

**ECO-FRIENDLY ELECTROLYTE BASED ON PECTIN AND  
SODIUM IODIDE FOR SODIUM-ION BATTERIES**

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**21PCH001**

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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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*Aishwarya*  
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*Incredible things can be done simply if we are committed to making them happen.*

*- Sadhguru*

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

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## ABBREVIATIONS

<b>S. NO</b>	<b>ABBREVIATIONS</b>	<b>EXPANSION</b>
1.	NIB/SIB	Sodium-ion Battery
2.	LIB	Lithium-ion Battery
3.	LSV	Linear Sweep Voltammetry
4.	EIS	Electrochemical Impedance Spectroscopy
5.	SBEs	Solid Biopolymer Electrolytes
6.	FT-IR	Fourier Transform Infrared
7.	TGA	Thermal Gravimetric Analysis
8.	PS	Pectin- Sodium iodide
9.	P-NaI-1,3-DOL	Pectin- Sodium iodide- 1,3-Dioxalane

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# **INTRODUCTION**

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# CHAPTER 1

## INTRODUCTION

### 1.1 INTRODUCTION

Energy storage technologies are essential for increasing the efficiency, safety, and economics of power generation and are an efficient way to advance the green economy. They also provide widespread access to renewable energy sources.

To maximize the energy efficiency of all types of energy systems and make it possible for the usage of renewable energy to rise, energy storage's objective is to assist in the research, development, implementation, and integration of energy storage technologies. An essential part of energy-efficient and sustainable energy systems is storage technology.

In the 21<sup>st</sup> century, Energy Storage Systems have become an essential part of the evolving clean energy systems. Energy storage presents a major business opportunity for India. Ambitious objectives, concentrated efforts, and a collaborative approach may help India meet its emission reduction targets while reducing its reliance on battery packs and cell imports. This may increase India's manufacturing capacity, encourage the creation of jobs, and position the nation as a hub for cutting-edge research and innovation. Achieving these objectives will require the nation's strengths in manufacturing and information technology, as well as its entrepreneurial spirit and expanding private sector. [Akshay Srivastava *et al.* (2019)]

### 1.2 BATTERY

A device that stores chemical energy and releases it as electrical energy is called a *battery*. So, a battery, cell, or storage battery is a device that transforms chemical energy into electrical energy. The first battery was created in 1800 by an Italian physicist named *Alessandro Volta*. As a source of direct electric current at a constant voltage, batteries are electrochemical cells that are frequently coupled in series in electrical devices.

Batteries can be used to store energy when needed. An advanced technological solution that allows energy to be stored in various ways for later use is the battery energy storage system. Battery systems are essential for utilities, organizations, and homes to provide a continuous power flow given the chance that an energy source may encounter changes owing to weather, disruptions, or geopolitical

causes. A battery energy storage system is now an essential component of any energy plan rather than a supplementary or auxiliary one.

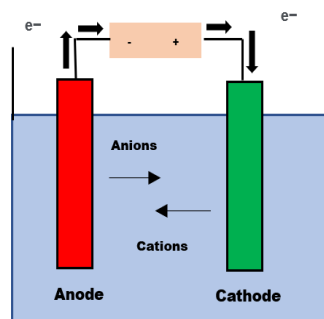
Based on energy density, charge and discharge efficiency, lifespan, and eco-friendliness of the devices, battery technologies for energy storage devices can be differentiated. The quantity of energy that may be stored in a single system per unit volume or per unit weight is known as energy density. Battery efficiency can be accessed using a performance scale called charge and discharge efficiency.

The life span of energy storage devices is a crucial performance component, and it has the most influence on evaluating economic efficiency. Eco-friendliness, or how recyclable and ecologically safe technology is a significant factor.

### 1.3 COMPONENTS OF A BATTERY

In its most basic form, a cell normally consists of three primary parts: two electrodes, an electrolyte, terminals, a separator, and a container. The anode and the cathode are two different kinds of electrodes found in electrodes.

The negative electrode is the anode. It loses electrons to the outside circuit and oxidizes as a result of the electrochemical reaction. On the other side, the cathode is the positive electrode (also called an oxidizing electrode). It absorbs electrons from the external circuit and undergoes reduction during the electrochemical reaction (**Figure 1**). Therefore, an electrochemical oxidation-reduction reaction is responsible for the energy conversion in the battery. The electrolyte is a cell's third crucial component. An electrolyte serves as a conduit for the movement of charge between the two electrodes in the form of ions. As a result, the electrolyte is also known as an ionic conductor.



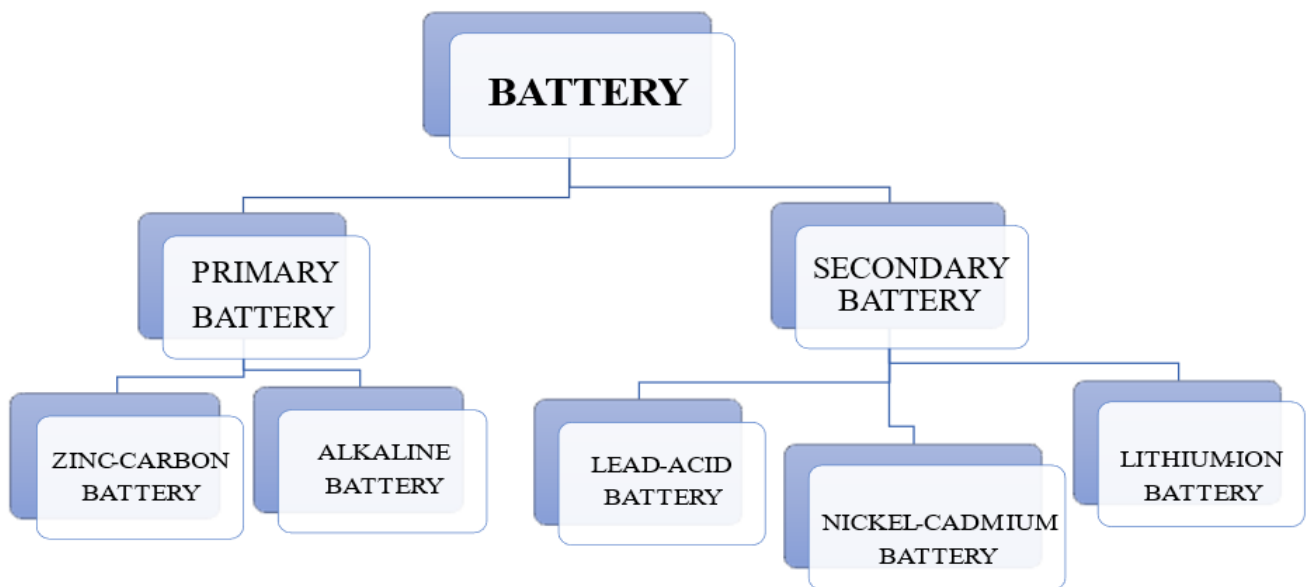
**Figure 1: Pictorial Representation of Battery**

## 1.4 Different Types of Batteries

All electrochemical cells and batteries are classified into two types:

- Primary battery
- Secondary battery

Even though there are several other classifications within two types of batteries, these two are the basic types as shown in **Flowchart 1**. Primary batteries are non-rechargeable batteries i.e., they cannot be recharged electrically while secondary batteries are rechargeable batteries i.e., they can be recharged electrically.



**Flowchart 1: Classification of Battery**

### 1.4.1 Primary Batteries

Due to a chemical reaction, the primary batteries generate electricity. There is just one way in which the reaction can go. It is impossible to stop this phenomenon. The battery eventually runs out of power as a result.

A primary battery cannot be recharged or used again. Primary batteries are often affordable, lightweight, compact, and extremely practical to use with little to no maintenance.

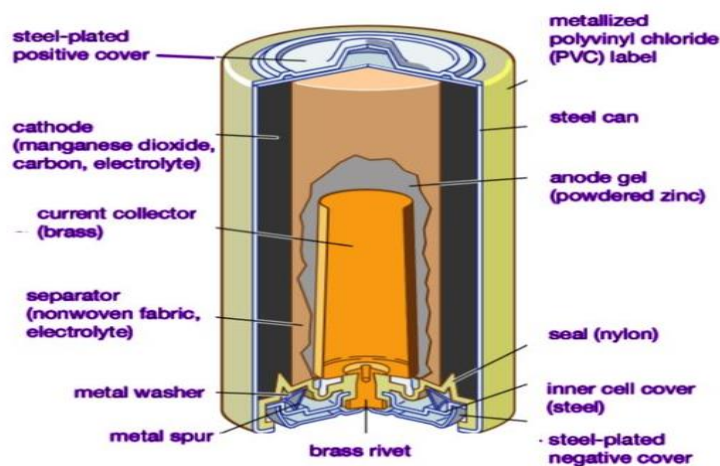
One example of primary batteries is:

### (i) Alkaline Battery

An alkaline battery is a type of primary battery that gets its power from the reaction of zinc metal and manganese dioxide. Additionally, it is a disposable battery (**Image 1**).

The Potassium hydroxide (KOH), an alkaline electrolyte, is what gives the alkaline battery its name rather than the zinc chloride ( $\text{ZnCl}_2$ ) or acidic ammonium chloride ( $\text{NH}_4\text{Cl}$ ) used in zinc-carbon batteries. Other battery designs also use alkaline electrolytes, even though the electrodes' active elements are different.

While giving the same voltage as zinc-carbon batteries in the Leclanché cell or zinc chloride batteries, alkaline batteries offer a higher energy density and a longer lifespan.



**Image 1: Alkaline Battery**

### 1.4.2 Secondary Batteries

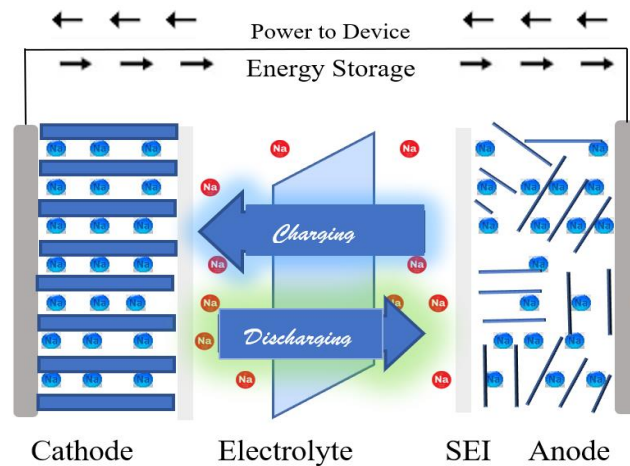
After being used in its pre-discharge condition, the secondary cell or battery is electrically recharged by running a current through the circuit in the opposite direction from the discharge current.

One example of secondary batteries is:

❖ **Sodium-ion Battery**

A type of rechargeable battery known as a sodium-ion battery (NIB/SIB) uses sodium ions (Na<sup>+</sup>) as its charge carriers. It's operation and cell design resemble those of lithium-ion batteries (LIB) types, although sodium is used in place of lithium. Sodium-ion battery development took place in the 1970s and early 1980s. The natural availability of sodium is the main advantage of sodium-ion batteries.

A liquid electrolyte composed of dissociated sodium salts in polar protic or aprotic solvents serves as the electrolyte in SIB cells, which also include an anode (which need not be sodium-based). Sodium ions migrate from the cathode to the anode during charging while electrons move through the external circuit. The process is reversed during discharge (**Figure 2**). [ **Jean-Marie Tarascon *et al.* (2022)**]



**Figure 2: Sodium-ion Battery**

## 1.5 SWITCHED OVER TO GREEN BATTERIES

The word and the colour green have tremendous momentum in the modern era. To prevent significant harm to the ecosystem, both producers and consumers want to discover ways to follow the trend towards creating less waste and environmental damage. One such way is with rechargeable batteries.

Although they are not new, rechargeable batteries have gained popularity in recent years. Since the lead-acid cell was invented in 1959 by French physicist Gaston Plante, rechargeable batteries have existed.

It is desirable to use energy from sustainable and renewable sources because environmental issues brought on by fossil fuels are a growing concern. However, efficient energy storage devices are essential for the most sustainable energy sources, such as solar and wind energy. Rechargeable batteries are one of many alternative technologies that have received a lot of attention due to their adaptability to different scales, low maintenance costs, and superior energy storage capabilities when compared to other energy storage technologies. Lithium-ion batteries (LIBs) with high energy density have seen quick advancements and commercialization in portable electronic gadgets and electric vehicles, making them one of the most promising rechargeable battery systems. However, if LIBs are widely employed in energy storage systems, which are several orders of magnitude larger than electronic gadgets and electric vehicles in scale, lithium may become scarce and expensive due to the limited lithium resources on the earth. As a result, there is an urgent need for the creation of next-generation rechargeable battery systems with high energy density, long cyclic life, and low cost. [Suqing Wang *et.al.*(2015)]

To create more affordable and sustainable energy storage systems based on the availability and abundance of Na, rechargeable battery systems using Na as a guest ion have been intensively studied. Na is the sixth most common element in the crust of the Earth (2.6%), and seawater provides practically limitless Na resources. [Hyungsub Kim *et al*(2016)]

Many people like the concept of rechargeable batteries and reducing waste because it results in a healthier environment. It is simple to exploit the current environmental movement to market productions by having more ecologically friendly goods and productions. The primary objective of manufacturers is to increase sales, and they can do this by appealing to consumers through the environmental movement and the colour green. Rechargeable batteries are meant to be less hazardous to the environment to help reduce waste and consumption. Through effective advertisements that utilize the green aspect and movement in this age, producers have created a compelling way to sell their products with influence already over their consumers. The utilization of colours, words, and timing things can be made to appeal and to compel a person towards the 'green' product.

## 1.6 Biopolymer Electrolyte

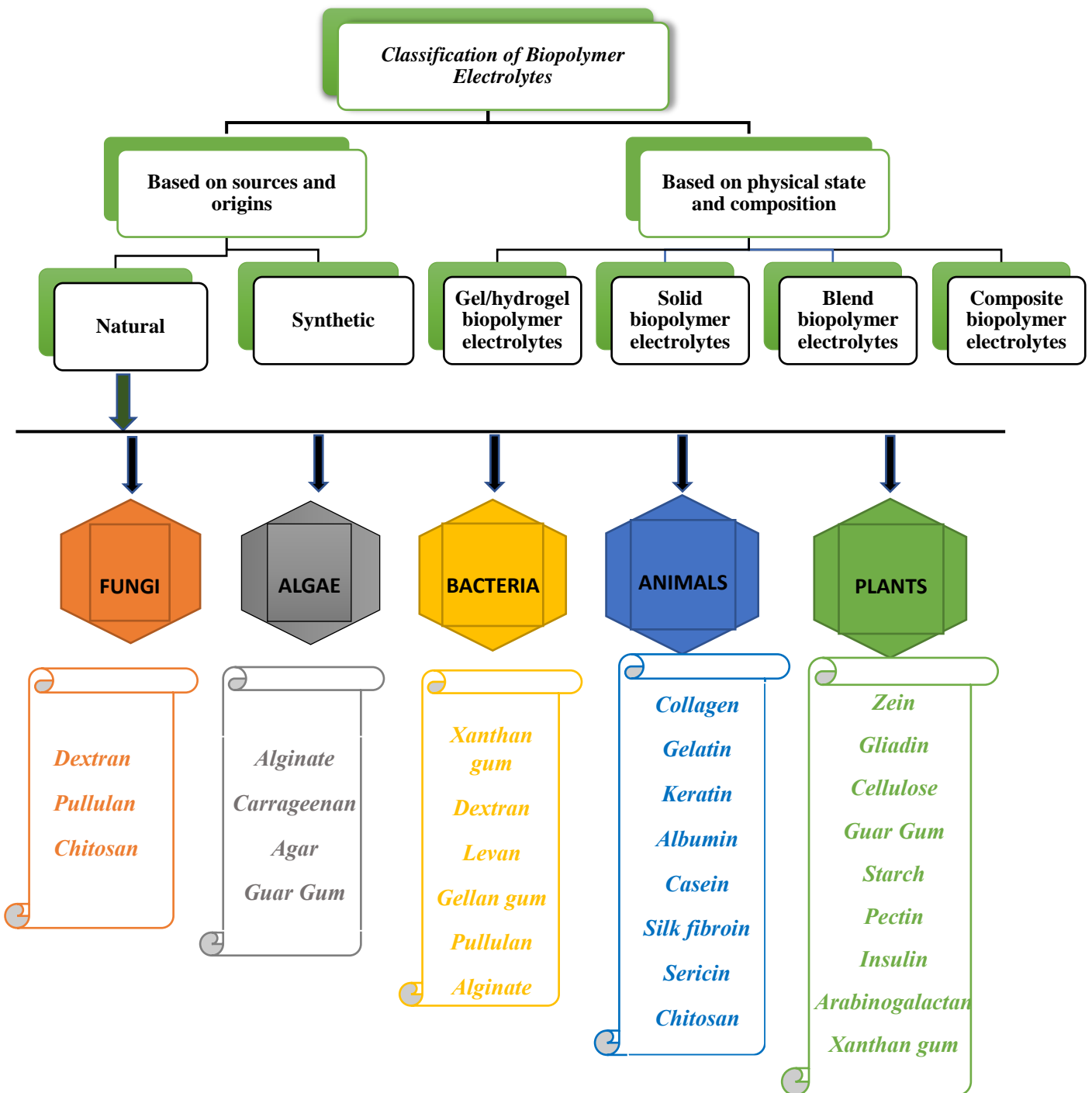
Biopolymers have received more attention in recent years. Prior to now, the three main uses of biopolymers were in the fields of medicine, agriculture, and packaging for consumer goods. One of the fundamental issues facing modern business and society is the storage, production, and distribution of energy. The development of solid-state ionic conductors has potential applications in the fields of microsensors and biomedical devices, as well as novel types of memory and computer architecture.

Modern methods for energy generation and storage have been made possible by the development of novel materials that can be used as solid electrolytes. Among the various poly(ethylene oxide)-based electrolytes, natural polymers like hydroxyethylcellulose, hydroxypropylcellulose, or carboxymethylcellulose (polysaccharides), starch, polyvinyl alcohol, polyethylene glycol, and chitosan, as well as proteins like gelatin, are regarded as polymer electrolytes. These polymers are known as biopolymer electrolytes because they exhibit inorganic dopants, acids, and gelation to increase ionic conductivity while also undergoing biodegradation.

## 1.7 Classification of Biopolymer Electrolyte

Biopolymer electrolytes are classified on the basis of their sources and origin, that is there are two types of biopolymer electrolytes: synthetic and natural. And biopolymer electrolytes can be categorized into four different types based on their physical state and composition. They are gel/hydrogel biopolymer electrolytes, solid biopolymer electrolytes, blend biopolymer electrolytes and composite polymer electrolytes as shown in **Flowchart 2**.

Based on their synthesis and place of origin, biopolymers can be divided into three primary types. The first category includes polymers including starch, cellulose, chitosan, and alginates that are directly derived from biomass. They are the largest and most plentiful source of bio-based polymers. The third group comprises polymers produced by microorganisms or bacteria, while the second category is concerned with polymers produced from bio-derived monomers.



**Flowchart 2: Classification of Biopolymer Electrolytes**

## Some Natural Biopolymer Electrolytes are:

### ❖ Starch

Due to its wide variety, biodegradability, accessibility, and abundance in nature, starch has been the subject of extensive research. The by-product of photosynthesis in plants is starch. It is a naturally occurring polymer made mostly from carbohydrate sources, such as corn, potatoes, wheat, tapioca, and rice [10]. Starch is used in a wide range of diverse industries and is not just restricted to major food products. Other uses for starch include encapsulants, binders, adhesives, and absorbents. Depending on the plant sources, natural starch is a mixture of linear amylose or poly( $\alpha$ -1,4-d-glucopyranose) and  $\alpha$ -1,6-branched amylopectin. The starch-based polymer appears as a promising candidate to be employed as a polymer host for electrolyte applications because these two chemicals contain hydroxyl groups.

### ❖ Cellulose

The most common and important renewable resource on earth is cellulose. It is the fundamental part of plant cell walls that serves as the skeleton and structural support. The linear homopolysaccharide polymer found in cellulose has a high molecular weight and is made up of  $\beta$ -d-glucopyranose units in the  ${}^4C_1$  form connected by (1 $\rightarrow$ 4) glycosidic linkages. Two anhydroglucose units make up the repeating ingredient. Many researchers have described the role of cellulose and its derivatives as hosts in a polymer electrolyte system, and cellulose and its derivatives have by far been researched concerning polymer electrolytes.

### ❖ Chitosan

Chitosan has drawn a lot of interest from the polymer field. It exhibits a variety of interesting characteristics, including being non-toxic, biodegradable, and biocompatible. 1,4 linked-2-deoxy-2-amino glucose, which is produced by the deacetylation process of chitin, makes up chitosan. A natural polymer known as chitin can be found in a variety of fungi and the exoskeleton of arthropods.

It's interesting to note that this polymer is used in polymer electrolyte applications. Many of the polar groups found in chitosan, including the hydroxyl and amino groups, can function as donors and combine with inorganic salts to form complexes. The amorphous polymer chitosan is said to have a glass transition temperature of about 200 °C. These requirements allow chitosan to be used as a

polymer host for salt solvation. Research on chitosan for polymer electrolyte applications began in 1995, making it the first biopolymer to do so.

#### ❖ **Gum**

Gums are substances classified under the category of polysaccharides and are of high commercial importance. They can be found in a variety of plant, animal, marine, and microbial sources. All gums exhibit the ability to thicken water and aqueous systems, though the rheological characteristics of the systems may differ depending on the specific types of gums being used.

#### ❖ **Agar**

Agar is a hydrocolloid substance that is formed naturally by extracting red seaweed. It is made up of a combination of the polysaccharide agarose and agarpectin. Agarose is a linear polymer that accounts for 70% of the combination made up of the agarobiose repeating unit in agar. A disaccharide known as agarobiose is composed of D-galactose and 3,6-anhydro-L-galactopyranose. Although the backbone of both compounds is made of galactose, agarpectin has acidic side groups like sulphate and pyruvate, whereas agarose is neutrally charged. As a potential location for complexation, the agar structure's abundance of oxygen atoms fits the condition of being a polymer host for an electrolyte.

#### ❖ **Carrageenan**

A variety of marine red seaweed called Rhodophyceae is used to make carrageenan, a linear sulphated polysaccharide polymer. It contains 3,6-anhydrogalactose, both sulphated and non-sulphated, and galactose repeating units that are amalgamated by alternating  $\alpha$ -(1,3) and  $\beta$ -(1,4) glycosidic linkages.

#### ❖ **Gelatin**

Collagen, a naturally occurring protein found in skin, cartilage, and bones, is the source of the liquid protein material known as gelatin. Gelatin is primarily obtained from bovine and porcine species, but it can also be obtained from fish and fowl. Numerous elements, including the source, the age of the animal, and the kind of collagen, can affect the qualities of gelatin. It can be used as an emulsifier, foaming agent, biodegradable packaging, and colloid stabiliser, among many other things. Gelatin is a polydisperse protein made up of many chain types with differing molecular weights.

[**Marwah Rayung *et al* (2020)**]

## 1.8 Objectives of the Study

The present study is carried out with the following objectives.

- To prepare solid biopolymer electrolytes using Pectin, Guar gum, Sodium sulphite, Sodium nitrite, Sodium iodide and 1,3-Dioxalane by Solution Casting Technique.
- To characterize the prepared solid biopolymer electrolytes by using Fourier Transform-Infrared Spectroscopy (FTIR), 3-D Laser Profilometry, and Thermogravimetry Analysis.
- To measure the Ionic conductivity through Electrical Impedance Spectroscopy (EIS), and Chronoamperometry.
- To determine the transport number of the prepared polymer electrolytes.

# **Review of literature**

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## **CHAPTER-II**

### **REVIEW OF LITERATURE**

This session explains the previous research work done in the field of solid polymer electrolytes and their related studies. The review of the literature was done to 1. To find the research gap. 2. To get an insight into the biopolymer electrolyte used in batteries. 3. To identify the techniques used for the preparation of the solid electrolyte.

#### **2.1 INTRODUCTION**

A literature survey is an overview of the research project that includes significant findings as well as theoretical and methodological development on a particular work. The present research work is mainly focused on the preparation and characterization of biopolymer electrolytes like pectin, guar gum, alginate, etc., and their application to battery systems. This chapter reviews current methodologies and technological advancements in polymer electrolytes as well as the creation of various techniques for enhancing the performance of polymer electrolytes in battery systems.

#### **2.2 BIOPOLYMERS AS ELECTROLYTES**

Biopolymer electrolytes are currently gaining popularity as alternatives to synthetic polymer electrolytes in electrochemical systems because they are carbon neutral, sustainable, and easily biodegradable. They also reduce reliance on non-renewable fossil fuels. Research is being done on a variety of biopolymers, including chitosan, pectin, agar-agar, guar gum, cellulose acetate, and carrageenan.

This review is based on different biopolymers doped with different salts prepared using different compositions of host and salt by solution casting method are shown in Tables 1 to 4.

**Table 1: Review based on biopolymer Agar Agar, Carrageenan, and Cellulose doped with different salts**

S.NO	TITLE OF THE PAPER	ELECTROLYTE	METHOD	CONCENTRATION (g/wt%)	IONIC CONDUCTIVITY	REFERENCE
1.	Characterization of biodegradable solid polymer electrolyte system based on agar-NH <sub>4</sub> Br and its comparison with NH <sub>4</sub> I	Agar and Ammonium Bromide	Solution Casting Technique	50M.wt% Agar 50M.wt% NH <sub>4</sub> Br	$1.33 \times 10^{-4} \text{ S cm}^{-1}$	Selvalakshmi <i>et al.</i> , Journal of Solid State Electrochemistry (2019) 23:1727–1737
2.	Performance of solid-state Li-ion conducting battery using biopolymer electrolyte based on agar–agar/lithium chloride	Agar–agar (AA) and lithium chloride (LiCl)	Solution Casting Technique	20 mol% Agar Agar 80 mol% LiCl	$3.12 \pm 0.11 \times 10^{-4} \text{ S cm}^{-1}$	S. Aafrin Hazaana <i>et al.</i> , Journal of Solid State Electrochemistry (2022)
3.	Preparation of primary magnesium battery based on kappa carrageenan with magnesium perchlorate and its application to electrochemical devices	Kappa carrageenan and magnesium perchlorate Mg(ClO <sub>4</sub> ) <sub>2</sub>	Solution Casting Technique	Kappa carrageenan (1g) 0.5 Mwt% of Mg(ClO <sub>4</sub> ) <sub>2</sub>	$6.28 \times 10^{-3} \text{ S cm}^{-1}$	P. Sangeetha <i>et al.</i> , Polymer Bulletin (2023)
4.	Proton-Conducting Biopolymer Electrolytes Based on Carboxymethyl Cellulose Doped with Ammonium Formate	Carboxymethylcellulose (CMC) and ammonium formate (AFT)	Solution Casting Technique	50M.wt% Ammonium Formate	$1.47 \times 10^{-4} \text{ S cm}^{-1}$	M. I. H. Sohaimy <i>et al.</i> , Polymers2022, 14, 3019

5.	Structural, thermal and electrochemical characterization of cellulose acetate-based solid biopolymer electrolyte for zinc ion batteries	Cellulose acetate (CA) and zinc nitrate $Zn(NO_3)_2$	Solution Casting Technique	45 M.wt% CA 55 M.wt% $Zn(NO_3)_2$	$2.7 \times 10^{-3} \text{ S cm}^{-1}$	B.Bhuvaneshwari <i>et al.</i> , Ionics (2022) 28:3865–3875
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### 2.2.1 Agar Agar

**S. Selvalakshmi *et al.* (2019)** have studied agar-based proton-conducting polymer electrolytes with  $NH_4Br$  in various ratios by using a solution-casting process with double-distilled water as the solvent. The 50 M.wt%  $NH_4Br$ -doped agar polymer complex had a maximum conductivity of  $1.33 \times 10^{-4} \text{ S cm}^{-1}$  at room temperature, according to the impedance analysis. The linear sweep voltammetry for the 50 M.wt% agar-50 M.wt%  $NH_4Br$  system was found to be 2.5 V.

**S. Aafrin Hazaana *et al.* (2022)** have studied biopolymer electrolytes based on agar-agar (AA) and lithium chloride (LiCl) which have been prepared using solution casting technique, and they are characterized using a variety of characterization techniques. The membrane's high ionic conductivity of  $3.12 \pm 0.11 \times 10^{-4} \text{ S cm}^{-1}$  was produced with a mixture of 20 mol% AA: 80 mol% LiCl.

### 2.2.2 Carrageenan

In the study of **P. Sangeetha *et al.* (2022)**, biodegradable solid polymer electrolyte films were prepared utilizing the solution casting method at room temperature with 1 g of kappa carrageenan (K-C) with various Mwt% ratios of magnesium perchlorate ( $Mg(ClO_4)_2$ ). The highest conductivity of  $6.28 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature was obtained for K-C (1 g):0.5 Mwt% ( $Mg(ClO_4)_2$ ). Linear Sweep Voltammetry is found to be 2.8 V for the required voltage for electrochemical applications in the electrochemical stability.

### 2.2.3 Cellulose

**M.I.H. Sohaimy *et al.* (2022)** have investigated a carboxymethylcellulose-ammonium formate biopolymer electrolyte system using carboxymethylcellulose (CMC) doped with varying amounts (10–50 wt%) of ammonium formate (AFT) to study the effect of AFT on the biopolymer-salt system. With the addition of AFT, they found the ionic conductivity of the CMC-AFT biopolymer electrolytes have increased and reached its greatest value of  $1.47 \times 10^{-4} \text{ S cm}^{-1}$ .

**B. Bhuvaneshwari *et al.* (2022)** have studied a zinc ion conducting biopolymer electrolyte based on cellulose acetate (CA) and various concentrations of zinc nitrate ( $\text{Zn}(\text{NO}_3)_2$ ) using the solution casting technique. Electrochemical impedance spectroscopy (EIS) was used to analyze the polymer electrolytes, and the sample with the composition 45 M.wt% CA:55 M.wt% ( $\text{Zn}(\text{NO}_3)_2$ ) achieved the highest conductivity at  $2.7 \times 10^{-3} \text{ S cm}^{-1}$ . The electrochemical stability of the electrolyte, according to the linear sweep voltammetry (LSV) study, was 3.03 V.

## 2.2.4 Sodium Alginate

**Table 2: Review based on biopolymer Alginate doped with different salts**

S.NO	TITLE OF THE PAPER	ELECTROLYTE	METHOD	CONCENTRATION (g/wt%)	IONIC CONDUCTIVITY	REFERENCE
1.	Investigation of N-S-based graphene quantum dot on sodium alginate with ammonium thiocyanate (NH <sub>4</sub> SCN) biopolymer electrolyte for the application of electrochemical devices	Sodium Alginate (SA) and Ammonium Thiocyanate (NH <sub>4</sub> SCN) salt	Solution Casting Technique	30 Mwt% Sodium Alginate  70 Mwt% NH <sub>4</sub> SCN	8.72 x 10 <sup>-3</sup> S cm <sup>-1</sup>	N. Vanitha <i>et al.</i> , J Mater Sci: Mater Electron (2022) 33:14847–14867
2.	A physicochemical elucidation of sodium perchlorate incorporated alginate biopolymer: toward all-solid-state sodium-ion battery	Sodium Alginate and Sodium Perchlorate (NaClO <sub>4</sub> )	Solution Casting Technique	60 wt.% NaClO <sub>4</sub>  40 wt.% Sodium Alginate	2.29 x 10 <sup>-3</sup> S cm <sup>-1</sup>	M. Infanta Diana <i>et al.</i> , J Mater Sci (2022) 57:8211–8224
3.	Sodium alginate incorporated with magnesium nitrate as a novel solid biopolymer electrolyte for magnesium-ion batterie	Sodium Alginate and Magnesium Nitrate (Mg(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O)	Solution Casting Technique	40 M wt.% Sodium Alginate  60 M wt.% Mg(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	4.58 x 10 <sup>-3</sup> S cm <sup>-1</sup>	R. TAMILISAI <i>et al.</i> , J Mater Sci: Mater Electron (2021) 32:22270–22285

4.	Characterization of Biopolymer Blend-based on Alginate and Poly (vinyl Alcohol) as an Application for Polymer Host in Polymer Electrolyte	Sodium Alginate and Poly (vinyl Alcohol)	Solution Casting Technique	70 M wt.% Sodium Alginate 30 M wt.% Poly (vinyl Alcohol)	$7.52 \times 10^{-8} \text{ S cm}^{-1}$	N M Ghazali <i>et al.</i> , IOP Conf. Series: Materials Science and Engineering 2021
5.	Studies on structural and ionic transport in biopolymer electrolytes based on alginate-LiBr	Sodium Alginate and Lithium Bromide	Solution Casting Technique	85M wt.% Sodium Alginate 15 wt.% LiBr	$7.46 \times 10^{-5} \text{ S cm}^{-1}$	A. F. Fuzlin <i>et al.</i> , Ionics (2020) 26:1923–1938
6.	Conduction Properties Study on Alginate Incorporated with Glycolic Acid-Based Solid Biopolymer Electrolytes	Sodium Alginate and Glycolic Acid	Solution Casting Technique	80M wt.% Sodium Alginate 20 wt. % of Glycolic Acid	$5.32 \times 10^{-5} \text{ S cm}^{-1}$	P. Perumal <i>et al.</i> , Ionics (2018) 24:3259–3270
7.	Investigations on Na-ion conducting electrolyte based on sodium alginate biopolymer for all-solid-state sodium-ion batteries	Sodium Alginate and Sodium Thiocyanate (NaSCN)	Solution Casting Technique	NaSCN salt (70 wt%)	$1.22 \times 10^{-5} \text{ S cm}^{-1}$	M. Infanta Diana <i>et al.</i> , Journal of Solid State Electrochemistry (2021) 25:2009–2020

8.	Effect of graphene quantum dot on sodium alginate with ammonium formate (NH <sub>4</sub> HCO <sub>2</sub> ) biopolymer electrolytes for the application of electrochemical devices	Sodium Alginate and Ammonium Formate (NH <sub>4</sub> HCO <sub>2</sub> )	Solution Casting Technique	30 M.wt% SA 70 M.wt% NH <sub>4</sub> HCO <sub>2</sub>	2.77 x 10 <sup>-3</sup> S cm <sup>-1</sup>	N. Vanitha <i>et al.</i> , 2022 Ionics (2022) 28:2731–2749
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The review below tells us about preparing solid biopolymer electrolyte Alginate as a host with different salts.

**N. Vanitha *et al.* (2022)** have used the solution casting technique to prepare a proton-conducting polymer electrolyte using the biopolymer sodium alginate (SA) and ammonium thiocyanate (NH<sub>4</sub>SCN) salt. The composition of 30 M.wt% SA: 70 M.wt% NH<sub>4</sub>SCN has the highest proton conductivity of 8.72 x 10<sup>-3</sup> S cm<sup>-1</sup>.

In **2022**, the water-soluble biopolymers sodium alginate and sodium perchlorate (NaClO<sub>4</sub>) were used to develop and analyse ion-conducting solid electrolyte membranes by **M. Infanta Diana *et al.*** Within the compositions, 100:0, 80:20, 60:40, 40:60, and 20:80 wt% of sodium alginate and NaClO<sub>4</sub>, 60 wt% NaClO<sub>4</sub>: 40 wt% SA exhibited maximum ion conductivity of 2.291 x 10<sup>-3</sup> S cm<sup>-1</sup> at room temperature. The electrochemical stability of the electrolyte membrane was found to be 3.4 V

The natural solid biopolymer electrolytes that consist of sodium alginate as the host biopolymer and magnesium nitrate (Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O) was investigated by **R. Tamilsai *et al.* (2021)**. The optimum ionic conductivity value was found by the AC impedance spectroscopy of the solid biopolymer electrolyte composition of 40 M wt% NaAlg:60 M wt% Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O was 4.58 x 10<sup>-3</sup> S cm<sup>-1</sup>. The highest magnesium ion-conducting membrane was studied using linear sweep voltammetry which exhibited the electrochemical stability of 3.5 V.

An electrolyte of a combination, polyvinyl alcohol (PVA) and alginate with different compositions was prepared using the solution casting technique. **N M Ghazali *et al.* (2020)** have

observed  $7.52 \times 10^{-8}$  S/cm to be the highest conductivity value of the Alginate-PVA polymer blend with a ratio of 70:30 Alginate: PVA.

The development of solid biopolymer electrolytes (SBEs) system based on alginate doped with LiBr was studied by **A.F. Fuzlin *et al.* (2020)** using the solution casting method. At ambient temperature, the alginate doped with 15 wt% LiBr had a maximum ionic conductivity of  $7.46 \times 10^{-5}$  S  $\text{cm}^{-1}$ , indicating both good conducting stability and an amorphous phase. Based on the LSV study, they have implied that the current SBEs have the potential to be applied to electrochemical devices.

The work of **Ahmad Faizrin Ahmad Fuzlin *et al.* (2020)** is based on the investigation of the conduction properties of solid biopolymer electrolytes (SBEs) which were made of alginate doped with various glycolic acid compositions. They have revealed that the sample containing 20% GA had an optimum ionic conductivity of  $5.32 \times 10^{-5}$  S  $\text{cm}^{-1}$ , at room temperature (303 K).

**M. Infanta Diana *et al.* (2021)** have analyzed the solid biopolymer electrolyte membranes based on sodium alginate. The sodium alginate biopolymer was prepared at various concentrations of sodium thiocyanate (NaSCN) using the solution casting technique. Large amounts of NaSCN salt were accommodated by the biopolymer host material (30 wt%), which had an ionic conductivity of  $1.22 \times 10^{-2}$  S  $\text{cm}^{-1}$ . The linear sweep voltammetry (LSV) of the biopolymer electrolyte was found to be 2.7 V.

A proton-conducting solid biopolymer electrolyte membrane made of sodium alginate (SA) combined with ammonium formate ( $\text{NH}_4\text{HCO}_2$ ) has been developed through solution casting technique by **N. Vanitha *et al.* (2022)**. The membrane with the composition of 30 M wt%SA:70 M wt%  $\text{NH}_4\text{HCO}_2$  has shown the highest ionic conductivity of  $2.77 \times 10^{-3}$  S  $\text{cm}^{-1}$ . The biopolymer electrolyte membrane's electrochemical stability was found to be 1.90 V using the LSV technique

## 2.2.5 Pectin

**Table 3: Review of biopolymer Pectin doped with different salts**

S.NO	TITLE OF THE PAPER	ELECTROLYTE	METHOD	CONCENTRATION (g/wt%)	IONIC CONDUCTIVITY	REFERENCE
1.	Conducting biopolymer electrolyte based on pectin with magnesium chloride salt for magnesium battery application	Pectin and Magnesium Chloride	Solution Casting Technique	30 M wt% Pectin 70 M wt% MgCl <sub>2</sub>	$1.14 \times 10^{-3} \text{ S cm}^{-1}$	S. Kiruthika <i>et al.</i> , Polymer Bulletin (2020) 77:6299–6317
2.	Proton-conducting biopolymer electrolytes based on pectin doped with NH <sub>4</sub> X (X=Cl, Br)	Pectin and Ammonium Bromide	Solution Casting Technique	40 mol% NH <sub>4</sub> Br	$1.07 \times 10^{-3} \text{ S cm}^{-1}$	N. Vijaya <i>et al.</i> , Ionics (2017) 23:2799–2808
3.	Characterization of biopolymer pectin with lithium chloride and its applications to electrochemical devices	Pectin and Lithium Chloride	Solution Casting Technique	50 mol% LiCl	$2.08 \times 10^{-3} \text{ S cm}^{-1}$	P. Perumal <i>et al.</i> , Ionics (2018) 24:3259–3270
4.	Preparation and Characterization of Biopolymer Electrolytes Based on Pectin and NaNO <sub>3</sub> for Battery Applications	Pectin and NaNO <sub>3</sub>	Solution Casting Technique	9% NaNO <sub>3</sub>	$4.2 \times 10^{-6} \text{ Scm}^{-1}$	M. Vahini <i>et al.</i> , Polymer Science, Series A, 2019, Vol. 61, No. 6, pp. 823–831

The review below tells us about preparing the solid biopolymer electrolyte Pectin as a host with different salts.

The biopolymer electrolytes were prepared from different compositions of pectin with different concentrations of MgCl<sub>2</sub> salt using a solution casting technique by **S. Kiruthika *et al.* (2019)**. The highest ionic conductivity for 30 M wt% pectin: 70 M wt% MgCl<sub>2</sub> was found to be  $1.14 \times 10^{-3} \text{ S cm}^{-1}$  and the electrochemical stability was investigated to be 2.05 V for the highest conducting sample.

**N. Vijaya *et al.* (2017)** focussed on the proton-conducting polymer electrolytes based on the biopolymer pectin doped with ammonium chloride and ammonium bromide which was prepared by solution casting method at room temperature. Pure pectin membrane has shown an ionic conductivity of  $9.41 \times 10^{-7} \text{ S cm}^{-1}$ , which was increased to  $4.52 \times 10^{-4} \text{ S cm}^{-1}$  and  $1.07 \times 10^{-3} \text{ S cm}^{-1}$  for the polymer systems with 30 mol% NH<sub>4</sub>Cl-doped pectin and 40 mol% NH<sub>4</sub>Br-doped pectin respectively.

Natural anionic polysaccharide pectin-based flexible electrolytes with different compositions of lithium chloride have been prepared by **P. Perumal *et al.* (2018)** using solution casting technique. The pectin-lithium chloride with 50 M.wt%: 50 M.wt% complex exhibited the highest ionic conductivity in the order of  $2.08 \times 10^{-3} \text{ S cm}^{-1}$ . They have also constructed the primary lithium-ion battery with an open-circuit voltage of 1.93 V.

**M. Vahini *et al.*** have been prepared pectin-based biopolymer electrolytes by solution casting technique with various sodium nitrate concentrations. The ionic conductivity of  $2.7 \times 10^{-9} \text{ S cm}^{-1}$  of pure pectin was enhanced to  $4.2 \times 10^{-6} \text{ S cm}^{-1}$  by adding 9% NaNO<sub>3</sub> salt. They have attained high ionic conductivity, minimal relaxation time, and the highest cationic transference number for 9% NaNO<sub>3</sub> doped biopolymer electrolyte.

**M. Muthukrishnan *et al.* (2018)** made an effort to synthesize a polymer electrolyte based on the biopolymer pectin and ammonium thiocyanate (NH<sub>4</sub>SCN) salt using the solution casting method. The highest conductivity was found to be  $1.5 \times 10^{-3} \text{ S cm}^{-1}$  for the sample with 40 mol% pectin and 60 mol% NH<sub>4</sub>SCN. The highest conducting sample's electrochemical stability was also investigated by using linear sweep voltammetry (LSV) which was found to be 3.69 V.

An eco-friendly biopolymer electrolyte pectin with magnesium nitrate salt Mg(NO<sub>3</sub>)<sub>2</sub> was studied by **S. Kiruthika *et al.* (2019)** using the solution casting method. The biopolymer electrolyte 50 Mwt% pectin:50 Mwt% Mg(NO<sub>3</sub>)<sub>2</sub> has the highest ionic conductivity of  $2.65 \times 10^{-4} \text{ S cm}^{-1}$ . The

electrochemical stability of the biopolymer electrolytes has been determined to be 3.8 V using LSV. They have also fabricated magnesium ion batteries with this biopolymer electrolyte and investigated the battery performance.

Biopolymer electrolytes based on pectin doped with different salts such as LiClO<sub>4</sub>, KCl, LiClO<sub>4</sub>-Ir(III), and KCl-Ir(III), have been prepared and characterized by **R. Leones *et al.* (2014)**. The ionic conductivity of the Pectin and KCl samples have the highest conductivity of 1.45 x 10<sup>-3</sup> S cm<sup>-1</sup> at 25 °C and 6.31 x 10<sup>-3</sup> S cm<sup>-1</sup> at 90 °C, respectively. This material has an appropriate stability window for application in solid-state electrochemical devices, based on its overall redox stability of 7.0 V.

**Abdullahi Abbas Adam *et al.*** have prepared the methylcellulose/pectin/potassium phosphate (MC/PC/K<sub>3</sub>PO<sub>4</sub>) based SBEs that have been plasticized with glycerol for electrochemical devices. The sample with 50% K<sub>3</sub>PO<sub>4</sub> and 50% glycerol exhibited the maximum ionic conductivity of around 7.5 x 10<sup>-4</sup> Scm<sup>-1</sup> at room temperature and a broad potential window of 3.99V.

**Abdullahi Abbas Adam *et al.* (2022)** have prepared polymer electrolytes using methylcellulose/pectin/potassium phosphate electrolyte, and ethylene carbonate (EC) by the solution casting method. The electrolyte with 25 wt% of EC has gained the highest ionic conductivity (5.9 x 10<sup>-4</sup> Scm<sup>-1</sup>) at ambient temperature with a t<sub>ion</sub> of 0.95 and a high stability window of 4.24 V.

The biopolymer pectin was combined with Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and was prepared by **P Perumal *et al.* (2019)** using solution casting technique. A maximum ionic conductivity of 1.69 x 10<sup>-5</sup> Scm<sup>-1</sup> was attained for the mixture of 60 (M.wt%) pectin and 40 (M.wt%) Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> due to the highly disordered atomic configurations caused by the addition of Dilithium borate salts in the pectin polymer.

**S. Kiruthika *et al.* (2019)** have investigated pectin with magnesium chloride salt in magnesium batteries using solution casting technique. They have generated the polymer electrolyte with a 30 M wt% pectin: 70 M wt% MgCl<sub>2</sub> ratio had the highest ionic conductivity 1.14 x 10<sup>-3</sup> Scm<sup>-1</sup> for all the polymer electrolytes. The highest conducting sample have an electrochemical stability of 2.05 V.

**R. Manjuladevi *et al.* (2018)** have prepared using the solution casting technique based on pectin doped with various compositions of lithium nitrate and exhibited the highest ionic conductivity of 3.97 x10<sup>-3</sup> Scm<sup>-1</sup> for 30 wt% pectin: 70 wt% LiNO<sub>3</sub>.

## 2.2.6 Guar gum

**Table 4: Review based on biopolymer Guar Gum doped with different salts**

S.NO	TITLE OF THE PAPER	ELECTROLYTE	METHOD	CONCENTRATION (g/wt%)	IONIC CONDUCTIVITY	REFERENCE
1.	Polymer electrolyte based on guar gum and ammonium thiocyanate for proton battery application	Guar Gum and Ammonium Thiocyanate	Solution Casting Technique	1.2 g of GG 0.6 g Ammonium Thiocyanate	$4.91 \times 10^{-3} \text{ Scm}^{-1}$	K. Venkatesh <i>et al.</i> , Polymer Bulletin (2022)
2.	Preparation and characterization of Guar gum-based solid biopolymer electrolyte doped with lithium bis(trifluoromethane sulphonyl)imide (LiTFSI) plasticized with glycerol	Guar Gum and lithium bis(trifluoromethane sulphonyl)imide (LiTFSI)	Solution Casting Technique	60 wt% GG 40wt% LiTFSI.	$2.04 \times 10^{-3} \text{ Scm}^{-1}$	M Abirami <i>et al.</i> , Bull. Mater. Sci. (2020) 43:254
3.	The Structural and Electrical properties of Guar Gum based Green Electrolyte	Guar gum and Zinc Sulphate heptahydrate salt ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ )	Solution Casting Technique	80 wt% GG 40wt% ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ )	$2.5 \times 10^{-5} \text{ Scm}^{-1}$	B. Srinivas <i>et al.</i> , Research Square (2023)

The review below tells us about preparing the solid biopolymer electrolyte Guar Gum as a host with different salts.

**K. Venkatesh *et al.* (2022)** have studied a proton conducting electrolyte based on guar gum and ammonium thiocyanate have been synthesized by the solution casting method with distilled water as the solvent at room temperature. The film, comprising 1.2 g of guar gum and 0.6 g of ammonium thiocyanate, have an ionic conductivity of  $4.91 \times 10^{-3} \text{ S cm}^{-1}$ . From LSV studies the electrochemical stability of the polymer electrolyte was found to be 2 V.

The guar gum (GG) - lithium bis(trifluoromethane sulphonyl)imide (LiTFSI)- glycerol-based solid biopolymer have been investigated by **M. Abirami *et al.* (2020)**. The highest optimum ionic conductivity for the film containing 60 wt% GG-40 wt% LiTFSI was found to be  $2.041 \times 10^{-3} \text{ S cm}^{-1}$ .

**B. Srinivas *et al.* (2023)** have prepared solid-state composite Green-polymer electrolytes based on Guar gum, Zinc Sulphate heptahydrate salt ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) using the solution casting method. Bulk resistance has been used at room temperature and various temperatures to calculate ionic conductivity. They have obtained the highest ionic conductivity for a pure guar gum sample was  $2.5 \times 10^{-5} \text{ S cm}^{-1}$  at  $100^\circ\text{C}$ .

**MATERIALS AND**

**METHODS**

## CHAPTER 3

### MATERIALS AND METHODS

This chapter deals with the materials used and methodologies adopted to prepare and characterized Solid Biopolymer Electrolytes [SBE].

#### 3.1 Materials

The materials used for preparing biopolymer electrolytes are listed below

- Guar Gum
- Pectin
- 1,3-Dioxalane
- Sodium Sulphite
- Sodium Nitrite
- Sodium iodide

#### 3.2 Pectin

Pectin is an important polysaccharide that originates from plants (**Image 2**). It mainly comprises d-galacturonic acid units joined in chains by  $\alpha$ , d-(1-4) glycosidic linkages, wherein several carboxyl or hydroxyl groups are dispersed along the backbone while a small percentage of neutral sugars may be present as side chains.



**Image 2: Pectin**

### 3.2.1 Properties of Pectin

Host Polymer:	Pectin
Source:	Apples and Citrus fruit
Chemical name:	Poly-D-Galacturonic acid
Molecular Formula:	$C_6H_{10}O_7$
Molecular Weight:	194.1394 g/mol
Appearance:	Fine powder
Colour:	Yellowish White



**Image 3: Pectin powder**

### 3.3 Guar Gum

Gums are prime examples of environmentally benign, green biopolymers, and these natural polysaccharides and their derivatives have been exploited to create a wide range of materials for various uses. Guar Gum is one of the cheapest sources of galactomannan, obtain from the endosperm of *Cyamopsis tetragonolobus* or *Cyamopsis psoraloides*, which belongs to the family Leguminosae (**Image 4**). Guar Gum is also known as Glucotard, Guaran, Cluster bean, Cyamopsis, Cuarina and Calcutta lucern. It is a high molecular weight polysaccharide with a white to yellowish-white appearance and is odourless which is acquired from the guar plant. The guar plant is about 0.6m with pods of 5-12.5cm in length. Guar Gum consists of high molecular weight polysaccharides of galactomannans which are linear chains of (1-4)-linked  $\beta$ -D-mannopyranosyl units with (1-6)-linked  $\alpha$ -D-galactopyranosyl residue as a side chain.



**Image 4: Guar gum**

### 3.3.1 Properties of Guar Gum

Host Polymer:	Guar gum
Source:	Guar gum plant, <i>Cyamopsis tetragonolobus</i>
Chemical name:	<i>Cyamopsis tetragonoloba</i>
Molecular Formula:	$C_{18}H_{32}O_{16}$
Appearance:	Coarse Powder
Colour:	Dirty White



**Image 5: Guar gum powder**

### 3.4 Properties of Sodium Sulphite

Ionic Salt:	Sodium Sulphite
Chemical Formula:	$Na_2SO_3$
Molecular Weight:	126.043 g/mol
Appearance:	Fine powder
Molecular Weight:	535.1452 g/mol
Colour:	White



**Image 6: sodium sulphite salt**

### 3.5 Properties of Sodium Nitrite

Ionic Salt:	Sodium Nitrite
Chemical Formula:	$NaNO_2$
Molecular Weight:	68.9953 g/mol
Appearance:	Crystalline solid
Colour:	Off White



**Image 7: Sodium nitrite salt**

### 3.6 Properties of Sodium iodide

Ionic Salt:	Sodium iodide
Chemical Formula:	NaI
Molecular Weight:	149.89 g/mol
Appearance:	Fine powder
Colour:	White



**Image 8: Sodium iodide salt**

### 3.7 Properties of 1,3-Dioxalane

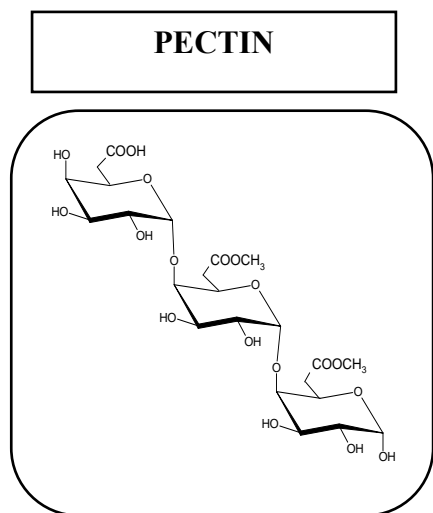
Plasticizer:	1,3-Dioxalane
Molecular Formula:	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>
Molecular Weight:	74.08 g/mol
Appearance:	Clear liquid
Colour:	Colourless



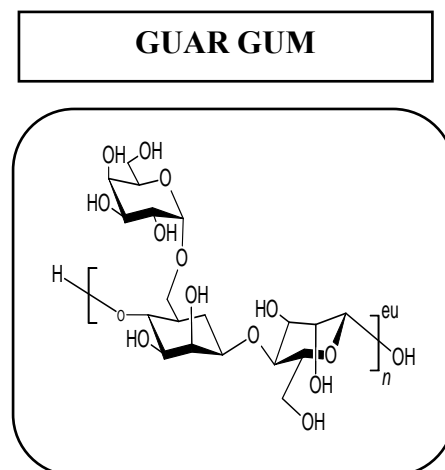
**Image 9: 1,3-Dioxalane**

### 3.8 Structures

Structures of Pectin (**Structure 1**), Guar gum (**Structure 2**), Sodium sulphite (**Structure 3**), Sodium nitrite (**Structure 4**), Sodium iodide (**Structure 5**), and 1,3-Dioxalane (**Structure 6**) are represented below.

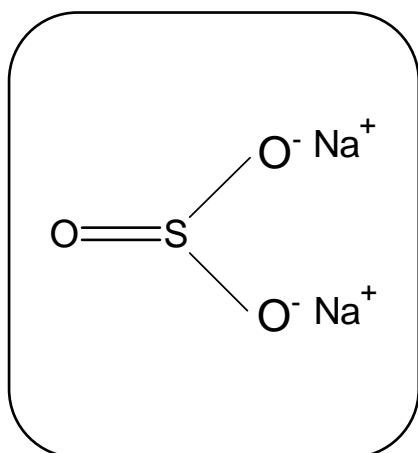


**Structure 1**



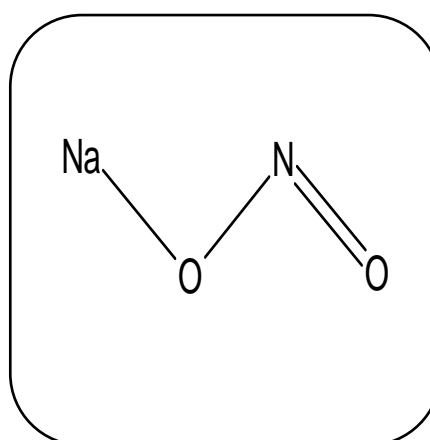
**Structure 2**

**SODIUM SULPHITE**



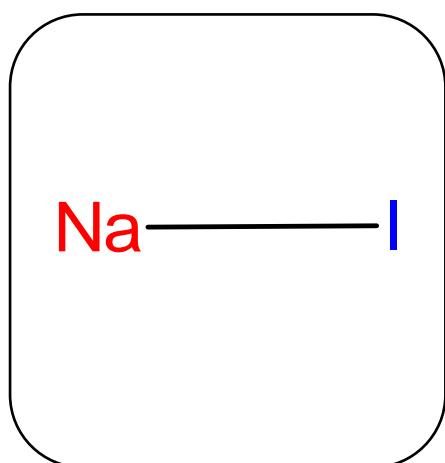
**Structure 3**

**SODIUM NITRITE**



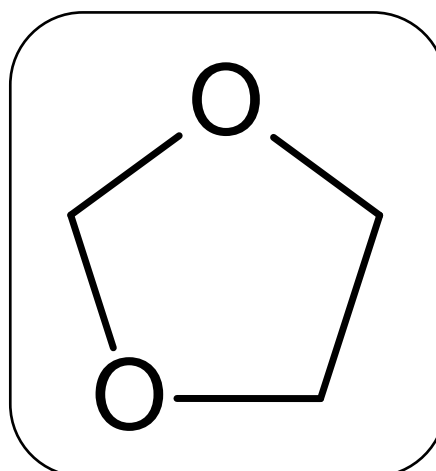
**Structure 4**

**SODIUM IODIDE**



**Structure 5**

**1,3-DIOXALANE**



**Structure 6**

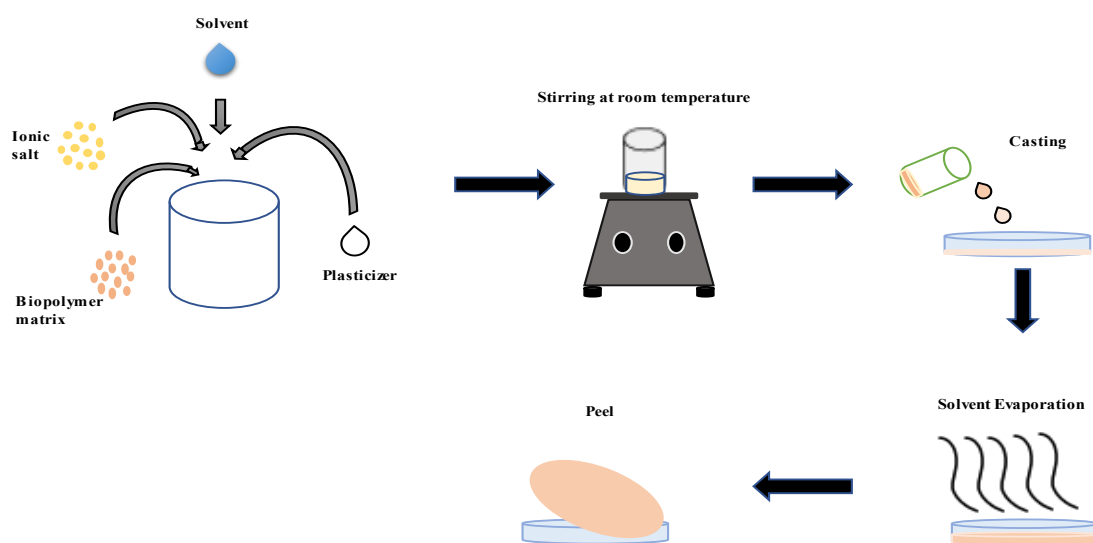
### **3.9 Method**

#### **Solution Casting Technique**

Polymer solution casting is a technique that can replace film extrusion to deliver high-quality films with superior optical, mechanical and physical film properties.

The biopolymer pectin has been blended with 40ml distilled water till it dissolves in a magnetic stirrer, then sodium iodide salt and 1,3-dioxolane as a plasticizer are added and kept in stirring for 24 hours to obtain a homogeneous mixture. The mixture was poured onto the Petri dishes

and kept in an air oven for 24 hours at 40°C and stored in a desiccator for avoiding moisture content for further characterization. (Figure 3)



**Figure 3: Solution Casting Technique**

### 3.10 Preparation of Polymer Electrolyte

A similar procedure was adopted to prepare other biopolymer electrolytes by using the following compositions (Table 5)

**Table 5: Composition of Biopolymer, salt, and 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	Pectin	Sodium Sulphite	1,3-Dioxalane	Pectin- Sodium Sulphite- 1,3-Dioxalane	70:25:5 60:35:5 50:45:5 40:55:5
2	Pectin	Sodium Sulphite		Pectin- Sodium Sulphite	70:30 60:40
3	Pectin	Sodium Nitrite	1,3-Dioxalane	Pectin- Sodium Nitrite- 1,3-Dioxalane	70:25:5 60:35:5
4	Pectin	Sodium Nitrite		Pectin- Sodium Nitrite	70:30 60:40
5	Guar Gum	Sodium Sulphite	1,3-Dioxalane	Guar Gum- Sodium Nitrite- 1,3-Dioxalane	70:25:5 60:35:5

6	Guar Gum (0.6g)	Sodium Sulphite	1,3-Dioxalane	Guar Gum- Sodium Sulphite- 1,3-Dioxalane	Salt 1 wt% 0.75 wt% 0.50 wt% 0.25 wt% 0.10 wt% 0.05 wt%
7	Guar Gum	Sodium Nitrite	1,3-Dioxalane	Guar Gum- Sodium Nitrite- 1,3-Dioxalane	70:25:5 60:35:5
8.	Pectin	Sodium iodide	1,3-Dioxalane	Pectin- Sodium iodide- 1,3-Dioxalane	50:45:5 55:40:5 60:35:5

### 3.11 Characterization

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

#### 3.11.1 Fourier Transform Infrared (FTIR)

FTIR spectroscopy is a technique used for characterizing organic molecules as it is sensitive to functional groups such as hydroxyls, carboxyls, esters and amides that are present in these molecules.

The basic principle of FTIR is that it is an analytical technique that is used to identify polymeric, organic and inorganic substances. Infrared light is used in this technique to scan test materials and examine their physical and chemical characteristics (**Image 10**).

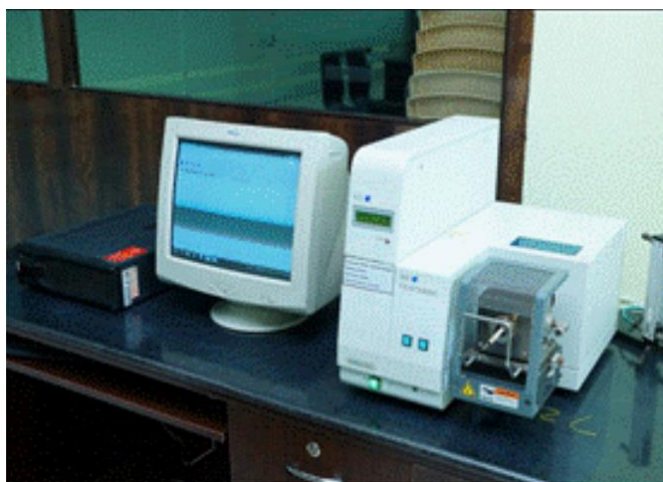
FTIR is the preferred method of infrared spectroscopy. When IR radiation passes through the sample at 10,000 to 100cm<sup>-1</sup>, in which some radiation is absorbed by the sample and some radiation gets transmitted. The spectrum of absorbed light represents a ‘fingerprint’ of the molecular structure of the sample in which the wave number is from 4000 to 400cm<sup>-1</sup>.



**Image 10: FTIR Spectrometer (Miracle 10 SHIMADZU)**

### 3.11.2 Thermal Gravimetric Analysis (TGA)

The temperature at which oxidation, reduction, or degradation takes place is measured by the Thermal Gravimetric/ Differential Thermal Analysis. In a single experiment, thermal analysis, also known as TGA, can characterize a sample while its weight is recorded on an analytical balance that is kept outside the oven. If a heat event results in the loss of a volatile component, there is a mass loss in the TGA (**Image 11**). A technique where the sample temperature is programmed into a given atmosphere and the temperature differential between the sample and a reference material is monitored against time or temperature. Knowing the drying and ignition temperatures of materials, as well as the temperatures at which compounds are most stable, are all possible with the use of the TGA data. To calculate the temperatures of transitions, reactions, and melting points of substances, the TGA data is employed.



**Image 11: TG/DTA 6300 Model instrument (EXSTAR)**

### 3.11.3 3-D Optical Profilometer

3-D Optical Profilometer is a measuring device used to measure the profile of a surface to quantify its roughness. It works on the principle of non-contact mode where the light source is used to analyze the surface of the material hence true imaging is possible where area measurements can be determined. This technique can be used to extract topographical data from a surface. This can be a single point, a line scan or even a full three-dimensional scan (**Image 12**). The main objective is to get the morphology of the surface, pitch heights and roughness of the surface.



**Image 12: 3-D Optical Profilometer (Zeta-20)**

### **3.11.4 Impedance studies**

Impedance spectroscopy is a high-performance measurement method, which is often used in many fields of science and technology. It refers to the measurement of complex impedance over a frequency range and provides opportunities for the separation of relaxation effects, accurate measurements and non-accessible quantity measurements. In physical science, impedance spectroscopy makes it possible to characterize complex conductivity.

Impedance spectroscopy is a powerful device for analysing the electric properties of solid electrolytic material and their interfaces (**Image 13**). Ion conductivity is dependent on their mobility and the conductive species. This method is used to determine the conductivity mechanism, observing the participation of the polymer chain and supporting generation processes. The solid polymer film mixture remained between the two aluminium electrodes. The values for real and imagined impedance have been taken. A plot of real impedance on the X-axis versus negative imaginary impedance on the Y-axis was drawn. The graph shows two well-defined regions, a semicircle in the high-frequency range and an inclined peak in the low-frequency region. From the complex impedance graph, the bulk strength ( $R_b$ ) can be calculated from the point of intersection of the semicircle and the inclined spike.

Knowing the total resistance, the conductivity of the sample can be determined using the relationship.

$$\rho = L/R_bA$$

Where A and L are the respective surface and thickness of the film.

$\rho$  → Impedance

$R_b$  → Bulk resistance



**Image 13: Ametek (PARSTAT MC – 1000)**

### 3.10.5 Transport Number Measurement

#### Chronoamperometry technique

The chronoamperometry technique is used to measure the transfer count that identifies if the conductivity in the polymer electrolyte is due to the presence of ions or electrons (Image 14). The transference number is calculated using Wager's polarization formula

$$t_{ion} = (I_f - I_i) / I_i$$

Where,

$t_{ion}$  is the transfer of ions,

$I_i$  is the initial current and

$I_f$  is the final current.

**RESULTS AND**

**DISCUSSION**

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Introduction

This chapter deals with the study and characterization of solid biopolymer electrolytes prepared from different compositions of Pectin, Guar gum, Sodium nitrite, and Sodium iodide. Also, it includes the study of the ionic conductivity and transport number of the prepared electrolytes.

The following biopolymer solid electrolytes with different compositions of Pectin, Guar gum, Sodium nitrite, and Sodium iodide were prepared for the present work.

- i. Pectin / Sodium nitrite
- ii. Pectin / Sodium nitrite / 1,3- dioxolane
- iii. Guar gum / Sodium nitrite / 1,3- dioxolane
- iv. Pectin / Sodium iodide / 1,3- dioxolane

For combinations i, ii, and iii, films were formed and FTIR was recorded, but the peaks were not obtained properly showing that there is no complex formed between the salt and the biopolymer. Hence further characterization was not carried out for these three polymer electrolytes.

The following session deals with the polymer electrolyte prepared with Pectin / Sodium iodide / 1,3- dioxolane.

The solid polymer electrolytes were prepared by solution casting technique using the biopolymer Pectin and Sodium iodide salt with the addition of plasticizer 1,3-Dioxalane with water as a solvent. Code PS 1, PS 2, and PS 3 and composition of 50:45:5, 55:40:5, and 60:35:5 (**Table 6**) were selected for the present study and thin films were obtained.

Fourier Transform-Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA), and 3D Optical Profilometry were used to characterize the prepared electrolytes. Electrical Impedance Spectroscopy and Chronoamperometry were used for the study of the ionic conductivity and transport number.

**Table 6: Pectin / Sodium iodide / 1,3-Dioxalane**

CODE	COMPOSITION (wt%)
PS 1	Pectin (50): Sodium iodide (45): 1,3-DOL (5)
PS 2	Pectin (55): Sodium iodide (40):1,3-DOL (5)
PS 3	Pectin (60): Sodium iodide (35): 1,3-DOL (5)

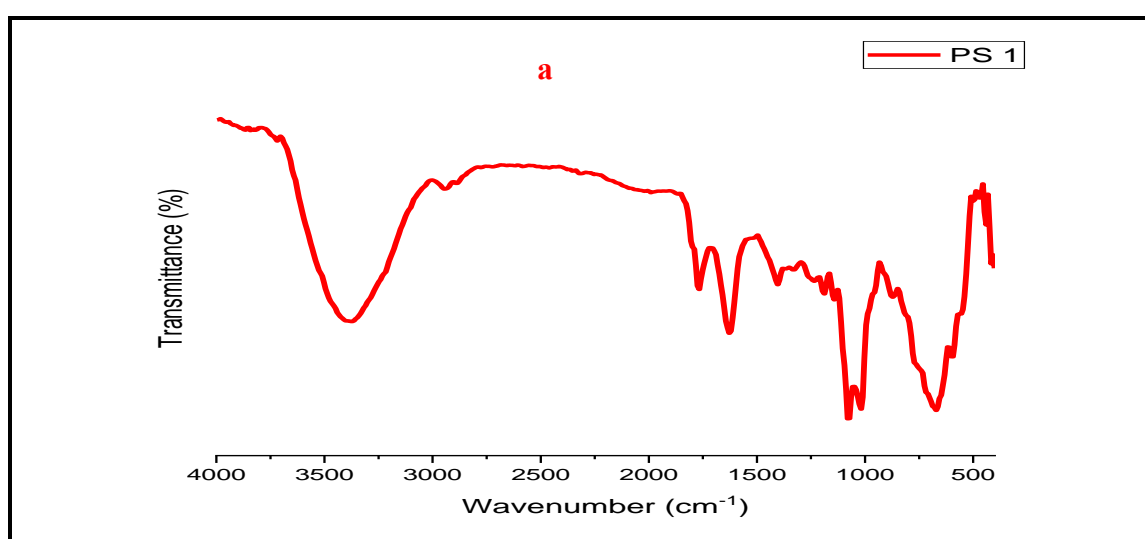
## 4.2 Characterization

### 4.2.1 Fourier Transform Infrared Analysis (FT-IR)

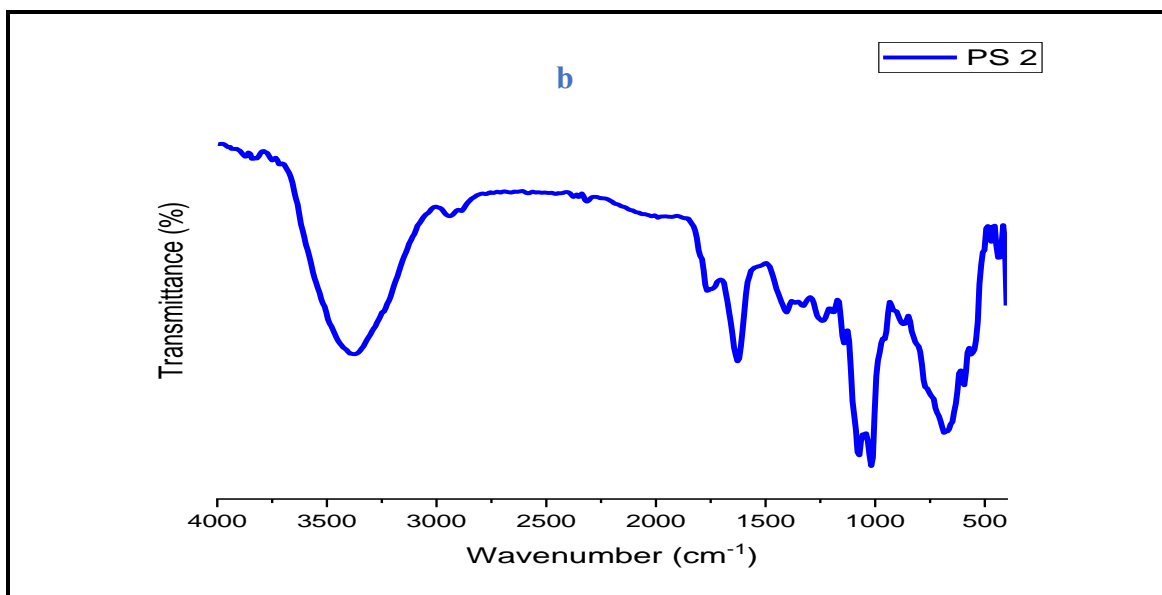
The FTIR peaks obtained for pure pectin and the prepared electrolytes for combinations of Pectin-NaI-1,3-DOL (50:45:5, 55:40:5, 60:35:5 wt%) are shown in **Figures 4a, 4b, and 4c** and the peak values are given in **Table 7**. For pure pectin a broad and strong absorption band due to the OH stretching vibration was observed around  $3294\text{ cm}^{-1}$  which is shifted to  $3380$ ,  $3374$ , and  $3363\text{ cm}^{-1}$  in the electrolytes PS 1, PS 2, and PS 3 respectively. These shifts are due to the presence of a hydroxyl group in the pectin. The aliphatic CH stretching vibration gives rise to the absorption band at  $2893\text{ cm}^{-1}$  in the pure pectin which is shifted to  $2947$ ,  $2949$ , and  $2931\text{ cm}^{-1}$  for PS 1, PS 2, and PS 3 respectively. The peak at  $1635\text{ cm}^{-1}$  is assigned to C=O stretching vibration is shifted to  $1627\text{ cm}^{-1}$  (PS-1, PS-2), and  $1620\text{ cm}^{-1}$  (PS-3). The peak appearing at  $1419\text{ cm}^{-1}$  in the case of pure pectin corresponds to O=C-O stretching shifted to  $1406\text{ cm}^{-1}$  (PS-1), and  $1404$  (PS-2, PS-3)  $\text{cm}^{-1}$ . A peak at  $1342\text{ cm}^{-1}$  attributed to OH bending vibration is moved to  $1327\text{ cm}^{-1}$  in the electrolytes of PS-1, PS-2 and PS-3 respectively. The  $1026\text{ cm}^{-1}$  peak of the -CH-O-CH stretch is shifted to  $1080$ ,  $1072$ , and  $1010\text{ cm}^{-1}$ . A new peak appears at  $671\text{ cm}^{-1}$  (PS-1), and  $686\text{ cm}^{-1}$  (PS-2, PS-3) in the electrolyte indicating the C-I stretching.

**Table 7: Peak assignments of Pectin/ Sodium iodide/ 1,3-Dioxalane polymer electrolytes**

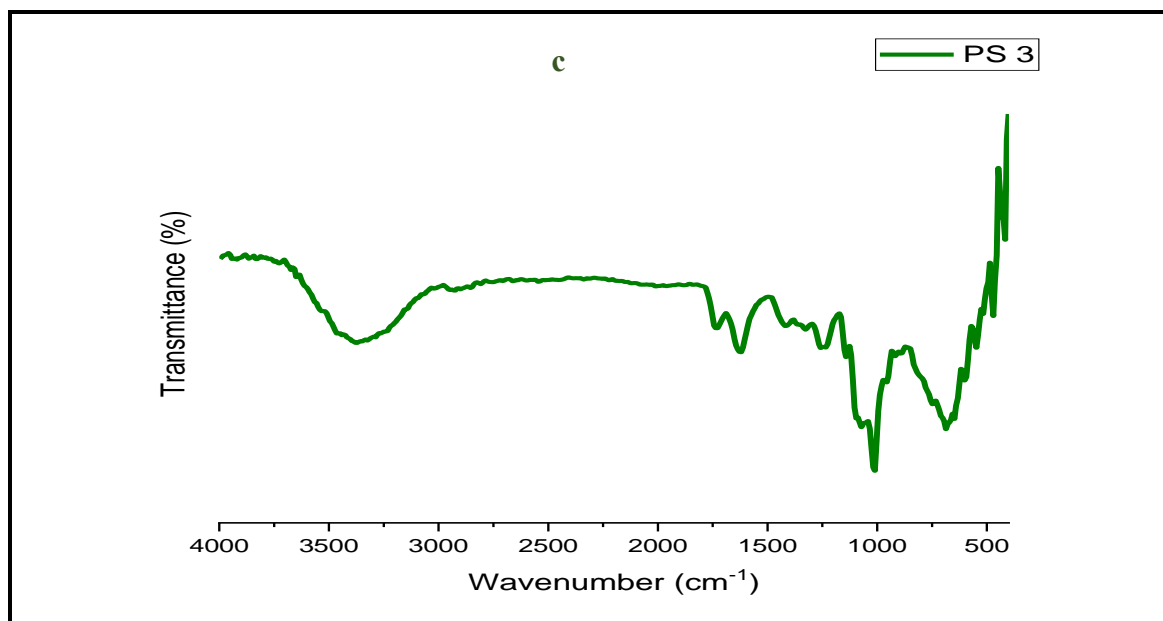
Pure Pectin	Wavenumber (cm <sup>-1</sup> )			Characteristic group
	60:35:5	50:45:5	55:40:5	
3294	3380	3374	3363	O-H stretching
2893	2947	2949	2931	-C-H stretching
1635	1627	1627	1620	C=O stretching
1419	1406	1404	1404	O=C-O stretching
1342	1327	1327	1327	O-H bending
1249	1242	1234	1234	-CH-OH stretching
1026	1080	1072	1010	-CH-O-CH stretching
-	671	686	686	C-I stretching



**Figure 4a: FTIR spectra of PS 1**



**Figure 4b: FTIR spectra of PS 2**



**Figure 4c: FTIR spectra of PS 3**

The appearance of a new peak and a shift in the wavenumber of the characteristic absorption peaks is due to the interaction of salt with the polymer matrix, confirming the complex formation between the sodium iodide and the biopolymer pectin.

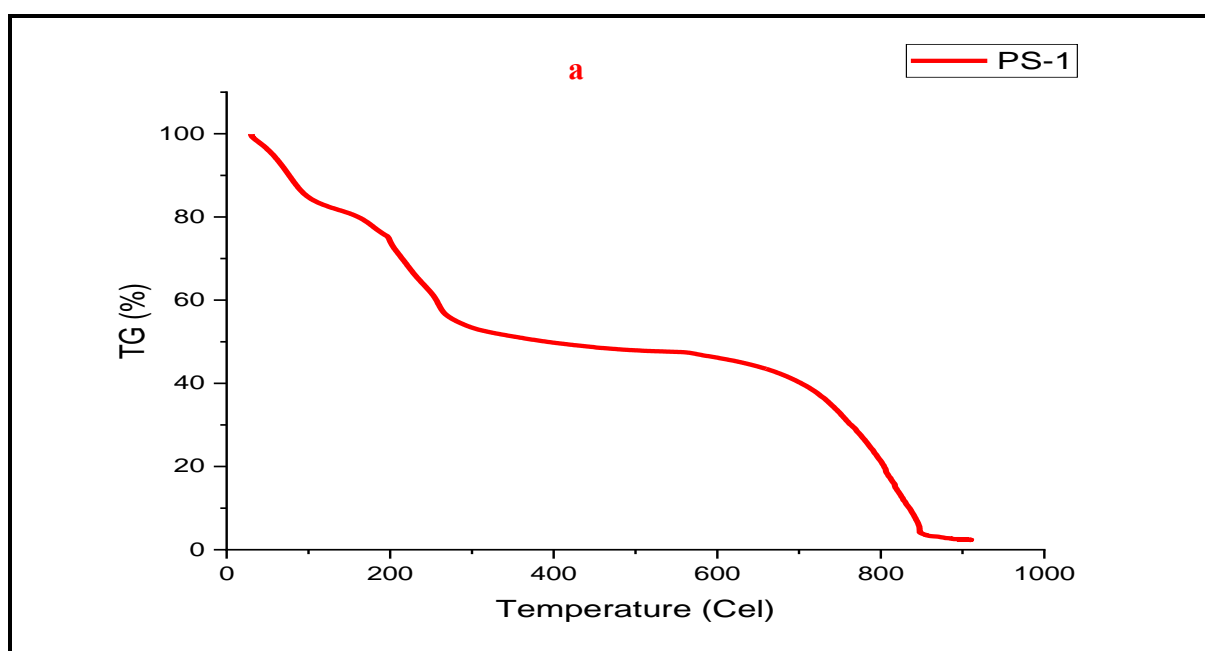
## 4.2.2 Thermal Gravimetric Analysis (TGA)

The TGA of Pectin – NaI – 1,3-Dioxalane electrolytes in the ratio of 50:45:5, 55:40:5, and 60:35:5 wt% is shown in **Figures 5a, 5b** and **5c**.

For the composition 50:45:5 wt%, the first weight loss of 14% of the initial mass, which occurs for pure pectin and pectin/NaI/1,3-DOL samples at 94°C, is due to the loss of water molecules. Then, at 257°C, there is a weight loss of about 34% for the prepared electrolyte, which is due to the pyrolytic breakdown, the end product of primary and secondary decarboxylation involving the acid group and carbon in the anhydrous glucose ring, which causes this weight loss. The weight loss of 52% that has taken place between 658<sup>0</sup> C to 864<sup>0</sup> C due to the sodium iodide degradation. [R. Leones et al, 2014] show that the prepared electrolyte is stable up to 864<sup>0</sup> C.

Similarly, for the composition 55:40:5 wt%, the first weight loss of 12% of the initial mass, which occurs for pure pectin and pectin/NaI/1,3-DOL samples at 95°C, is due to the loss of water. Then, at 264°C, there is a weight loss of about 41% for the prepared electrolyte. There is a 47% weight loss that takes place between 663<sup>0</sup> C to 850<sup>0</sup> C. Thermal stability is stable up to 850<sup>0</sup> C.

For 60:35:5 wt% composition for the first weight loss of 10% occurs at 90°C, corresponds to a loss of water molecules and is followed by the second weight loss of 32% at 240°C. Between 656°C and 820°C there is a weight loss of 58% due to the degradation of sodium iodide showing that the electrolyte with a composition of 60:35:5 wt% is stable up to 820°C.



**Figure 5a: TGA Curve of PS 1**

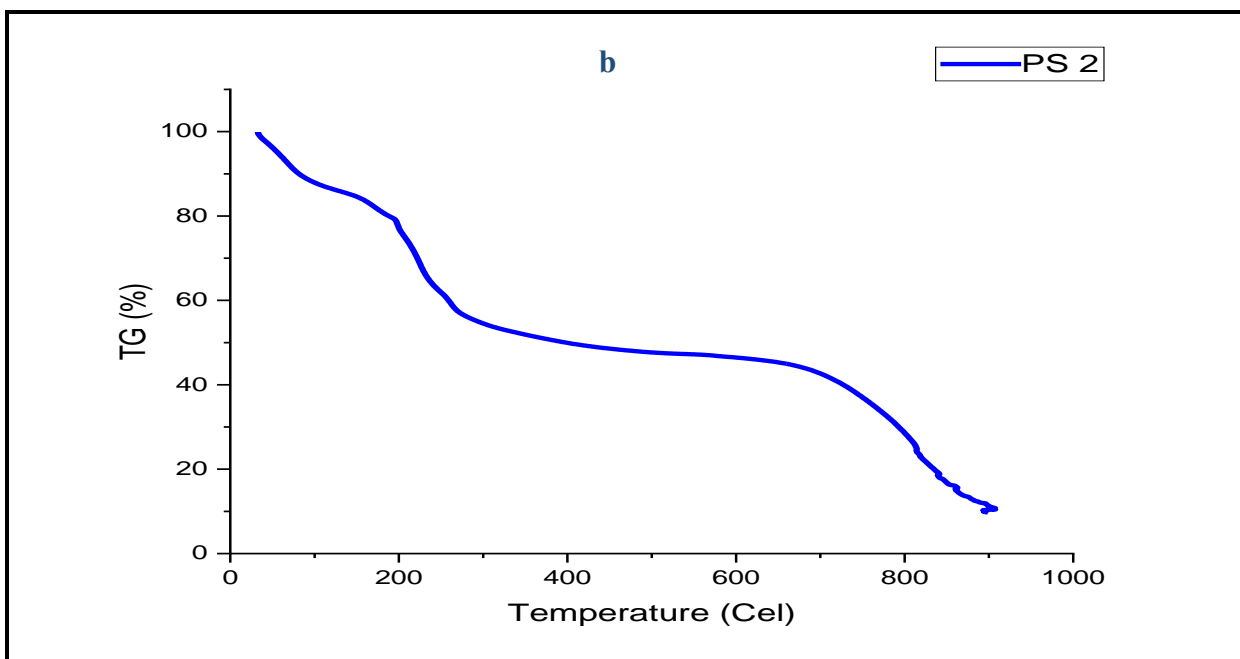


Figure 5b: TGA Curve of PS 2

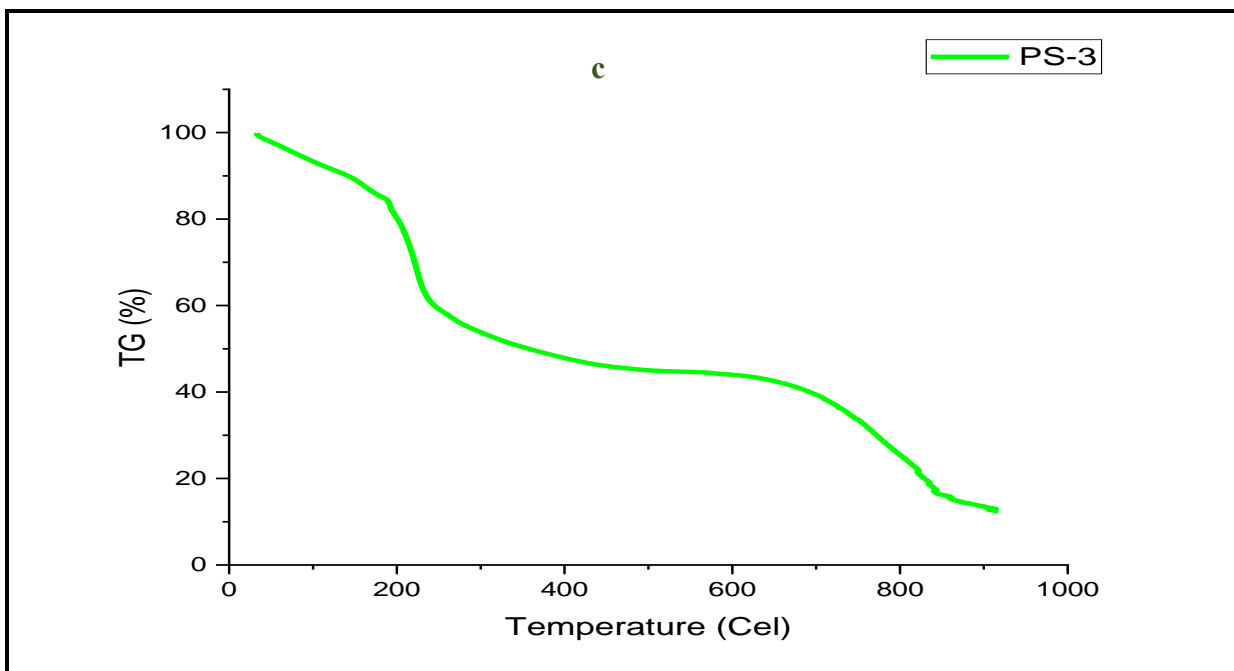


Figure 5c: TGA Curve of PS 3

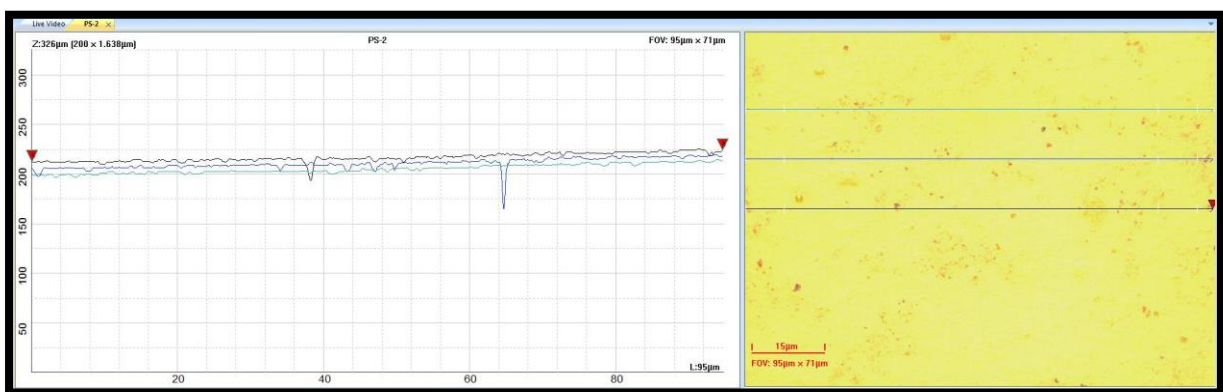
The thermal stability for the pectin-Sodium iodide-1,3-Dioxalane polymer electrolytes in the ratio of 60:35:5, 50:45:5, and 55:40:5 wt% is given in **Table 8**.

**Table 8: Thermal stability of Pectin / Sodium Iodide / 1,3-Dioxalane polymer electrolytes**

<b>Code</b>	<b>Composition of Pectin / Sodium Iodide / 1,3-Dioxalane polymer electrolytes (wt %)</b>	<b>Thermal stability (°C)</b>
<b>PS 1</b>	50:45:5	864
<b>PS 2</b>	55:40:5	850
<b>PS 3</b>	60:35:5	820

### 4.2.3 3D Laser Profilometry Analysis

3D laser profilometric analysis is a powerful technique used for analyzing surface morphology at a micro-scale, which is currently being utilized to evaluate the uniformity and roughness of the surface. 3D Laser Profilometry analysis images for Pectin-NaI- 1,3-DOL polymer electrolytes (50:45:5, 55:40:5, 60:35:5 wt%) are shown in **images 14 (PS-1), 15 (PS-2), 16 (PS-3)** respectively and average roughness ( $R_a$ ) measurement values are 6.12, 18.9, and 18.2 for PS-1, PS-2, PS-3 respectively are shown in **Table 9**. It is observed that the surface roughness of the sample varied with different concentrations of polymer electrolytes.



Topographical representation of surface features of PS-1

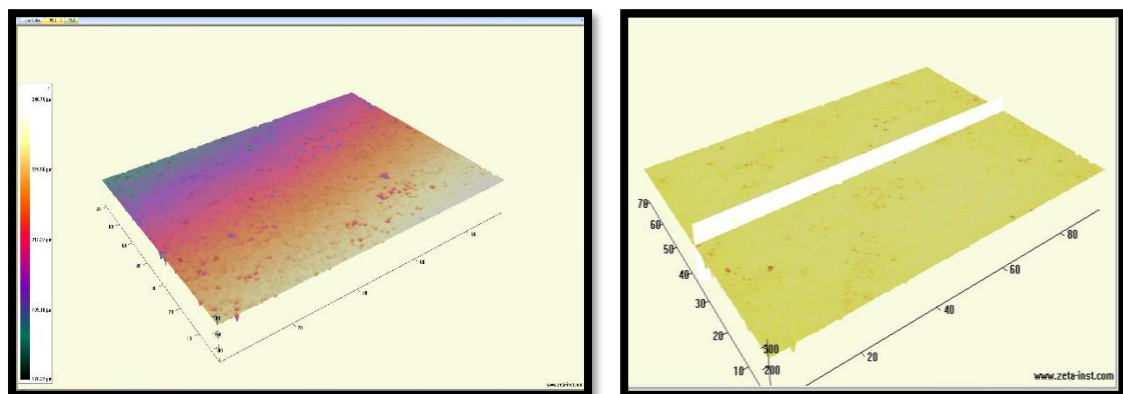
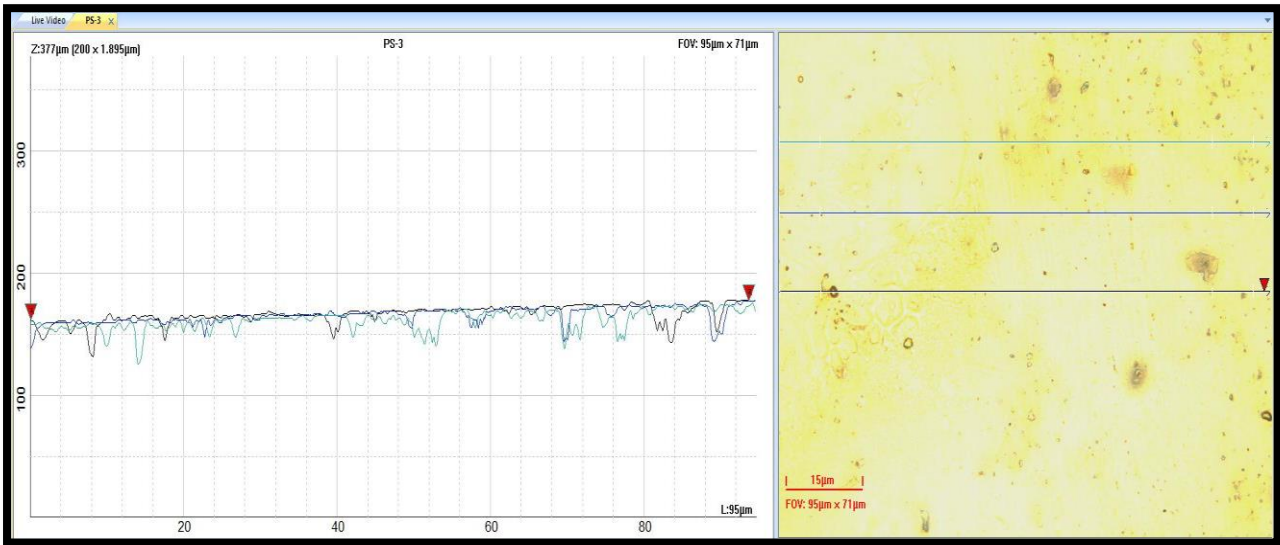
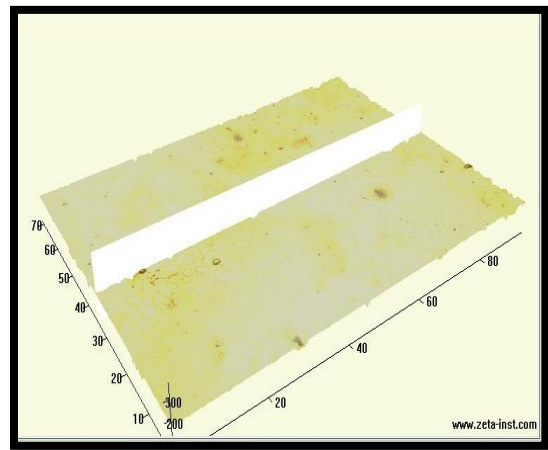
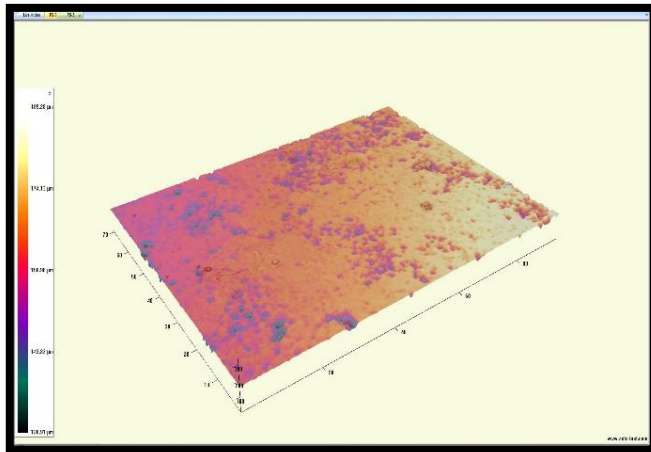


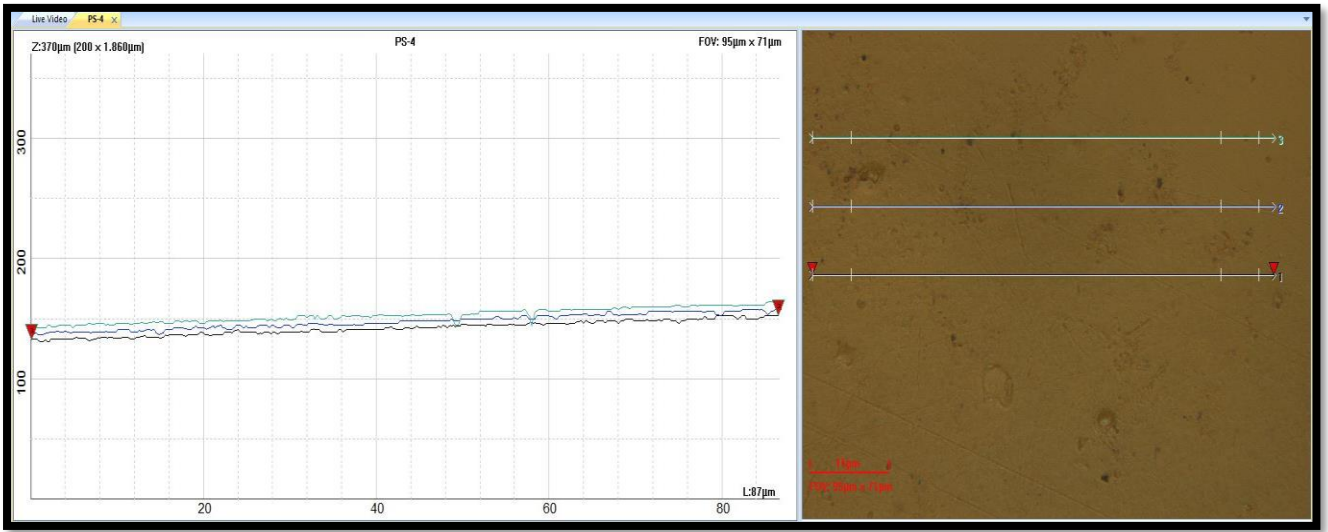
Image 14: Zeta images of PS-1



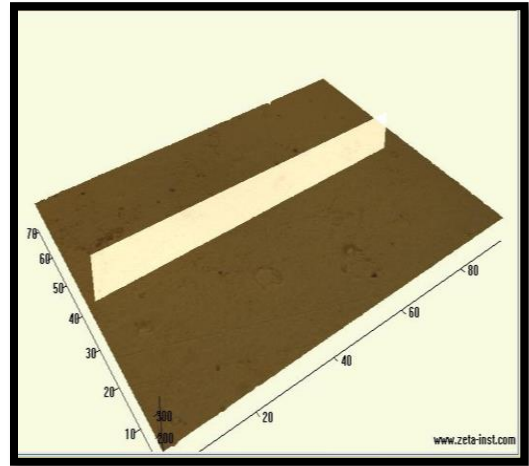
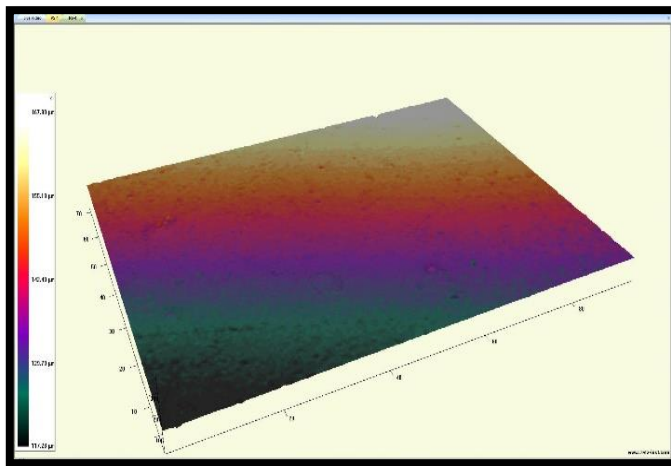
**Topographical representation of surface features of PS-2**



**Image 15: Zeta images of PS-2**



**Topographical representation of surface features of PS-3**



**Image 16: Zeta images of PS-3**

**Table 9: Average roughness values of Pectin- NaI -1,3-DOL polymer electrolyte**

S.No	Compositions of Pectin- NaI- DOL (wt%)	Average roughness (R <sub>a</sub> ) (%)
1.	PS-1 50:45:5	18.2
2.	PS-2 55:40:5	6.12
3.	PS-3 60:35:5	18.9

The images obtained showed three-dimensional surface areas with average roughness (R<sub>a</sub>) values of 18.2 %,6.12 %, and 18.9 % for PS-1, PS-2, and PS-3 respectively. Among the three electrolytes, PS-2 (55:40:5) has the lowest R<sub>a</sub> value (6.12 %), which is smoother than PS-1 (18.2) and PS-3 (18.9). The proper blending of the electrolyte is revealed by the surface roughness value (R<sub>a</sub>).

The presence of a large number of spherulites having different sizes indicates the presence of a crystalline phase, whereas the small voids correspond to an amorphous phase [Shujahdeen B. Aziz *et al.* (2018)]. Due to the complex interactions between NaI and the polymer-pectin chains, the size of spherulites decreased as the weight percentage of NaI increased which was subsequently accompanied by an increase in the amorphous region. Due to the small size of the spherulites and their surrounding voids, the PS-2 sample appears to have the most amorphous. [K. K. Maury *et al.* (1995)]

## 4.2.4 Impedance Studies

The nature of the electrochemical system can be studied using impedance plots over a wide range of frequencies at different temperatures by applying an AC voltage or current. The high-frequency semi-circle is due to the parallel combination of bulk resistance which is due to the migration of ions and bulk capacitance which is due to immobile polymer chains.

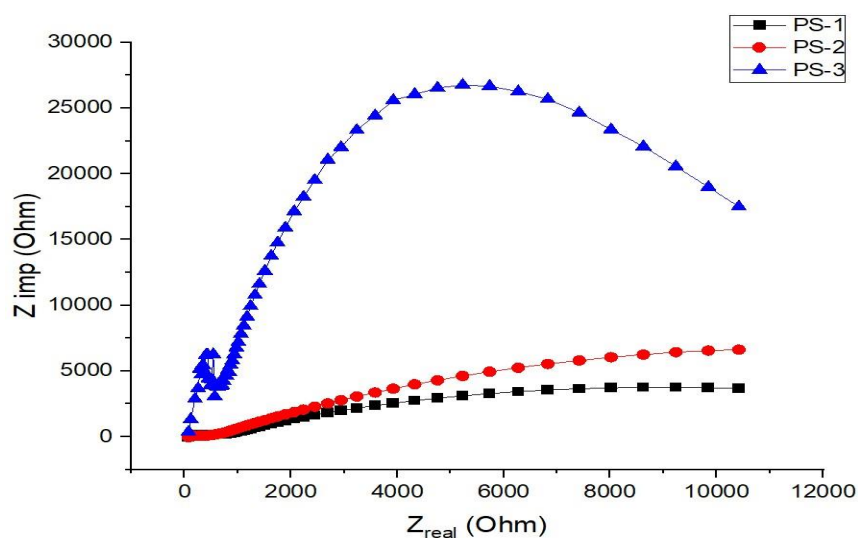
The ionic conductivity values obtained for various compositions of NaI doped with polymer Pectin with plasticizer DOL at room temperature (303K) are given in **Table 10**.

**Table 10. Conductivity values of Pectin/ NaI / 1,3-DOL polymer electrolytes**

Code	Composition (wt%)	Conductivity (S/cm)
PS 1	50:45:5	$1.16 \times 10^{-5}$
PS 2	55:40:5	$1.49 \times 10^{-5}$
PS 3	60:35:5	$5.6 \times 10^{-7}$

Pectin doped with various concentrations of NaI with plasticizer DOL at ambient temperature (303K) is shown in **Figure 6**. It is evident from Table 10 that the film containing 55:40:5 wt%

(PS-2) exhibits higher conductivity of  $1.49 \times 10^{-5}$  S/cm. The ionic conductivity of the electrolyte is related to the smoothness of the film. When smoothness increases the conductivity of the film also increases, this is evident from the 3-D profilometric analysis.



**Figure 6: Nyquist plot for PS-1, PS-2, and PS-3**

#### 4.2.5 Transport number measurement

The transport number was determined using the chronoamperometry technique and the transference number for cations ( $t_+$ ) and anions ( $t_-$ ) has been evaluated using the formula

$$t_+ = (I_i - I_f) / I_i$$

$$t_- = (I_i - I_f) / I_i$$

where  $I_i$  is the initial current, and

$I_f$  is the final current.

**Figure 7** shows the transport number curve of the electrolyte. The transport number values of Pectin/ NaI/ DOL are given in **Table 11**.

**Table 11: Transport number for Pectin/ NaI/ DOL polymer electrolyte**

Code	Composition	Transport number ( $t_{ion}$ )	
		$t_+$	$t_-$
PS 1	50:45:5	0.69	0.30
PS 2	55:40:5	0.51	0.49
PS 3	60:35:5	0.58	0.42

It is obvious from Table 11, that the transference number ( $t_{ion}$ ) of the polymer PS 2 (55:40:5 M wt%) of Pectin/ NaI/ 1,3-DOL with a maximum ionic conductivity of  $1.49 \times 10^{-5} \text{ S/cm}$  was found to be 0.51 for  $\text{Na}^+$  ions and 0.49 for  $\text{I}^-$  ions. The highest ionic conductivity may be due to the mobility of both anions and cations.

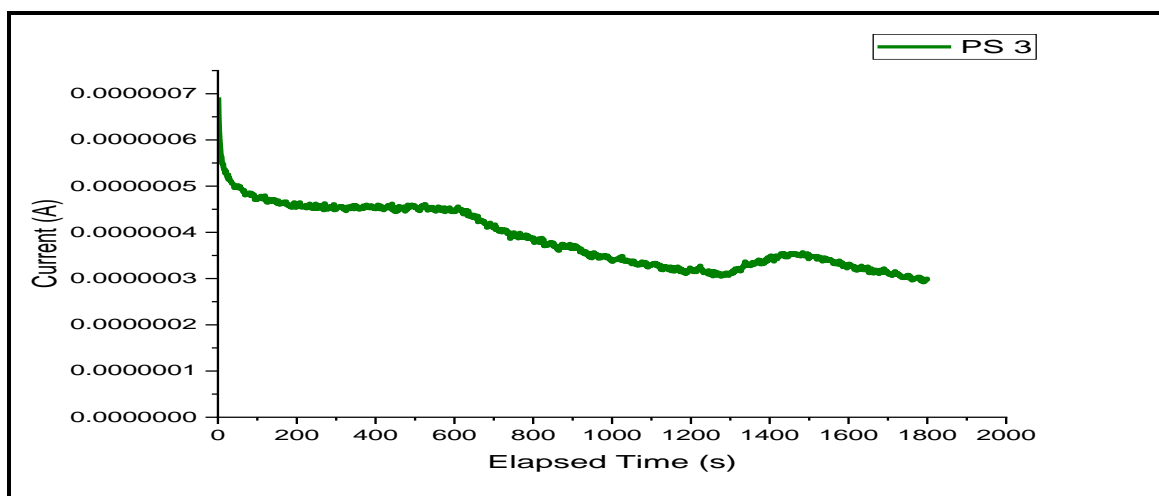
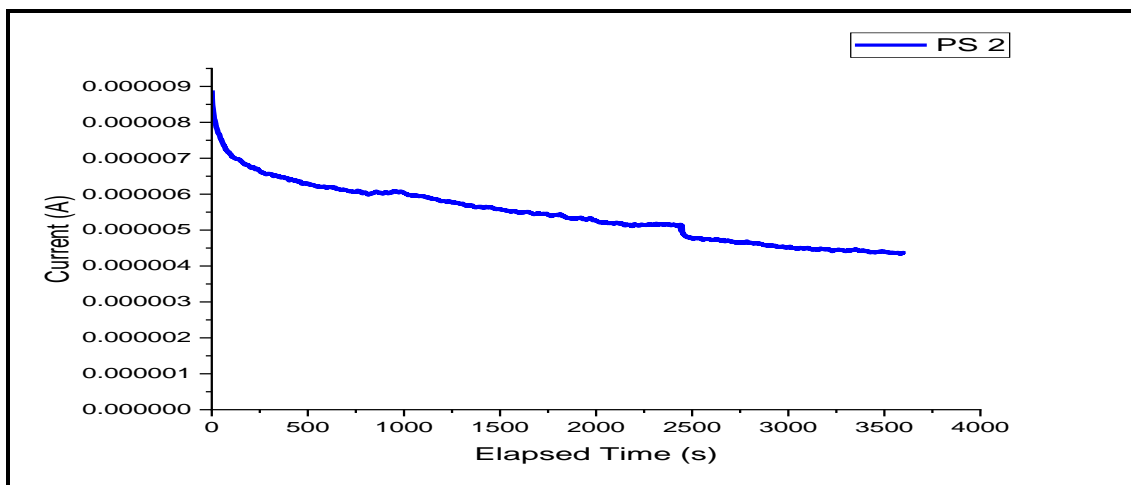
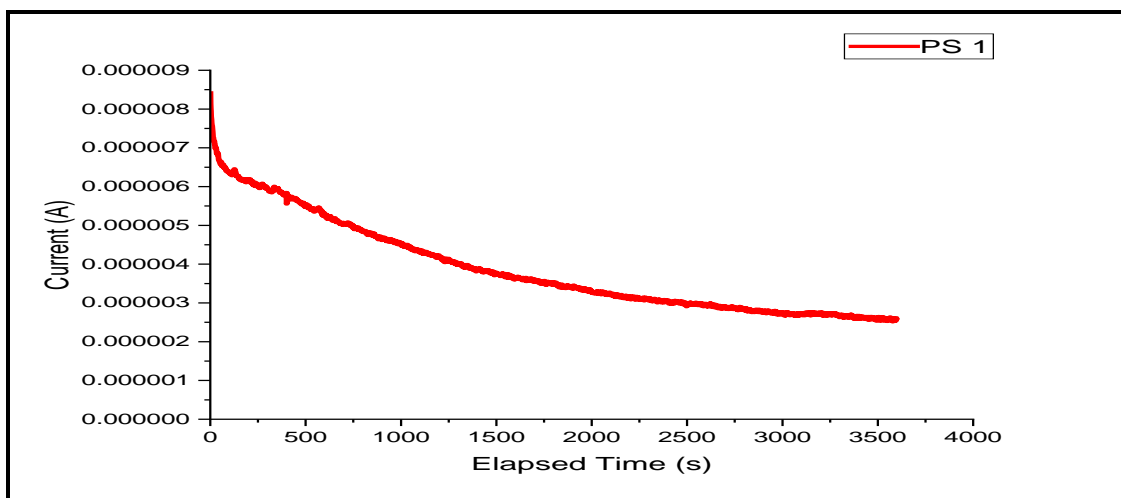


Figure 7: Transport number curve of PS 1, PS 2, and PS

**SUMMARY AND**

**CONCLUSION**

## Chapter V

### SUMMARY AND CONCLUSION

In the present study, " **ECO-FRIENDLY ELECTROLYTE BASED ON PECTIN AND SODIUM IODIDE FOR SODIUM-ION BATTERIES**," the preparation and characterization of environmentally friendly polymer electrolytes based on the biopolymer Pectin and Sodium iodide as ionic salt is summarized and concluded in this chapter.

#### Summary

Pectin / Sodium nitrite, Pectin / Sodium nitrite / 1,3- dioxolane, Guar gum / Sodium nitrite / 1,3- dioxolane, and Pectin / Sodium iodide / 1,3- dioxolane have been prepared using the solution casting technique. Among the four electrolytes, Pectin / Sodium nitrite, Pectin / Sodium nitrite / 1,3- dioxolane, and Guar gum / Sodium nitrite / 1,3- dioxolane film was formed and FTIR was recorded, but the peaks were not obtained properly showing that there is no complex formed between the salt and the biopolymer. Hence further characterization was not carried out for these three polymer electrolytes. Therefore further study proceeded with Pectin / Sodium iodide / 1,3- dioxolane.

FTIR study shows the complex formation of the prepared solid biopolymer electrolyte and the thermal stability of Pectin / Sodium iodide / 1,3- dioxolane with the composition of 50:45:5, 55:35:5, and 60:35:5 are 864, 850, and 820<sup>0</sup>C respectively were revealed by TGA analysis.

The topographical study is carried out using 3-D Optical Laser Profilometry and is observed that the electrolyte with composition 55:40:5 (PS-2) has a Ra value of 6.12 % which is smoother than the other two compositions 50:45:5 (18.2 %), and 60:35:5 (18.9 %), hence exhibited highest ionic conductivity of  $1.49 \times 10^{-5}$  S/cm analysed through impedance measurements.

The chronoamperometry technique was used to determine the transport number and the transference number for cation and anion was found to be 0.51 for Na<sup>+</sup> ions and 0.49 for I<sup>-</sup> ions for the highest ionic conducting electrolyte of composition 55:40:5 (PS-2).

## **Conclusion**

Biodegradable polymer electrolyte Pectin / Sodium iodide / 1,3- dioxolane of PS-1(50:45:5), PS-2 (55:40:5), and PS-3(60:35:5) were prepared and the highest ionic conductivity of  $1.49 \times 10^{-5}$  S/cm for PS-2 (55:40:5) was obtained at room temperature. Hence this electrolyte may be used to fabricate coin cells with suitable electrodes for sodium-ion batteries.

## **RECOMMENDATIONS**

- 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 Na-ion batteries.
- The electrolytes may be prepared by varying the composition of the ionic dopant.

# **BIBLIOGRAPHY**

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## Bibliography

Aafrin Hazaana, S., Joseph, A., Selvasekarapandian, S., Meera Naachiyar, R., Vengadesh Krishna, M., & Muniraj Vignesh, N. (2022). Development and characterization of biopolymer electrolyte based on gellan gum (GG) with lithium chloride (LiCl) for the application of electrochemical devices. *Polymer Bulletin*. <https://doi.org/10.1007/s00289-022-04316-w>

Abbas Adam, A., Soleimani, H., Fadhlullah Bin Abd Shukur, M., Ojur Dennis, J., Mudassir Hassan, Y., Abubakar Abdulkadir, B., Yetunde Yusuf, J., & Asyiqin Bt Shamsuri, N. (n.d.). *PHYSICOCHEMICAL AND ELECTROCHEMICAL PERFORMANCE OF GLYCEROL PLASTICIZED SOLID BIOPOLYMER ELECTROLYTES BASED ON METHYLCELLULOSE/PECTIN BLEND DOPED WITH POTASSIUM SALT*. <https://ssrn.com/abstract=4032235>

Adam, A. A., Soleimani, H., Shukur, M. F. B. A., Dennis, J. O., Hassan, Y. M., Abdulkadir, B. A., Yusuf, J. Y., Ahmed, O. S. S., Salehan, S. S., Ayub, S., & Abdullahi, S. S. (2022). Novel composite polymer electrolytes based on methylcellulose-pectin blend complexed with potassium phosphate and ethylene carbonate. *Biomass Conversion and Biorefinery*. <https://doi.org/10.1007/s13399-022-03202-9>

Allen J. Bard and Larry R. Faulkner (2001), “Electrochemical Methods fundamental and applications”.

Awang, F. F., Hassan, M. F., & Kamarudin, K. H. (2023). Investigation of structural and electrical properties of a biopolymer materials with its potential application in solid-state batteries. *Polymer Bulletin*, 80(2), 1463–1476. <https://doi.org/10.1007/s00289-022-04124-2>

Aziz, S. B., Faraj, M. G., & Abdullah, O. G. (2018). Impedance Spectroscopy as a Novel Approach to Probe the Phase Transition and Microstructures Existing in CS:PEO Based Blend Electrolytes. *Scientific Reports*, 8(1). <https://doi.org/10.1038/s41598-018-32662-1>

Azzahari, A. D., Abdul Mutalib, N. F., Rizwan, M., Naceur Abouloula, C., Selvanathan, V., Sonsudin, F., & Yahya, R. (2018). Improved ionic conductivity in guar gum succinate–based polymer electrolyte membrane. *High Performance Polymers*, 30(8), 993–1001. <https://doi.org/10.1177/0954008318775790>

Bhuvaneswari, B., Sivabharathy, M., Prasad, L. G., & Selvasekarapandian, S. (2022). Structural, thermal and electrochemical characterization of cellulose acetate–based solid biopolymer electrolyte for zinc ion batteries. *Ionics*, 28(8), 3865–3875. <https://doi.org/10.1007/s11581-022-04616-1>

Carvalho, D. V., Loeffler, N., Hekmatfar, M., Moretti, A., Kim, G. T., & Passerini, S. (2018). Evaluation of guar gum-based biopolymers as binders for lithium-ion batteries electrodes. *Electrochimica Acta*, 265, 89–97. <https://doi.org/10.1016/j.electacta.2018.01.083>

Dennis, J. O., Adam, A. A., Ali, M. K. M., Soleimani, H., Shukur, M. F. B. A., Ibnaouf, K. H., Aldaghri, O., Eisa, M. H., Ibrahim, M. A., Bashir Abdulkadir, A., & Cyriac, V. (2022). Substantial Proton Ion Conduction in Methylcellulose/Pectin/Ammonium Chloride Based Solid Nanocomposite Polymer Electrolytes: Effect of ZnO Nanofiller. *Membranes*, 12(7). <https://doi.org/10.3390/membranes12070706>

Diana, M. I., Selvasekarapandian, S., Selvin, P. C., & Krishna, M. V. (2022). A physicochemical elucidation of sodium perchlorate incorporated alginate biopolymer: toward all-solid-state sodium-ion battery. *Journal of Materials Science*, 57(17), 8211–8224. <https://doi.org/10.1007/s10853-022-07185-w>

Diana, M. I., Selvin, P. C., Selvasekarapandian, S., & Krishna, M. V. (2021). Investigations on Na-ion conducting electrolyte based on sodium alginate biopolymer for all-solid-state sodium-ion batteries. *Journal of Solid State Electrochemistry*, 25(7), 2009–2020. <https://doi.org/10.1007/s10008-021-04985-z>

Evanovich, J., & King, L. (n.d.). *Hardcore twenty-four : a Stephanie Plum novel*.

Fuzlin, A. F. A., Misnon, I. I., & Samsudin, A. S. (2020). Conduction properties study on alginate incorporated with glycolic acid based solid biopolymer electrolytes. In *Materials Science Forum: Vol. 981 MSF* (pp. 34–39). Trans Tech Publications Ltd. <https://doi.org/10.4028/www.scientific.net/MSF.981.34>

Fuzlin, A. F., Nagao, Y., Misnon, I. I., & Samsudin, A. S. (2020). Studies on structural and ionic transport in biopolymer electrolytes based on alginate-LiBr. *Ionics*, 26(4), 1923–1938. <https://doi.org/10.1007/s11581-019-03386-7>

Ghazali, N. M., Mazuki, N. F., & Samsudin, A. S. (2021). Characterization of Biopolymer Blend-based on Alginate and Poly (vinyl Alcohol) as an Application for Polymer Host in Polymer

Electrolyte. *IOP Conference Series: Materials Science and Engineering*, 1092(1), 012047. <https://doi.org/10.1088/1757-899x/1092/1/012047>

Gunasekaran, A., Sorrentino, A., Asiri, A. M., & Anandan, S. (2020). Guar gum-based polymer gel electrolyte for dye-sensitized solar cell applications. *Solar Energy*, 208, 160–165. <https://doi.org/10.1016/j.solener.2020.07.084>

Hazaana, S. A., Joseph, A., Selvasekarapandian, S., Naachiyar, R. M., & Vignesh, N. M. (2022). Performance of solid-state Li-ion conducting battery using biopolymer electrolyte based on agar–agar/lithium chloride. *Journal of Solid State Electrochemistry*. <https://doi.org/10.1007/s10008-022-05348-y>

[https://books.google.co.in/books/about/Biopolymer\\_Electrolytes.html?id=6YRfDwAAQBAJ&redir\\_esc=y#v=onepage&q&f=false](https://books.google.co.in/books/about/Biopolymer_Electrolytes.html?id=6YRfDwAAQBAJ&redir_esc=y#v=onepage&q&f=false)

[https://books.google.co.in/books?hl=en&lr=&id=zgmmEAAAQBAJ&oi=fnd&pg=PA389&dq=electrodes+in+sodium+ion+batteries&ots=Sj\\_Vo3t7Yr&sig=DY53OrHoysoNypITdnghMDFa630&redir\\_esc=y#v=onepage&q=electrodes%20in%20sodium%20ion%20batteries&f=false](https://books.google.co.in/books?hl=en&lr=&id=zgmmEAAAQBAJ&oi=fnd&pg=PA389&dq=electrodes+in+sodium+ion+batteries&ots=Sj_Vo3t7Yr&sig=DY53OrHoysoNypITdnghMDFa630&redir_esc=y#v=onepage&q=electrodes%20in%20sodium%20ion%20batteries&f=false)

[https://books.google.co.in/books?id=6YRfDwAAQBAJ&printsec=frontcover&source=gbs\\_ge\\_summary\\_r&ad=0#v=onepage&q&f=true](https://books.google.co.in/books?id=6YRfDwAAQBAJ&printsec=frontcover&source=gbs_ge_summary_r&ad=0#v=onepage&q&f=true)

[https://books.google.co.in/books?id=so7zDwAAQBAJ&printsec=frontcover&dq=BATTERIES&hl=en&newbks=1&newbks\\_redir=0&sa=X&ved=2ahUKEwin4LyLif79AhWOSGwGHWBNNBBMQ6AF6BAgJEA#v=onepage&q=BATTERIES&f=false](https://books.google.co.in/books?id=so7zDwAAQBAJ&printsec=frontcover&dq=BATTERIES&hl=en&newbks=1&newbks_redir=0&sa=X&ved=2ahUKEwin4LyLif79AhWOSGwGHWBNNBBMQ6AF6BAgJEA#v=onepage&q=BATTERIES&f=false)

<https://drive.google.com/file/d/1mBToo4WsTdwzEmyBDUfR-o5UVpZnC0hK/view>

[https://drive.google.com/file/d/1t8m\\_z-UGX76Yk8dvVyiflG8kfNye-LJU/view](https://drive.google.com/file/d/1t8m_z-UGX76Yk8dvVyiflG8kfNye-LJU/view)

[https://en.wikipedia.org/wiki/Alkaline\\_battery](https://en.wikipedia.org/wiki/Alkaline_battery)

[https://en.wikipedia.org/wiki/Sodium-ion\\_battery](https://en.wikipedia.org/wiki/Sodium-ion_battery)

<https://www.adb.org/sites/default/files/publication/479891/handbook-battery-energy-storage-system.pdf>

<https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7078607/>

<https://www.niti.gov.in/sites/default/files/2019-10/ISGF-Report-on-Energy-Storage-System-%28ESS%29-Roadmap-for-India-2019-2032.pdf>

Kiruthika, S., Malathi, M., Selvasekarapandian, S., Tamilarasan, K., Moniha, V., & Manjuladevi, R. (2019). Eco-friendly biopolymer electrolyte, pectin with magnesium nitrate salt, for

application in electrochemical devices. *Journal of Solid State Electrochemistry*, 23(7), 2181–2193. <https://doi.org/10.1007/s10008-019-04313-6>

Kiruthika, S., Malathi, M., Selvasekarapandian, S., Tamilarasan, K., & Maheshwari, T. (2020). Conducting biopolymer electrolyte based on pectin with magnesium chloride salt for magnesium battery application. *Polymer Bulletin*, 77(12), 6299–6317. <https://doi.org/10.1007/s00289-019-03071-9>

Kumar, L. S., Selvin, P. C., Selvasekarapandian, S., Manjuladevi, R., Monisha, S., & Perumal, P. (2018). Tamarind seed polysaccharide biopolymer membrane for lithium-ion conducting battery. *Ionics*, 24(12), 3793–3803. <https://doi.org/10.1007/s11581-018-2541-3>

Leones, R., Botelho, M. B. S., Sentanin, F., Cesarino, I., Pawlicka, A., Camargo, A. S. S., & Silva, M. M. (2014). Pectin-based Polymer Electrolytes with Ir(III) Complexes. *Molecular Crystals and Liquid Crystals*, 604(1), 117–125. <https://doi.org/10.1080/15421406.2014.968049>

Maithilee, K., Sathya, P., Selvasekarapandian, S., Chitra, R., Krishna, M. V., & Meyvel, S. (2022). Na-ion conducting biopolymer electrolyte based on tamarind seed polysaccharide incorporated with sodium perchlorate for primary sodium-ion batteries. *Ionics*, 28(4), 1783–1790. <https://doi.org/10.1007/s11581-022-04440-7>

Majumdar, S., Sen, P., & Ray, R. (2022). High-performance graphene oxide-grafted chitosan-starch solid biopolymer electrolytes for flexible hybrid supercapacitors. *Journal of Solid State Electrochemistry*, 26(2), 527–547. <https://doi.org/10.1007/s10008-021-05093-8>

Manjuladevi, R., Selvin, P. C., Selvasekarapandian, S., Shilpa, R., & Moniha, V. (2018). Lithium ion conducting biopolymer electrolyte based on pectin doped with Lithium nitrate. *AIP Conference Proceedings*, 1942. <https://doi.org/10.1063/1.5029206>

Maurya, K. K., Bhattacharya, B., & Chandra, S. (1995). Hydrogen Ion Transport Studies in PEO : NH<sub>4</sub>HSO<sub>4</sub>, Polymer Electrolyte. In *phys. stat. sol. (a)* (Vol. 147).

Mendes, J. P., Esperança, J. M. S. S., Medeiros, M. J., Pawlicka, A., & Silva, M. M. (2017). Structural, morphological, ionic conductivity, and thermal properties of pectin-based polymer electrolytes. *Molecular Crystals and Liquid Crystals*, 643(1), 266–273. <https://doi.org/10.1080/15421406.2016.1263111>

Muthukrishnan, M., Shanthi, C., Selvasekarapandian, S., Manjuladevi, R., Perumal, P., & Christopher Selvin, P. (2019). Synthesis and characterization of pectin-based biopolymer electrolyte for electrochemical applications. *Ionics*, 25(1), 203–214. <https://doi.org/10.1007/s11581-018-2568-5>

Nandhinilakshmi, M., Vanitha, D., Nallamuthu, N., Anandha Jothi, M., & Sundaramahalingam, K. (2022). Structural, electrical behavior of sodium ion-conducting corn starch–PVP-based solid polymer electrolytes. *Polymer Bulletin*. <https://doi.org/10.1007/s00289-022-04230-1>

Perumal, P., Christopher Selvin, P., & Selvasekarapandian, S. (2018). Characterization of biopolymer pectin with lithium chloride and its applications to electrochemical devices. *Ionics*, 24(10), 3259–3270. <https://doi.org/10.1007/s11581-018-2507-5>

Perumal, P., Christopher Selvin, P., Selvasekarapandian, S., & Abhilash, K. P. (2019). Bio-host pectin complexed with dilithium borate based solid electrolytes for polymer batteries. *Materials Research Express*, 6(11). <https://doi.org/10.1088/2053-1591/ab4724>

Rani, M. S. A., Rudhziah, S., Ahmad, A., & Mohamed, N. S. (2022). Effects of different iodide salts on the electrical and electrochemical properties of hybrid biopolymer electrolytes for dye-sensitized solar cells application. *Polymer Bulletin*, 79(11), 9813–9832. <https://doi.org/10.1007/s00289-021-03980-8>

Sangeetha, P., Selvakumari, T. M., Selvasekarapandian, S., & Mahalakshmi, M. (2023). Preparation of primary magnesium battery based on kappa carrageenan with magnesium perchlorate and its application to electrochemical devices. *Polymer Bulletin*. <https://doi.org/10.1007/s00289-022-04669-2>

Selvalakshmi, S., Mathavan, T., Selvasekarapandian, S., & Premalatha, M. (2019). Characterization of biodegradable solid polymer electrolyte system based on agar-NH<sub>4</sub>Br and its comparison with NH<sub>4</sub>I. *Journal of Solid State Electrochemistry*, 23(6), 1727–1737. <https://doi.org/10.1007/s10008-019-04262-0>

Selvalakshmi, S., Vanitha, D., Saranya, P., Selvasekarapandian, S., Mathavan, T., & Premalatha, M. (2022). Structural and conductivity studies of ammonium chloride doped agar–agar biopolymer electrolytes for electrochemical devices. *Journal of Materials Science: Materials in Electronics*, 33(32), 24884–24894. <https://doi.org/10.1007/s10854-022-09198-2>

Shilpa, R., & Saratha, R. (2020). Biodegradable pectin- Guar gum blend electrolyte for solid-state lithium-ion batteries. *AIP Conference Proceedings*, 2270. <https://doi.org/10.1063/5.0019432>

Shipla R, PhD thesis, Electrochemical Performance of Composite Solid Biopolymer Electrolytes (Pectin and Guar gum) with Lithium Salts and Disparately Processed NM Cathodes (2021)

Sohaimy, M. I. H., & Isa, M. I. N. (2022). Proton-Conducting Biopolymer Electrolytes Based on Carboxymethyl Cellulose Doped with Ammonium Formate. *Polymers*, 14(15). <https://doi.org/10.3390/polym14153019>

Spinei, M., & Oroian, M. (2022). The Influence of Extraction Conditions on the Yield and Physico-Chemical Parameters of Pectin from Grape Pomace. *Polymers*, 14(7). <https://doi.org/10.3390/polym14071378>

Srinivas, B., Srinivas, B., Sreekanth, T., & Rajesh, S. (2023). *The Structural and Electrical properties of Guar Gum based Green Electrolyte*. <https://doi.org/10.21203/rs.3.rs-2700949/v1>

Suvarna, K., Kirubavathy, S. J., Selvasekarapandian, S., Krishna, M. V., & Ramaswamy, M. (2022). Corn silk extract-based solid-state biopolymer electrolyte and its application to electrochemical storage devices. *Ionics*, 28(4), 1767–1782. <https://doi.org/10.1007/s11581-021-04415-0>

Tamilisai, R., Palanisamy, P. N., Selvasekarapandian, S., & Maheshwari, T. (2021). Sodium alginate incorporated with magnesium nitrate as a novel solid biopolymer electrolyte for magnesium-ion batteries. *Journal of Materials Science: Materials in Electronics*, 32(17), 22270–22285. <https://doi.org/10.1007/s10854-021-06713-9>

Vahini, M., Muthuvinayagam, M., & Isa, M. I. N. (2019). Preparation and Characterization of Biopolymer Electrolytes Based on Pectin and NaNO<sub>3</sub> for Battery Applications. *Polymer Science - Series A*, 61(6), 823–831. <https://doi.org/10.1134/S0965545X19060129>

Vanitha, N., Shanmugapriya, C., Selvasekarapandian, S., Krishna, M. V., & Nandhini, K. (2022). Investigation of N-S-based graphene quantum dot on sodium alginate with ammonium thiocyanate (NH<sub>4</sub>SCN) biopolymer electrolyte for the application of electrochemical devices. *Journal of Materials Science: Materials in Electronics*, 33(18), 14847–14867. <https://doi.org/10.1007/s10854-022-08404-5>

Vanitha, N., Shanmugapriya, C., Selvasekarapandian, S., Naachiyar, R. M., Krishna, M. V., Aafrin Hazaana, S., Nandhini, K., & Ramaswamy, M. (2022). Effect of graphene quantum dot on sodium alginate with ammonium formate (NH<sub>4</sub>HCO<sub>2</sub>) biopolymer electrolytes for the application of electrochemical devices. *Ionics*, 28(6), 2731–2749. <https://doi.org/10.1007/s11581-022-04522-6>

Venkatesh, K., Jenova, I., Karthikeyan, S., Madeswaran, S., Arivanandhan, M., Joice Sheeba, D., & Nithya, S. (2022). Polymer electrolyte based on guar gum and ammonium thiocyanate for proton battery application. *Polymer Bulletin*. <https://doi.org/10.1007/s00289-022-04572-w>

Vijaya, N., Selvasekarapandian, S., Sornalatha, M., Sujithra, K. S., & Monisha, S. (2017). Proton-conducting biopolymer electrolytes based on pectin doped with NH<sub>4</sub>X (X=Cl, Br). *Ionics*, 23(10), 2799–2808. <https://doi.org/10.1007/s11581-016-1852-5>

Wu, P. M., Chung, C. Y., Chen, Y. R., Su, Y. H., Chang-Liao, K. S., Chi, P. W., Paul, T., Chen, Y. J., Chen, Y. L., Wang, S. F., Badgular, P., Chen, B.-N., Cheng, C. L., & Wu, M. K. (2022). Vibrational and electrochemical studies of pectin—a candidate towards environmental friendly lithium-ion battery development. *PNAS Nexus*, 1(4). <https://doi.org/10.1093/pnasnexus/pgac127>