline battery of comparable size. The reactions are



Lithium-ion battery

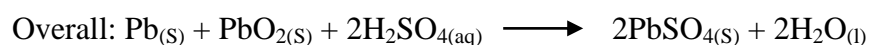
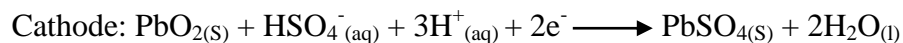
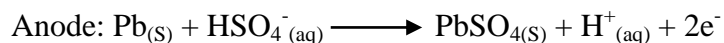
Among the most widely used rechargeable batteries, lithium-ion batteries are found in a variety of portable electronic devices. The reactions are



Lithium batteries are well-liked because they can supply a lot of current, are lighter than comparable batteries of other types, produce a practically constant voltage as they drain, and lose their charge very gradually when kept in storage.

Lead-acid battery

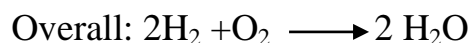
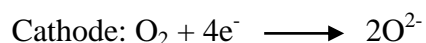
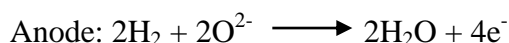
The secondary battery that is used in an automobile is a lead-acid battery. It can generate the high current needed by automobile starter motors and is reasonably priced. The reactions for a lead acid battery are



Fuel cells

In a fuel cell, chemical energy is transformed into electrical energy. Unlike batteries, fuel cells need a constant supply of fuel, often hydrogen. As long as fuel is available, they will keep producing electricity. Vehicles, boats, submarines, spacecraft, satellites, and space capsules have all employed hydrogen fuel cells to power the propulsion systems.

The air's oxygen combines with hydrogen in this hydrogen fuel-cell design to create water and energy. In a hydrogen fuel cell, the reactions are



A significant power source, electrochemical batteries are employed in a wide range of consumer, commercial, and military applications. Global sales top \$50 billion each year. Battery use is expanding quickly, which is mostly due to developments in electronics technology, decreasing power requirements, and the creation of portable devices that are best powered by batteries. The rise in demand for battery-powered products, the opening of numerous new markets for battery applications, including everything from small portable electronics to electric cars, and utility power load leveling are further contributing reasons [DK Kim, S Yoneoka, 2018].

1.6 Upgradation of Green Batteries- Eco-friendly


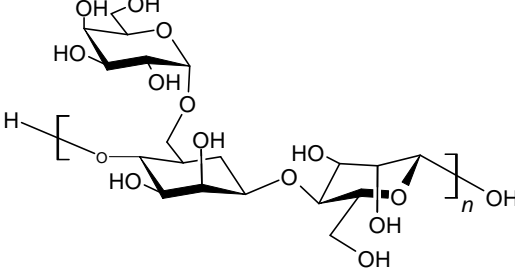

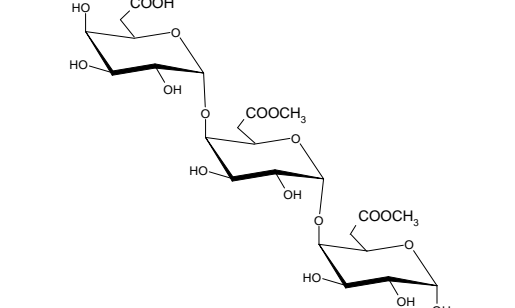

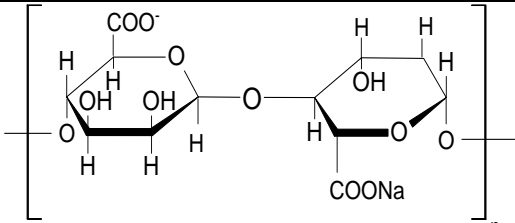

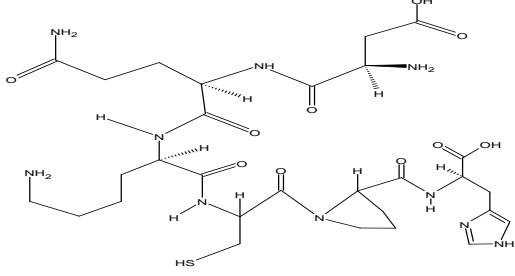

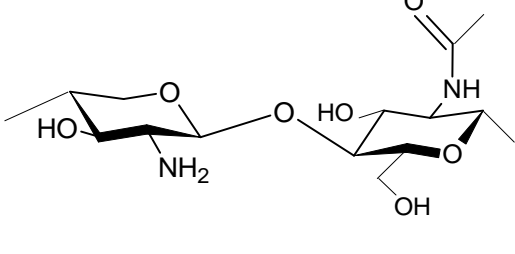
Futuristic batteries are lighter, have greater range, charge more quickly, and are biodegradable. A challenge has been aroused in disposing of the primary batteries. The solution to this problem is to reuse them, by recharging the batteries. Liquid electrolytes have disadvantages such as flammability, leakage, poor chemical stability, and poor safety. Solid electrolyte becomes a promising option to mitigate these issues. Among every solid electrolyte, polymer-based solid electrolytes have such advantages as good flexibility, low flammability, high safety, and excellent mechanical, chemical, and thermal stability. But it has one major disadvantage i.e., they are not biodegradable. To overcome this problem, the world is seeking new innovative materials which have to be used as electrolytes. So, the research has been directed toward finding out eco-friendly materials for energy storage devices.

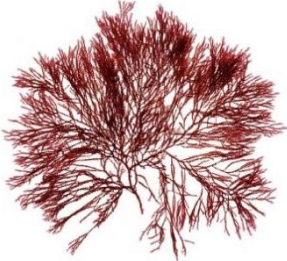
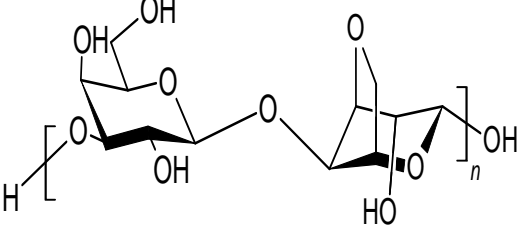

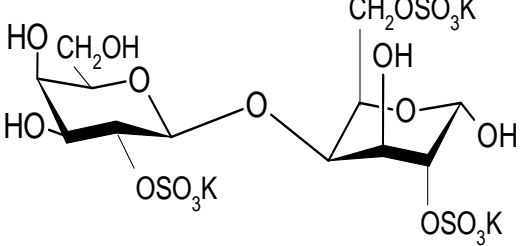

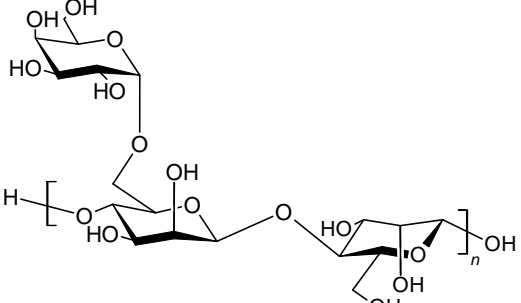

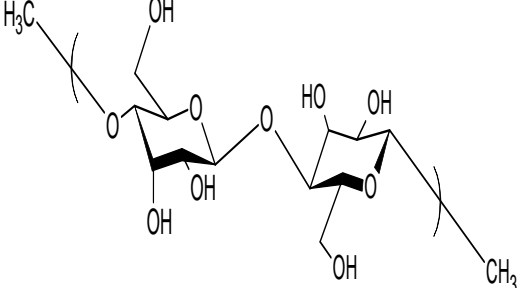

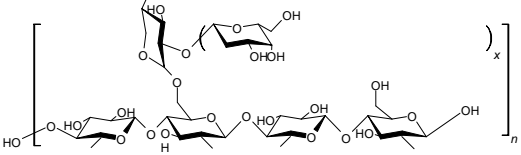
Recent and developing battery uses include the storage of electrical energy produced by natural energy sources such as solar or wind generators, electric and electric hybrid vehicles, portable electronics, and electric utility energy storage. The efficiency, life, and cost requirements for the batteries used for a variety of new and existing applications have also increased. It's possible that the present generation of batteries cannot fulfill these performance requirements. As a result, it is necessary to have both natural battery storage with improved performance and new battery technology with features like high power and energy densities, long life, low cost, little to no service, and a high safety profile. Biopolymer electrolyte has certain advantages like low cost, eco-friendly, good film formability, degradability, water-solubility, renewability, adhesive property, and biocompatibility [Chandra, A *et al.*, 2016].


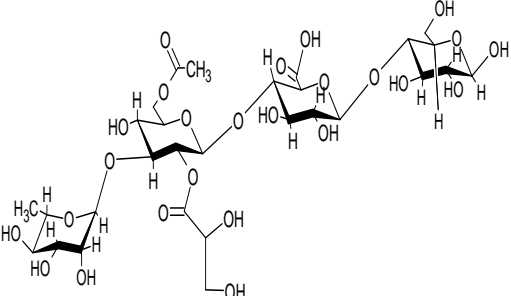

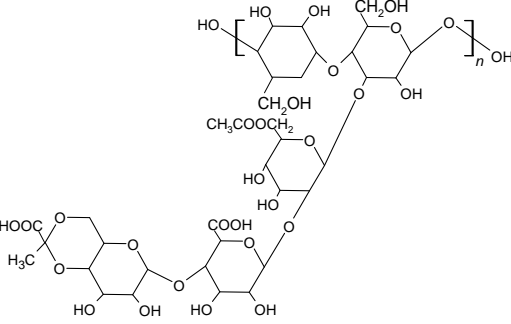

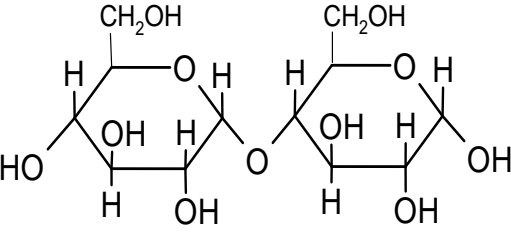

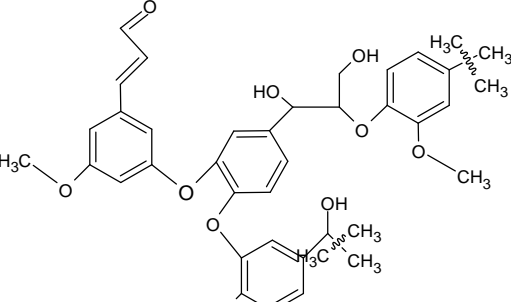

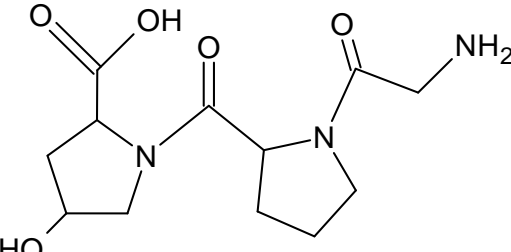
1.7 Biopolymer Solid Electrolytes for Batteries


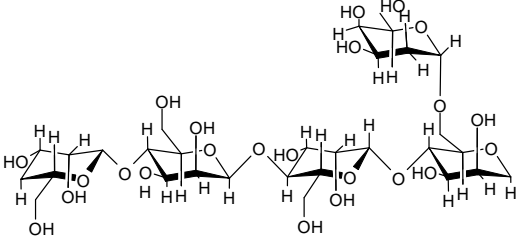

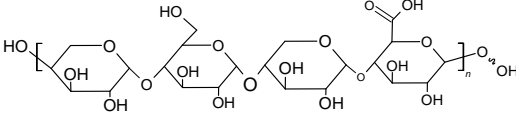
The biopolymers, also known as bio-macromolecules, are produced from living creatures or from biomass, a material that breaks down quickly in the environment. In addition, utilizing a biopolymer rather than conventional polymers significantly lowers production costs. Using renewable and natural resources gives products with distinct characteristics like affordability, outstanding compatibility, ease of film formation, and abundance. Biopolymer uses in electrical equipment are not only attractive but also essential for environmental safety. Biopolymers are perfectly applied for electrochemical and electrochromic sensing applications because they have strong physicochemical features. The Biopolymers and their Structures are tabulated in **Table 1**.

Table 1: Biopolymers & their Structures

BIOPOLYMER	PICTORIAL REPRESENTATION OF BIOPOLYMER	STRUCTURE
Guar gum		
Pectin		
Alginate		
Gelatin		
Chitosan		

<p>Agarose/ Agar</p>		
<p>Carrageenan</p>		
<p>Gum Arabic</p>		
<p>Cellulose</p>		
<p>Tamarind seed</p>		

<p>Gellan- gum</p>		
<p>Xanthan gum</p>		
<p>Starch</p>		
<p>Lignin</p>		
<p>Collagen</p>		

Locust bean gum		
Peach gum		

The above are some of the Biopolymers used in Energy Storage Applications. These Biopolymers are naturally abundant, cost-effective, Biodegradable, Eco-friendly, and hydrophilic. They can be easily soluble in water and are an excellent film-forming polymer in nature & used as a thickening and stabilizing agent. The various Bio-based polymers, their sources, and their uses are tabulated in **Table 2**.

1.8 Guar gum (GG)

The plant *Cyamopsis Tetragonoloba*, which belongs to the *Leguminosae* family, produces guar gum from its seeds. One of the largest molecular weights of a naturally occurring water-soluble polymer is found in the polysaccharide guar. A large component of guar gum is made up of high molecular weight galactomannan polysaccharides, which are linear chains of (14)-linked -D-Mannopyranosyl units with (16)-linked -D-Galactopyranosyl residues as lateral chains.

1.9 Pectin

Being a naturally occurring molecule present in berries, apples, plums, oranges, guavas, and other citrus fruit, biopolymer pectin is attracting a lot of attention. Pectin is composed of a long polygalacturonic acid chain bonded by (1-4) glycoside linkages with side chains made of arabinans, galactans, rhamnose, and xylose. Pectin is used as a gelling agent. In addition, it is employed as a stabilizer and thickening agent. Pectin was chosen by researchers to serve as the polymer electrolyte for electrochemical applications because of its non-toxic, renewable, water-soluble, and biodegradable qualities.

1.10 Other Biopolymers

- One of the most useful naturally occurring biopolymers is **gelatin**. A mixture of single- and multistranded polypeptides comprised of glycine and proline residues that contain both hydrophilic and hydrophobic groups is known as gelatin.
- A substance termed **alginate**, commonly referred to as alginic acid, is present in the cell walls of brown algae. Because it is most frequently spontaneously taken from cells as a polysaccharide, it is regarded as being extremely safe. The two uronic acids that makeup alginates are d-mannuronic acid (M) and l-guluronic acid (G), which are taken from the brown seaweed family Phaeophyceae.
- **Chitosan** is a naturally occurring, bioactive polysaccharide made up of copolymers of glucosamine and N-acetyl glucosamine that is generated from chitin.
- A polymer called **agarose** is extracted and refined from agar or marine algae that contain agarose. It is a naturally occurring polymer whose chemical composition alternates between 3,6-anhydro-L-galactose and -D-galactose units of agarose.
- Sulfated Galatians, such as **carrageenan**, are typically extracted from marine red algae. The building blocks of carrageenan are d-galactose. It consists of 1,4-linked and 1,3-linked d-galactose chains.
- **Gum Arabic** is a heteropolysaccharide with branched chains that can be neutral, mildly acidic, or both. It is most frequently encountered as a salt mixture of polysaccharide acids like magnesium and potassium. Gum Arabic comprises 1,3-linked -d-galactopyranosyl units as well as l-arabinose, l-rhamnose, and d-glucuronic acid.
- A polymer of beta glucose units with a 1-4 unbranched glycosidic bond makes up **cellulose**.
- A neutral xyloglucan (XG) called **tamarind seed polysaccharide** (TSP) also referred to as tamarind gum, is taken out of the tamarind seed kernels. It has a -(1,4)-d-glucan backbone and -(1,6)-d-xylose branches with -(1,2)-d-galactose largely replaced.
- Pseudomonas elodea produces **gellan gum**, an anionic polysaccharide that is water-soluble and made up of two residues of D-glucose, one residue of each of D-glucuronic acid and L-rhamnose, and two residues of D-glucose.
- The bacteria Xanthomonas campestris secretes the polysaccharide known as **xanthan gum**. It is made up of glucose, mannose, and glucuronic acid pentasaccharide repeat unit.

Table 2: Various Bio-based polymers, sources & uses [Singh, R *et al.*, 2016]

Biopolymer	Sources	Uses
Guar gum	Cyamopsis tetragonoloba	Thickening agent
Pectin	Citrus fruits	Emulsifier, gelling agent, thickener & stabilizer
Alginate	Brown algae (Phaeophyceae)	Gelling, thickening, stabilizing, or emulsifying agent
Xanthan gum	Sugar from Corn, Wheat	Thickening & stabilizing agent
Chitosan	Crustaceans, especially crab, prawns, and shrimp shells	Thickening agent
Carrageenan	Red seaweed	Thickening & suspending agent
Collagen	Berries	Supplementary & thickening agent

1.11 Perspectives on the polymer electrolyte

The electrolyte either exists as a liquid, gel, or solid. Although liquid electrolytes still predominate in many applications, they have a variety of disadvantages, including corrosion, flammability, leakage, and reactions with the electrodes. A polymer electrolyte (PE) has advantageous qualities that overcome issues brought on by the all-solid-state condition. The pictorial representation of Liquid and Polymer Electrolytes is shown in Fig 4.

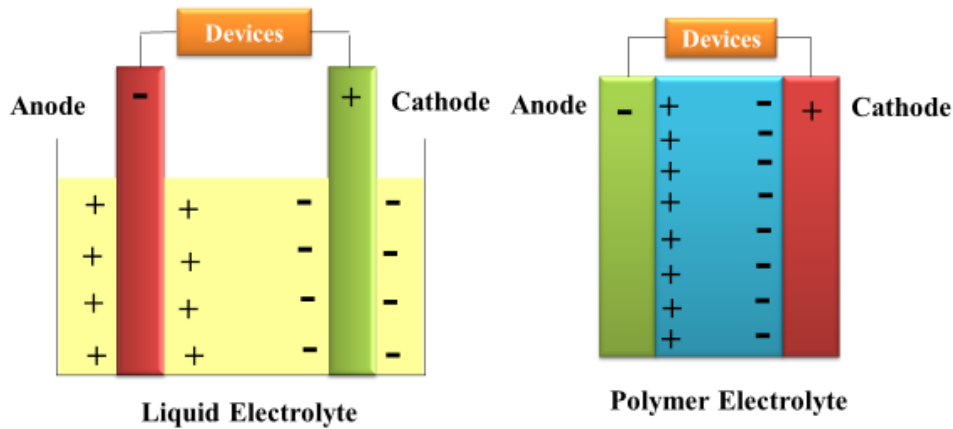
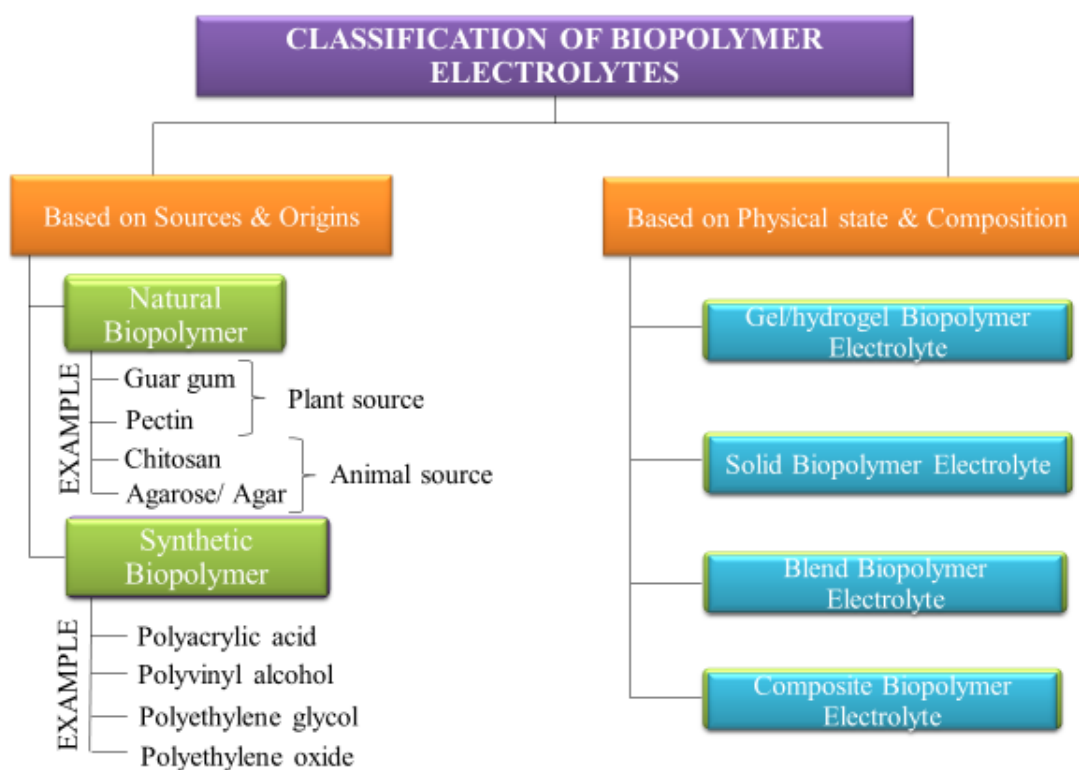


Fig 4: Pictorial representation of Liquid & Polymer Electrolyte

1.12 Classification of Biopolymer Electrolytes

According to their sources and places of origin, biopolymer electrolytes can be divided into two categories: synthetic & natural. Starch, chitosan, and cellulose are some examples of natural biopolymer electrolytes frequently employed in research. Based on their physical status and composition, biopolymer electrolytes can also be divided into four primary types: Gel biopolymer electrolytes/hydrogel biopolymer electrolytes, solid biopolymer electrolytes, blended biopolymer electrolytes, and composite polymer electrolytes. [Yin, H *et al.*, 2021] A flowchart of the classification of Biopolymer Electrolytes is given below (**Flowchart 2**).



Flowchart 2: Classification of Biopolymer Electrolytes

To attain greater ionic conductivity, the proposed work attempts to produce biopolymer electrolytes with sodium salts. The biocompatibility, environmental friendliness, economic viability, and non-toxic properties of biopolymers are factors in their selection.

1.13 Sodium Salts

A sodium-ion battery (NIB) system is a form of energy storage that depends on the electrochemical charge and discharge reactions between a positive electrode (cathode) made of layered materials containing sodium and a negative electrode (anode), which is typically made of hard carbons or intercalation compounds. Lithium and sodium are both alkali metals, which means that they both possess comparable chemical traits, including ionicity, electronegativity, and electrochemical reaction. As a result, they have nearly equivalent synthetic techniques and electrochemical results, demonstrating that Na-ion batteries might be successfully constructed based on previously established approaches or methods employed for the lithium counterpart. The sodium-ion battery offers the following benefits: inexpensive raw material costs; corrosivity-free chemical reactions; lengthy charge times without battery damage, degradation, or self-discharge; and high cycle life.

Sodium salts used in NIBs are sodium chloride [Jothi MA *et al.*, 2022], sodium perchlorate [Diana *et al.*, 2022], Sodium- difluoro (oxalato) borate (NaDFOB) [Chen, J *et al.*, 2015], Sodium triflate- (NaCF_3SO_3) [Zhang, Y *et al.*, 2021], Sodium bis(fluorosulfonyl)imide ($\text{Na}(\text{SO}_2\text{F})_2$, NaFSI), Sodium thiocyanate (NaSCN), sodium nitrate (NaNO_3) [Vahini, M *et al.*, 2019], Sodium iodate salt- (NaIO_3), sodium iodide (NaI) etc.,

1.14 Objectives of the study

With the above introductory part, the present study is carried out with the following objectives.

- To prepare solid polymer electrolytes using Guar Gum, Pectin, Sodium Nitrite, Sodium Bromide, and 1,3- Dioxolane by Solution Casting Technique.
- To characterize the prepared polymer electrolyte by using the techniques such as Fourier Transform-Infrared Spectroscopy (FTIR), 3-D Laser Profilometry, and Thermogravimetric analysis (TGA).
- To measure the Ionic Conductivity of the prepared solid polymer electrolytes through Electrical Impedance Spectroscopy (EIS) and Chronoamperometry (CA).
- To determine the transport number for the prepared solid polymer electrolytes.

REVIEW OF LITERATURE

CHAPTER II

REVIEW OF LITERATURE

2.1 Introduction

This chapter explains the research work done in the field of solid bio-polymer electrolytes and their related studies. The review of the literature was focused on three areas, to find the research gap, to get an insight into the biopolymer electrolyte used in batteries, and to identify the techniques used for the preparation of the solid electrolytes.

The present research work is focused on preparing biopolymer electrolytes for sodium-ion batteries. The review provides a detailed insight into the use of biodegradable polymers like Pectin, Guar Gum, Alginate, etc., and their application towards sustainable battery systems. Recent approaches and technological developments of polymer electrolytes and the progress of some methods used in improving the performance of the polymer electrolytes in Sodium-ion battery systems are reviewed in this chapter. Reviews on electrolytes in batteries are summarized well in many reports.

The review based on different **biopolymers doped with sodium salts** as a promising electrolyte is shown in **Table 3**.

The review based on different **Synthetic polymers doped with sodium salts** as a promising electrolyte is shown in **Table 4**.

The Review based on **Guar gum doped with different salts** as a promising electrolyte is shown in **Table 5**.

2.2 Review of different Bio-polymers with Sodium salts

2.2.1 Alginate with Sodium salt

- **M. Infanta Diana *et.al* (2021)** have been reported the biopolymer electrolyte membrane with Alginate & NaSCN by using a solution casting technique. The maximum ionic conductivity for host material 30% and salt 70% was found to be $1.22 \times 10^{-2} \text{ S cm}^{-1}$. They constructed a battery with the above-mentioned composition with an open cell potential of 2.87 V.

2.2.2 Pectin with Sodium salt

- Biopolymer electrolytes based on Pectin and Sodium Nitrate were proposed by **M. Vahini *et al*** by solution casting method. The ionic conductivity was found to be increased from the pure Pectin (2.7×10^{-9}) to $4.2 \times 10^{-6} \text{ S/cm}$ by doping with NaNO_3 salt. They have also discussed the dielectric characteristics of the prepared Pectin - NaNO_3 electrolytes. They attained the high ionic conductivity, lowest relaxation time (41.2 mS), and highest cationic transference number for 9% of the NaNO_3 -doped biopolymer electrolytes.

2.2.3 Tamarind seed polysaccharide (TSP) with Sodium salt

- Na-ion conducting biopolymer electrolyte based on tamarind seed polysaccharide (TSP) with sodium perchlorate salt was prepared by **K.Maithilee *et al*** using a solution casting technique. One gram of TSP was mixed with 0.8 grams of NaClO_4 to get the highest ionic conductivity, measuring $1.70 \times 10^{-3} \text{ Scm}$, out of all the adopted biopolymer electrolytes. Differential scanning calorimetry (DSC) was used to determine the membranes' glass transition temperatures (T_g). Linear sweep voltammetry (LSV) was found to be 3.24 V for the best-conducting biopolymer electrolyte. By fabricating the primary sodium battery with the highest conducting biopolymer electrolyte they were able to measure the open-circuit cell potential of 3.15 V.

2.2.4 Cellulose with Sodium salt

- A unique polymer electrolyte with pyranose rings was proposed by **F. Col *et al*** based on a traditional polyethylene oxide (PEO) backbone, sodium carboxymethyl cellulose (Na-CMC), and sodium perchlorate by using a solution casting technique. It was determined that Na-CMC could be used effectively as both an electrode binder and an electrolyte additive, which would improve the pathways for establishing an ideal electrode/electrolyte interface.

2.2.5 Chitosan/ Dextran with Sodium salt

- **Ahmad *et al*** have synthesized the polymer electrolyte system of chitosan/dextran-NaTf with different glycerol concentrations by solution casting method. According to the electrical impedance spectroscopy (EIS) investigation, they reported that Glycerol enhances the electrolyte's ionic conductivity at ambient temperature. The maximum DC ionic conductivity was found to be 6.10×10^{-5} S/cm for the highest-conducting plasticized electrolyte. They also examined the impact of plasticizers on film morphology using field emission scanning electron microscopy (FESEM).

2.2.6 Chitosan/ Polyvinyl Alcohol with Sodium salt

- CS-PVA-NaI-based bio-polymer electrolyte membranes were prepared by **D. Bharati and A. Saroj** using a solution casting technique and characterized the prepared samples using FTIR, XRD, TGA, Impedance Spectroscopy, ITN, LSV, and CV measurements. At 30°C, the sample, BPBE#15IL, had an optimal dc conductivity of 1.7×10^{-4} S/cm which was caused by ions due to the measurement of the ionic transference number (ITN)[ITN ~ 0.99]. They also revealed that the electrochemical stability window (ESW) value as ~ 2.3 V.

2.2.7 Corn Starch with Sodium salt

- A new solid polymer electrolyte (SPE) based on corn starch was synthesized by **F. F. Awang *et al*** with a different sodium bisulfite concentration by using a solution casting technique. The sample containing 15% NaHSO₃ had the maximum ionic conductivity, which was found to be 2.22×10^{-4} Scm⁻¹ at ambient temperature. At room temperature, the cell produced an open circuit voltage of 1.55 V while its discharge characteristics were also investigated.

2.2.8 Chitosan with Sodium salt

- The chitosan-NaI electrolyte was successfully prepared via a simple and upscalable solution casting technique. **N.A. Rahman *et al*** have reported the best ionic conductivity with values equal to 1.11×10^{-4} S/cm. They also investigated the efficiency along with short-circuit density and open-circuit voltage.

Table 3: Review based on different biopolymers doped with sodium salts as a promising electrolyte

S.NO	TITLE OF THE PAPER	NATURAL POLYMER ELECTROLYTE	METHOD	CONCENTRATION (g/wt%)	IONIC CONDUCTIVITY	REFERENCE
1	Investigations on Na-ion conducting electrolyte based on sodium alginate biopolymer for all-solid-state sodium-ion batteries	Sodium thiocyanate (NaSCN) Sodium Alginate	Solution casting method	Biopolymer host material (30 wt%) NaSCN salt (70 wt%)	$1.22 \times 10^{-2} \text{ S cm}^{-1}$	M. Infanta Diana <i>et.al</i> Journal of Solid State Electrochemistry (2021)
2	Preparation and Characterization of Biopolymer Electrolytes Based on Pectin and NaNO ₃ for Battery Applications	Pectin NaNO ₃	Solution casting method	91% Pectin : 9% NaNO ₃	$4.2 \times 10^{-6} \text{ Scm}^{-1}$	M. Vahini <i>et al.</i> Polymer Science, Series A, 2019.
3	Na-ion conducting biopolymer electrolyte based on tamarind seed polysaccharide incorporated with sodium perchlorate for primary sodium-ion batteries	Tamarind seed polysaccharide (TSP) sodium perchlorate (NaClO ₄)	Solution casting method	1 g TSP: 0.8 g NaClO ₄	$1.70 \times 10^{-3} \text{ S cm}^{-1}$	K. Maithilee <i>et al.</i> Ionics (2022)

4	Cellulose-based novel hybrid Polymer electrolytes for green and efficient Na-ion Batteries	Sodium carboxy methyl cellulose (Na-CMC) Sodium perchlorate (NaClO ₄)	Solution casting method	89:9:9	-	F. Colò <i>et al.</i> / <i>Electrochimica Acta</i> 174 (2015)
5	Plasticized Sodium-Ion Conducting Polymer Blend Electrolyte Membranes Based on Chitosan/ Dextran Biopolymers	Chitosan/Dextran-sodium triflate (NaTf) Glycerol	Solution casting method	CS –dextran (60:40) wt.% NaTf 40 wt%	$6.10 \times 10^{-5} \text{cm}^{-1}$	Ahmad <i>et al.</i> <i>Polymers</i> 2021
6	Plasticization effect of ionic liquid on structural, thermal, and ion transport properties of CS-PVA-NaI-based bio-polymer electrolyte membranes	Chitosan (CS) Polyvinyl Alcohol (PVA) 1-ethyl-3-methylimidazolium methyl sulfate Sodium Iodide (NaI)	Solution casting method	CS (10 wt%) (90 wt%) of PVA 15 wt% of IL NaI (40 wt%)	$1.7 \times 10^{-4} \text{S/cm}$	D. Bharati and A. Saroj <i>polymer-plastics technology and materials</i> 2023

7	Investigation of structural and electrical properties of biopolymer materials with its potential application in solid-state batteries	Corn Starch Sodium Bisulphite	Solution casting method	1 g of Corn Starch 15 wt.% NaHSO ₃	$2.22 \times 10^{-4} \text{ Scm}^{-1}$	F. F. Awang, M. F. Hassa & K. H. Kamarudin Polymer Bulletin (2023) 80:1463–1476
8	Chitosan as a paradigm for biopolymer electrolytes in solid-state dye-sensitized solar cells	Chitosan NaI	Solution casting method	Chitosan 70 wt% NaI 30 wt%	$1.11 \times 10^{-4} \text{ s/cm}$	N.A. Rahman et al. Polymer 230 (2021) 124092

2.3 Review of different Synthetic polymers with Sodium salts

2.3.1 Polyethylene Oxide (PEO) with Sodium salts

- The blend electrolyte of succinonitrile (SN), sodium triflate (NaCF₃SO₃), and polyethylene oxide (PEO) was prepared by **M. Patel *et al*** using a solution casting technique. Ionic conductivity in PEO-NaCF₃SO₃ was greatly improved by the addition of SN. The prepared polymer-plastic composite electrolyte's ionic conductivity was found to be $1.1 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ at 50% SN concentration (relative to the weight of the polymer), which was 45 times more than PEO-NaCF₃SO₃.

- **J. Siva Kumar *et al*** have carried out their work to develop a polymer electrolyte based on PEO complexed with sodium salt (NaClO_3) by using the solution casting method. The conductivity of the electrolyte (PEO + NaClO_3) at normal temperatures was found to be approximately 103 times greater than that of pure PEO. They revealed that the measurements of the transport number of the polymer electrolyte system's ions were primarily responsible for charge transport. Additionally, they have also investigated the open circuit voltage (2.97 V) and short circuit current (346 μA), respectively.
- **Yiwei Yao *et al*** have proposed an inorganic solid electrolyte (beta-alumina) filler which was used to demonstrate poly (ethylene oxide) (PEO) solid polymer electrolytes with increased ion conductivity. In the presence of conductive beta-alumina filler, the ion conductivity of the PEO polymer electrolyte was increased from 2.5×10^{-4} to $3.95 \times 10^{-4} \text{ S cm}^{-1}$.
- **Koduru *et al*** have investigated the polymer blend electrolytes based on polyvinyl pyrrolidone (PVP) and polyethylene oxide (PEO) complexed with NaIO_4 salt using the solution casting method. They measured the electrical conductivity of the mixed polymer complexes between the temperatures of 303 K and 343 K with the frequency range of 1 Hz to 1 MHz by using complex impedance spectroscopy. They also presented a study on the electrical conductivity characteristics of GO-doped "salt complexed electrolyte" systems.
- By using a solution casting technique, a PEO-based solid polymer electrolyte was formulated by **Yatim Lailun Ni' mah *et al***. They investigated the ionic conductivities of the films by using impedance analysis with the ratio EO: Na = 20, which was found to be $1.35 \times 10^{-4} \text{ S/cm}$. By the addition of TiO_2 (3.4 nm, 5 wt%) at 60°C , the ionic conductivity was increased to $2.62 \times 10^{-4} \text{ S/cm}$.
- **G. Chen, *et al*** have synthesized hyperbranched polyether for composite polymer electrolytes with PEO and NaTFSI using the solution casting method. The ionic conductivity was found to be $5.7 \times 10^{-4} \text{ S/cm}$ at room temperature.

- Polymer electrolytes based on poly(ethylene oxide) (PEO) have been extensively studied with sodium perchlorate salt along with Pyr₁₃FSI by **Guanghai Chen *et al*** using a solution casting technique. They have incorporated Pyr₁₃FSI into the PEO–NaClO₄ electrolyte to investigate the plasticizing effect by infrared spectrum characterizations and DFT calculations.

2.3.2 Polyethylene Glycol (PEG) with Sodium salt

- A new composite polymer electrolyte (CPE) was developed and reported by **Xuejing Zhang *et al*** using the solution casting method. The CPE showed strong ionic conductivity ($1.46 \times 10^{-4} \text{ Scm}^{-1}$ at 70 °C). The CPE was made of poly(methacrylate), poly(ethylene glycol), α - Al₂O₃ with acidic surface sites, and sodium chloride.

2.3.3 Poly(methyl-methacrylate) (PMMA) with Sodium salt

- **P. Chandra Sekhar *et al*** have investigated the effect of plasticizers on the conductivity of polymer electrolyte systems using DMF as a plasticizer, Poly(methyl-methacrylate), and Sodium perchlorate by solution casting technique. The ionic conductivity was found to be increased on adding a plasticizer to $1.94 \times 10^{-6} \text{ S/cm}$. They also measured the open-circuit voltage, short-circuit current and discharge time.

2.3.4 Polyvinyl pyrrolidone (PVP) with Sodium salt

- A sodium ion-conducting polymer electrolyte based on polyvinyl pyrrolidone (PVP) complexed with NaClO₄ was prepared using the solution-cast technique. **Ch.V. Subba Reddy *et al*** have investigated the ionic conductivity and transference number.

2.3.5 Poly(vinylidene fluoride) (PVdF) with Sodium salt

- **Sundari *et al*** have carried out their work on a new solid polymer electrolyte system consisting of PVdF polymer and sodium perchlorate as salt using a solution casting technique. They have reported the maximum ionic conductivity for 60 PVdF+ 40 NaClO₄ system as $1.78 \times 10^{-5} \text{ S/cm}$ at room temperature. They have also investigated various cell parameters like open circuit voltage, short circuit current, power density, and energy density.

Table 4: Review based on different synthetic polymers doped with sodium salts as a promising electrolyte

S. NO	TITLE OF THE PAPER	SYNTHETIC POLYMER ELECTROLYTE	METHOD	CONCENTRATION (g/wt%)	IONIC CONDUCTIVITY	REFERENCE
1	Increasing ionic conductivity of polymer–sodium salt complex by addition of a non-ionic plastic crystal	Poly(ethyleneoxide) (PEO), sodium triflate (NaCF ₃ SO ₃), Succinonitrile (SN), Anhydrous acetonitrile	Solution casting method	60%PEO 40%NaCF ₃ SO ₃ (EO: Na= 6:1)	$1.1 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$	M. Patel <i>et al.</i> / Solid State Ionics 181 (2010) 844–848
2	Preparation and study of properties of polymer electrolyte system (PEO + NaClO ₃)	PEO and NaClO ₃	Solution casting method	PEO+ NaClO ₃ (70:30)	$3.36 \times 10^{-7} \text{ S cm}^{-1}$	J. Siva Kumar <i>et al.</i> / Materials Letters 60 (2006) 3346–3349
3	Promoted ion conductivity of sodium salt–poly(ethylene oxide) polymer electrolyte induced by adding conductive beta-alumina and Application in all-solid-state sodium batteries	PEO-NaClO ₄ -beta-alumina	Solution casting method	(nEO:nNa = 20:1) beta-alumina - 10 wt%	$3.95 \times 10^{-4} \text{ S cm}^{-1}$	Yiwei Yao <i>et al.</i> / Energy materials J Mater Sci (2021) 56:9951–9960

4	A novel PMA/PEG-based composite polymer electrolyte for all-solid-state sodium-ion batteries	azodiisobutyronitrile (AIBN) poly(ethylene glycol) (PEG) acetone NaClO ₄	Solution casting method	100 mg of azodiisobutyronitrile (AIBN) 5.81 g of PEG 600 Acetone dissolved nano- α -Al ₂ O ₃ 0.6 M NaClO ₄	1.46×10^{-4} S·cm ⁻¹	Xuejing Zhang <i>et al.</i> / Nano Res. 2018, 11(12): 6244–6251
5	Investigations on Poly (ethylene oxide) (PEO) - blend-based solid polymer electrolytes for sodium-ion batteries	Graphene Oxide (GO) PEO Sodium Periodate (NaIO ₄)	Solution casting method	0.4 wt% GO 10 wt% NaIO ₄	1×10^{-6} Scm ⁻¹	Koduru <i>et al.</i> Journal of Physics: Conference Series 764 (2016)
6	Solid-State polymer nanocomposite electrolyte of TiO ₂ /PEO/NaClO ₄ for sodium-ion batteries	PEO Anhydrous acetonitrile NaClO ₄	Solution casting method	EO:Na = 20 Addition of TiO ₂	1.35×10^{-4} S/cm 2.62×10^{-4} S/cm	Yatim Lailun Ni'mah <i>et al.</i> Journal of Power Sources (2014)
7	Hyperbranched polyether boosting ionic conductivity of polymer electrolytes for all-solid-state sodium-ion batteries	PEO NaTFSI	Solution casting method	PMH9-1/1-3 NaTFSI)	5.7×10^{-4} S cm ⁻¹	G. Chen, <i>et al.</i> Chemical Engineering Journal 394 (2020) 124885

8	Effect of plasticizer on conductivity and cell parameters of (PMMA+NaClO ₄) polymer electrolyte system	Poly(methyl-methacrylate) (PMMA) Dimethyl formamide (DMF) Sodium perchlorate (NaClO ₄)	Solution casting method	80:20 DMF - 2 ml	1.94×10^{-6} S/cm	P. Chandra Sekhar <i>et al.</i> IOSR Journal of Applied Physics Volume 2, Issue 4, PP 01-06, 2012.
9	Preparation and characterization of (PVP + NaClO ₄) electrolytes for battery applications	Polyvinyl pyrrolidone (PVP) NaClO ₄	Solution casting method	30% polymer 70% salt	-	Ch.V. Subba Reddy <i>et al.</i> Eur. Phys. J. E 19, 471–476 (2006)
10	Structural and A.C. Conductivity Studies of (PVdF + NaClO ₄) Solid Polymer Electrolyte System for an Electrochemical Cell Applications	Poly(vinylidene fluoride) (PVdF) Sodium perchlorate	Solution casting method	60 PVdF + 40 NaClO ₄	1.78×10^{-5} S/cm	Sundari <i>et al.</i> Asian J. Chem Vol. 25, Suppl. Issue (2013)
11	Inhibition of Crystallization of Poly(ethylene oxide) by Ionic Liquid: Insight into Plasticizing Mechanism and Application for Solid-State Sodium-Ion Batteries	N-methyl-N-propylpyrrolidinium bis(fluorosulfonyl)imide (Pyr ₁₃ FSI) PEO NaClO ₄	Solution casting method	20:1 (EO: Na) 40 wt% PEO	6.8×10^{-5} S cm ⁻¹	Guanghai Chen <i>et al.</i> ACS Appl. Mater. Interfaces 2019, 11, 43252–43260

2.4 Review of Guar gum- based polymer with different salts

- A proton-conducting natural polymer electrolyte based on guar gum and ammonium thiocyanate was prepared by **K. Venkatesh *et al*** using the solution casting method. They have calculated the ion transport number using the FTIR deconvolution method. The ionic conductivity was found to be 4.91×10^{-3} S/cm for the film containing 1.2 g of GG and 0.6 g of NH_4SCN . They have also investigated the transference number and LSV studies. OCV and short circuit current were also measured.
- The solution casting method was employed to prepare solid-state composite Green-polymer electrolytes using Guar gum, Zinc Sulphate heptahydrate salt ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) which was synthesized and studied by **B. Srinivas *et al***. Anisometric morphology was investigated using the Scanning Electron Microscopy (SEM) technique. The ionic conductivity was found to be 6.78×10^{-8} S/cm.
- GG-based solid biopolymer electrolytes with LiTFSI- glycerol has been synthesized via the solution casting method by **M. Abirami *et al***. The best optimum ionic conductivity was found to be 2.041×10^{-3} S/cm for the film containing 60 wt% GG-40 wt% LiTFSI.
- Guar gum Succinate- based polymer electrolyte has been investigated with succinate anhydride, 4-dimethylaminopyridine blend with ethylene carbonate (EC), carboxymethyl cellulose (CMC), lithium triflate (LiTf), and lithium iodide (LiI) by **Ahmad Danial Azzahari *et al*** using solution casting technique. The highest ionic conductivity was found to be 6.29×10^{-4} S cm^{-1} and 2.10×10^{-4} S cm^{-1} for the compositions GGS: EC(1.0:0.6) with 30wt% LiTf and GGS:CMC: EC(0.5:0.5:0.6) with 25wt% LiI respectively.
- **Ahalya Gunasekaran *et al*** have investigated Guar gum- based biopolymer electrolytes using LiI/I2, 4- tert-butylpyridine, 1-methyl-3-propylimidazolium iodide, and polyethylene glycol by solution casting method. They have also fabricated the solar cells using the prepared polymer gel electrolyte. Photochemical characterization had been carried out for the fabricated device.

- **R. Shilpa and R. Saratha** have found the maximum ionic conductivity as $1.59 \times 10^{-4} \text{ Scm}^{-1}$ for the prepared polymer blend electrolyte, which was prepared by solution casting technique with 0.25wt% of LiTFSI.
- The highly flexible and conductive eco-friendly electrolyte had been synthesized using Guar gum, Zinc Sulphate along with Manganese Sulphate by solution casting technique. At room temperature, they found the highest ionic conductivity of $1.07 \times 10^{-2} \text{ Scm}^{-1}$. **Y. Huang *et al*** have also reported the capacity and durability of the prepared electrolyte.
- **J. Wang, Y. Huang, B. Liu, *et al*** have carried out the natural hydrogel electrolyte with the blend of Guar gum and Sodium alginate and electrolyte solution of Zinc sulfate and Manganese sulfate using the solution casting method. The highest ionic conductivity was found to be 6.19 mScm^{-1} .

Table 5: Review based on Guar gum doped with different salts as a promising electrolyte

S. NO	TITLE OF THE PAPER	GUAR GUM (GG)- BASED ELECTROLYTE	METHOD	CONCENTRATION (g/wt%)	IONIC CONDUCTIVITY	REFERENCE
1	Polymer electrolyte based on guar gum and ammonium thiocyanate for proton battery application	Guar gum- Ammonium thiocyanate (NH ₄ SCN)	Solution casting method	1.2 g GG 0.6 g NH ₄ SCN	4.91×10^{-3} S/cm	K. Venkatesh <i>et al.</i> , (2022) Polymer Bulletin
2	The Structural and Electrical properties of Guar Gum Based Green Electrolyte	Guar gum- Zinc Sulphate heptahydrate (ZnSO ₄ .7H ₂ O)	Solution casting method	90:10 (GG: salt)	6.78×10^{-8} S/cm	B. Srinivas <i>et al.</i> , (2023)
3	Preparation and characterization of Guar gum-based solid biopolymer electrolyte doped with lithium bis(trifluoromethanesulphonyl)imide (LiTFSI) plasticized with glycerol	Guar gum- lithium bis(trifluoromethane sulphonyl)imide (LiTFSI)- Glycerol	Solution casting method	60GG : 40LiTFSI	2.041×10^{-3} Scm ⁻¹	M. Abirami <i>et al.</i> , (2020), Bull. Mater. Sci. (2020) 43:254

4	Improved ionic conductivity in guar gum succinate-based polymer electrolyte membrane	Guar gum(GG)- Succinate anhydride, ethylene carbonate (EC), carboxy methyl cellulose (CMC), lithium triflate (LiTf), and lithium iodide (liI)	Solution casting method	GGs: EC (1.0:0.6) 30 wt% LiTf GGs:CMC: EC(0.5:0.5:0.6) 25 wt% LiI	$6.29 \times 10^{-5} \text{ S cm}^{-1}$ $2.10 \times 10^{-4} \text{ S cm}^{-1}$	Ahmad Danial Azzahari <i>et al.</i> , (2018) High-Performance Polymers 1-9
5	Guar gum-based polymer gel electrolyte for dye-sensitized solar cell applications	Guar gum-LiI/I ₂ , 4- tert-butylpyrdine, 1-methyl-3-propylimidazolium iodide, and polyethylene glycol	Solution casting method	0.6 g of Guar gum	1.46 S cm^{-1}	Ahalya Gunasekaran <i>et al.</i> , (2020) Solar Energy 208 (2020) 160–165
6	Biodegradable pectin- guar gum blend electrolyte for solid-state lithium-ion batteries	Guar gum- Pectin LiTFSI	Solution casting method	1 g Guar gum-1 g Pectin 0.25wt% of LiTFSI	$1.59 \times 10^{-4} \text{ S cm}^{-1}$	R. Shilpa and R. Saratha, (2020) ICPCMNEA
7	Flexible and stable quasi-solid-state zinc ion battery with conductive guar gum electrolyte	Guar gum ZnSO ₄ MnSO ₄	Solution casting method	0.6 g GG 2M ZnSO ₄ + 0.1 M MnSO ₄	$1.07 \times 10^{-2} \text{ Scm}^{-1}$	Y. Huang <i>et al.</i> / Materials Today Energy 14 (2019) 100349

8	Flexible and anti-freezing zinc-ion batteries using a guar-gum/sodium-alginate/ethylene-glycol hydrogel electrolyte	Guar gum(GG)-Sodium alginate(SA) Ethylene glycol(EG)	Solution casting method	0.4 g SA 0.2 g GG 10 ml (2M ZnSO ₄ + 0.1M MnSO ₄) solution 30% EG	16.81 mScm ⁻¹	J. Wang, Y. Huang, B. Liu <i>et al.</i> Energy Storage Materials 41 (2021) 599–605
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MATERIALS AND METHODS

CHAPTER III

Materials and Methods

This chapter deals with the materials used and methodologies adopted to prepare and characterize the Solid Biopolymer Electrolytes (SPE)

3.1 Materials

The materials used for preparing biopolymer electrolytes were listed below:

- Guar Gum
- Pectin
- Sodium Nitrite
- Sodium Bromide
- 1,3-Dioxolane

3.2 Properties and Appearance of Guar Gum

Host Polymer:	Guar Gum
Source :	Guar plant- <i>Cyamopsis Tetragonolobus</i>
Family:	Leguminosae
Chemical Name:	<i>Cyamopsis tetragonoloba</i>
Molecular Formula:	$C_{18}H_{32}O_{16}$
Molecular Weight:	535.145 g/mol
Appearance:	Coarse Powder
Color:	Dirty White



Image 1: Appearance of Guar Gum

3.3 Properties and Appearance of Pectin

Host Polymer: Pectin
Source: Apples and Citrus Fruits
Chemical Name: Poly-D-Galacturonic acid
Molecular Formula: $C_6H_{10}O_7$
Molecular Weight: 194.1394 g/mol
Appearance: Fine powder
Color: Yellowish white



Image 2: Appearance of Pectin

3.4 Properties and Appearance of Sodium nitrite

Ionic salt: Sodium nitrite
Chemical formula: $NaNO_2$
Molecular weight: 68.9953 g/mol
Appearance: Crystalline solid
Color: Off-white



Image 3: Appearance of Sodium Nitrite

3.5 Properties and Appearance of Sodium bromide

Ionic salt: Sodium bromide
Chemical formula: $NaBr$
Molecular weight: 102.894 g/mol
Appearance: Crystalline granular powder
Color: White



Image 4: Appearance of Sodium

3.6 Properties and Appearance of 1,3-Dioxolane

Plasticizer: 1,3-Dioxolane

Molecular formula: $C_3H_6O_2$

Molecular weight: 74.08 g/mol

Appearance: Clear liquid

Color: Colourless



Image 5: Appearance of 1,3-Dioxolane

Table 6: Structures of polymer, salt, and plasticizer

S.NO	NAME OF THE COMPOUND	STRUCTURE
1	Guar Gum	The structure of Guar Gum is given in the previous chapter
2	Pectin	The structure of Pectin is given in the previous chapter
3	Sodium nitrite	
4	Sodium bromide	
5	1,3-Dioxolane	

Structures of polymer, salt, and plasticizer are listed in **Table 6**.

3.7 Method

Solution casting technique:

The biopolymer Guar Gum and Pectin have been complexed with two different ionic salts namely sodium nitrite and sodium bromide to prepare three ion-conducting biopolymer electrolytes with the plasticizer 1,3-Dioxolane. The biopolymer electrolyte has been prepared by using the solution casting method. Among the different types of methods, this method of preparing electrolytes is widely used because of its ease of preparation. The advantage of this method is its cost-effectiveness and laboratory use. The preparation of electrolytes is shown in **Figure 5** and the method of preparation is given in **Flowchart 3**.

3.8 Preparation of Electrolyte

Solvent: Water

Biopolymers: Guar Gum & Pectin

Salts: Sodium nitrite & Sodium bromide

Plasticizer: 1,3-Dioxolane

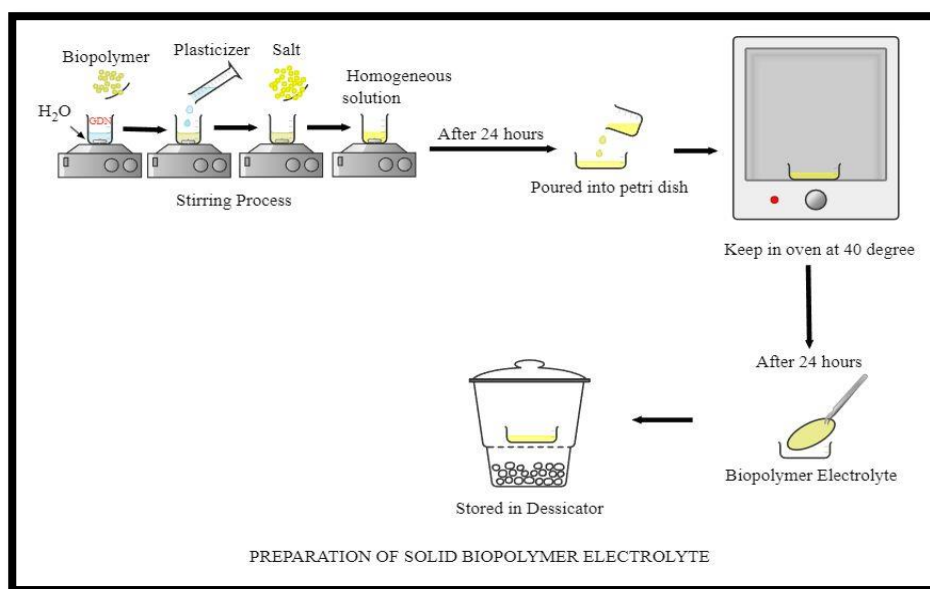
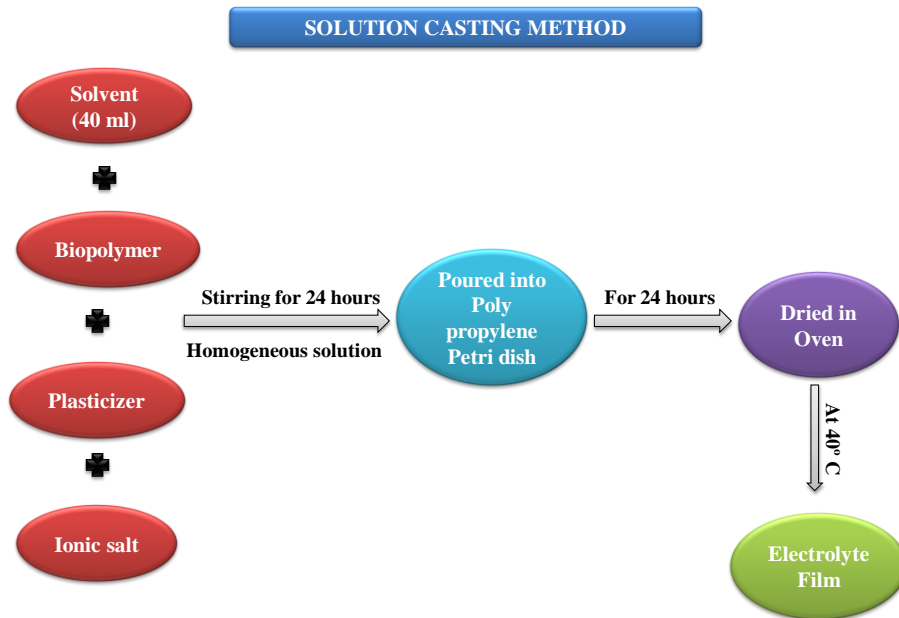


Fig 5: Preparation of Electrolyte



Flowchart 3: Method of preparation of Biopolymer Electrolyte

Table 7a: Ratios (wt%) of biopolymer, salt & plasticizer/ionic liquid

S.NO	Name of the Biopolymer	Name of the salt	Name of the plasticizer/ ionic liquid	Name of the Biopolymer Electrolyte	Ratios (wt%)
1	Guar Gum	Sodium nitrite	1,3- Dioxolane	Guar Gum- Sodium nitrite- 1,3- Dioxolane	70:25:5 60:35:5 50:45:5 40:55:5 30:65:5
2	Guar Gum	Sodium bromide	1,3- Dioxolane	Guar Gum- Sodium bromide- 1,3- Dioxolane	90:5:5 80:15:5 70:25:5 60:35:5

Table 7b: Compositions (g/wt%) of biopolymer, salt & plasticizer/ionic liquid

S.NO	Name of the Biopolymer	Name of the salt	Name of the plasticizer/ ionic liquid	Name of the Biopolymer Electrolyte	Salt Concentration (g/wt%)
1	Guar Gum (0.4 g)	Sodium nitrite	1,3- Dioxolane (2 ml)	Guar Gum- Sodium nitrite- 1,3- Dioxolane	1 wt% 0.75 wt% 0.50 wt% 0.25 wt% 0.10 wt% 0.05 wt%
2	Guar Gum (1.2 g)	Sodium nitrite	1,3- Dioxolane (2 ml)	Guar Gum- Sodium nitrite- 1,3- Dioxolane	0.1 g 0.2 g 0.3 g 0.4 g 0.5 g 0.6 g
3	Guar Gum (0.6 g)	Sodium nitrite	1,3- Dioxolane (2.5 ml)	Guar Gum- Sodium nitrite- 1,3- Dioxolan e	1 wt% 0.75 wt% 0.50 wt% 0.25 wt% 0.10 wt% 0.05 wt%
4	Pectin (1.2 g)	Sodium nitrite	-	Pectin- Sodium nitrite- 1,3- Dioxolane	0.1 g 0.2 g 0.3 g 0.4 g 0.5 g

5	Guar Gum (0.6 g)	Sodium nitrite	-	Guar Gum- Sodium nitrite- 1,3- Dioxolane	0.1 g 0.2 g 0.3 g 0.4 g 0.5 g 0.6 g
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3.8.1 Guar Gum/ Sodium nitrite/ 1,3-Dioxolane:

The biopolymer Guar Gum have been blended with 40 ml of distilled water in a magnetic stirrer, then Sodium nitrite salt and 1,3-Dioxolane as a plasticizer are added and kept in stirring for 24 hours to obtain a homogeneous solution. The solution was poured onto the Petri dishes and kept in a hot air-oven for 24 hours at 40⁰ C. The ratios (wt%) of Guar gum/ Sodium nitrite/ 1,3-Dioxolane were given in **Table 7**.

3.8.2 Pectin/ Sodium nitrite

The biopolymer Pectin have been blended with 40 ml of distilled water in a magnetic stirrer, then Sodium nitrite salt was added and kept in stirring for 24 hours to obtain a homogeneous solution. The solution was poured onto the Petri dishes and kept in a hot air-oven for 24 hours at 40⁰ C. The concentrations (g) of Pectin/ Sodium nitrite were given in **Table 8**.

3.8.3 Guar Gum/ Sodium nitrite

The biopolymer Guar Gum have been blended with 40 ml of distilled water in a magnetic stirrer, then Sodium nitrite was added and kept in stirring for 24 hours to obtain a homogeneous solution. The solution was poured onto the Petri dishes and kept in a hot air-oven for 24 hours at 40⁰ C. The concentrations (g) of Guar gum/ Sodium nitrite were given in **Table 8**.

3.8.4 Guar Gum/ Sodium bromide/ 1,3-Dioxolane

The biopolymer Guar Gum have been blended with 40 ml of distilled water in a magnetic stirrer, then Sodium bromide salt and 1,3-Dioxolane as a plasticizer are kept in stirring for 24 hours to obtain a homogeneous solution which is shown in **Image 6**. The solution was poured onto the Petri dishes and kept in a hot air-oven for 24 hours at 40⁰ C. The concentrations (M wt%) of Guar gum/ Sodium bromide/ 1,3-Dioxolane were given in **Table 8**. The solid polymer electrolytes are shown in **Image 7**.

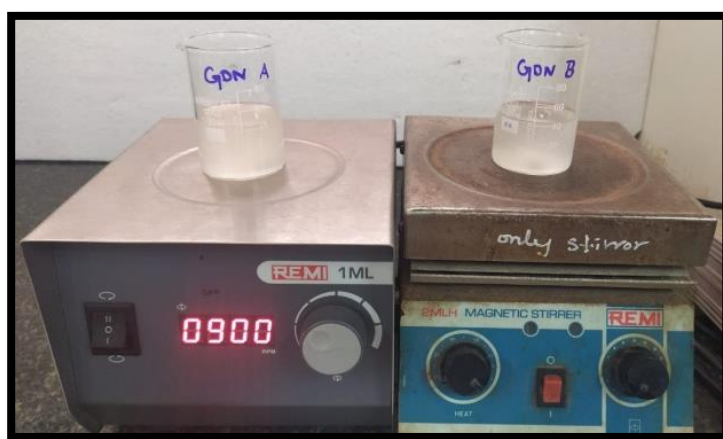


Image 6: Blending of mixture

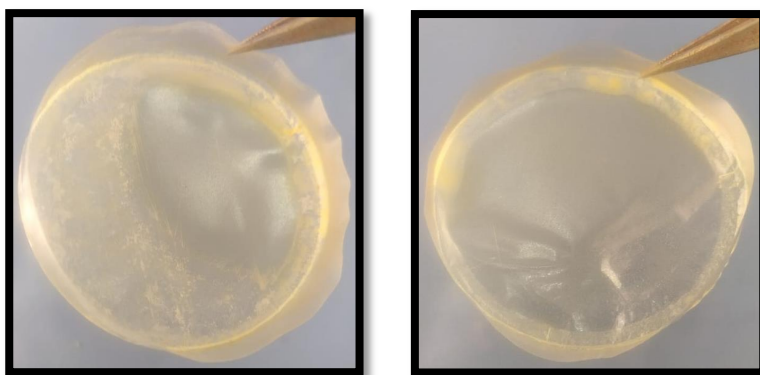


Image 7: Solid polymer film of GG-NaBr-1,3-DOL

3.9 Characterization Techniques

3.9.1 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared spectroscopy provides a simultaneous, almost instantaneous recording of the entire spectrum. In the FTIR spectroscopic principle, infrared (IR) radiation (about 10,000 to 100 cm^{-1}) passes through a sample, and part of the radiation is absorbed. The radiation that passes through the sample is recorded. Because different molecules with different structures produce different spectra, spectra can be used to identify and discriminate between molecules. It has a wide range of applications, from monitoring processes for identifying compounds to determining components within a mixture. **Figure 6** shows the FT-IR instrument.

FTIR analysis is applied to:

- Identify and characterize unknown materials (e.g., films, solids, powders, or liquids)
- Identify contamination on or in a material (e.g., particles, fibers, powders, or liquids)
- Determine additives after extraction of a polymer matrix.
- Identify oxidation, decomposition, or untreated monomer in failure analyses.



Fig 6: FTIR Spectrometer Instrument (Miracle 10 SHIMADZU)

3.9.2 Thermal Gravimetric Analysis (TGA)

Thermogravimetric analysis measures the temperatures at which degradation, reduction or oxidation occurs. Thermal analysis or TGA is a simultaneous thermal analyzer that can characterize several thermal properties of a sample in a single experiment. The TGA analysis is carried out by gradually increasing the temperature of a sample in an oven, as its weight is measured on an analytical balance that remains outside the oven. In the TGA, there is a loss of mass if a thermal event leads to the loss of a volatile component. A technique where the temperature difference between the specimen and a reference material is monitored against time or temperature, the sample temperature is programmed into a given atmosphere. The data obtained in TGA is useful in determining the purity and composition of materials, drying and ignition temperatures of materials, and knowing the stability temperatures of compounds. The data obtained in the DTA is used to determine temperatures of transitions, reactions, and melting points of substances. **Figure 7** shows the TGA instrument.



Fig 7: TGA 6300 Model instrument (EXSTAR)

3.9.3 3-D Optical Profilometer

A profilometer is a measuring instrument used to measure the profile of an area to quantify its roughness. Critical dimensions such as step, bend, and flatness are calculated from the surface topography. The optical profile meter operates on the principle of contactless mode where the light source is used to analyze the surface of the materials, so true imaging is possible where surface measurements can be obtained. The roughness map (or gloss map) defines the way light disperses through the surface of the 3D model. A 0 for roughness results in a high gloss surface like plastic while a 1 is a more matte look. **Figure 8** shows the 3D optical profilometer instrument.



Fig 8: 3-D Optical Profilometer (Zeta-20)

3.9.5 Impedance Studies

Impedance spectroscopy is a powerful instrument to analyze the electrical properties of solid electrolytic material and its interfaces. Ion conductivity is dependent on their mobility and the conductive species. This method is used to establish the conductivity mechanism, observing the involvement of the polymer chain and the carrier generation processes. The solid polymer film mixture was retained between the two aluminum electrodes. Both real and imaginary impedance values were taken. A plot of the actual impedance on the X axis concerning the negative imaginary impedance on the Y axis has been drawn. The graph shows two well-defined regions, a semi-circle in the high-frequency range and a peak inclined to the low-frequency region. From the complex impedance plot, the bulk resistance (R_b) can be calculated from the point of intersection of the semi-circle and the inclined tip. The impedance instrument is shown in **Figure 9**. By knowing the bulk resistance, the conductivity of the sample may be determined using the relation,

$$\rho = L/R_b A$$

In which,

ρ → Impedance

R_b → Bulk resistance

A & L are respectively the **surface** and the **thickness** of the film.



Fig 9: Ametek PARSTAT MC – 1000

3.9.6 Transport number measurement

Chronoamperometry technique

Chronoamperometry is an analytic technique in which the electrical potential of the working electrode is stepped. The current resulting from faradaic processes occurring on the electrode (caused by the potential step) is monitored over time. The chronoamperometric technique is used to measure the transference number that identifies whether the conductivity in the polymer electrolyte is due to the presence of ions or electrons. The Chronoamperometric instrument and probe setup are shown in **Figures 10a and 10b** respectively. The transference number is determined using the equation,

$$t_{\text{ion}} = I_s / I_0 \text{ and } t_{\text{ion}} = (I_0 - I_s) / I_0$$

where,

t_{ion} → Transfer of ions

I_0 → Initial current

I_s → Steady state current



Fig 10a: Ametek PARSTAT MC – 1000 (Chronoamperometry)



Fig 10b: Thin film probe set up

RESULTS AND DISCUSSION

CHAPTER IV

RESULT AND DISCUSSIONS

4 Introduction

This chapter deals with the results obtained through various techniques and measurements of the prepared polymer electrolytes and the discussions based on the results. The following sets of biopolymer solid electrolytes with different compositions of Guar gum, pectin, Sodium nitrite, Sodium bromide, and 1,3 Dioxalane were prepared for the present work.

- a) Guar gum/ Sodium nitrite/ 1,3- Dioxalane
- b) Guar gum/ Sodium nitrite
- c) Pectin/ Sodium nitrite
- d) Guar gum/Sodium bromide/ 1,3-Dioxalane

Out of the prepared electrolytes mentioned above, the electrolytes (c) prepared from different compositions of Pectin with sodium nitrite were not properly formed which is shown in **Image 8**. Hence, further characterizations for these polymer electrolytes were not able to be carried out. For (a) and (b) polymer electrolytes only Fourier Transform Infra-Red Spectroscopy (FT-IR) characterization had been done. The prepared electrolytes of (a) and (b) are shown in **Images 9a and 9b** and their FT-IR spectrum are shown in **Figures 11(a-d) and 12(a-f)**. Since proper peaks were not obtained, the Figure shows that there was no reaction between polymer and sodium salt.

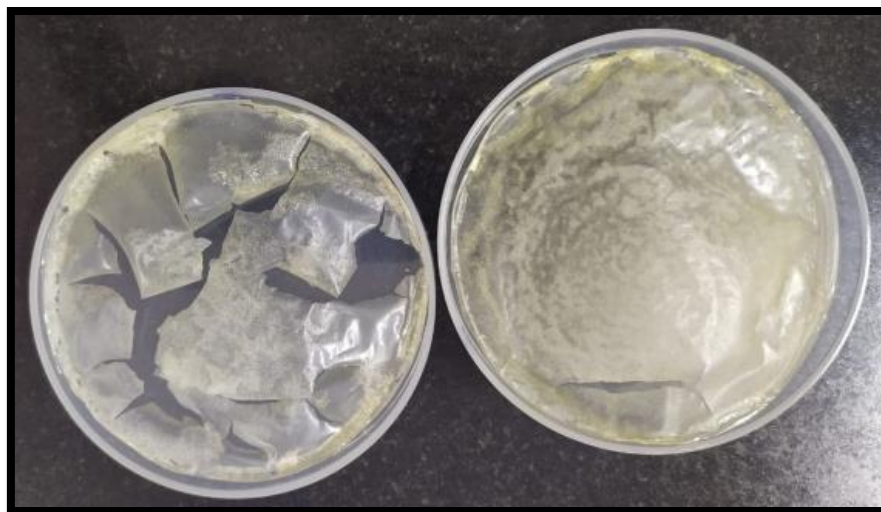
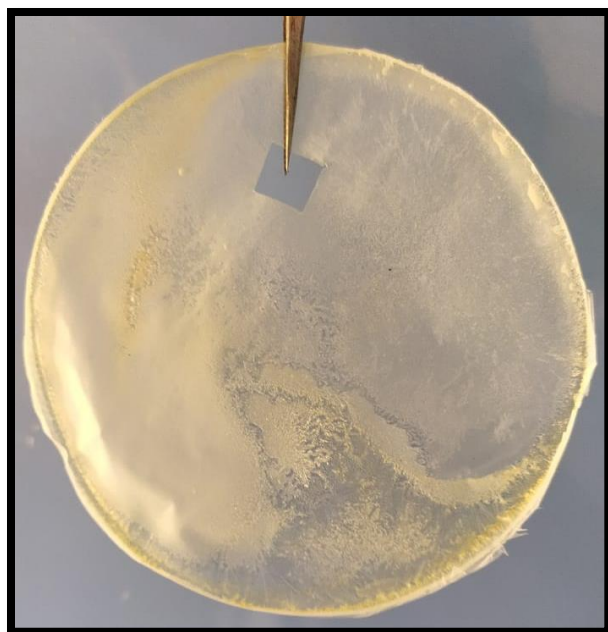


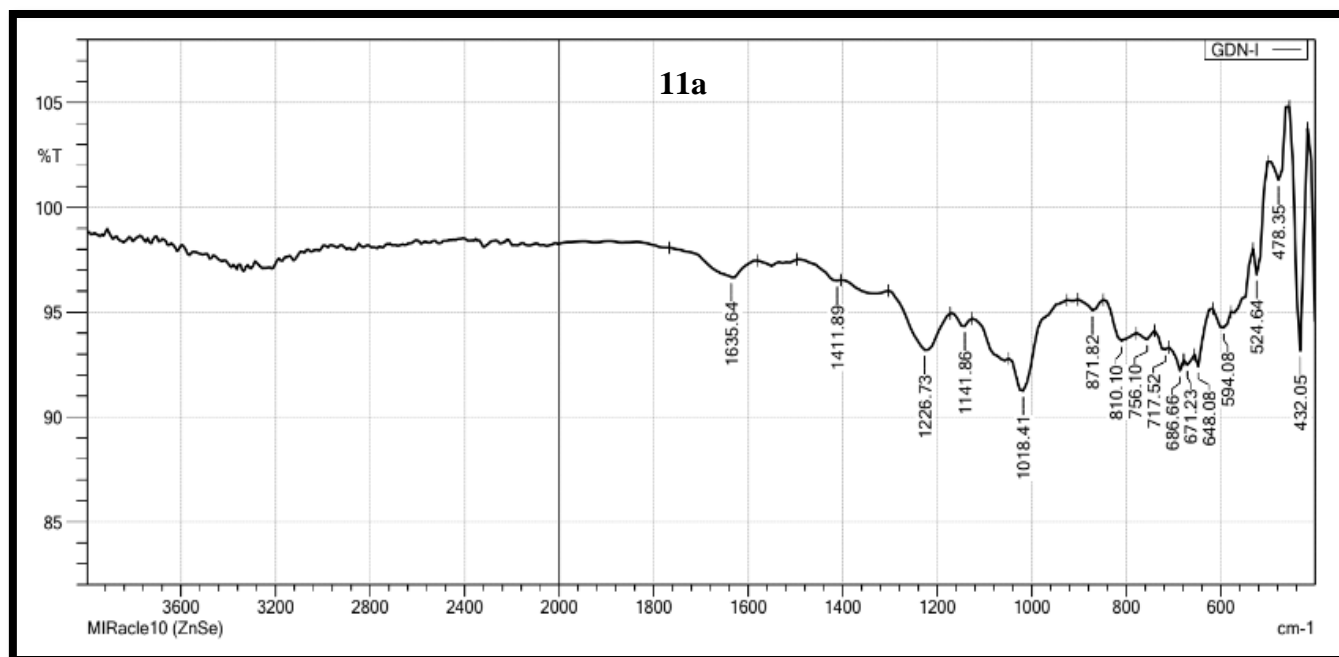
Image 8: Solid polymer film



**Image 9a: Solid polymer film of Guar gum/
Sodium nitrite/ 1,3- Dioxalane**



**Image 9b: Solid polymer film of Guar gum/
Sodium nitrite**



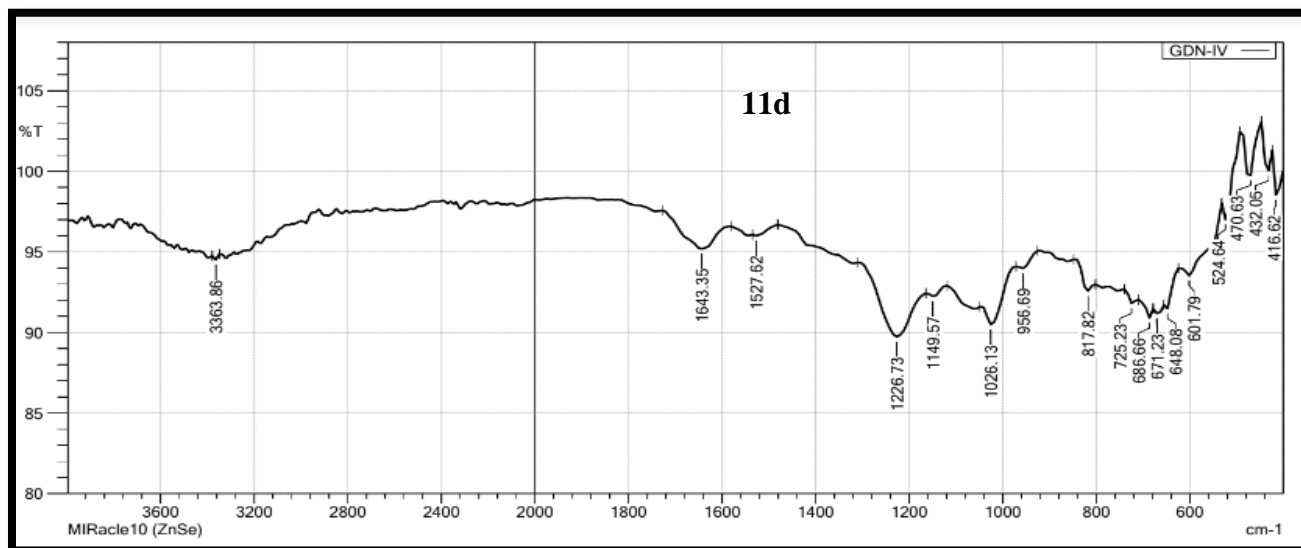
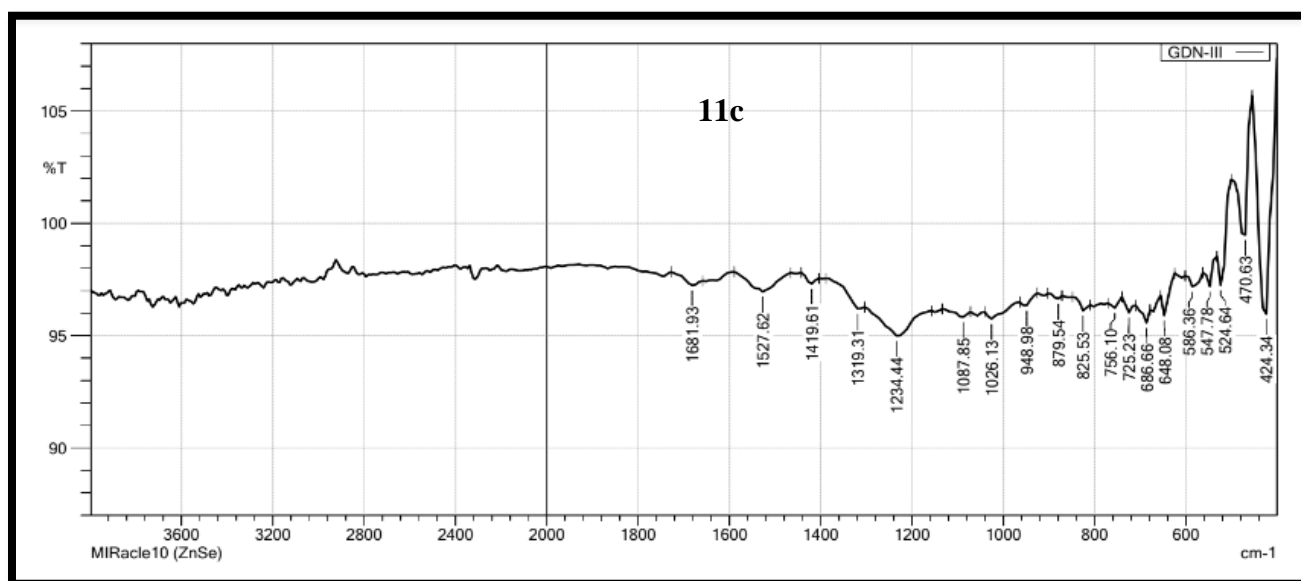
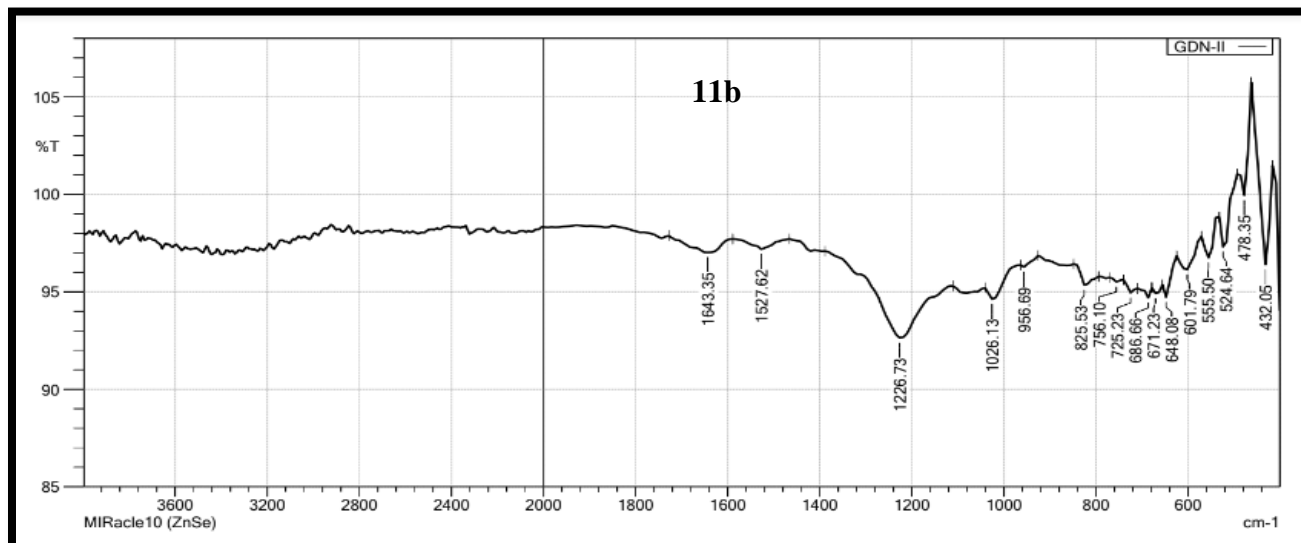
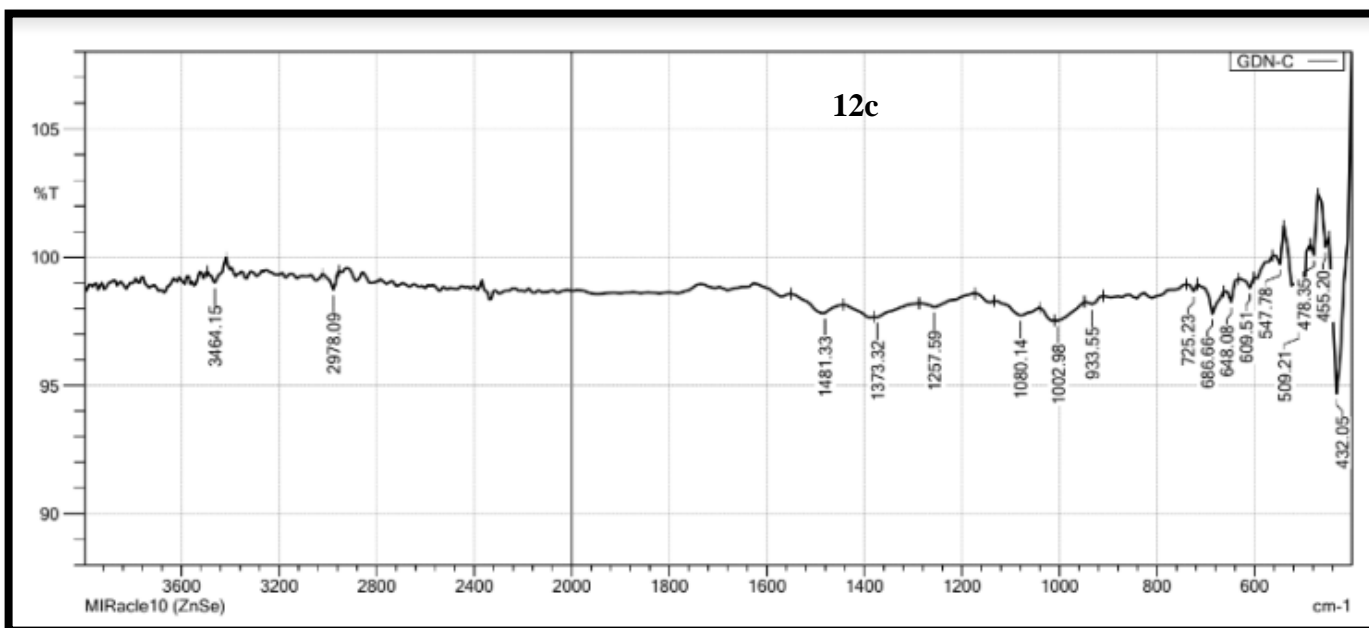
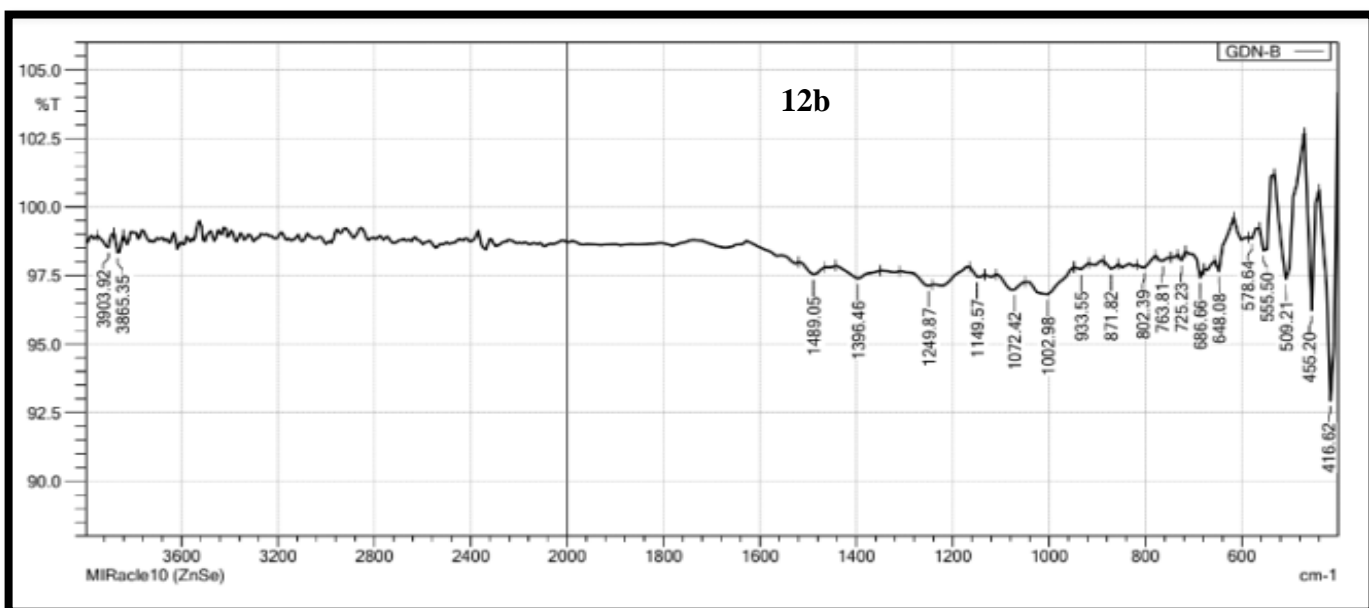
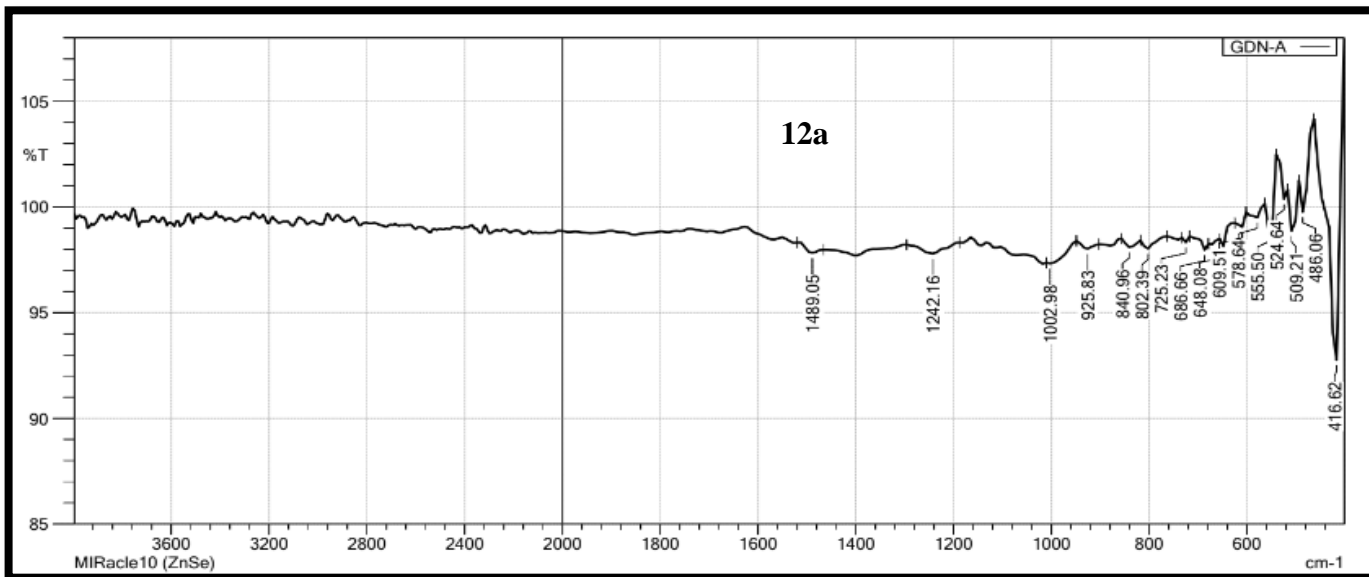


Fig 11(a-d): FT-IR spectrum of Guar gum/ Sodium nitrite/ 1,3- Dioxalane



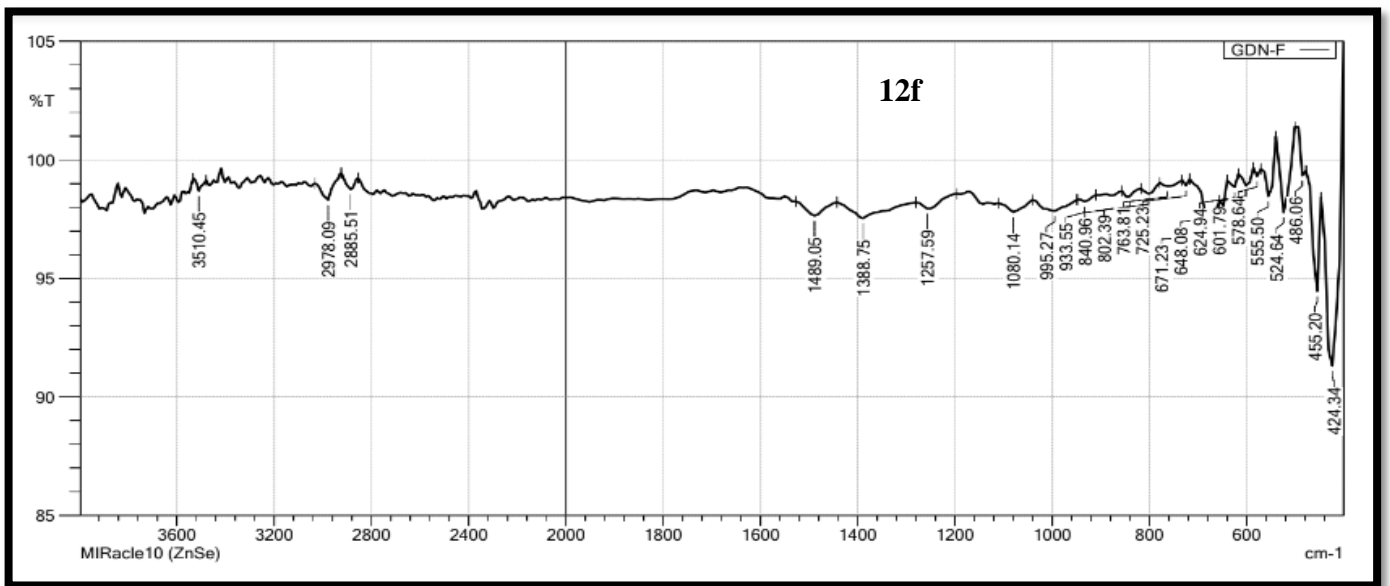
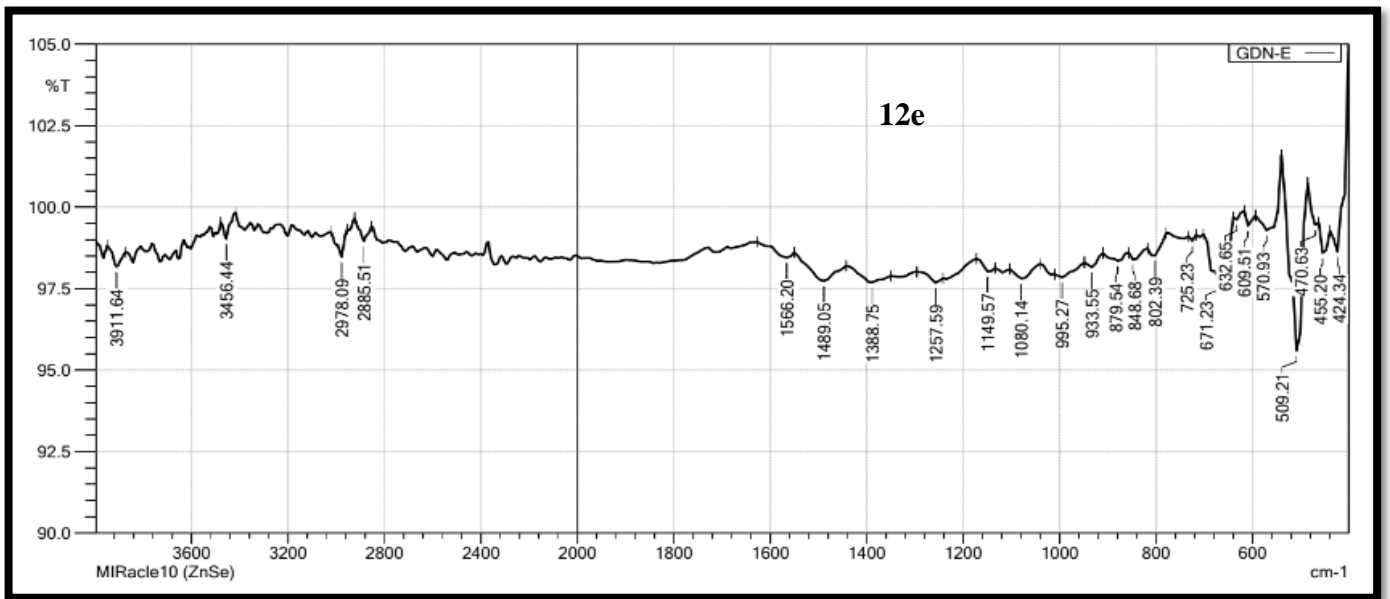
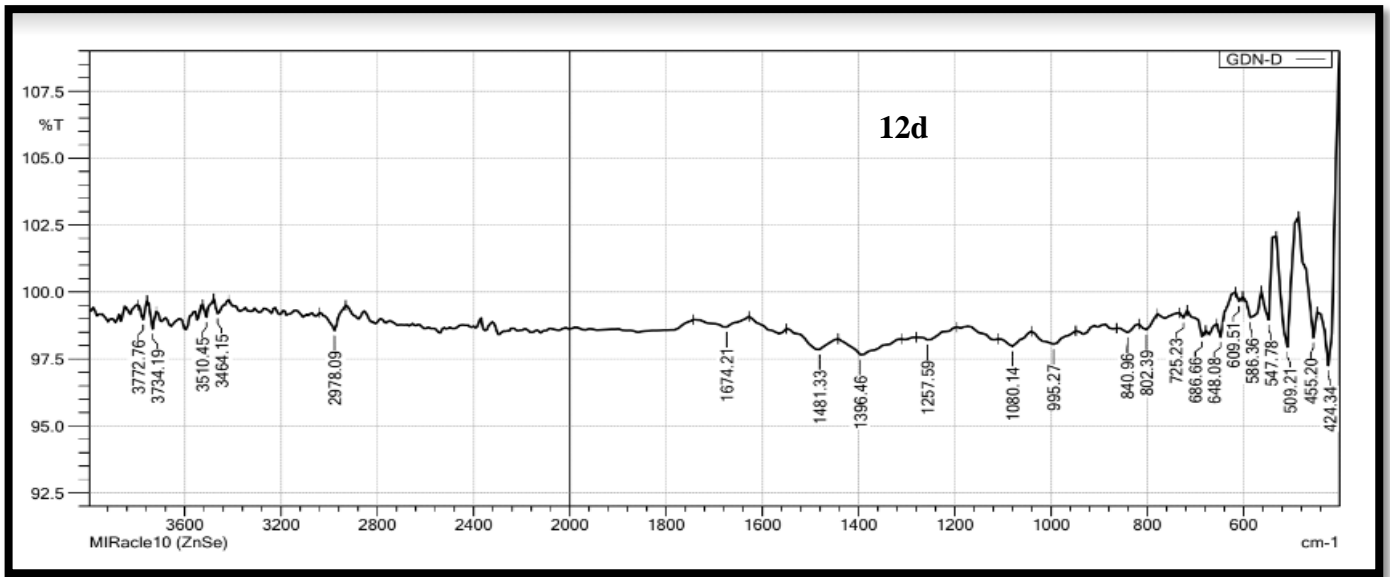


Fig 12(a-f): FT-IR spectrum of Guar gum/Sodium nitrite

The prepared polymer electrolytes (d) of different compositions of Guar gum/Sodium bromide/1,3-Dioxalane are shown in **Images 10 to 13**. The code and compositions assigned for the solid biopolymer electrolytes were given in **Table 8**.

Table 8: The code and compositions assigned for the solid biopolymer electrolytes (Guar gum/ Sodium Bromide/ 1,3-Dioxalane)

Code	Composition (M wt%)
GDN 1	Guar gum (90): Sodium Bromide (5): 1,3-DOL(5)
GDN 2	Guar gum (80): Sodium Bromide (15): 1,3-DOL(5)
GDN 3	Guar gum (70): Sodium Bromide (25): 1,3-DOL(5)
GDN 4	Guar gum (60): Sodium Bromide (35): 1,3-DOL(5)

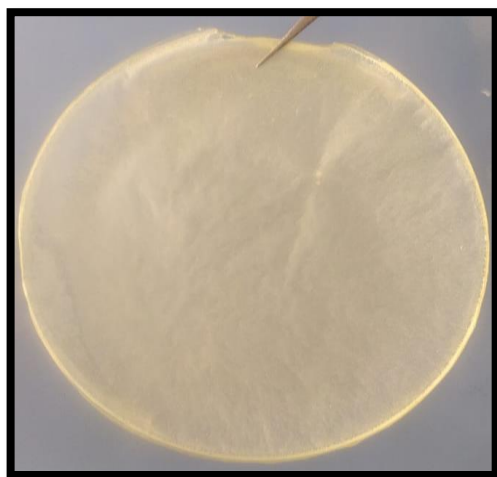


Image 10: Solid polymer film of GDN 1

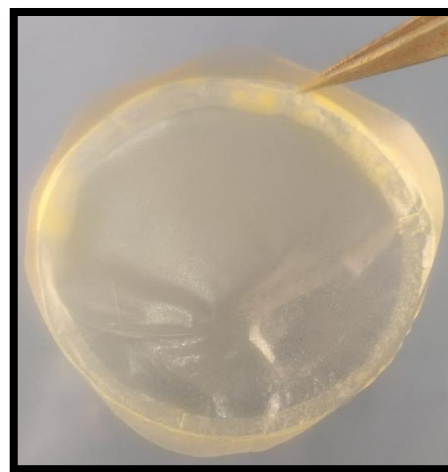


Image 11: Solid polymer film of GDN 2

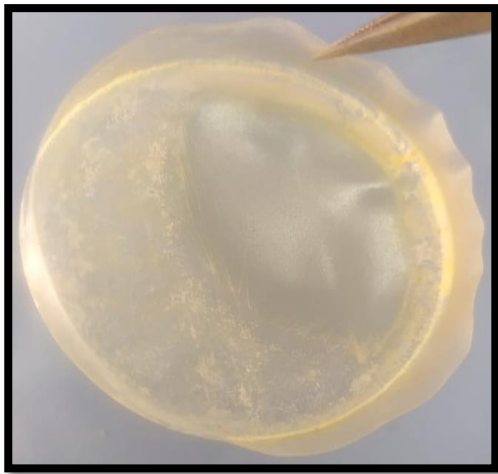


Image 12: Solid polymer film of GDN 3

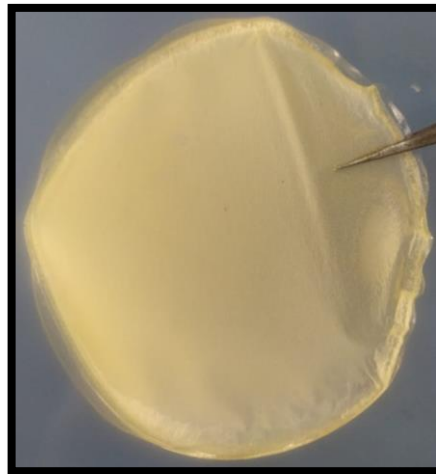


Image 13: Solid polymer film of GDN 4

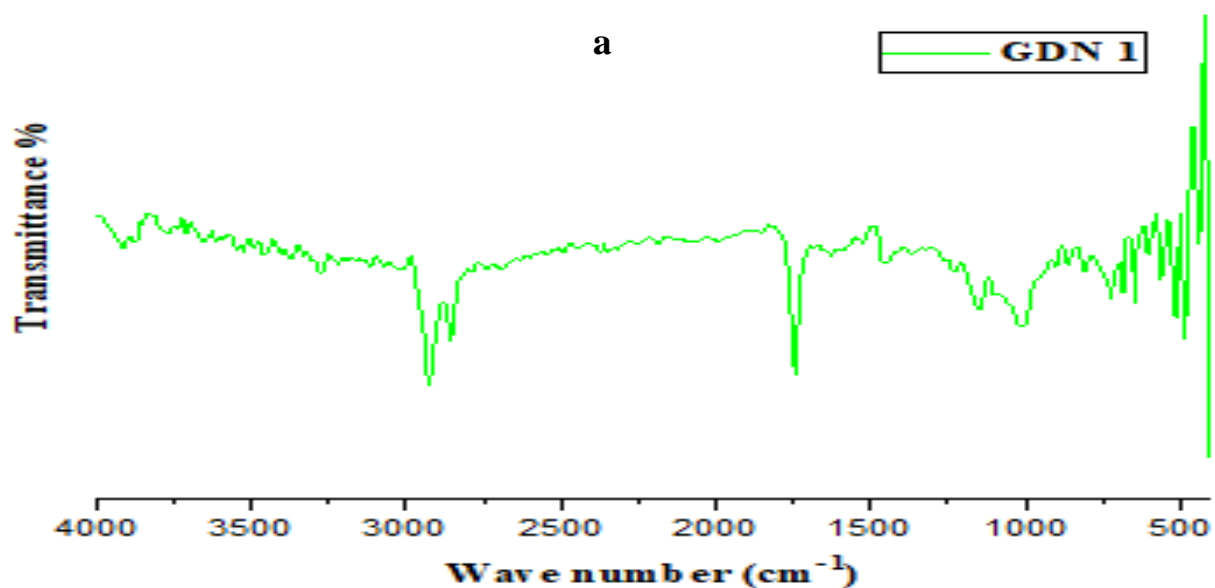
The thin transparent films obtained were characterized by various techniques.

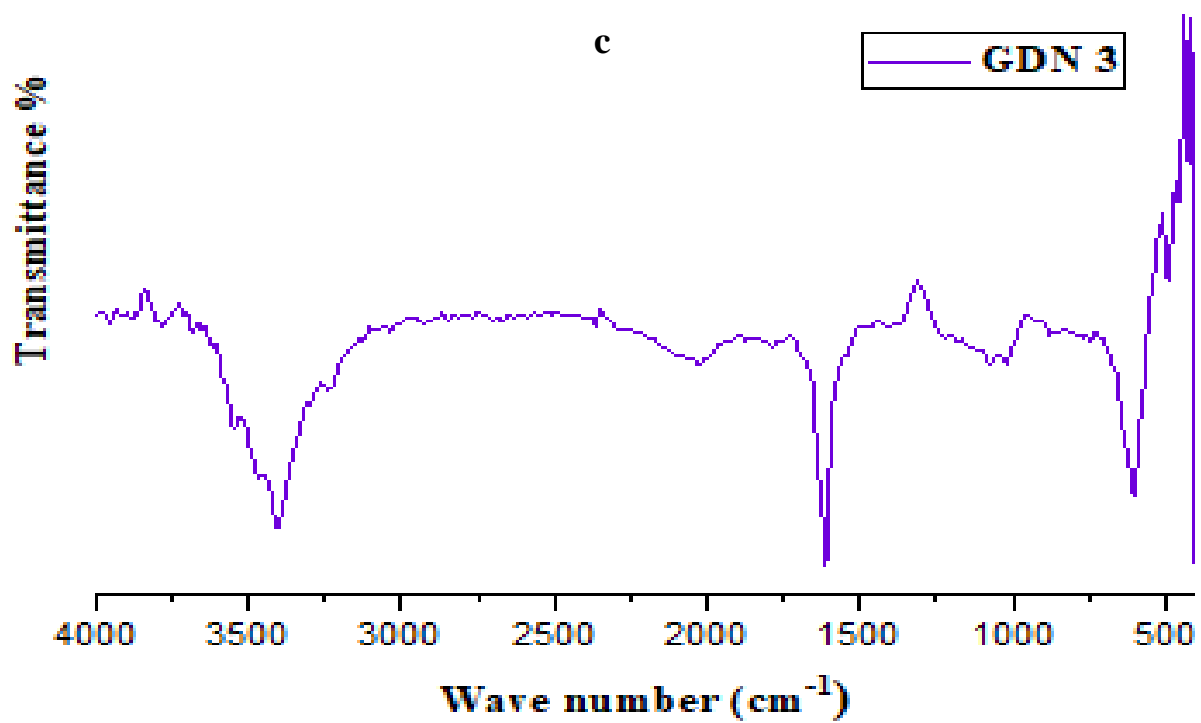
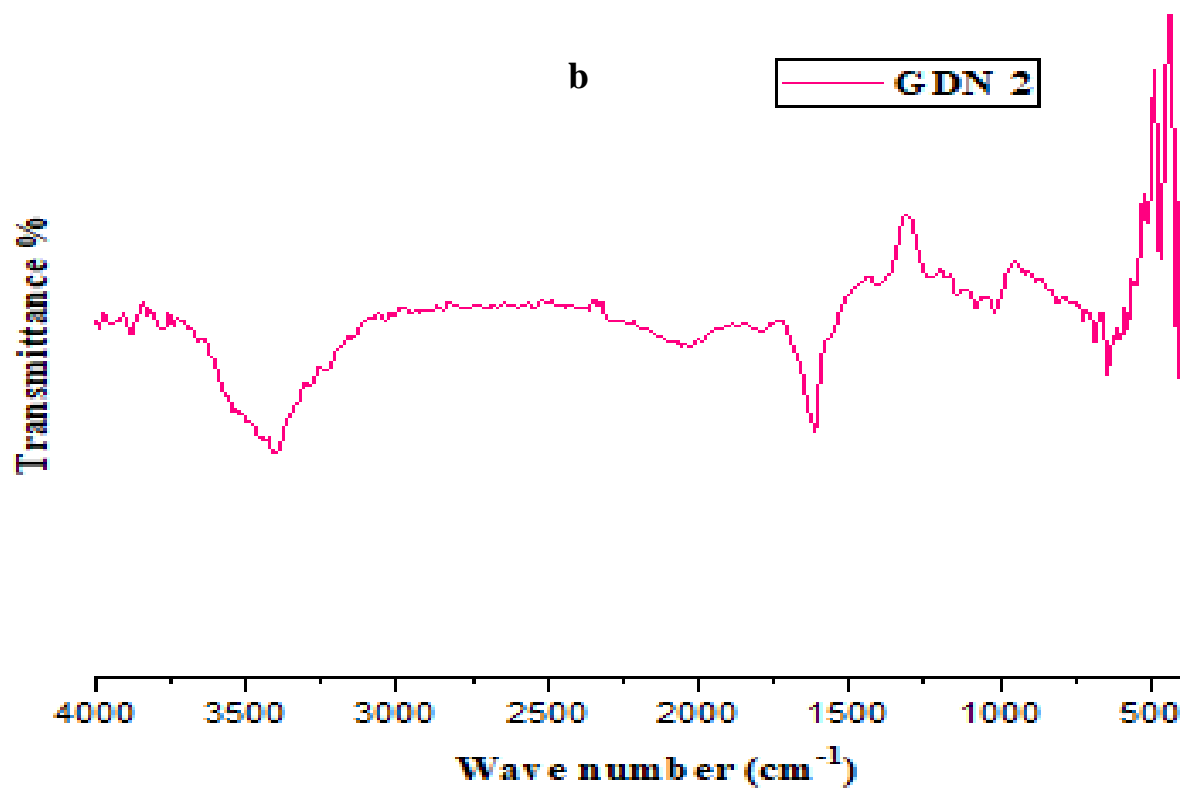
4. Characterization

The prepared biopolymer solid electrolytes have been characterized by the following techniques/analysis:

4.1 FT-IR Analysis

The FT-IR transmission spectra obtained for different compositions of Guar gum-Sodium bromide-1,3-Dioxalane polymer electrolytes are shown in **Figure 13 (a-d)** and the corresponding peak values in terms of wavenumber (cm^{-1}) are given in **Table 9**.





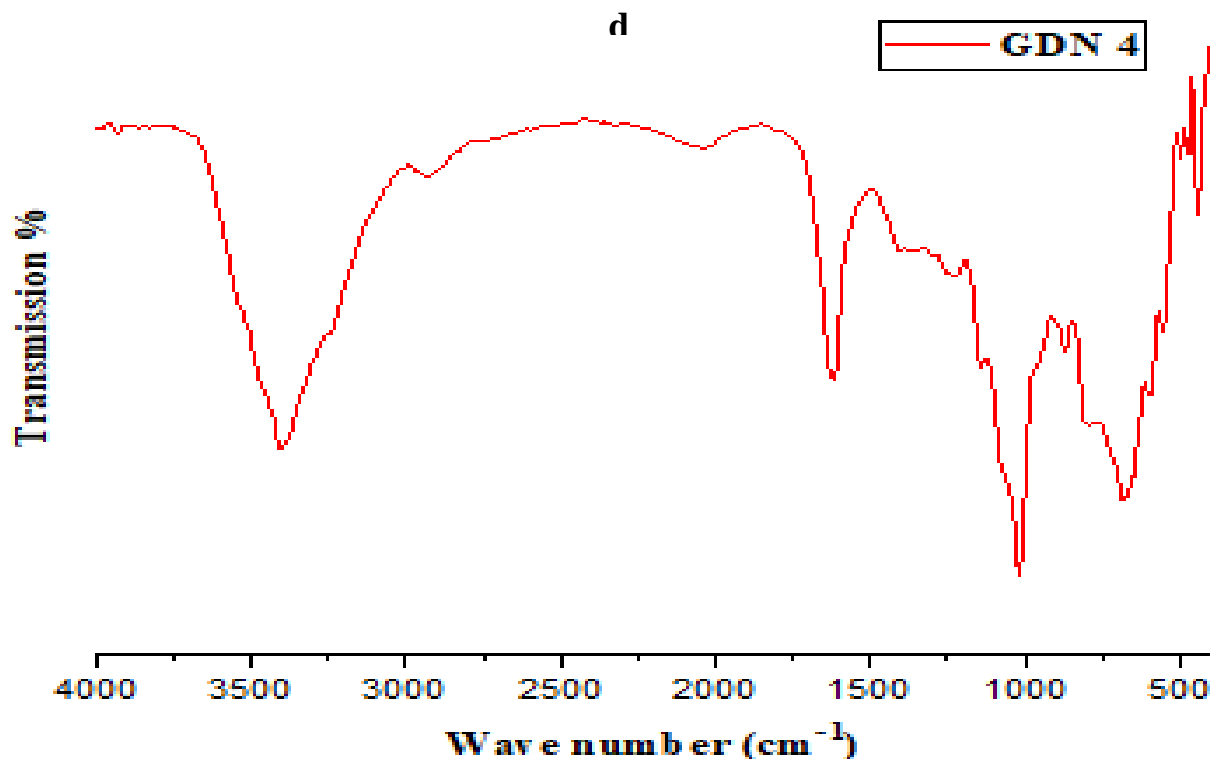


Fig 13(a-d): FTIR spectra of Guar gum- Sodium Bromide- 1,3-Dioxalane

For pure GG, a broad and strong absorption band due to OH stretching vibration was observed around 3328 cm^{-1} . This broadband is due to the hydroxyl groups present in the polymer. The aliphatic CH stretching vibration gives rise to the absorption band at 2925 cm^{-1} . The peaks appearing at 1365 cm^{-1} are assigned to OH bending vibration associated with water molecules. The peak appearing at 1155 cm^{-1} in the case of pure GG corresponds to $-\text{CH-OH}$ stretching vibrations. The polymer backbone peaks present within the region $1200\text{-}800\text{ cm}^{-1}$, which corresponds to highly coupled C-C-O, C-OH, and C-O-C stretching. The glycosidic linkages that belong to the absorption bands at 876 cm^{-1} are due to C-O-C stretching vibrations [R. Shilpa, Ph.D., thesis, 2021].

Table 9: FT-IR observed vibration peak values in terms of wavenumber (cm^{-1}) of Guar gum/ Sodium bromide/ 1,3-Dioxalane polymer electrolytes

Wavenumber (cm^{-1})					Characteristic functional groups
Pure Guar gum	GDN 1	GDN 2	GDN 3	GDN 4	
3328	-	3402.43	3402.43	3394.72	OH-stretching vibration
2925	-	2931.80	-	-	C-H stretching of the CH_2 group
1735	-	-	-	-	C=O stretching
1648	-	1620.21	1612.49	1612.49	O=C-O stretching
1365	-	-	-	-	O-H bending
1155	-	1141.86	1141.86	1141.86	-CH-OH stretching
1015	-	1018.41	1018.41	1018.41	C-O-C stretching
876	-	871.82	748.38	810.10	C-O-C stretching
770	-	794.67	748.38	725	(1-4), (1-6) linkages of galactose and mannose
-	-	601.79	601.79	601.79	C-Br stretching

In the case of Guar gum-based polymer electrolytes for composition GDN 1 (90:5:5), there were no vibrational peaks observed showing the absence of complex formation of ionic dopant and host polymer at this mentioned composition. However, for the compositions (80:15:5, 70:25:5, and 60:35:5), the above-mentioned peaks are present with slight shifting on the addition of Sodium Bromide (Na-Br) salt and those values are given in **Table 2**. A new small peak at 601.79 cm^{-1} is obtained on the addition of NaBr salt. The peak appears due to the **C-Br stretching**, which is a characteristic peak corresponding to Na-Br. The peak corresponding to Na^+ vibration appears in the region of the broad OH stretching band which is due to the addition of salt. A peak obtained at 3346 cm^{-1} (GG) is shifted to 3402 cm^{-1} (GDN 2, GDN 3), and 3394 cm^{-1} (GDN 4) attributed to OH stretching vibration. The shift in the vibrational bands and the evolution of new peaks corresponding to Na-Br prove the complex electrolyte formation between the host polymer and the salt.

4.2 Thermal Gravimetric Analysis (TGA)

The thermal stability studies were undertaken by thermogravimetric analysis (TGA). Thermal stability is very important for polymeric materials because the end use and processability of these depend on them [Mohammad Saleem Khan and Abdul Shakoor, 2015]. For native Guar gum, the initial weight loss of 13.8% observed at 86⁰C was due to the degradation of entrapped moisture content in the prepared electrolytes. With a further increase in temperature, a major weight loss of 60% at 250⁰C is observed [Abirami M *et al*, 2020]. The TGA curve for Guar gum- Sodium bromide- 1,3-Dioxalane electrolytes in the ratio of 80:15:5, 70:25:5, and 60:35:5 wt% are shown in **Figures 14a, 14b, and 14c**.

For 80:15:5 M wt% GG-NaBr-1,3-DOL polymer electrolyte, the weight loss of 11% observed at 115⁰C was due to the degradation of entrapped moisture content in the prepared electrolyte. With a further increase in temperature, a major loss of 48% at 320⁰ is observed which is assigned to the breakage of C-O-C bonds in mannose and galactose backbones, resulting in CO₂ expulsion from the guar gum backbone. The remaining 41% weight loss takes place between 700⁰C to 900⁰C indicating the decomposition of NaBr salt.

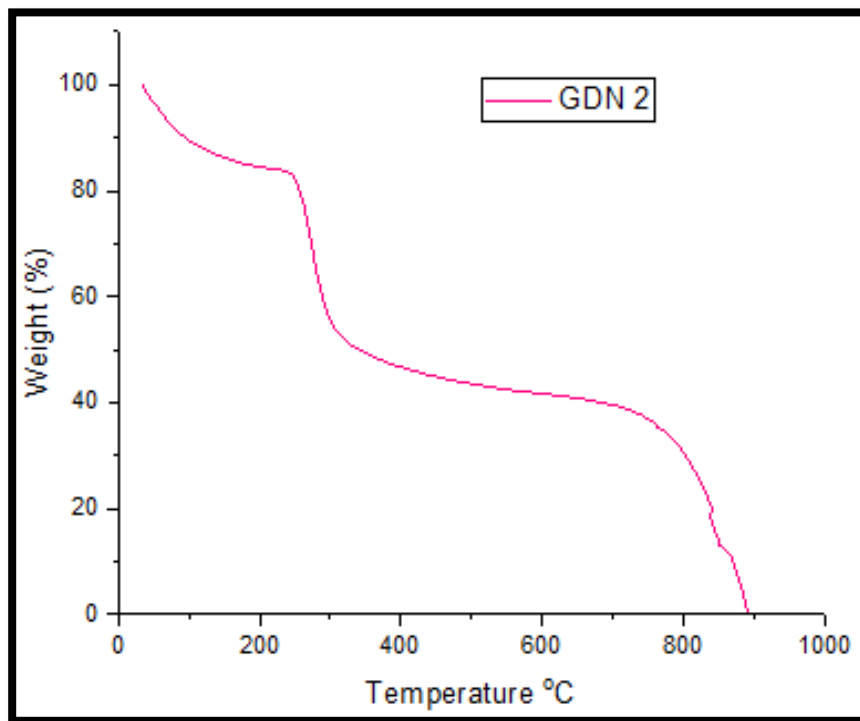


Fig 14a: TGA curve of GDN 2

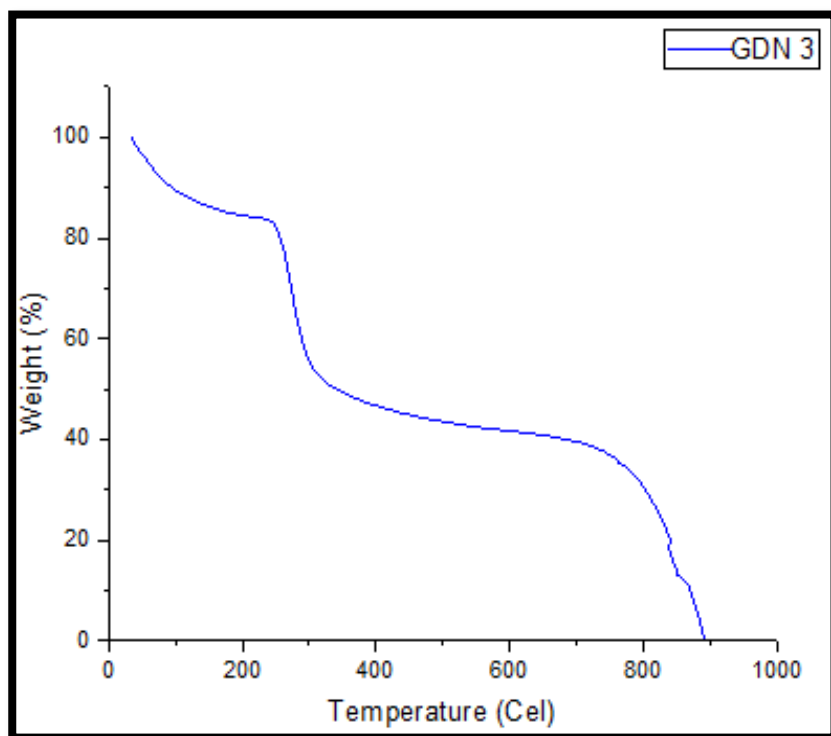


Fig 14b: TGA curve of GDN 3

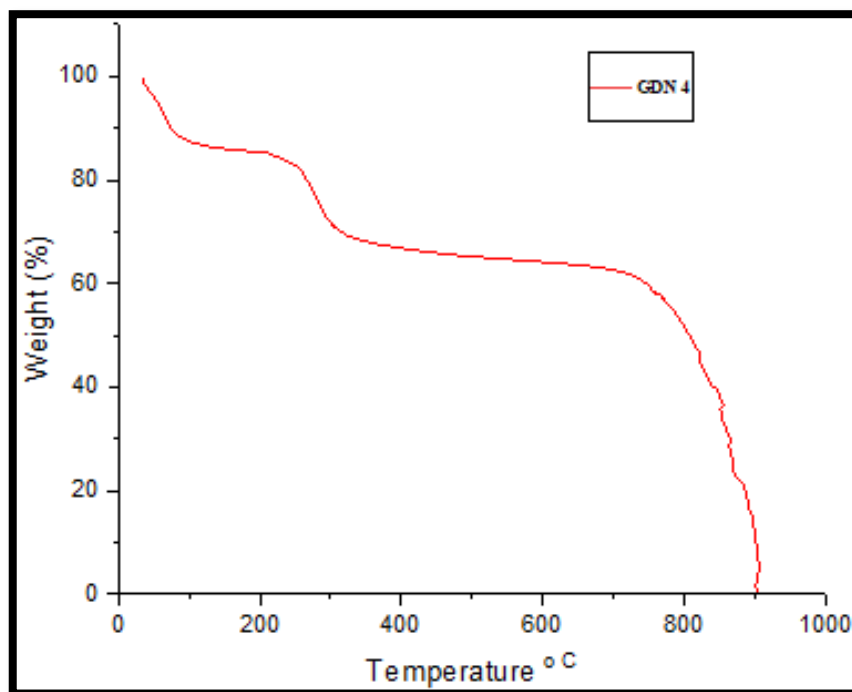


Fig 14c: TGA curve of GDN

A weight loss of 11% observed at 107⁰C is due to the degradation of entrapped moisture content in the prepared electrolyte of the composition 70:25:5 M wt% (GDN 3). With a further increase in temperature, a mass loss of 32% at 300⁰ is observed which is assigned to the breakage of C-O-C bonds in mannose and galactose backbones, resulting in CO₂ expulsion from the guar gum backbone. The remaining 57% weight loss takes place between 700⁰C to 900⁰C indicating the decomposition of NaBr salt.

A weight loss of 11% is observed due to the degradation of entrapped moisture content in the prepared electrolyte of the composition 60:35:5 M wt% (GDN 4) at 107⁰C. A weight loss of 28% at 300⁰C was observed for GDN 4 polymer electrolytes assigned to the breakage of C-O-C bonds in mannose and galactose backbones, resulting in CO₂ expulsion from the guar gum backbone. A major loss of 61% weight loss takes place due to the high concentration of salt, between the temperature range from 700⁰C to 900⁰C indicating the decomposition of NaBr salt.

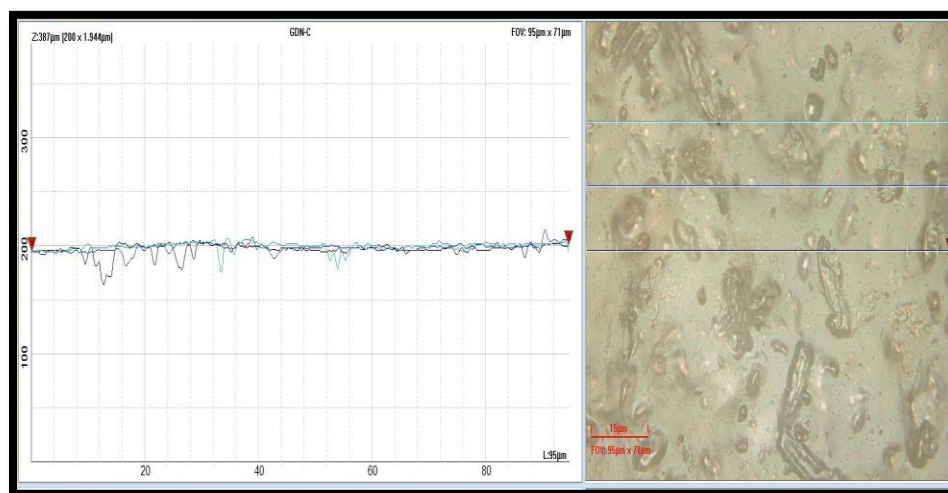
Table 10: Thermal stability of Guar gum- Sodium bromide- 1,3-Dioxalane polymer electrolytes

S. NO	Code	Composition of GG-NaBr-1,3-DOL polymer electrolytes (M wt %)	Thermal stability (°C)
1	GDN 2	80:15:5	905.10
2	GDN 3	70:25:5	858.37
3	GDN 4	60:35:5	898.78

From TGA results, it can be concluded that on adding plasticizer and dopant the thermal stability of polymer membranes was significantly affected [Dodi G *et al*, 2011]. The prepared GG-NaBr-1,3 DOL-based polymer electrolytes are stable up to 900 °C. In comparison with the pure polymer (thermal stability of pure GG is up to 80⁰C), the thermal stability of the doped and plasticized samples has been affected, which was supported by FTIR data witnessing the interaction of the salt and the polymer [Sudhakar *et al.*, 2014]. The thermal stability of the prepared polymer electrolytes is increased due to the interaction of the polymer and salt. The thermal stability for the Guar gum-Sodium bromide-1,3-Dioxalane polymer electrolytes in the ratio 80:15:5, 70:25:5, and 60:35:5 are given in **Table 10**.

4.3 3D Laser Profilometry Analysis

The topography of the surface and its features of prepared polymer films were studied using a 3D-Laser Profilometer. The roughness of the sample with different ratios of polymer electrolytes surface varies accordingly. The topographic surface features and 3D zeta images of the Guar gum-Sodium bromide-1, 3-DOL polymer electrolytes (80:15:5, 70:25:5, and 60:35:5 wt%) are shown in **Image 14 (80:15:5)**, **15 (70:25:5)** and **16 (60:35:5)**. The images exhibited three-dimensional surface areas with the average roughness (Ra) values ranging from 15.6 to 27.5 % which are given in **Table 11**.



Topographical representation of surface features of GDN 2

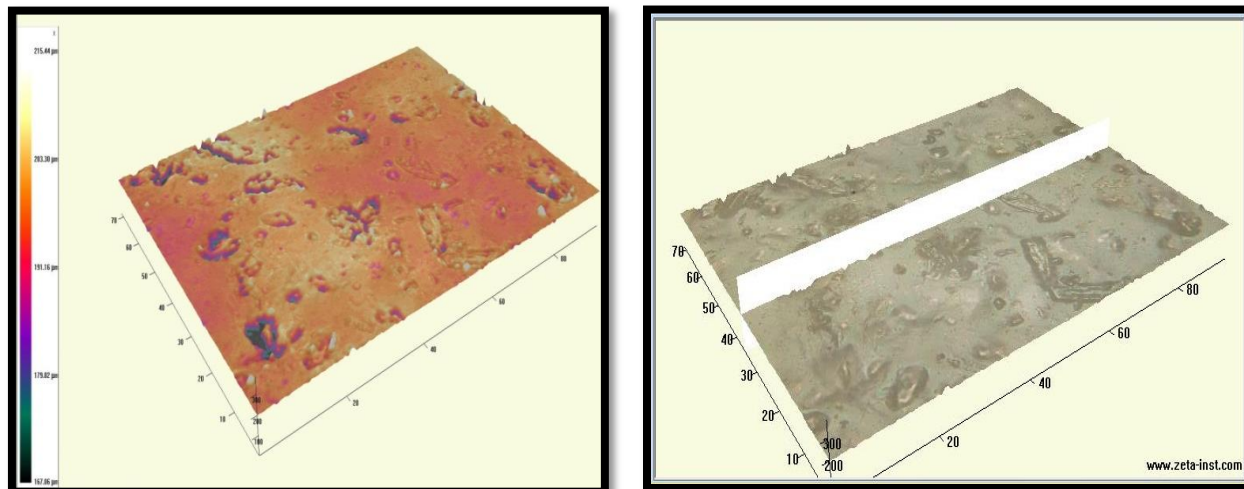
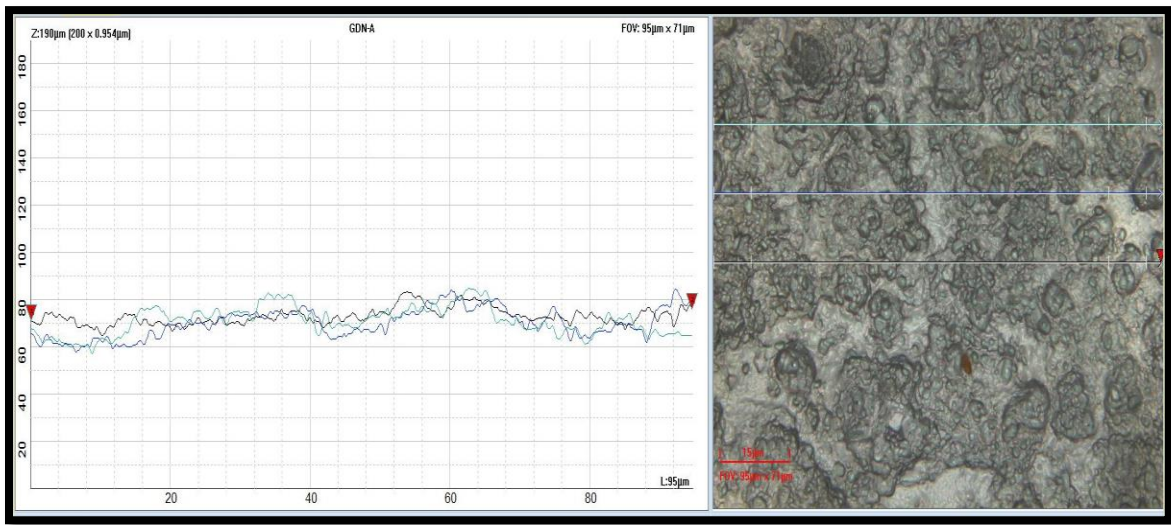


Image 14: Zeta images of GDN 2



Topographical representation of surface features of GDN 3

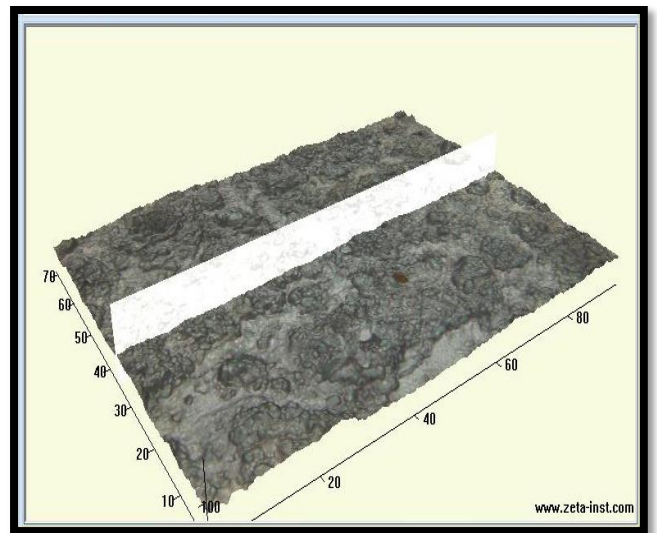
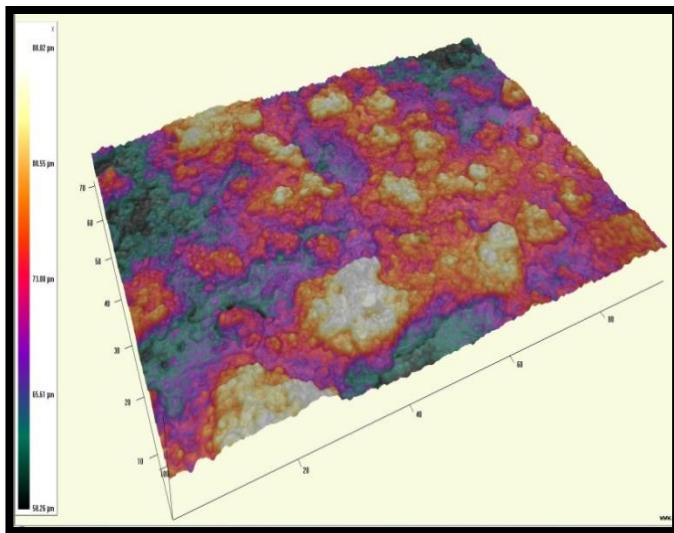
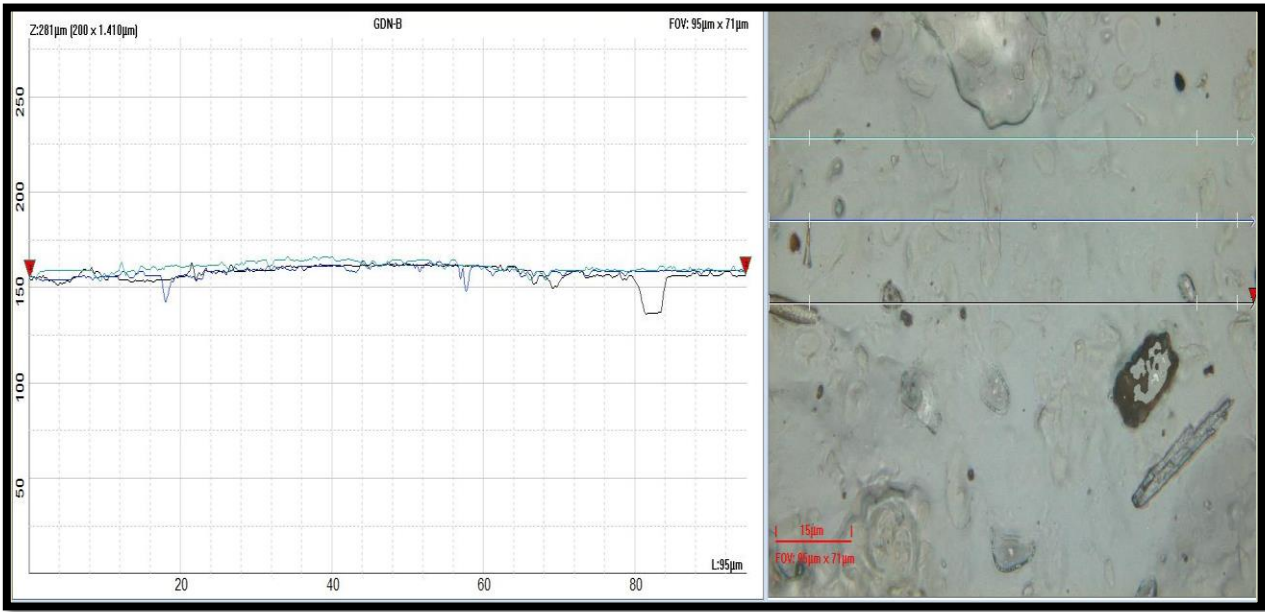


Image 15: Zeta images of GDN 3



Topographical representation of surface features of GDN 4

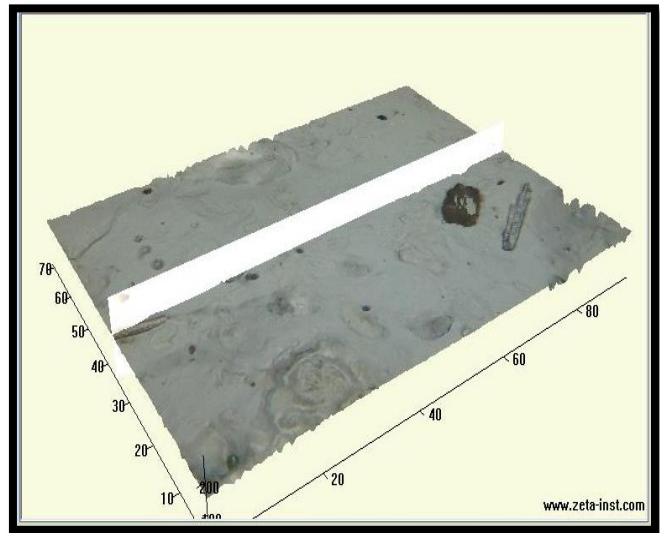
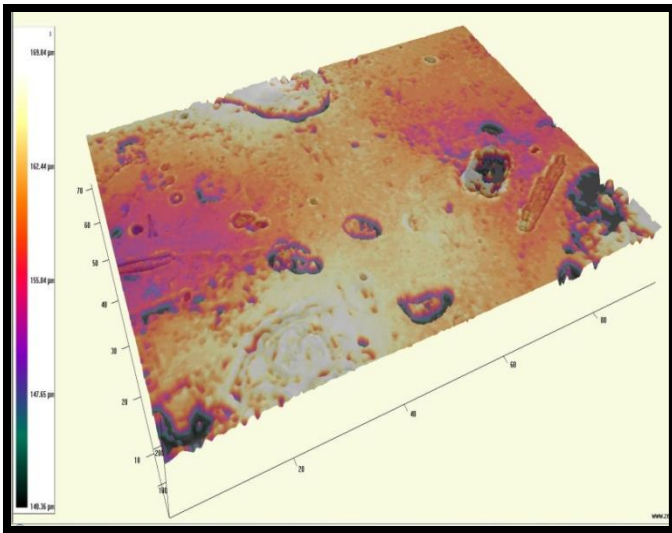


Image 16: Zeta images of GDN 4

Table 11: Average roughness values of GG-NaBr-1,3-DOL polymer electrolytes

Code	Composition of Guar gum- Sodium bromide- 1,3-DOL (M wt%)	Average roughness (Ra) values (%)
GDN 2	80:15:5	15.6
GDN 3	70:25:5	25.1
GDN 4	60:35:5	27.5

It is also observed that, as the concentration of the Sodium bromide salt increased, the surface roughness of the film increases. Among the prepared biopolymer thin films of Guar gum- Sodium bromide- 1,3- Dioxalane, GDN 2 exhibited lesser average roughness values (R_a) of 15.6 % and GDN 3 exhibited higher average roughness values of 27.5%. This study may be concluded that the mobility of ionic species decreases by the increase in crystalline nature of the prepared films which causes low ionic conductivity [Mohammad Saleem Khan and Abdul Shakoor, 2015]. Thus, GDN 3 is comparatively amorphous than GDN 4.

4.4 Impedance studies

The Nyquist plot represents the impedance behavior through the variation of real impedance vs imaginary impedance for different frequency domains. The Nyquist plot shows two well-defined regions, a semicircle in the high-frequency range is related to the conduction process in the bulk of the electrolytes (R_b), and the linear region in the low-frequency range can be attributed to the effect of blocking electrodes. The electrical conductivity values are estimated using the following equation.

$$\rho = l/R_b A$$

where,

ρ is conductivity (Scm^{-1})

l is the thickness of the sample (mm)

R_b is resistance (ohm)

A is an area of the sample (cm^2)

The thickness of the obtained films was found using a screw gauge and the area of the impedance measurement was $1 \times 1 \text{ cm}^2$. The observed thickness and bulk resistance for the GG-NaBr-1,3-DOL polymer electrolytes are tabulated in **Table 12**.

Table 12: Thickness and Bulk resistance for GG-NaBr-1,3-DOL polymer electrolytes

Code	Composition	Thickness (mm)	Bulk Resistance (Ω)
GDN 2	80:15:5	0.012	6124
GDN 3	70:25:5	0.042	18615
GDN 4	60:35:5	0.034	46740

The conductivity values for various concentrations of ionic salt (NaBr) doped with polymer guar gum at room temperature (303 K) with plasticizer (1,3- Dioxalane) are given in **Table 13**.

Table 13: Conductivity values of Guar gum- Sodium bromide- 1,3-Dioxalane polymer electrolytes

Code	Composition	Conductivity (S/cm)
GDN 2	80:15:5	1.96×10^{-7}
GDN 3	70:25:5	2.26×10^{-7}
GDN 4	60:35:5	7.29×10^{-8}

It is evident from Table 13, that the film containing 70:25:5 M wt% of GDN 3 exhibits higher conductivity of 2.26×10^{-7} S/cm. The reason for such an increase in conductivity may be due to the increased interaction of Na^+ ions [Aziz, S. B., & Abidin, Z. H. Z., 2013]. Also, GDN 3 has a relatively higher transport number (t_{ion}) of 0.76, which is given in **Table 14**. Further, on the addition of salt, the conductivity will be found in future research. Nyquist plots for Guar gum doped with various concentrations of NaBr with plasticizer 1,3-Dioxalane at ambient temperature (303 K) were shown in **Figure 15**.

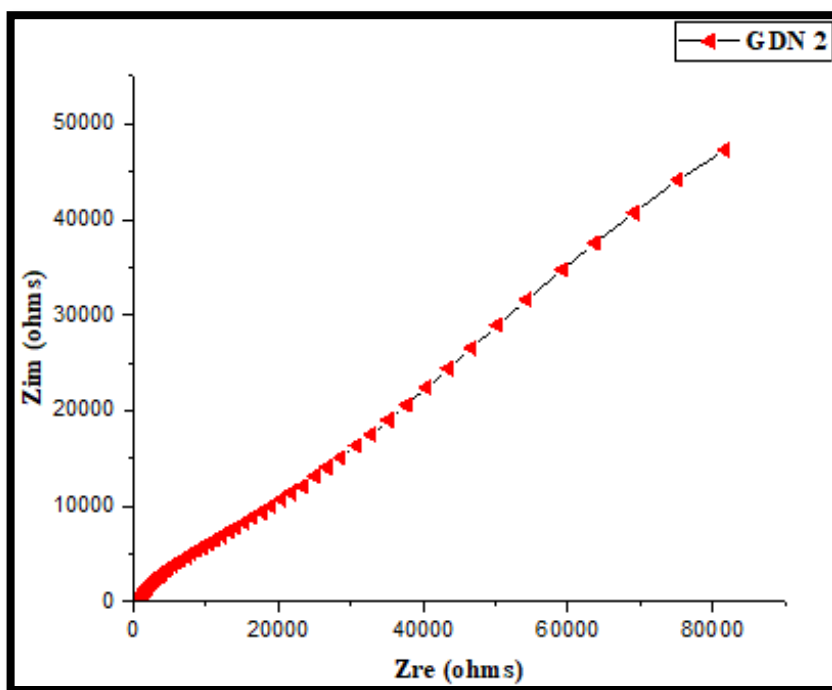


Fig 15a: Nyquist plot of GDN 2

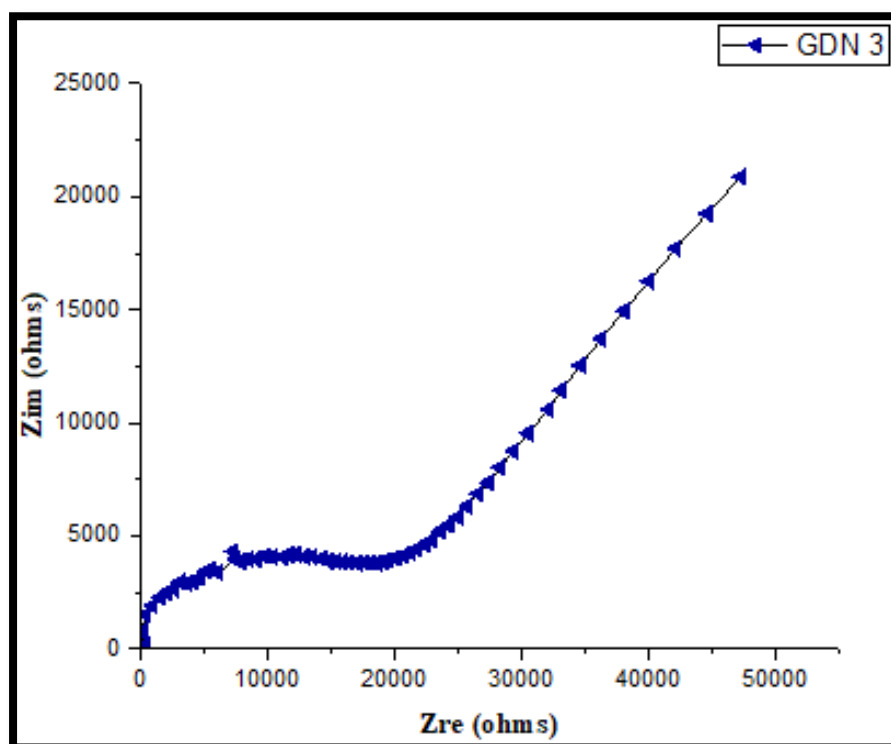


Fig 15b: Nyquist plot of GDN 3

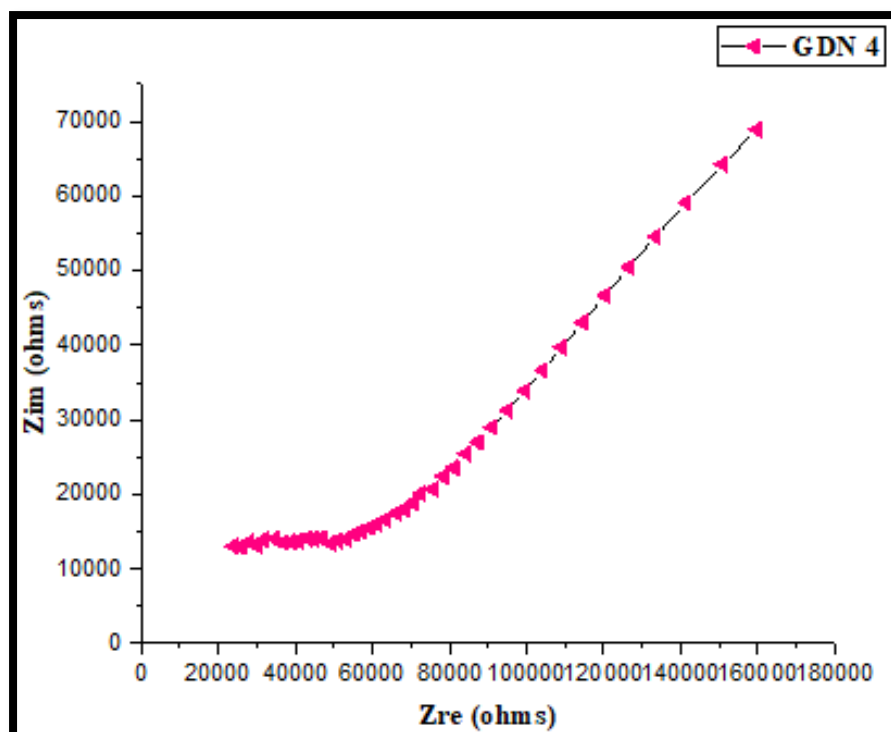


Fig 15c: Nyquist plot of GDN 4

Fig 15: Nyquist plot for GG-NaBr-1,3-DOL

4.5 Transport number measurement

The Chronoamperometric (CA) technique was used to measure the ion transference number which identifies whether the conductivity in the polymer electrolyte is due to the presence of ions or electrons. The ionic transport number was calculated using Wager's polarization formula,

$$t_{\text{ion}} = I_s/I_0 \text{ or } t_{\text{ion}} = (I_0 - I_s)/ I_0$$

where,

t_{ion} is the transference number

I_0 is the initial current and

I_s is the steady state current

The cation (t_+) and anion (t_-) transport numbers have been calculated from initial and final current values from the current vs time plot. The current vs time plot for GG-NaBr-1,3-DOL of 3 different compositions is shown in **Figure 16**. All the electrolytes have maximum cation transport numbers compared to anion transport number which is shown in **Table 14**.

Table 14: Transport number of prepared polymer electrolyte at room temperature

Code	Composition	Transport number (t_{ion})
		t_+
GDN 2	80:15:5	0.59
GDN 3	70:25:5	0.76
GDN 4	60:35:5	0.70

It is observed from **Table 14**, that the prepared electrolytes from various compositions of GG-NaBr-1,3-DOL were found to have higher transport numbers for cations than anions which proves that Na^+ ions are more than e^- in the prepared biopolymer matrix. Moreover, the highest t_+ value of 0.76 exhibited in electrolyte GDN 3 proves the highest ionic conductivity of the GDN 3 polymer electrolyte.

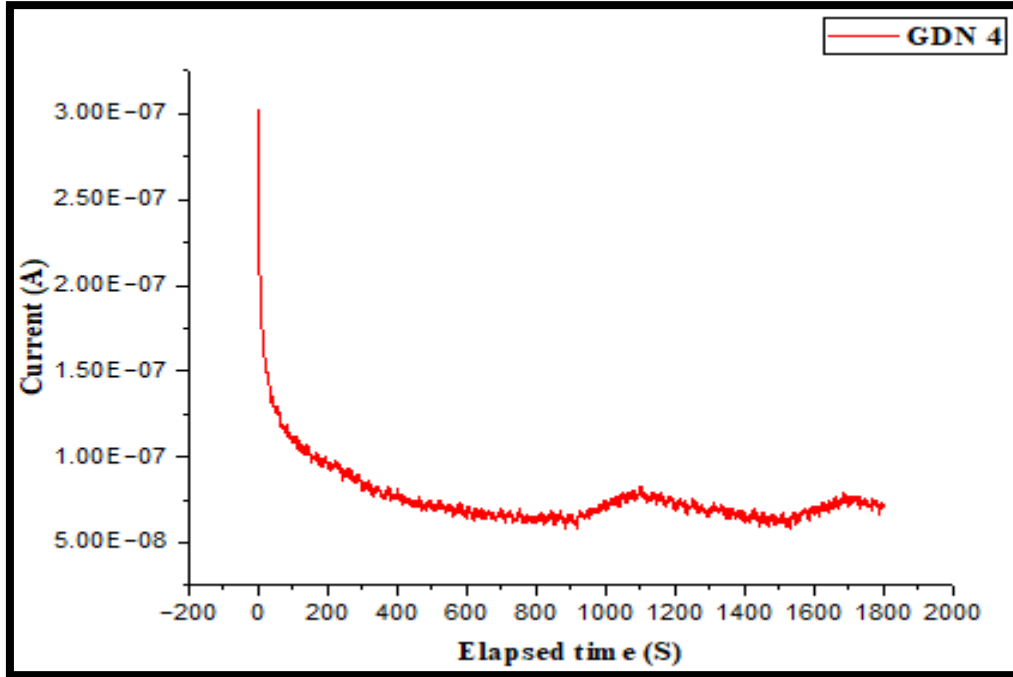
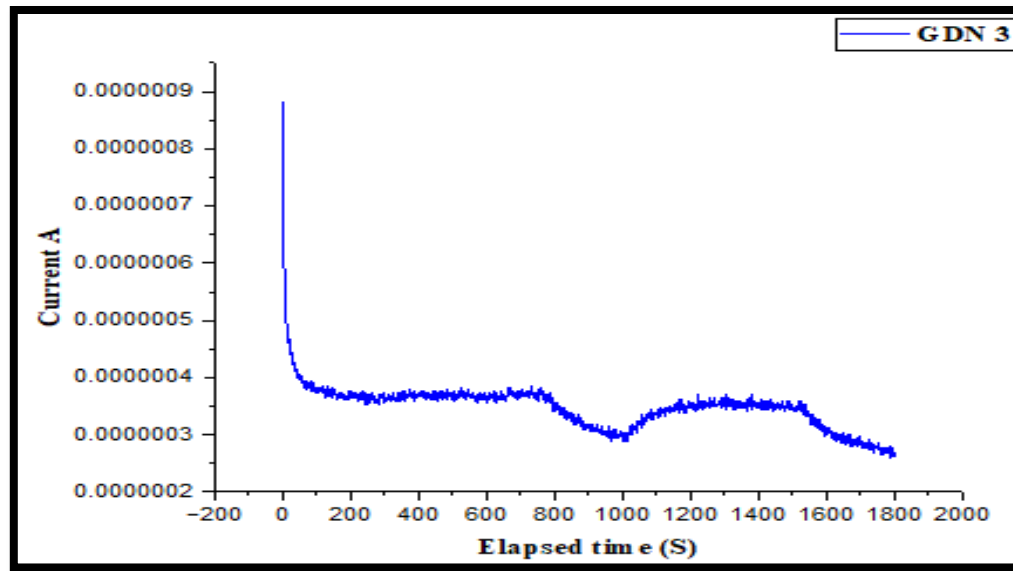
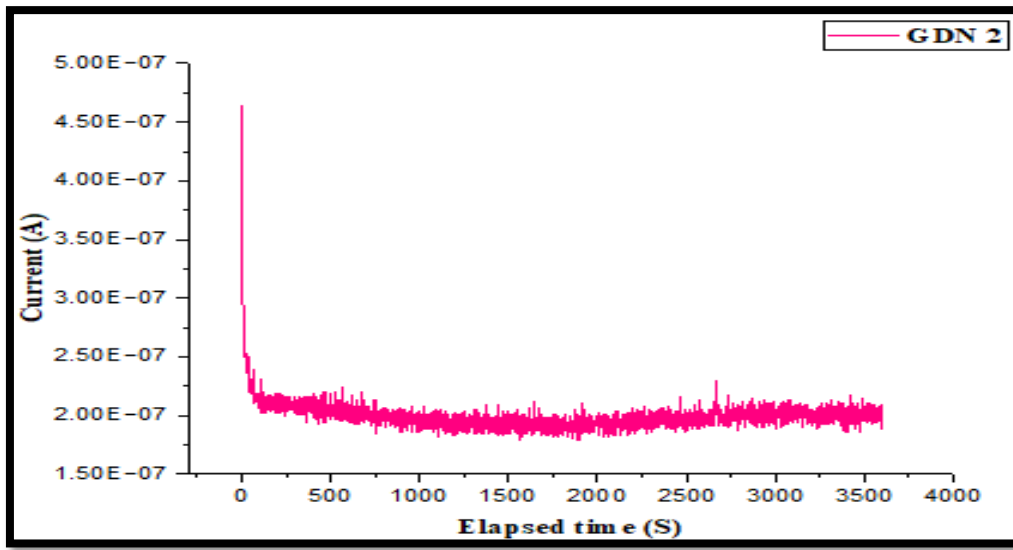


Fig 16: Transport number curve of GDN 2, GDN 3, and GDN 4
70

SUMMARY AND CONCLUSION

CHAPTER V

SUMMARY AND CONCLUSION

This chapter summarizes the major findings of the present study entitled, “**BIO-HOST GUAR GUM COMPLEXED WITH SODIUM BROMIDE BASED SOLID ELECTROLYTES FOR SODIUM-ION BATTERIES**”.

- Out of the four prepared electrolytes, there was no proper complexation with the combination of Pectin and Sodium Nitrite.
- Two out of the remaining three, (Guar gum/Sodium nitrite/1,3-Dioxalane and Guar gum/Sodium nitrite) were characterized using FTIR Spectroscopy. Since there were no proper peaks obtained, further characterizations were not done.
- From the FTIR study, the results show that the complexation has occurred in the prepared polymer electrolyte system of Guar gum/Sodium bromide/1,3-Dioxalane. Hence, further characterizations were carried out for this particular composition.
- The thermal stability of the prepared thin films was carried out by TGA and the results showed that all the polymer films were thermally stable up to 900⁰ C.
- The morphology study of the prepared electrolyte Guar gum/Sodium bromide/1,3-Dioxalane has been carried out by 3D Laser profilometry analysis and the results showed that GDN 2 (80:15:5) and GDN 3 (70:25:5) of Guar gum/Sodium bromide/1,3-Dioxalane were comparatively smoother than GDN 4 (60:35:5).
- From the impedance study, it has been found that the film GDN 3 (70:25:5) exhibits the highest conductivity of $2.26 \times 10^{-7} \text{ S cm}^{-1}$.
- A maximum transport number of 0.76 was obtained by Chronoamperometry technique for the film GDN 3 (70:25:5 of Guar gum/Sodium bromide/1,3-Dioxalane)

CONCLUSION

In this study, the main aim is to prepare biopolymer electrolytes with the highest ionic conductivity. The biopolymer electrolyte based on Guar gum/Sodium Nitrite/1,3-Dioxalane of the composition 70:25:5 M wt% (GDN 3) is found to have the highest conductivity of $2.26 \times 10^{-7} \text{ S cm}^{-1}$ with a transport number of 0.76. Hence, this cost-effective and eco-friendly biopolymer electrolyte may be used with suitable electrodes for sodium-ion batteries.

RECOMMENDATION

1. New electrolyte can be prepared using biopolymers with other sodium salts using the same Guar Gum as a biopolymer and 1,3-Dioxalane as plasticizer.
2. Repeatedly and reproducibility studies can be carried out to ascertain the result so as to find out the applicability of these electrolytes for the fabrication of sodium-ion batteries.

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