Preparation and characterization of polymer electrolyte based on pectin-lithium nitrate for energy storage devices

By

Candidate

R.Shilpa

REG NO: 15PCH014

A Dissertation submitted to

Avinashilingam Institute for Home science and

Higher Education for Women University

(Estd. u/s 3 of UGC Act 1956)

Coimbatore-641 043, Tamil Nadu, India

In partial fulfilment of the requirement for

the Master's Degree in Chemistry

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Signature of the
Supervisor

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Signature of the
Head of department

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S.No	CONTENTS	Page No
	CHAPTER- I	
1.1	INTRODUCTION	1
1.2	CHARACTERISTICS FEATURES OF FAST IONIC CONDUCTORS	1
1.3	ROLE OF IONIC MATERIALS IN ELECTROCHEMICAL POWER SOURCES	2
1.4	LITHIUM ION BATTERIES	3
1.5	CLASSIFICATION OF POLYMER ELECTROLYTES	4
1.6	SELECTION OF POLYMER AND SALT	7
1.7	ION CONDUCTION IN POLYMER ELECTROLYTES	7
1.8	APPLICATIONS OF FAST IONIC CONDUCTORS	9
	CHAPTER- II	
2.1	INTRODUCTION	10
2.2	REVIEWS BASED ON NATURAL POLYMERS AND LITHIUM SALTS	10
2.3	PRESENT STUDY	21
	CHAPTER- III	
3.1	INTRODUCTION	23
3.2	SOLUTION CAST METHOD	23

3.3	DETAILS OF MATERIALS USED IN THE PRESENT STUDY	26
3.4	FORMATION OF POLYMER - DOPANT COMPLEX	27
3.5	COMPLEX IMPEDANCE SPECTRA	27
	CHAPTER IV	
4.1	INTRODUCTION	29
4.2	AC IMPEDANCE SPECTROSCOPY ANALYSIS	30
4.3	CONDUCTANCE SPECTRA	32
4.4	INFRARED SPETRA	33
4.5	X-RAY DIFFRACTION	36
4.6	FABRICATION AND CHARACTERIZATION OF LITHIUM BATTERY	37

INTRODUCTION

INTRODUCTION

1.1 Introduction

Electrical conduction in solids is attributed to the motion of electrons or ions. Solid materials can be classified into different groups according to the type of charge carriers. In metals, an electric current has been carried by electron. If the conduction is due to ions then the conductor is termed as ionic conductor. The study of these conductors is ‘’**Solid State Ionics’’.** The term solid state ionics has been coined by ‘’Takehiko Takahashi’’ in 1960. If the charge carriers consist of both electrons and ionic motion, they are called as mixed conductors. Generally ionic solids have the conductivity about 10^{-12} Scm^{-1} at room temperature. If the ionic conductivity of the material lies between $10^{-4} – 10^{-1}$ Scm^{-1} they are termed as super ionic conductors or fast ionic conductors.

1.2 Characteristic features of fast ionic conductors

In fast ionic conductors,

i. The bonding is essentially ionic in nature.
ii. The electronic conductivity is low ($<10^{-8}$ S cm^{-1}) in order to avoid the self-damage of the device, thus resulting in a long shelf life.
iii. Good chemical and electrochemical compatibility and good adhesion for mechanical contact with solid electrode materials are observed.
iv. Transport of ions occurs through the favourable conduction pathways across and along particles

1.3 Role of materials in electrochemical power sources

Due to industrialization and modernization there has been a tremendous demand for new efficient power systems through which we can overcome the increasing energy crisis and the threatening global warming. An immediate theme that catches our attention in this context is relaying our power needs on super ionic devices such as batteries, fuel cells, electro chromic display devices, sensors etc., Our special focus is on the indigenous technology development of specific types of lithium ion batteries employing polymer electrolyte.

The research in lithium ion batteries started with G.N Lewis in 1912. Lithium is more suitable material for the fabrication of solid state batteries since it has high electropositive nature than all metals in the periodic table and also it is the lightest of all metals. Hence it easily gives up electrons to form positive lithium [Li+] ions which act as the charge carrier for conduction mechanism. Moreover lithium has high specific capacity, compared to lead-acid, Ni-Cd and Ni-MH batteries.

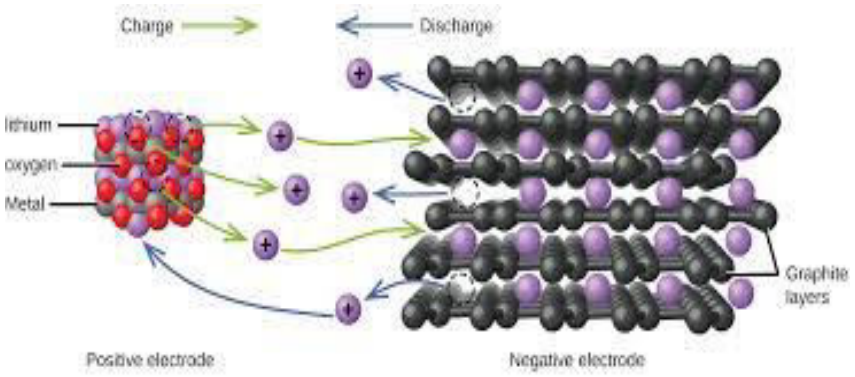
1.4 Lithium ion battery

A battery is a device that stores chemical energy and makes it available in the electrical form. A lithium ion rechargeable battery is based simply on the theory of lithium ion migration. Li-ion battery consists of three major components. They are anode, cathode and an electrolyte. Anode is the electrode where oxidation takes place and the cathode is the electrode where reduction takes place during discharge. Such electrodes are called the intercalation hosts which have the key properties of

(1) Open crystal structures which allow the insertion or extraction of lithium ions

(2) The ability to accept compensating electrons at the same time.

Here electrolyte provides the medium for ion transport between the two electrodes of the cell. Lithiated transition metal oxides like $LiCO_2$, $LiMn_2O_4$, and $LiNiO_2$ serve as cathode materials in conjunction with a hard carbon or graphite anode. During charging lithium is extracted from the cathode and inserted into the carbonaceous anode. The discharge process involves the deinsertion of lithium from the anode and insertion into the cathode material. This process is completely reversible. The back and forth motion of lithium ions between the electrodes gave them the name of ‘’swing’’ or ‘’rocking chair’’ batteries. Schematically it is shown below

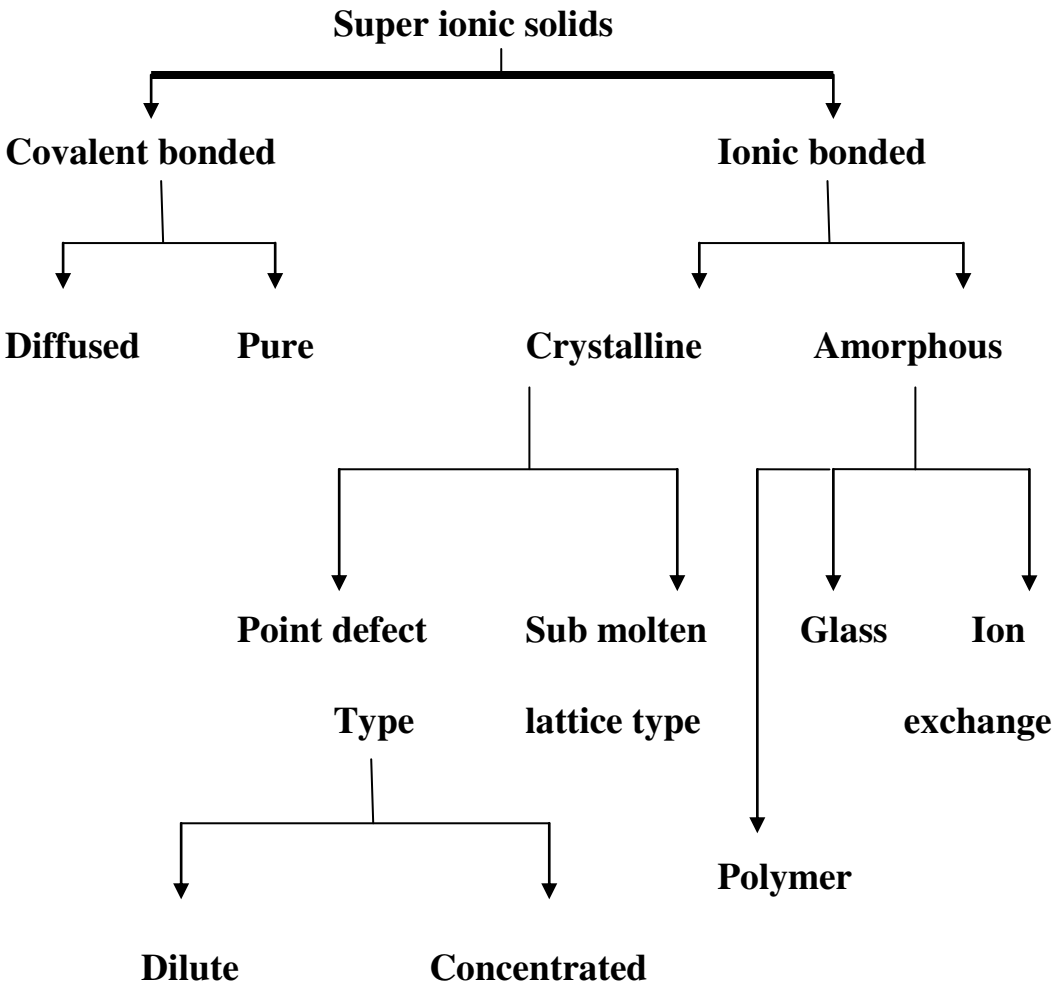


For better performance of the battery the following parameters have to be taken into account

- The cationic conductivity
- Wide electrochemical stability
- Improved safety

So the current witnessing is on polymer electrolytes satisfying the above criteria. The ionic conduction can be induced by doping insulating polymers with ionic salts. The structure and charge transport mechanism for polymer electrolytes greatly differ from those of inorganic solid electrolytes. The polymer host provides easy pattern for diffusion of ions. These polymers may be crystalline or amorphous but both forms exhibit high ionic conductivity.

1.5 Classification of polymer electrolytes



a) Solvent free polymer salt complexes

Solvent free polymer electrolytes have been obtained by dissolving a salt in a high molecular weight of polymer matrix. A large number of ion conducting polymers consisting of monovalent, divalent alkali, transition metal, ammonium salts with anion like ClO_4-, I-, SCN-, CH_3SO_3-, BF_4- etc., and host polymers like poly(ethylene oxide), poly(propylene oxide), poly(ethylene imine), poly(ethylene adipate), etc have been reported. The main disadvantages with most of these conventional polymer electrolyte systems are:

i. High crystallinity (-70%) with very low chain flexibility at room temperature.
ii. Conduction through both cations and anions which is undesirable for device applications.
iii. Tm < 100℃ making the temperature range of operation of these materials limited.

b) Polyelectrolytes

To increase the cationic transference number, researchers have synthesized polymers in which anions are covalently bonded to the polymer backbone. These polymers are called 'polyelectrolytes'. By virtue of the anions being effectively immobilized, all ionic conductivity is due to cationic transport. Nevertheless, such materials are usually not sufficiently flexible and exhibit ambient – temperature conductivities only around or below 10^{-6} S cm^{-1}. In fact, polyelectrolytes have no unique advantage for applications such as batteries. Unlike polymer electrolytes, polyelectrolyte are not susceptible to the bulid-up of potentially resistive layers of high or low salt concentration at the electrode/electrolyte interfaces during charging and discharging. Polystyrene sulphonate and perfluorosulfonated polymers like Nafion belong to this group. The conductivity of these polymers is very low (~10^{-10}-10^{-15} S cm^{-1})

c) Solvent swollen polymers

The solvent swell the basic polymer host and the ionic solute are accommodated in the swollen lattice which permit the ionic motion in solvent rich swollen region of the polymer host. The conductivity of these materials depends on the ambient and the concentration of the solvent in the swollen region. Nafion, PVA-H_3PO_4, PVP-H_3PO_4 are some of the examples of this group.

d) Plasticized electrolytes

The plasticized electrolytes have been obtained by adding small amount of a high dielectric constant solvent to a conducting polymer electrolyte to enhance its conductivity. Normally, Propylene carbonate (PC) and Ethylene carbonate (EC) and sometimes water may be used as plasticizing agent. Poly(acrylonitrile) (PAN),

Poly (vinylidene fluoride) (PVdF), Poly (methylmethaacrylate) (PMMA) have been proposed as frame works for the plasticized polymer electrolytes.

e) Nano composite electrolytes

The nano particulate ceramics or dual-phase block copolymers have been added to the polymer electrolytes and these electrolytes are called as nano composite polymer electrolytes. Introducing ceramic powders (Al_2O_3, SiO_2, ZrO_2, etc.,) with nanometer sized grains to polymer electrolytes may improve mechanical strength, conductivity and interfacial properties.

Examples are Poly (ethylene oxide) PEO-$LiClO_4$-Al_2O_3, PMMA-$LiClO_4$-DMP-CeO_2.

f) Rubbery electrolytes

Rubbery or polymer-in–salt, essentially a liquid electrolyte comprising a low temperature molten salt mixture, reduced to rubbery condition by addition of a small amount of high molecular weight polymer. On a structural level, these electrolytes have some factors in common with gel electrolytes. An example is Poly (acrylonitrile) (PAN) - Lithium (trifluromethylsulphonyl)imide (TFSI).

1.6 Selection of polymer and salt

For effective complexation/salvation of salts in polymers, the following criterion can be taken as 'thump rules'

(1) The polymer should be of low glass transition temperature (Tg) for their flexible backbone, which will ensure the complexation.
(2) The concentration of polar groups (or salvation heteroatoms) responsible for complexation of cations, should be as large as possible.
(3) The lattice energy of the salts should be lower for which, salts of larger atoms such as I-, ClO_4-, CF_3SO_3-, SCN- etc are preferred.

1.7 Ion conduction in polymer electrolytes

In polymer electrolytes the segmental motions are thought to promote ion motion by making and breaking of the co-ordination sphere of the solvated ion and by the electric field. The crystalline polymer salt complexes exhibit inferior conductivity to the amorphous complexes above their T_g (the temperature below which the segments is glassy and brittle and above which it is soft and flexible) where the segments of the polymer are in rapid motion. This indicates the importance of the polymer segmental motion ion transport. The importance of the polymer segmental motion has focused most on amorphous materials with low T_g. The segmental motion occurs in the vicinity of T_g and becomes more rapid above T_g.

Arrhenius theory

The variation of ionic conductivity with temperature can be expressed by Arrhenius equation which is given as

$$\sigma T = \sigma_0 \exp(-E_a/kT)$$

where,

σ_0 is the pre-exponential factor,

E_a is the activation energy &

K is the Boltzmann constant.

The lnσVs 1/T plot is linear for Arrhenius behavior. However sometimes non-linear behaviour is observed for higher temperatures. This non-linearity can be explained by Vogel-Tamman-Fulcher theory.

VTF Theory

Vogel-Tamman-Fulcher (VTF) theory is also known as free volume theory. According to VTF theory, the ion transport mechanism in the polymer electrolyte results from the segmental motions. This process promotes ion movement through the formation and destruction of a co-ordinating sphere of the solvated ion, thereby, creating a free volume into which the ion can diffuse under the influence of electric field. The conductivity is calculated using VTF equation as follows

$$\sigma = \sigma_0/T_1/2 \exp\,[-B/k(T-T_0)]$$

where,

σ_0 is the exponential factor

B is the pseudo activation energy

T is the absolute temperature

T is the thermodynamic glass transition temperature &

k is the Boltzmann constant

1.8 Applications of fast ionic conductors

I. Fuel Cells

Batteries and fuel cells are both electrochemical devices that have high efficiency. A battery stores its energy in its electrodes. Electricity is released as the electrodes are consumed. In contrast fuel cells produce electricity using fuel from an external tank. It can operate continuously as long as fuel is supplied and the tank can be quickly refueled, avoiding a time consuming recharging process. Chemically, a fuel cell takes in hydrogen and air, creates electricity and produces by products of water and heat. Hence fuel cell is pollution free.

II. Electrochromic display devices

These devices are based on colour changes of certain kind of materials due to electrochemical reduction and oxidation. This phenomenon which can be produced by the application of an electric field is called electrochromism. Organic compounds like dipthalocyanin complexes containing lanthanide elements or polythiophene exhibits electrochromism.

III. Electrochemical sensors

The electrochemical sensors generally contain a physical transducer and a chemically selective layer. These sensors act as a transducer for detecting elements and provide vital information about the specific chemical constituents in the environment. Biosensors, chemical sensors, ion selective sensors are few of its types. In these, polymer electrolytes, have gained an extremely wide application in the field of sensors because they are

- Relatively low cost material and
- Their fabrication technique is simple.

REVIEW OF LITERATURE

Literature review

2.1 Introduction

The purpose of a literature review is

- To establish a theoretical framework for the topic / subject area
- To define key terms, definitions and terminology
- To identify studies, models, case studies etc., supporting the topic
- To define / establish your area of study, ie the research topic.

2.2 Reviews Based On Natural Polymers and Lithium Salts

Earlier literature regarding the natural polymers and lithium salts are given below

T.M. Di Palma,*et al*., (2017) Xanthan and κ-carrageenan were used to prepare alkaline hydrogels to be used as electrolytes in aluminium air primary batteries. Two pasty gels were obtained starting from xanthan and KOH solutions (1 M and 8 M), while only the 8 M KOH solution permitted the formation of a stable, elastic and gumminess hydrogel with κ-carrageenan.

Weisheng He,*et al.,* (2017) investigated that the classic poly(ethylene oxide) (PEO) based solid polymer electrolyte suffers from poor ionic conductivity of ambient temperature, low lithium ion transference number and relatively narrow electrochemical window (<4.0 V vs. Li^+/Li). Herein, the carbonate-linked PEO solid polymer such as poly(diethylene glycol carbonate) (PDEC) and poly(triethylene glycol carbonate) (PTEC) were explored to find out the feasibility of resolving above issues.

Hongli Zhu,*et al.,* (2017) found cellulose is the most abundant renewable material in nature. In this work, ordered cellulose nanocrystals (CNCs) have been transformed into porous carbon with an increased short-range ordered lattice and percolated carbon nano fiber at a relatively low carbonization temperature of 1000 °C. When evaluated as anode for sodium-ion batteries (SIBs), the CNC derived porous carbon shows superior performances including a high reversible capacity of 340 mA h/g at a current density of 100 mA/g, which is one of the highest capacity carbon anodes for SIBs

Aqdas Noreen,*et al.,*(2017) reported Pectins are natural complex heteropolysaccharides, composed of (1, 4)-linked α-d-galacturonic acid residues and variety of neutral sugars such as rhamnose, galactose and arabinose. It is second most abundant component of the cell wall of all land plants. It has wide applications in various fields due to its use as gelling, emulsifying or stabilizing agent and as well as its non-toxic, biocompatible and biodegradable nature.

GabrijelaHorvat, *et al.,*(2017) developed a novel high methoxyl pectin–xanthan aerogel coating on medical-grade stainless steel, prepared by ethanol-induced gelation and subsequent supercritical drying. Two non-steroidal anti-inflammatory drugs, *i.e.*diclofenac sodium and indomethacin, were incorporated into the aerogel coating. Electrochemical analyses were performed on the coated samples using electrochemical impedance spectroscopy and cyclic polarization techniques.

Aleksandra Nesic, *et al.,* (2017) prepared pectin based films including different amounts of sodium alginate by casting method. All the films, with and without polyglycerol as plasticizer, were crosslinked with zinc ions in order to extend their potential functionality. The development of junction points, occurring during the crosslinking process with zinc ions, induced the increasing of free volume with following changing in chemico-physical properties of films.

Reza Younesi, *et al.,*(2017) found presently lithium hexafluorophosphate ($LiPF_6$) is the dominant Li-salt used in commercial rechargeable lithium-ion batteries (LIBs) based on a graphite anode and a 3–4 V cathode material. While $LiPF_6$ is not the ideal Li-salt for every important electrolyte property, it has a uniquely suitable combination of properties (temperature range, passivation, conductivity, etc.) rendering it the overall best Li-salt for LIBs. However, this may not necessarily be true for other types of Li-based batteries.

Qi Li,*et al.,* (2016) reported that owing to almost unmatched volumetric energy density, Li-based batteries have dominated the portable electronic industry for the past 20 years. Not only will that continue, but they are also now powering plug-in hybrid electric vehicles and zero-emission vehicles. There is impressive progress in the exploration of electrode materials for lithium-based batteries because the electrodes (mainly the cathode) are the limiting factors in terms of overall capacity inside a battery.

FarhadMohazabrad, *et al.,* (2016) reported developing batteries with high specific capacity and power density is essential in many applications such as electric vehicles and portable electronic devices. The Li-oxygen battery has a very high theoretical energy density of 11 kWh kg^{-1} and is considered as a promising battery technology. The concentration of the lithium ion in battery electrolyte is typically 1 M in both Li-ion and Li-oxygen batteries. Considering the high cost of the lithium salt and low current rates of Li-oxygen battery, this study investigated effects of salt concentration (LiPF6 in Tetraethylene glycol dimethyl ether) on battery performance through experiments and model simulations.

Jianhui Wang, *et al*, (2016) found a viable electrolyte for next-generation 5 V-class lithium-ion batteries is of primary importance. A long-standing obstacle has been metal-ion dissolution at high voltages. The L_{iPF6} salt in conventional electrolytes is chemically unstable, which accelerates transition metal dissolution of the electrode material, yet beneficially suppresses oxidative dissolution of the aluminium current collector; replacing L_{iPF6} with more stable lithium salts may diminish transition metal dissolution but unfortunately encounters severe aluminium oxidation.

AlexandruSonoc, *et al.,* (2015) determineda high recovery of lithium from recycled lithium ion batteries (LIBs) is essential to ensure the growth and sustainability of the electrical vehicle market. Without recycling, lithium demand is predicted to outstrip supply in 2023. Current industrial processes are focused on recovering cobalt and other valuable metals because, given lithium's current low price, it is economically unfavorable to recover it. As part of our efforts to create a process where the recovery of lithium is economically viable we have analyzed the current industrial processes.They have determined that, when applied to recycling automotive LIBs, they are needlessly energy intensive and complicated.

Francesca Colo, *et al.,* (2015) reported in the present work, a novel pyranose ring laden polymer electrolyte is proposed for all solid Na-ion secondary cells that can operate at moderate temperatures. The prepared fully solid polymer electrolyte film is based on a classic polyethylene oxide (PEO) backbone, homogeneously blended with sodium carboxymethyl cellulose (Na-CMC) and sodium perchlorate. The favourable use of Na-CMC as electrode binder as well as electrolyte additive is evaluated, which would enhance the pathways for forming an optimised electrode/electrolyte interface.

K. Padhi, *et al.,* (2015) reported reversible extraction of lithium from (triphylite) and insertion of lithium into at 3.5 V vs. lithium at 0.05 mA/cm^2 shows this material to be an excellent candidate for the cathode of a low-power, rechargeable lithium battery that is inexpensive, nontoxic, and environmentally benign. Electrochemical extraction was limited to ~0.6 Li/formula unit; but even with this restriction the specific capacity is 100 to 110 mAh/g.

Boor Singh Lalia, *et al.,* (2014) investigated on cellulose which is the main building block of plant's cell wall that provides structural stability. This idea inspired us to use modified cellulose (Networked cellulose) to provide thermal and mechanical stability to a polymer electrolyte system. The system composed of polyethylene glycol (PEG) (or tetraethylene glycol dimethyl ether (TEGDME)), polyethylene oxide (PEO), networked cellulose (NC) and $LiCl_{O4}$ as a salt.

Xinxin Jiang, *et al.,* (2014) proved copper nitrate hydrate ($Cu(NO_3)_2 \cdot 2.5H_2O$) exhibits superior high lithium storage capacity (2285 mAh g^{-1}) as anode material for lithium-ion batteries. The structural transformation and lithium storage mechanism of $Cu(NO_3)_2 \cdot 2.5H_2O$ are thoroughly studied by various advanced analytical techniques. It is found that the lithium storage process of $Cu(NO_3)_2 \cdot 2.5H_2O$ is associated with a quasi-reversible electrochemical conversion reaction.

NurUmiraTaib,*et al.,* (2014) synthesized solid polymer electrolytes consisting of chitosan, lithium bis (trifluoromethylsulfonyl) imide (LiTFSI) as a salt and succinonitrile as a plastic crystal are prepared by using the solution casting method. Electrochemical impedance spectroscopy is used to examine the ionic conductivity of the films at the temperature range of 303–383 K. Chitosan–LiTFSI containing 50 wt% succinonitrile exhibits high ionic conductivity at a room temperature of 0.4×10^{-3} S cm^{-1}, a high lithium ion transference number (0.598) and wide electrochemical window.

Lili Chai, *et al.,* (2013) investigated when chitosan was applied as the electrode binder material for a spherical graphite anode in lithium-ion batteries. Compared to using poly (vinylidene fluoride) (PVDF) binder, the graphite anode using chitosan exhibited enhanced electrochemical performances in terms of the first Columbic efficiency, rate capability and cycling behavior. With similar specific capacity, the first Columbic efficiency of the chitosan-based anode is 95.4% compared to 89.3% of the PVDF-based anode.

Yuki Yamada, *et al.,*(2013) reported a major unsolved problem with rechargeable Li/O2 batteries is the identification of electrolyte compositions that allow efficient and stable cycling of both Li metal and O2 electrodes simultaneously. Previously, lithium nitrate (LiNO3) was employed in a rechargeable Li/O2 battery to stabilize the solid−electrolyte interphase on Li metal in an electrolyte based on N,N-dimethylacetamide (DMA), a solvent with favorable properties vis-a-vis the O` 2 electrode.

Renáta Orinakova, *et al.,*(2013) found rechargeable lithium-ion batteries (LIBs) have been the most commonly used batteries in the portable electronics market for many years. Polypyrrole (PPy) was now investigated as a conducting addition agent to enhance the cathode and anode materials performance in LIBs. Actual development in the synthesis and modification of the most promising cathode materials, $LiFeP_{O4}$, is described in this mini-review.

John B. Goodenough, *et al.,* (2013) found each cell of a battery stores electrical energy as chemical energy in two electrodes, a reductant (anode) and an oxidant (cathode), separated by an electrolyte that transfers the ionic component of the chemical reaction inside the cell and forces the electronic component outside the battery. The output on discharge is an external electronic current I at a voltage V for a time Δt.

Paolone*, et al.,* (2012) reported the Young's modulus and the elastic energy dissipation of polyethylene oxide (PEO)-based lithium battery electrolyte membranes have been studied in this work. The membranes, formed by pure PEO and doped by $LiCF_{3}S_{O3}$, $L_{i2}S$ and Zr_{O2}, were studied within a 90 K - 400 K temperature range. We observed the glass transition around 230 K and the first-order phase transformation from the crystalline to the amorphous phase around 330 K on heating.

Armstrong, *et al.,* (2011) found the importance of exploring new low-cost and safe cathodes for large-scale lithium batteries has led to increasing interest in Li2FeSiO4. The structure of Li2FeSiO4 undergoes significant change on cycling, from the prepared s form to an inverse II polymorph; therefore it is important to establish the structure of the cycled material. In s half the LiO4, FeO4, and SiO4 tetrahedral point in opposite directions in an ordered manner and exhibit extensive edge sharing. Transformation to the inverse II polymorph on cycling involves inversion of half the SiO4, FeO4, and LiO4 tetrahedral, such that they all now point in the same direction, eliminating edge sharing between cation sites and flattening the oxygen layers. As a result of the structural changes, Li+ transport paths and corresponding Li-Li separations in the cycled structure are quite different from the prepared material

Haiyan Sun, *et al.,* (2009) reported the fabrication of binder-free anodes for lithium-ion batteries (LIBs) based on graphenenanoflakes on-demand designed and produced by liquid phase exfoliation of graphite. A solvent exchange process is exploited to first remove the N-methyl-2-pyrrolidone used for the exfoliation of graphite and then to re-disperse the exfoliated single-(SLG) and few-layer (FLG) graphene flakes, at a high concentration ($\sim$5 g L^{-1}), in an environmentally friendly solvent, i.e., ethanol.

Li Zhi Zhan,*et al.,* (2008) synthesized a novel thiolane polymer, poly[1,2,4,5-tetrakis(propylthio)benzene] (PTPB), by facile oxidative-coupling polymerization, characterized by FT-IR, XPS, XRD, TGA and EA, and tested as cathode active material in rechargeable lithium batteries. The FT-IR, XPS and elemental analysis confirm the occurrence of polymerization and show the existence of C–S–C bonds. The results show that the thiolane polymer has electrochemical activity as cathode material in lithium batteries and thioether bonds may be the centers of the electrode reaction.

C. Gerbaldi, *et al.,*(2008) synthesized a novel methacrylic gel-polymer membrane by free radical photo polymerisation (UV-curing technique). The polymerisation was very easy, fast and reliable and the membrane shows good behaviour in terms of both conductivity and cyclability in Li cells. The anode materials were prepared by high energy ball milling obtaining nanocrystalline Ni–Sn alloys.

V.Z. Barsukov, *et al.,*(2006) The mechanisms and reasons of catalytic activity of polyaniline (PANI)-type conducting polymers toward oxygen reduction in acidic and saline solutions are investigated by electrochemical and quantum-chemical methods. The PANI/thermally expanded graphite compositions were developed for realization of fully functional air gas-diffusion electrodes. Principally new concept for creation of rechargeable metal-air batteries with such type of catalysts is proposed.

RotemMarom, *et al.,*(2001) presented herein is a discussion of the forefront in research and development of advanced electrode materials and electrolyte solutions for the next generation of lithium ion batteries. The main challenge of the field today is in meeting the demands necessary to make the electric vehicle fully commercially viable. This requires high energy and power densities with no compromise in safety. Three families of advanced cathode materials (the limiting factor for energy density in the Li battery systems) are discussed in detail.

Takeshi Ogasawara, *et al.,* (2001) reported that the rechargeable lithium batteries represent one of the most important developments in energy storage for 100 years, with the potential to address the key problem of global warming. However, their ability to store energy is limited by the quantity of lithium that may be removed from and reinserted into the positive intercalation electrode, Li_xCoO_2, 0.5 <x<1 (corresponding to 140 mA·h g^{-1} of charge storage). Abandoning the intercalation electrode and allowing Li to react directly with O_2 from the air at a porous electrode increases the theoretical charge storage by a remarkable 5−10 times

Lithium ion conductingpolymer electrolyte	**Device/ property studied**	**Conductivity (Scm^{-1})**	**References**
PVA: PAN: $LiBF_4$	Gel electrolytes for lithium ion batteries	10^{-3}	[Fabio A et al., (2007)]
PAN: $LiPF_6$: EC: DMC	Lithium ion cell	$1*10^{-3}$	[Dong-Won et al., (2002)]
PAN:$CF_3SO_3LI/(CF_3SO_3)_2Mg$: EC: PC	GPE: electro chemical double layer capacitor	10^{-3}	[S.Mithra et al., (2001)]
PAN: PC: $LiClO_4$	TiO2 Photo electro chemical cell	$4.2*10^{-4}$	[Rika Taslim et al., (2010)]

PVA: $LiCF_3SO_3$	-	10^{-4}	[Malathi J et al., (2010)]
PVA; PvdF: $LiCF_3SO_3$	Battery	$3.9*10^{-4}$	[P.Tamilselvi et al., (2014)]
PVP: PEO: $LiClO_4$	-	10^{-7}	[Young – Wook Park et al., (2005)
PVP: $LiClO_4$	NMR & FTIR studies	-	[Hew – Der Wu et al., (2001)]
PVA: PVP: LiBr	Structural, optical, thermal and electrical	$1.0061* 10^{-10}$	[Abdelrazek et al., (2010)]
P(ECHO-EO): $LiClO_4$: PEGM	-	$3.41*10^{-3}$	[S Kohjiya et al., (2000)]
PVS/PvdF: $LiN(CF_3SO_2)_2$/EC/C	Electrochemically stable up to 4.5 – 4.8 V	$\sim10^{-3}$ at 30^0C	[M.S.Choe (2000)]
PvdF: $LiCF_3SO_3$/ DMF	Pfg- NMR	-	[M.J.Williamson (1999)]
PAN: PVA/ $LiClO_4$, $LiBF_4$ copolymer	-	10^{-3} (RT)	[Fabio et al., (2007)]
PEO/PAN: $LiClO_4$: EC: Al_2O_3	-	$7.2*10^{-5}$	[Mingyeong Kim et al., (2013)]
PvdF: $LiC(CF_3SO_2)_3$/PC/DMF	AC impedance, 7Li NMR	$3* 10^{-4}$ at 25^0C	[F.Croce (1996)]
PAO:$LiClO_4$:ϒBL	-	10^{-3}	[Yoshiru Matsuda et al., (2003)]
PMMA: $LiN(CF_3SO_3)$: PC	-	10^{-4}	[Y Alias et al., (2005)]
PvdF: $LiBF_4$ in propylene carbonate (PC)	Electrochemical	10^{-4} at 30^0c	[Thierry Michot (2000)]
OUM/PPM 55: $LiBF_4$: $LiClO_4$: ϒBL	-	$\sim10^{-3}$	[O V Yarmolenko et al., (2003)]

PvdF: EC/PC/DMA/hydroxyl carboxylic acids	Ionic conductivity	10^{-4} at 20^0C	[S.S.Sekhon (2002)]
PMMA/PvdF: $LiCF_3SO_3$/ DMP	Electrochemical	0.914* 10-^{3} at 30^0C	[Rajendran (2007)]
PMMA: $LiN(CF_3SO_2)_2$: PC	-	$3.41*10^{-3}$	[Jacub Reiter et al., (2008)]
PvdF: $LiPF_6$, EC/DMC/DEC(1/1/1 weight)	Electrochemical/ Li-ion polymer battery	$1* 10^{-3}$ at 30^0C	[Jeong Rae Kim (2004)]
PvdF-co-HFP/PVK: EC/$LiBF_4$	Electrochemical/ Li battery	$0.7* 10^{-3}$ at 30^0C	[M.S.Micheal (2004)]
PvdF:: PEMA: ECD: PC	-	$1.5*10^{-3}$	[M Sivakumar et al., (2007)]
PVC: PAN: $LiClO_4$: PC	-	$8.35*10^{-3}$	[S Rajendran, Ravi Shankar et al., (2007)]
PvdF-co-HFP: $LiPF_6$(1M) in EC/DMC/DEC	Conductivity	$4* 10^{-3}$	[H.Huang (2001)]
PMMA: $LiPF_6$/EC/DEC	Electrochemical performance	$5.8* 10^{-3}$ at 20^0C	[H.S.Kim (2003)]
PMMA: $LiClO_4$/DMP/CeO_2	FTIR, AC Impedance spectroscopy	$0.5* 10^{-4}$ at 30^0C	[S.Rajendran (2002)]
PAN: $LiClO_4$: EC	-	$9.12*10^{-3}$	[Huang Hong et al., (1992)]
PVC/PMMA: EC/DMC/$LiClO_4$	Plastic Li ion battery	$1.1* 10^{-3}$ at 30^0C	[Nam-Soon Choi et al., (2001)]
PMMA: PC/$LiClO_4$	ECW	$2.3* 10^{-3}$ at 25^0C	[Bohnke et al., (1993)]

PMMA: PC/EC/LiN[$CF_3(SO_2)_2$]	Conductivity	7* 10^{-4} at 25^0C	[Scrosati (1994)]
PPO: LiTFSI: ϒBL	-	10^{-3}	[P AttricJannasch et al., (2001)]
PVAC: PMMA: LiClO4	-	1.76*10^{-3}	[R Baskaran et al., (2006)]
PMMA: $LiCF_2SO_2$/EC/PC	Conductivity	5.5* 10^{-3} at 30^0C	[Sekhon et al., (1998)]
PMMA: EC/PC/$LiASF_6$	Conductivity	8* 10^{-4} at 25^0C	[Scrosati (1994)]
PVA: $LiFePO_4$	-	10^{-5}	[Mohan et al., (2010)]
PVC/PMMA: $LiAsF_6$/DBP	Ionic conductivity	4.6* 10^{-6} at 30^0C	[S.Rajendran (2000)]
P(AN-CO-VEC): EVA: $LiCF_3SO_3$	-	6*10^{-3}	[Xinglan Huang et al., (2012)]
PVA: $LiCF_3SO_3$	-	10^{-4}	[Malathi et al., (2010)]
PMMA: $LiClO_4$/Dclay/EC	Composite PE	6* 10^{-4} at 30^0C	[H.W.Chen (2002)]
PMMA/ PvdF: $LiClO_4$: DMP	-	4.2*10^{-3}	[S Rajendran et al., (2002)]

2.3 Present study

In the present study, the biopolymer pectin is choosen since it is rarely used in battery applications. Pectin, a naturally available material, is a polysaccharide that is largely present in the cell wall of plants. Pectins, also known as pectic polysaccharides, are rich in galacturonic acid. Homogalacturonan is a linear chain of 1,4-linked α-Dgalactopyranosyluronic acid residues, in which some of the carboxyl groups are methyl esterified [Ridley BL (2001)]. At present, apple pomace and citrus peels are the main sources of commercially acceptable pectin. The commercial pectin usually has an esterification degree (DE) of 50 %, which gives the mark for commercial pectin classification as high (HM) and low (LM) methoxilated. It is mainly used as a gelling agent, thickening agent, and stabilizer in food industries. Pectin has unique gel-forming ability in presence of divalent cations, which makes it an ideal carrier for delivering bioactive agent. Pectin has been grafted with poly (Nisopropylacrylamide) and studied as a potential carrier for colon-targeted drug delivery of theophylline. [Mishra R. K et al. (2012)] developed novel polymer blend films based on pectin/PVP and pectin/gelatin for their respective applications in controlled drug delivery and wound-dressing applications.

A great deal of research is focused on using microencapsulation technology for drug encapsulation and drug delivery. Perera et al. developed pectin-4-aminothiophinole (ATP) conjugate microparticles for colon-specific drug delivery. Polysaccharides have recently been investigated for preparation of nanoparticles because of their excellent physicochemical properties and biocompatible nature which is beneficial for biomedical use. In a recent research, Coimbra etal.prepared pectin/chitosan polyelectrolyte complex scaffolds and Munarin et al. investigated pectin-based injectable biomaterials for possible bone tissue engineering applications.

Pectin has special place among available polysaccharides due to their biodegradable and non-toxic nature.

Hence, it has been selected as host polymer. The literature survey reveals that the polymer electrolytes based on pectin doped with inorganic salts/acids are scanty. The ionic conductivity of the plasticized pectin-based gel electrolytesprepared with glycerol and LiClO4 is found to be 4.7 × 10−4 S cm−1 at room temperature for the sample with 68 wt.% of glycerol by Andrade et al. Vijaya et al. have reported that the maximum ionic conductivity of pectin doped with NH4SCN at room temperature is 4.505 × 10−4 S cm−1 for 50 mol% pectin-50 mol% NH4SCN in the concentration range studied. In this work, ammonium salts are selected as doping salts because they are known to be good proton donors. The present work aims at developing new Lithium-ion conducting polymer electrolyte membranes based on the biopolymer pectin as host polymer matrix and lithium nitrate as doping salts. The prepared membranes are investigated using XRD, FTIR, and AC impedance techniques for their complexation behavior, nature (crystalline/amorphous), and electrical properties and characterized using AC impedance spectroscopy technique in the frequency ranging from 42Hz-1MHz.

MATERIALS AND METHODS

EXPERIMENTAL TECHNIQUES

3.1 Introduction

The host polymer Pectin has been doped with ionic dopant Lithium nitrate in order to prepare an ion conducting polymer electrolyte. The ionic dopant provides the mobile charges in the polymer matrix. The polymer electrolytes, Pectin has been prepared by solution cast technique with different salt concentrations. The solution cast method attracts more interest because of its easy preparation and suitability for mass production. Electrical characterization of the prepared polymer films has been performed using AC impedance technique. X-ray diffraction patterns exhibited by the electrolyte films were recorded at room temperature on a Philips X'Pert PRO diffractometer using CuKα radiation in the range of $2\theta = 10°–90°$. The electrolyte films were subjected to FTIR measurements using a Shimadzu-IRAffinity-1 spectrophotometer in the frequency range of 400–4000 cm−1 at room temperature. The prepared electrolyte films were sandwiched between two aluminum blocking electrodes, and impedance measurements were carried out in the frequency range of 42 Hz to 1 MHz at room temperature using HIOKI 3532–50 LCR HiTester.

3.2 Solution cast method

Polymer electrolytes have been prepared by complexing the salt (MX) having low lattice energy with polymers. Among the various methods of electrolyte preparation, solution cast method is one of the good techniques used worldwide due to its ease of preparation. A suitable amount of host polymer Pectin and salt, $LiNO_3$ have been dissolved separately in deionized water and these solutions have been mixed together and stirred well to obtain a homogeneous mixture. The mixtures have then been poured on to apetri dishes and evaporated slowly at room temperature. The smooth, uniform thin films which are transparent to visible light with have been obtained. Then the final product has been vacuum dried.

Preparation of the polymer electrolyte

Fig.1 The preparation method of different compositions of Pectin-LiNO3 polymer electrolyte

The schematic illustration of the preparation procedure of the polymer electrolyte film is shown in figure. 2

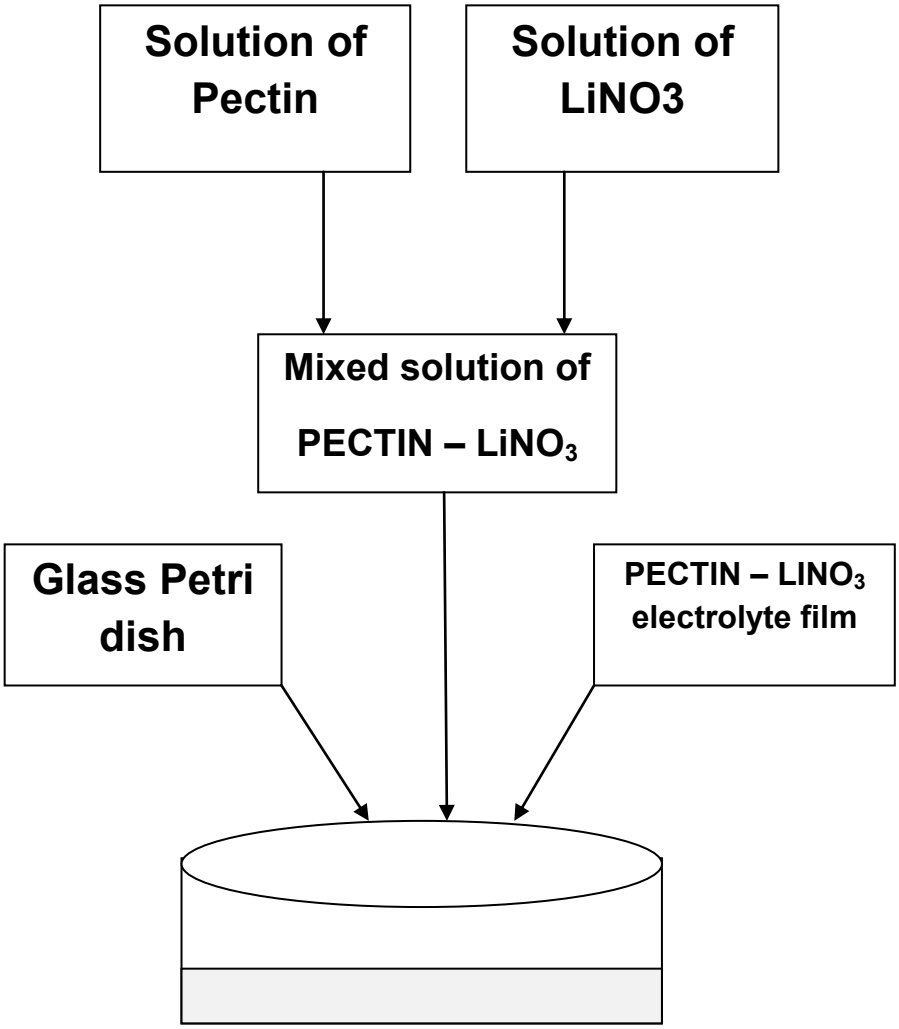
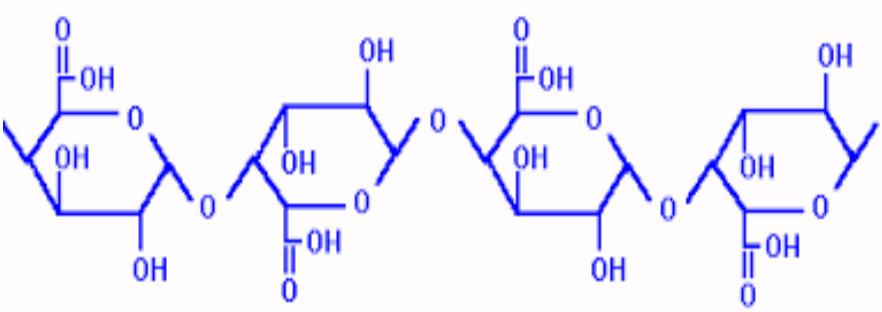


Fig2. Schematic illustrations of the preparation of the polymer electrolyte film (MX-Lithium nitrate)

3.3Details of materials used in the present study

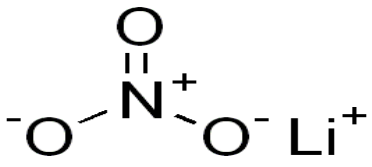
Structure of polymer

Host Polymer	:	Pectin
Molecular formula	:	$C_6H_{10}O_7$
Average Molecular Weight	:	194.1 kg/mol
State	:	White Powder
Solvent	:	Water



Structure of Ionic dopant

Ionic dopant	:	Lithium nitrate
Molecular weight	:	68.946 g/mol
State	:	Colorless, granules
Solvent	:	Deionised water



3.4 Formation of polymer – Dopant complex

When the ionic dopant is dissolved in the solvent, the dopant is dissociated into cation and anion. The dissociated salt is again dissolved in the polymer matrix. This mixture is then allowed to evaporate to eliminate the excess solvent and thin polymer electrolyte film has been formed. There are two energetically significant stages for the electrolyte formation. First, the ionic dopant has been dissociated into cation and anion by the process of dissolution. Then the dissociated salt is mixed with host polymer to obtain the polymer complex. In the case of polymer salt complex (Pectin-MX) cation coordinates with lone pairs of electrons on the oxygen in the polymer chain. The anion remains in close proximity to preserve local charge neutrality.

3.5 Complex impedance spectra

It is a relatively powerful method of characterizing many of the electrical properties of material and their interfaces with electronically conducting electrodes. It is used to investigate the dynamics of bound or mobile charges in the bulk or interfacial regions of any kind of solid or liquid material, ionic, semiconducting, mixed electronic-ionic and even insulators (dielectrics). In general electrical characterization can be done by dc and ac measurement techniques though the dc measurement technique is straight forward it cannot be implemented for solid electrolyte for the following reasons (i) as the dc field is applied to the electrolyte, the material gets polarized and ionic conductivity ceases. Therefore for solid electrolyte ac measurement of electrical conductivity is done to avoid polarization of the sample. The electrical conductivity measurements can be done in the following ways

1) Sample with non-blocking/reversible electrodes
2) Sample with blocking electrode

In the present study the electrical conductivity measurements were done with the help of blocking electrodes. The corresponding impedance plots have an additional low frequency dispersion region. In the low frequency region, polarization at the electrode electrolyte interface due to the double layer capacitance (Cdl) becomes dominant. The general approach is to apply an electrical stimulus (a known voltage or current) to the electrodes and observe the response (the resulting current or voltage). The most commonly used method is the impedance spectroscopy, i.e. to measure Impedance directly in the frequency domain by applying a single frequency voltage to the interface and measuring the phase shift and amplitude or real and imaginary parts of the resulting current at the frequency.

The most attractive aspects of impedance spectroscopy are

- It involves relatively simple electrical measurements that can readily be automated.
- The results can often be correlated with material variables such as composition, microstructure, defects, dielectric properties, chemical reactions etc.,

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

4.1 Introduction

In the recent years, there has been a tremendous interest in the preparation of polymer electrolytes with high ionic conductivity, good mechanical strength and thermal stabilities because these polymer electrolytes play a major role not only in lithium polymer/lithium ion batteries but, also in other electrochemical devices such as super capacitors, electrochromic devices etc. among the various types of polymer electrolyte systems used in lithium polymer batteries, solid polymer electrolyte systems used in lithium polymer batteries, solid polymer electrolytes (SPEs) have many advantages such as high ionic conductivity, high energy density, leak proof, solvent-free condition, wide electrochemical stability windows, easy process ability and light weight.

Lithium bis(trifluoromethanesulphone)imide, $LiN(SO_2CF_3)_2$, (LiTFSI) and $LiCLO_4$ are of a new family of bulky lithium salts which have great charge delocalization favorable to ionic dissociation in a solvating polymer such as poly(ethylene oxide) (PEO), good chemical, electrochemical and thermal stabilities and also a "plasticizing" effect which decreases the crystallinity of the host polymer and hence higher ionic mobility. In the present study Pectin: $LiClO_4$ polymer electrolytes for different composition have been prepared by solution cast technique and characterized by ac impedance spectroscopy technique. The results are presented and discussed in this chapter.

4.2 AC IMPEDANCE SPECTROSCOPY ANALYSIS

The typical impedance plots (Z' VS Z") for the polymer electrolyte Pectin:LiNO3 of different composition for 85% Pectin:15mol%LiNO3 are shown in fig 4.1 and fig 4.2 respectively. The complex impedance diagram shows two well defined regions a chord in the high frequency range which is related to conduction process in the bulk of the electrolytes and the linear region in the low frequency range can be attributed to the effect of blocking electrodes. At low frequency, the complex plot shows a straight line parallel to the imaginary axis, but the double layer at the blocking electrode causes the curvature. The disappearance of the chord portion in the complex impedance plot of 30mol% Pectin: 70mol%LiNO3 illustrate that the total conductivity is mainly the result of the ionic conduction.

It has been noted that the semi-circle at higher frequencies completely disappears when the temperature increases. This is because when the temperature is increased, only the resistive component of the polymer electrolyte prevails and the capacitive nature disappears at higher temperatures because of random orientations of dipoles in the side chains. In this case the migration of ions may occur through the free volume of polymer matrix

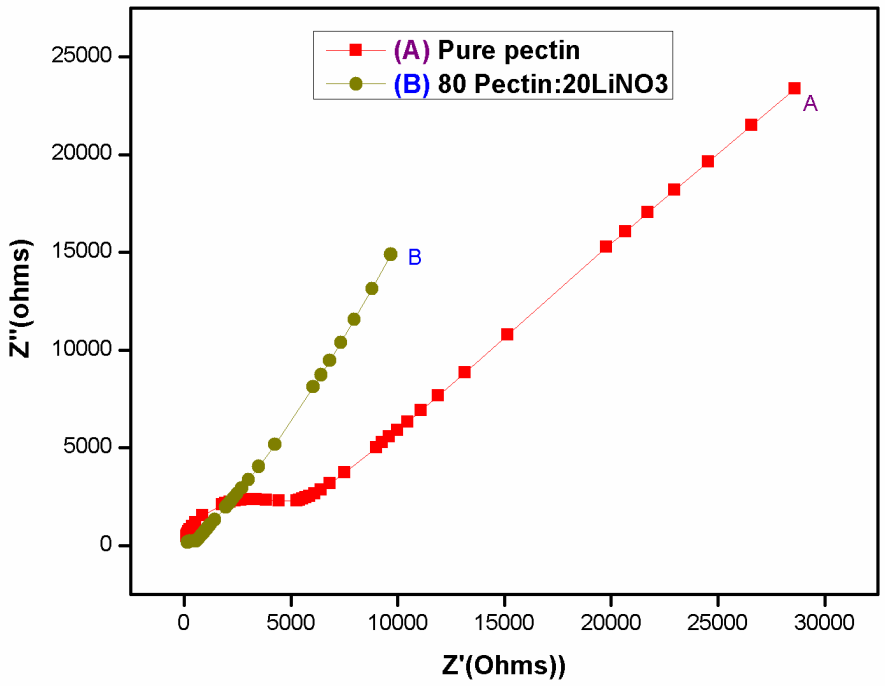
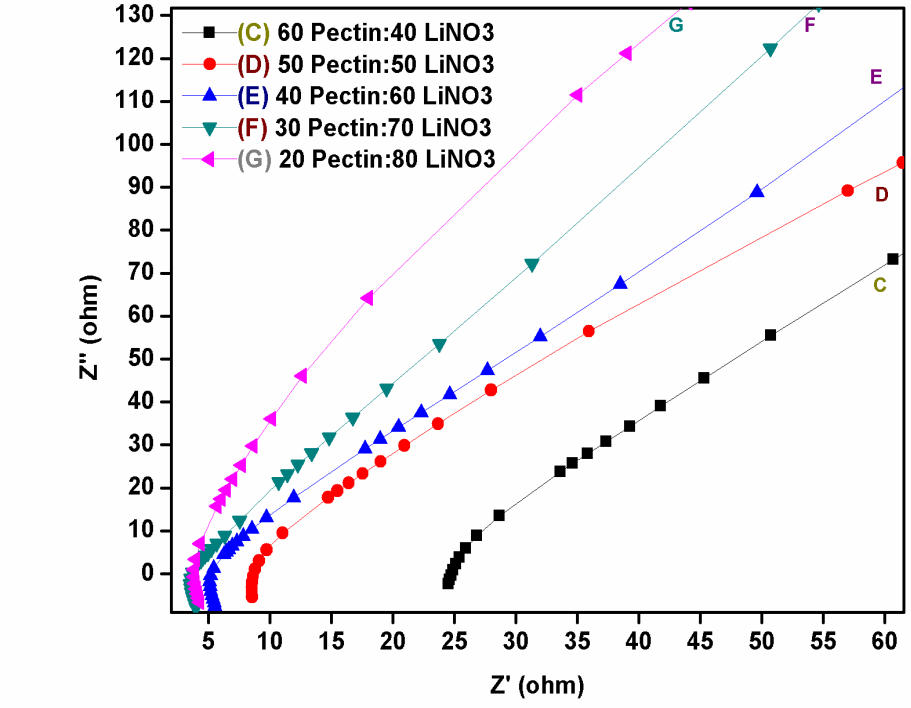


Fig 4.1 Impedance plot of two different compositions of Pectin : $LiNO_3$ polymer electrolyte



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g 4.2 Impedance spectra of Pectin and $LiNO_3$ at various compositions

4.3 Conductance spectra analysis

The conductance spectra of Pectin – LiNO3 with different concentrations are shown below in the figure 4.3. the plot shows three regions. The first one is low frequency dispersion region which is due to the space charge polarization at the blocking electrodes. The second region corresponds to the frequency independent plateau region and the explanation of the plateau region to zero frequency gives the value of dc conductivity. The final high frequency region corresponds to bulk relaxation phenomenon.

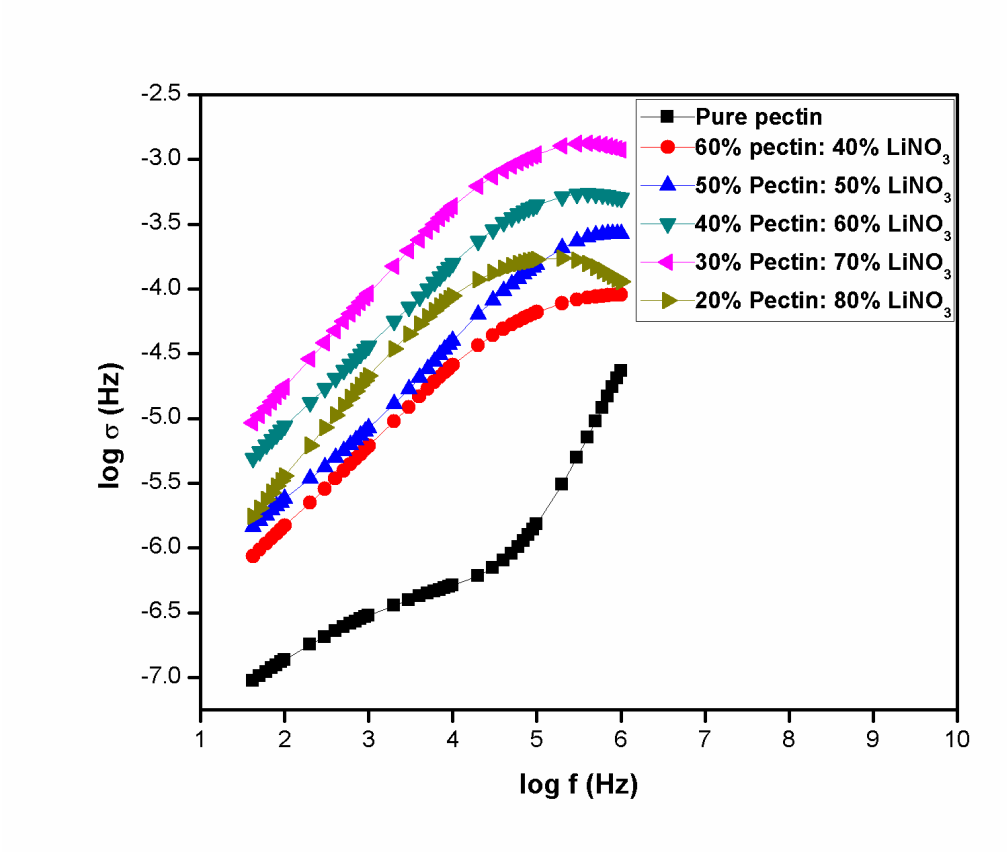


Fig 4.3 Conductance spectra of the Pectin-LiNO3 polymer electrolyte

4.4 FTIR Spectroscopic analysis

Fourier Transform Infrared Analysis

FTIR spectroscopy is a powerful technique for characterizing organic molecules as it is sensitive to functional groups such as hydroxyls, carboxyls, esters, and amides that are present in these molecules. On addition of salt into the polymer host, the cation of the salt is expected to coordinate with the polar groups in the host polymer matrix resulting in the complexation. This type of interaction influences the local structure of the polymer backbone, and certain infrared active modes of vibration will get affected. This indicates that the infrared spectroscopic studies provide the evidence of the complexation. The FTIR analysis of the pure pectin and the shift in the characteristic absorption bands due to these functional groups in the lithium salt-doped polymer electrolyte membranes. The FTIR spectra of various compositions of pectin doped with lithium nitrate are shown in Fig.1 respectively. The absorption peaks observed in pectin-$LiNO_3$ electrolyte films and their assignments are given in Table 1. The broad absorption band at 3394 cm−1, which can be attributed to O–H stretching vibration of the hydroxyl group observed in FTIR spectrum of pure pectin, is found to be shifted in the $LiNO_3$ salt-doped electrolytes as shown in Table 1. It has been observed that the band due to O–H stretching vibration gets broadened with the increase of salt concentration in both the polymer electrolytes. The introduction of a new peak in the salt-doped system may be due to the interaction of the salt with the host polymer matrix. The weak band at 2926 cm−1 in pure pectin is due to C–H stretching vibration and C–H stretching of CH_2 group, which is shifted to lower wave number with increased intensity in both the salt-doped polymer systems as shown in the table 1. The band that appears at 1716 cm−1 can be assigned to C=O stretching vibration of methyl-esterified carboxylic group (–$COOCH_3$) present in pectin. This band is found to be displaced with increased intensity in the alt-doped electrolyte films.

The peak at 1632 cm−1, which can be ascribed to vibrations of the O=C–O structure, are shifted in both the electrolytes. The intensity of the peak at 1632 cm−1 has been increased in both the systems.The two weak bands at 1361 cm−1 assigned to –OH bending vibration and 1119 cm−1 due to the presence of –CH–OH in aliphatic cyclic secondary alcohol of pure pectin get shifted in the pectin-$LiNO_3$ polymer electrolyte systems. The peak at 1022 cm−1 corresponding to –CH–O–CH– stretching vibration of pectin is found to be shifted in both the systems. The shift in the peak positions and change in the intensity of the characteristic peaks in the pectin-$LiNO_3$ polymer electrolyte systems may be due the interaction between the cation of the salts and pectin. Thus, the FTIR analysis confirms the complex formation between the biopolymer pectin and the lithium salts.

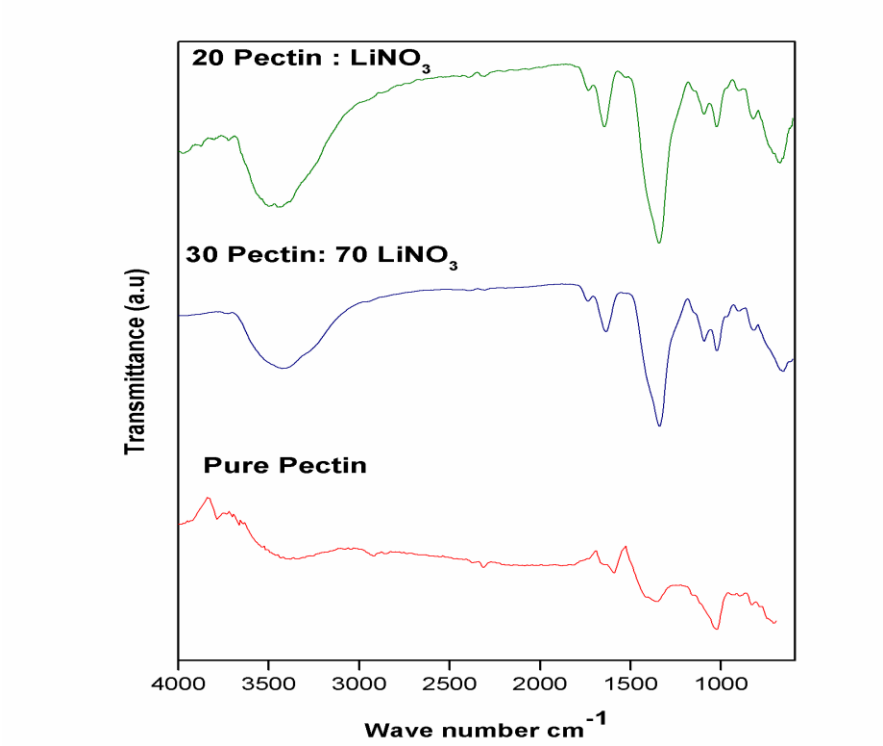


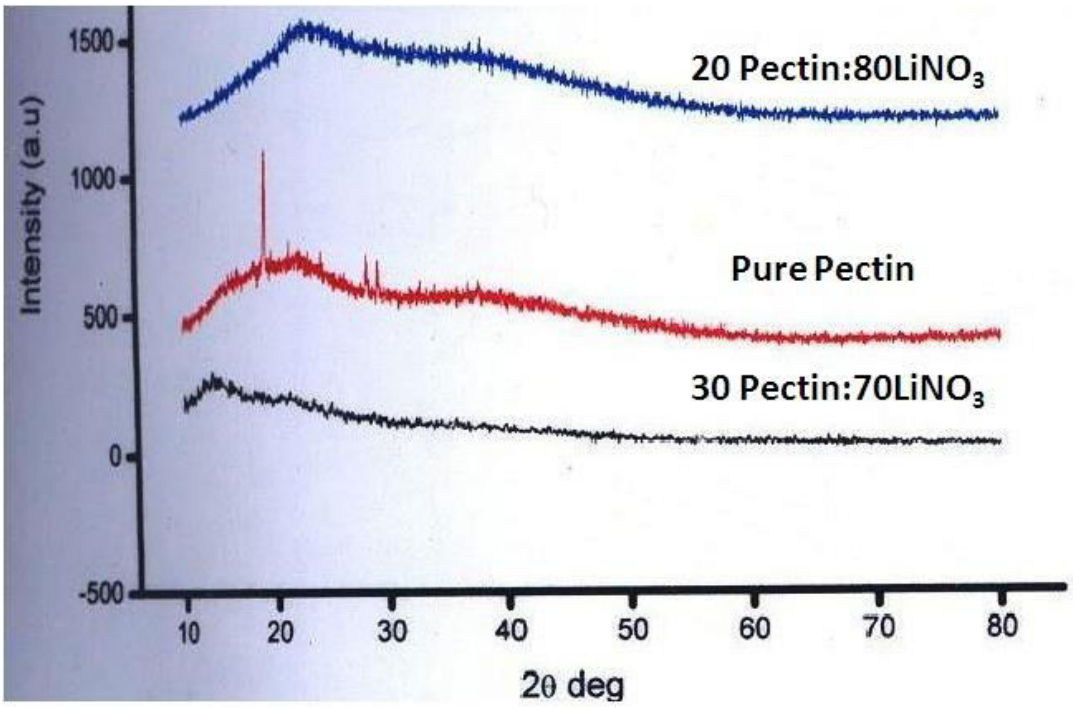
Fig 4.4:Absorption peaks observed in pectin-NH4Cl electrolyte films

TABLE 1: Absorption peaks observed in pectin-$LiNO_3$ electrolyte films

Wave number (cm−1)			Peak assignment
Composition of pectin-$LiNO_3$ (mol%)			
Pure pectin	30:70	20:80	
3394.1116	3410.1351	3442.1820	O–H stretching
2926.4258	2942.4493	2958.4728	-C–H stretching
1716.6519	1732.6754	1732.6754	C=O stretching
1632.4860	1635.5330	1635.5330	Vibrations of the O=C–O structure
1361.1306	1345.1072	1329.0837	–OH bending
1119.7768	1103.7533	1103.7533	–CH–OH in aliphatic cyclic secondary alcohol
1022.6343	1022.6343	1022.6343	–CH–O–CH stretching

4.5 X-ray diffraction analysis

The figure below represents the XRD pattern of pure Pectin, 70 and 80 mol% of $LiNO_3$ doped with Pectin which shows the semi crystalline nature of the pectin. A broad peak around 21.9° has been observed in the XRD pattern of pure Pectin. In the salt-added system, the peak (21.9°) has been found to increase in broadness and decrease in intensity with increase in the concentration of the salt. The decrease of intensity and the increase in full width half maximum of the characteristics peak reveal the amorphous nature of the polymer electrolyte. This amorphous nature increases as the salt content is increased No peaks corresponding to $LiNO_3$ have been observed which indicate a complete dissociation of salt in the polymer matrix. Polymer electrolyte 30% Pectin: 70% $LiNO_3$ has maximum amorphous nature.



4.5 Fabrication and characterization of primary lithium battery

The highest conducting sample in 30 Pectin: 70 LiNO3 polymer electrolyte systems were used as an electrolyte for battery fabrication. Preparations of the anode desired proportions (3:1:1) of zinc metal powder, ZnSO4·7H2O, and graphite powder were taken and mixed together and finally ground well. Then, the mixture was passed to form a thin pellet. Preparation of the cathode the ratio of (8:2:1) PbO2, V2O5, graphite, and polymer electrolyte was taken and mixed together and finally grind well. The above mixture was made into thin pellet. Graphite was added to introduce the electronic conductivity, while the addition of the polymer electrolyte helps in reducing the electrode polarization. The polymer electrolyte was sandwiched between the anode and cathode pellets. The open circuit voltage (OCV) of the cell was monitored for 30 days with configuration

Zn+ZnSO4·7H2O/ 30 PAN: 70 LiNO3/ PbO2+V2O5.

Anode reaction

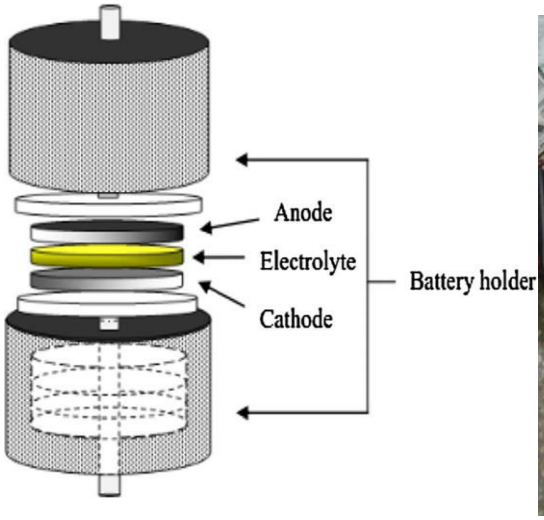
$$n\,Zn + ZnSO_4 \cdot 7H_2O \longrightarrow ZnSO_4.(7-2n)\,H_2O \cdot 2n\,(OH) + Li + 2ne-$$

Cathode reaction

$$PbO_2 + 4H + 2e^- \longrightarrow Pb_2^+ + 2H_2O$$

$$V_2O_5 + 6H + 2e^- \longrightarrow 2VO_2^+ + 3H_2$$

The OCV of a lithium cell is described as the difference between the equilibrium potentials at each electrode, with the positive and negative electrode potentials (Fig.3, battery holder). The stabilized voltage of 1.4 V observed for the cell is shown in Fig. 3.1. The discharge characteristics of stabilized voltage cell at room temperature for constantload 10 K ohm is presented Fig.3.2. This figure shows the cell potential decreasing during discharge. The initial sharp decrease in voltage of this cell may be due to polarization. While discharging through 10 K ohm load the voltage value of cell remains constant at 1.3 V for 27 days. The region in which the cell voltage remains constant is called as plateau region. Beyond the plateau region, voltage value of the cell drops again.



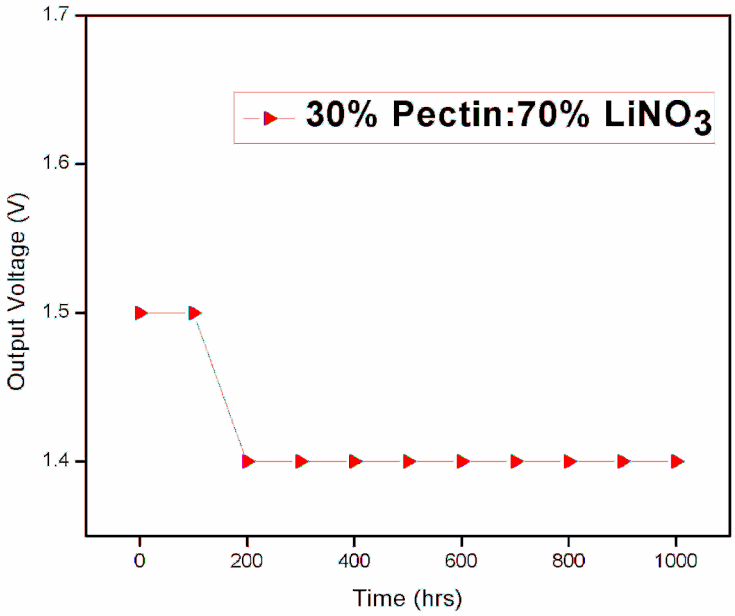


Fig 4.5Output circuit voltage as a function of time for 30 Pectin: 70 $LiNO_3$ polymer electrolyte

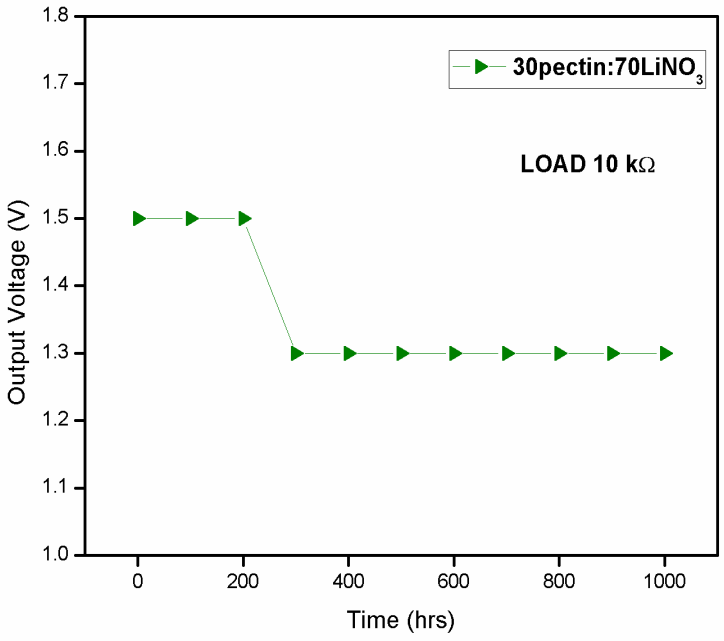


Fig 4.6Output circuit voltage as a function of time for 30 Pectin: 70 $LiNO_3$ polymer electrolyte with resistance

SUMMARY AND CONCLUSION

Summary and Conclusion

The main objective of this study is to electrically characterize the systems by complex impedance analysis, XRD and FTIR. Using this analysis the Cole –Cole plot, conductance spectra have been plotted. The results obtained from these studies can be summarized as follows

A series of homogeneous thin films of solid polymer electrolytes has been prepared from pectin and LiNO3 by solution casting method

The XRD study of polymer electrolyte that the amorphous nature of the polymer electrolyte has been increased by the addition of LiNO3. The conductivity of the polymer electrolyte increasing the amorphous nature of the polymer.

FTIR study shows that complexation has occurred in the prepared polymer electrolytes

From the impedance analysis it has been found that the high ionic conductivity of 1.113* 10-3Scm-1 has been found for30 mol% Pectin: 70 mol % LiNO3 polymer electrolyte.

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