Preparation and characterization of biopolymer electrolytes based on Carboxyl methyl cellulose and sodium salt with Sodium Tetrafluoroborate

Project Report Submitted to

AYYA NADAR JANAKI AMMAL COLLEGE, SIVAKASI

(Autonomous, affiliated to Madurai Kamaraj University, Re-accredited (4th Cycle) with ‘A^{+}’ grade (CGPA 3.48 out of 4) by NAAC and recognized as College of Excellence by UGC, STAR College by Ranked 58th at national level in NIRF 2020)

SIVAKASI-626 124

In partial fulfillment of the requirements for the
Degree of
MASTER OF SCIENCE
IN
PHYSICS
By
J P NIJANTHAN
(Register No: 19PP25)
Under the Guidance of
Dr. S. JAYA M.Sc., M.Phil., Ph.D.

CENTRE FOR RESEARCH AND POST GRADUATE STUDIES IN PHYSICS
(DST-FIST SPONSORED)
AYYA NADAR JANAKI AMMAL COLLEGE (Autonomous)
SIVAKASI-626 124.
MAY 2021

Dr. B. SUNDARESAN M.Sc., B.Ed., M.Phil., Ph.D.
Associate Professor and Head
Department of Physics (P.G)
Ayya Nadar Janaki Ammal College (Autonomous)
Sivakasi – 626 124.

CERTIFICATE

This is to certify that this project report entitled **“Preparation and characterization of biopolymer electrolytes based on Sodium carboxyl methyl cellulose with Sodium Tetrafluoroborate ”** is being submitted by **J P NIJANTHAN,** (**Reg. No.19PP25),** student of M.Sc., Degree course in Physics, Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi, affiliated to Madurai Kamaraj University, Madurai, is a bonafide record of work carried out by her under the guidance and supervision of **Dr. S. JAYA M.SC., M.Phil., Ph.D.** Assistant Professor in Physics (P.G.),Department of Physics, Ayya Nader Janaki Ammal College, Sivakasi.

It is further certified that this project report has been scanned for Plagiarism using Urkund software available in the college Library and the level of Plagiarism is found to be less than the level recommended by the Academic Integrity Committee of the college

Place: Sivakasi — Signature of the Head of the Department
Date: XX.05.2021 — (**Dr. B. SUNDARESAN)**

Dr. S. JAYA M.SC., M.Phil., Ph.D.
Assistant Professor,
Department of Physics (PG),
Ayya Nadar Janaki Ammal College (Autonomous),
Sivakasi – 626124.

CERTIFICATE

This is to certify that this project report entitled **“Preparation and characterization of biopolymer electrolytes based on Sodium Carboxyl methyl cellulose with Sodium Tetrafluoroborate”** being submitted by **J P NIJANTHAN** (**Reg. No.19PP25),** student of M.Sc., Degree course in Physics, Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi, affiliated to Madurai Kamaraj University, Madurai, is a bonafide record of work carried out by her under my guidance and supervision.

It is further certified that to the best of my knowledge, this project report or any part therefore has not been submitted in this University or elsewhere for any other Degree or Diploma.

Place: Sivakasi — Signature of the Guide

Date: XX.05.2021 — **(Dr. S. JAYA)**

J P NIJANTHAN
II M. Sc., Physics
Reg No.19PP25
Department of Physics (P.G)
Ayya Nadar Janaki Ammal (Autonomous)
Sivakasi- 626 124.

DECLARATION

I do hereby declare that the project report entitled **"Preparation and characterization of biopolymer electrolytes based on Carboxyl methyl cellulose and sodium salt with Sodium Tetrafluoroborate "**has been carried out by me under the guidance and supervision of **Dr. S. JAYA M.SC., M.Phil., Ph.D.** Assistant Professor Department of physics (P.G) and has not been submitted elsewhere for the award of any other degree or diploma.

Place: Sivakasi　　　　Signature of the student
Date:XX.05.2021　　　　(J P NIJANTHAN)

ACKNOWLEDGEMENT

I express my grateful thanks to our Principal, **Dr. C. ASHOK M.P.Ed., M.Phil., D.Y.Ed., Ph.D.,** and the staff of the Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi for providing all the necessary facilities to carry out this work.

I extend my sincere thanks to **Dr. B**. **SUNDARESAN, M.Sc., MPhil., B.Ed., Ph.D.,** Head and Associate Professor, Department of Physics (P.G), Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi, for his constant encouragement and valuable advice throughout the course.

I express my heartfelt and sincere gratitude to **Dr. S. JAYA M.SC., M.Phil., Ph.D.** Assistant Professor, Department of Physics (P.G), Ayya Nadar Janaki Ammal College (Autonomous) Sivakasi, for her stimulating guidance, invaluable suggestions and persistent encouragement.

I would like to thank **God Almighty** for having showered blessings upon me to complete my project successfully.

I express my sincere thanks to the faculties of the center For Research and Post Graduate Studies in Physics. I wish to express my heartfelt thanks to P.G And U.G Lab Assistant, for his kind and support throughout my project work.

I am indebted to my **Parents** for their constant encouragement and financial support to carry out my task successfully.

Finally, I express my thanks to my **friends** for their encouragement and providing the necessary co-operation and help to finish this project.

Place: Sivakasi Signature of the student
Date: XX.05.2021 (J P NIJANTHAN)

CONTENTS

CHAPTER I

INTRODUCTION

1.1 INTRODUCTION

A polymer is a very big molecule formed by the combination of a large number of small molecules or repeating units. In the other word, a polymer is defined as a large molecule which is formed by repetition of similar or different kinds of monomers. Monomer is a small molecule which repeats itself to form a polymer. The word polymer is derived from Greek word. Poly means “many”. Mer means “parts”. Polymer means “of many parts”. Polymer can be found all around us

There are three types of classification of polymers based on the source of availability.

- Natural polymer
- Synthetic polymer
- Semi synthetic polymer

Natural polymers: They are obtained naturally are called natural polymers. Ex: starch, cellulose, protein and natural rubber.

Synthetic polymers: The polymers are synthesized in the laboratory are called synthetic polymers. It is also called man-made polymers. Ex: polyethylene, polyvinyl chloride, Bakelite, nylon and synthetic rubber.

Semi-synthetic polymers: They are derived from naturally occurring polymers and undergo

Solid polymer electrolyte (SPE) are defined as a solvent-free salt solution in a polymer host material that conducts ions through the polymer chains. Compared to ISEs, SPEs are much easier to process, generally by solution casting, making them greatly compatible with large-scale manufacturing processes.

Proton conducting polymer materials are very useful for device application. As a matter of fact such proton conductor are equally an important class of polymer electrolyte owing to the low temperature and possibilities of application in fuel cell, sensors, and electro chromic devices(1).

Solid polymer electrolytes generally consist of a polymer host as solid matrix and disassociated salt as ion conductor (2). The polymer host should have a low glass transition temperature facilitating chain segments mobility and a high dielectric constant disassociated enough salt.

Solid polymer electrolytes offer outstanding advantage of high flexibility, easy process ability and low interfacial resistance over inorganic ceramic electrolytes. These merits qualify SPEs intriguing materials for large format and high energy solid state batteries (3).

Solid electrolytes can mainly be classified according to the nature of the ion conducting species as cation conductor (Li^+,Na^+,Cu^+,Ag^+,H^+)and anion conductor (F^-,O^{2-}). Since then in the last nearly four and half decades ,a large number of solids exhibiting fast ion transport involving variety of mobile species such as Li^+,Na^+,Cu^+,Ag^+,H^+ ,Mg^{2+}, F^-,O^{2-} etc. has been investigated extensively.

Solid polymer electrolytes, used in cell phone and lap top computers ,currently contain a liquid electrolyte . replacing the liquid electrolyte currently used has several advantage; it allows use of higher energy density solid lithium at the anode,removes toxic solvent , improves cycling ability,and eliminates the need for heavy casing.Despite the advantage of solid polymer electrolytes, their conductivity is not sufficient for use in batteries. Our aim is to fabricate a solid polymer electrolyte with maximum conductivity.

1.2 Polymer Electrolytes

Polymer electrolytes can be formed by mixing polymers having polar group and ionic salts. The distinct features of polymer electrolytes as compared to other solid electrolytes are greater flexibility, capacity to form thin films, good processing ability and lesser weight. The polymer electrolyte should act as good electrical insulator but at the same time it must possess high ionic conductivity. Methodologies like copolymerization plasticization, dispersion of organic and inorganic fillers and radiation of gamma rays are used in preparation of polymer electrolytes; tend to enhance the electrical conductivity, electrochemical and mechanical conductivity stability.

1.2.1Properties of polymer electrolytes

For successful practical application a polymer electrolyte must have a range of critical properties including the following:

- Adequate ionic conductivity, together with high electronic resistivity.

- High cation mobility (if possible with cation transference number t+=1).
- Good mechanical properties (e.g., not brittle like certain ceramics, but able to relax elastically when stress arising from, for example volume changes in adjacent phases).
- The ability to form good interfacial contacts with electrodes.
- Chemical and thermal stability and safety.

1.3 Types of polymer electrolyte

There are three types of polymer electrolytes based on physical state and composition.

- Solid polymer electrolyte
- Gel polymer electrolyte
- Blend polymer electrolyte
- Composite polymer electrolyte

1.3.1 Solid polymer electrolyte (SPEs)

Solid polymer electrolyte (SPE) are defined as a solvent-free salt solution in a polymer host material that conducts ions through the polymer chains. Compared to ISEs, SPEs are much easier to process, generally by solutioncasting, making them greatly compatible with large-scale manufacturing processes. Moreover, they possess higher elasticity and plasticity giving stability at the interface, flexibility and improved resistance to volume changes during operation.[1] A good dissolution of Li salts, low glass transition temperature (T_g), electrochemical compatibility with most common electrode materials, a low degree of crystallinity, mechanical stability, low temperature sensitivity are all characteristics for the ideal SPE candidate. The solid electrolyte can typically be classified as one of three types,

- Dry SPE
- Gelled SPE
- Porous SPE

1.3.2 Gel polymer electrolyte(GPEs)

Gel polymer electrolyte is also known as plasticized polymer electrolyte, which was first introduced by Fusillade and Perche in1957. GPE contains a plasticizer or gelled polymer matrix, which is swollen by addition of the plasticizers. It can be prepared by simply heating a mixture of polymer and Li salt with solvent. By introducing a plasticizer and/or solvent, the ion transport is not dominated by the segmental motion of polymer chains but occurs in the swollen gelled phase or liquid phase. In general, when the polymer is composed of interconnected microspores, the ionic conductivity of GPEs mainly depend on the properties of trapped liquid electrolyte. It should possess good mechanical strength, capability of holding a liquid electrolyte, high ionic conductivity and electrochemical stability towards both cathode and anode.

These polymer electrolytes have drawn considerable interest of researches due to its many attractive properties such as excellent thermal, chemical and electrochemical stabilities. It is able to dissolve a wide range of organic, inorganic and organo- metallic compounds. It is also a promising item for electrochemical potential window, wider decomposition temperature range, non-toxicity and non-volatility as well as non- flammability.

Doping of ionic liquid produces gel-like polymer electrolyte perhaps sticky gel polymer electrolyte. Sticky gel polymer electrolyte has advantage in electrochemical devices designing by providing a good contact between electrolyte and electrode.

1.3.3 Composite polymer electrolyte (CPEs)

Composite polymer electrolyte can significantly improve the performance in electrochemical devices such as lithium-ion batteries. The amorphous domains of semi-crystalline polymer facilities the ion transport, while an enhanced mobility of polymer chains contributes to high ionic conductivity. It is prepared by the addition of high surface inorganic fillers. The mechanical strength and stiffness of the system were improved.

Advantages of these composite materials include the ability to suppress PEO crystallization and the enhancement of mechanical properties. In many cases, composite electrolytes also show much higher conductivity and Li transference numbers, which are crucial for successful application in Li batteries.

1.3.4 Blend polymer electrolyte (BPEs)

A polymer blend or polymer mixture, is a member of a class of material analogous to metal alloys, in which at least two polymers are blended to create a new material with different physical properties

The properties of polymer blends depend on the physical and chemical properties of the participating polymers and on the state of the phase, whether it is in homogenous or heterogeneous phase. Polymer blending is one of the effective methods to reduce the crystalline content and to enhance the amorphous content. polymer blends often exhibit properties that are superior to the individual component polymers.

In our work, we prefer the first category that is solid polymer electrolyte to prepare proton conducting polymer electrolyte.

1.4 **Application**

There are wide of application in polymer electrolytes.

- batteries
- Fuel cells
- Sensors
- Electro chemical window
- Super capacitors

1.4.1 Batteries

An electro chemical emf will be developed when a solid electrolyte is stacked between two electrodes of different chemical potentials. Over the liquid electrolytes, galvanic cells have the advantage of long operating temperature range, long operating life and feasibility of miniaturization as the electrolyte could be coated as thin film.

A battery, which is actually an electric cell, is a device that produces electricity from a chemical reaction. A cell consists of a negative electrode; an electrolyte, which conducts ions; a separator also an ion conductor; and a positive electrode. If the electrolyte is a polymer electrolyte then the battery is called as solid polymer battery.

Electrolyte plays a key role in transporting the positive lithium ions between the cathode and anode. The most commonly used electrolyte is comprised of lithium salts, such as LiBr in an organic solution.

Electrolyte is the component which plays this important role. It serves as the medium that enables the movement of only lithium ions between the cathode and anode. For the electrolyte, materials with high ionic conductivity are mainly used so that lithium ions move back and forth easily.

The electrolyte of a battery consist of soluble salts, acids or other bases in liquid ,gelled and dry formats. Electrolyte also comes in a polymer as used in the solid state battery, solid ceramic and molten salts, as in the sodium –sulfur battery.

Electrolytes play an important role in Lead acid, Nickel cadmium ,Nickel-metal-hydride and Lithium ion batteries, Sodium polymer batteries and Silver polymer batteries.

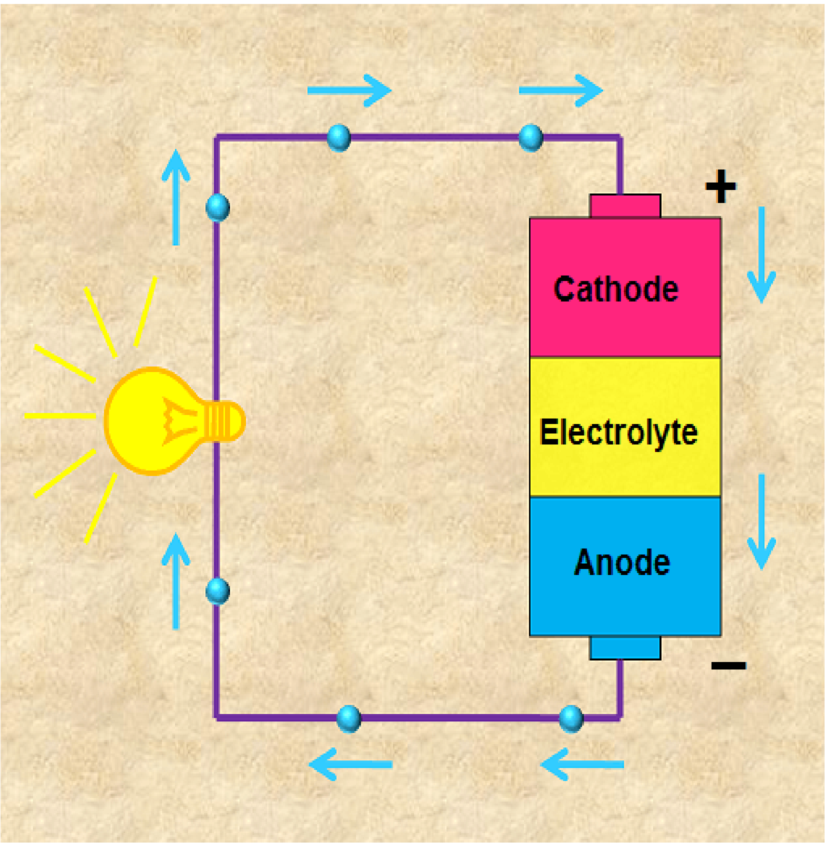


Figure 1.1 Shows the Battery image

1.4.2 Fuel cell

Every fuel cell consists of electrolytes, which essentially carry the electrically charged particles from the anode to the cathode and vice versa.Thus, electrolytes act as a catalyst which makes it possible for the chemical reaction to take place in a speedy manner. In the entire process, the electrolyte plays a major role in maintaining just the right proportion of ions to travel between the cathode and the anode. Any other freely travelling electrons could disrupt the ongoing chemical reaction in the fuel cell. Fuel cells are used in the transport vehicles such as cars and buses and as backup power units in electrically generating grids.

There are many types of fuel cells, but they all consist of an anode, a cathode, and an electrolyte that allows ions, often positively charged hydrogen ions, to move between the two sides of the fuel cell. At the anode a catalyst causes the fuel to undergo oxidation reactions that generate ions and electrons. The ion moves from the anode to the cathode through the electrolyte. At the same time, electron flow from the anode to the cathode through an external circuit, producing direct current electricity.

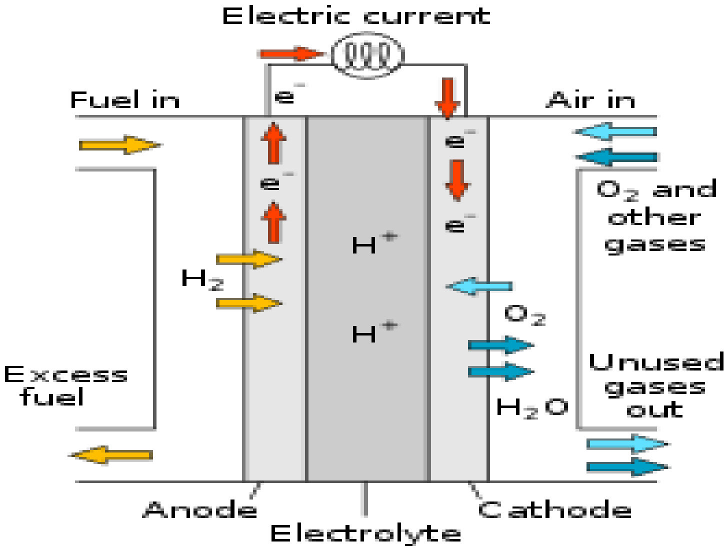


Figure 1.2 Shows the fuel cell image

1.4.3 Sensors

Electrochemical sensors are essentially fuel cells composed of noble metal electrodes in an electrolyte. The electrolyte is normally an aqueous solution of strong inorganic acids. When a gas is detected the cell generates a small current proportional to the concentration of the gas. An electrochemical sensor consists of a diffusion barrier, a sensing-electrode, a counter-electrode and an electrolyte. Their normal life expectancy may be up to three years from the date of manufacture.

1.4.4 Electrochemical window

The electrochemical window of a substance is the electrode electric potential range between which the substance is neither oxidized nor reduced. The electrochemical window is one of the most important characteristics to be identified for solvents and electrolytes used in electrochemical applications. It indicates the potential range and the potential difference

1.4.5 Super capacitors

Electric double layer capacitor also called super capacitor, has recently attracted considerable attention as promising energy storage device because of the high-power energy density and long cycle performance. For the first time carbon nano tubes modified polypropylene have been used as an active electrode material for the super capacitor assembly. The capacity value has found to be the order of 163F/g. PAN and PVDF-HHP (KF 2801) polymer matrices in a solution of LiCF3SO3 in EC-BL solvent mixture has been used in super capacitors.

A super capacitor also called an ultra-capacitor. It is a high-capacity capacitor with a capacitance value much higher than other capacitors, but with lower voltage limits, that bridges the gap between electrolytic capacitors and rechargeable batteries.

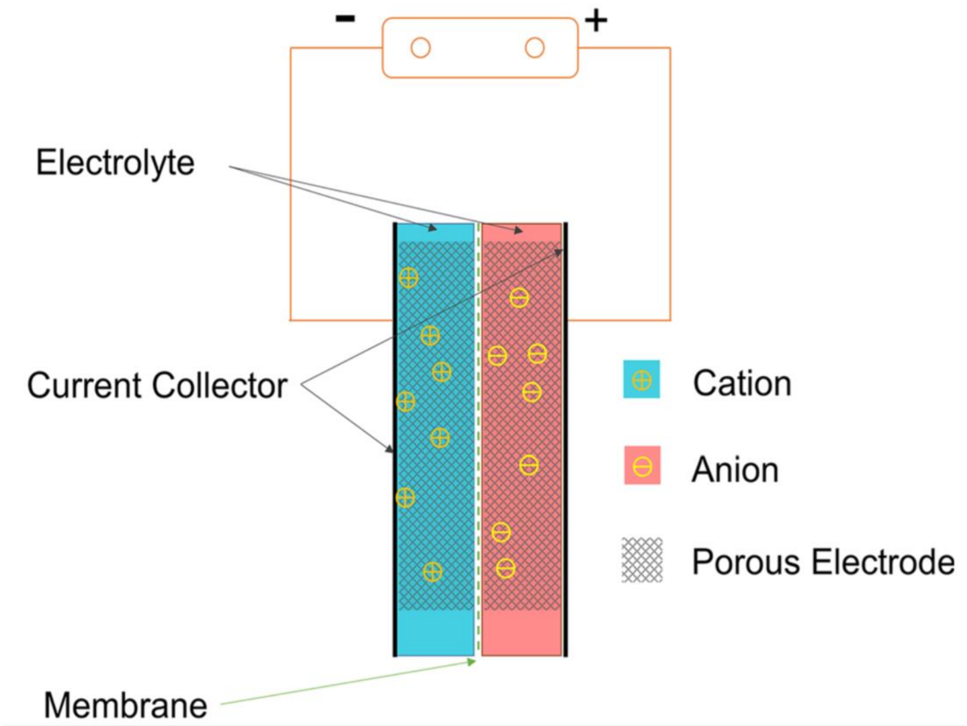


Figure 1.3 shows the Super capacitor image

1.5 Glass transition temperature (T_g)

T_g marks the temperature below which the polymer is hard, stiff and brittle and above which it is soft. The hare and brittle state is the glassy state and the soft and flexible state is known as rubbery state or viscoelastic state. At this temperature, amorphous polymers undergo a second-order phase transition from a amorphous solid, or from a crystalline solid (depending on the degree of crystallization) to a brittle, glassy amorphous solid. T_g may be engineered by altering the degree of branching or cross linking in the polymer or by the addition of plasticizer.

This behavior can be understood in terms of the structure of glassy materials which are formed by substances containing long chains, networks of linked atoms or those that possess a complex molecular structure. Normally, such materials have a high viscosity in the liquid state, when rapid cooling occurs to a temperature at which the crystalline state is expected to be the more stable, molecular movement is too hackwork to take up a crystalline confirmation.

1.6 Polymerization

It is the process of connecting these monomers together and creating large macromolecules of different sizes and shapes. Polymerization is similar to constructing a large building out of the same type of Lego blocks. The blocks can be connected in various ways to create a larger, more intricately shaped structure than the original Lego block on its own.

1.7 Classification of polymerization.

1.7.1 Addition Polymerization

Polymerization that occurs through the coupling of monomers using their multiple bonds is called addition polymerization. The simplest example involves the formation of polyethylene from ethylene molecules. In this reaction, the double bond in each ethylene molecule opens up, and two of the electrons originally in this bond are used to form new carbon-carbon single bonds with two other ethylene molecules.

Some common commercial addition polymers are:

- Polyethylene - films, packaging, bottles
- Polypropylene - kitchenware, fibers, appliances
- Polyvinyl chloride - pipe fittings, clear film for meat packaging

1.7.2 Condensation Polymerization

The chemical mechanism that cells use to make and break polymers are basically the same in all cases. Monomers are connected by a reaction in which two molecules are covalently bonded to each other through loss of a water molecule; this is called a condensation polymerization because the lost molecule is water. When a bond forms between two monomers, each monomer contributes part of the water molecule that is lost; one molecule provides a hydroxyl group, while the other provides hydrogen. To make a polymer, this reaction is repeated as monomers are added to the chain one by one.

1.7.3 Homopolymer and Heteropolymer

Homo polymer is produced in single monomer. A heteropolymer is produced in two or more monomers. And it is commonly known as co-polymer.

1.8 Based on Structure of Polymers

Structure is the main factor which differentiates the polymer from its monomer. This classification also deals with the solubility nature of the polymer. According to structure, the polymer has been classified as,

1. Linear Polymers

2. Branch chain Polymers

3. Crossed linked Polymer

(i) Linear polymers:

Linear polymers are similar in structure to a long straight chain which identical links connected to each other. The monomers in these are linked together to form a long chain. In other words, these polymers, which are composed of chainlike molecule, may be viscous

liquids or solids with varying crystallinity; a number of them can be dissolved in certain liquids and they soften or melt upon heating. These polymers have high melting points and are of higher density.

Example: Polyacrylonitrile (PAN), Poly-vinyl chloride (PVC).

(ii) Branch chain polymers:

The structure of these polymers is like branches originating at random points from a single linear chain. Monomers join together to form a long straight chain with some branched chains of different lengths. As a result of these branches, the polymers are not closely packed together. They are of low density having low melting points.

Example: Low-density polyethene (LDPE)

(iii) Crosslinked or Network polymers:

In this type of polymers, monomers are linked together to form a three-dimensional network. The monomers contain strong covalent bonds as they are composed of bi-functional and tri-functional in nature. These polymers are brittle and hard. Cross-linked polymers, in which the molecular structure is a network, do not dissolved in any solvents.

Example: Bakelite, Melamine

1.9 Based on Molecular Forces

Intra molecular forces are the forces that hold atoms together within a molecule. In Polymers, strong covalent bonds join atoms to each other in individual polymer molecules.

Intermolecular forces (between the molecules) attract polymer molecules towards each other. The properties exhibited by solid materials like polymers depend largely on the strength of the forces between these molecules [8]. According to this, Polymers can be classified into four types. They are,

1. Elastomers
2. Thermoplastics
3. Thermosetting
4. Fibers

i)Elastomers:

Elastomers are rubber-like solid polymers, that are elastic in nature. The polymer can be easily stretched by applying a little force. The polymer chains are held by the weakest intermolecular forces, hence allowing the polymer to be stretched. When the applied force is released the polymer returned to its original state. This happens as we introduce cross links between the polymer chains which help it in retracting to its original position, and taking its original form.

Example:

1. Rubber bands or hair bands . Applying a little stress elongates the band. While removing that stress also results in the rubber band taking up its original form.

2. Our car tires are made of Vulcanized rubber. This is when we introduce Sulphur to cross bond the polymer chains.

ii) Thermoplastics:

Thermoplastic polymers are long-chain polymers in which inter-molecular forces (Van der Waal’s forces) hold the polymer chains together. These polymers are softened when they are heated and hardened when they are allowed to cool down. They do not contain any cross bond and can easily be shaped by heating and using molds.

Example: Polystyrene or Poly-vinyl chloride (PVC) which is used in making pipes.

iii) Thermosetting:

Thermosetting plastics are polymers which are semi-fluid in nature with low molecular masses. When heated, they start cross-linking between polymer chains, hence becoming hard and infusible. They form a three-dimensional structure on the application of heat. This reaction is irreversible in nature.

Example: Bakelite, which is used in making electrical insulation.

iv) Fibres:

In the classification of polymers, these are a class of polymers which are a thread like in nature, and can easily be woven. They have strong inter-molecules forces between the chains giving them less elasticity and high tensile strength. The intermolecular forces may be hydrogen bonds or dipole-dipole interaction. Fibers have sharp and high melting points.

Example: Nylon-66, which is used in carpets and apparels.

1.10 APPLICATIONS OF POLYMER ELECTROLYTES

The polymer electrolyte is of tremendous interest to researchers because of its many advantages such as no leakage, flexible geometry, excellent safe performance and good compatibility with electrodes compared with its liquid counterpart. As a key technique in cell manufacture, progress in polymer electrolytes will bring about a revolution in cell manufacture. At the same time, it will make a great contribution to saving on total energy consumption, reducing the release of CO2 and suppressing the heating of the Earth.

Ion conducting polymers are of considerable interest because of their potential application as a solid polymer electrolyte. Typical applications are in Rechargeable batteries, super capacitor and Fuel cell ect.

a) Super capacitors

Super capacitors characterized by high capacitance values in the Farad ranges and low internal resistances are devices for applications requiring high current loads. Polymer electrolytes are receiving a great deal and lot of attention in electrochemical super capacitors. Super capacitors can be used as uninterruptable power sources, can be coupled with batteries to provide peak power and it can replace batteries for memory back up.

b) Rechargeable batteries

Rechargeable batteries are among the first commercial based ionic conducting polymers. Polymer electrolytes are most suitable for these batteries because they serve as heat resistive separators as well as conductors. Polymer electrolytes also play a very important role in miniaturizing the size of Li+ ion batteries.

c) Fuel Cells

A fuel cell us a device which converts chemical energy into electrical energy. They are used as power sources for space craft. Due to the awareness of limited energy supply, much effort is being made to develop a fuel cell as terrestrial power generator. Efforts are being taken to develop fuel cells based on proton conducting polymer electrolytes. Fuel cells of this type are most advantageous for power generation because of their structural simplicity. These polymer electrolytes serve both as ionic conductive layers and as an excellent gas separator.

1.11 REVIEW OF LITERATURE

Supriya Shetty,et.al.,[3] prepared Na+ ion-conducting solid polymer electrolyte (SPE) based on sodium salt of carboxymethyl cellulose (NaCMC) doped with sodium nitrate (NaNO3) was developed by solution casting method. FTIR technique confirmed the formation of hydrogen bonding between NO− 3 anion and functional groups of NaCMC. XRD study revealed the low degree of crystallinity that reduced upon doping. Impedance spectroscopy was adapted in order to analyze the conductivity and dielectric relaxation phenomena of the polymer-salt complex. FTIR deconvolution technique was employed to understand the factor that influences the ionic conductivity in SPE; concentration of mobile ions and ionic mobility both play a vital role. Ion transference number has been found out to be > 0.97 for all samples indicating that the conducting species are primarily ions. The highest ionic conductivity of 3×10^{-3} Scm^{-1} with the mechanical strength of 30.12 MPa was achieved for a host containing 30 wt.% NaNO3 at ambient temperature.

ErlantzLizundiaab et.al.,[4] prepared there is a growing demand for lithium ion batteries (LIBs) fabricated with environmentally-friendly materials to transition toward a more sustainable society based on a circular economy. Battery separator, typically a porous petroleum-polymer, plays a pivotal role as it serves to efficiently transfer ions between electrodes while preventing electrical short-circuits. To reduce our dependence on fossil resources, cellulose and its derivatives are being used as sustainable battery separators thanks to its easily controllable porosity, suitable mechanical and thermal properties, non-toxicity and inherent hydrophilicity. Here we first present the structure, physico-chemical properties and various types of cellulose derivatives, as well as the different manufacturing approaches to obtain porous cellulose membranes. Further, the most recent developments in the field of cellulose and its derivates for lithium ion battery separators and solid polymer electrolytes are discussed. Finally, the main issues and properties to be improved in the near future concerning cellulosic separators are shown.

Mohad Ikmar Nizam Mohamad et al., [9] reported solid polymer electrolytebased on (SPE) carboxymethyl cellulose (CMC) and ammonium chloride (NH4Cl) films were prepared by solution casting method. The ionic conductivity and electrical properties of SPE films were investigated using Electrical Impedance Spectroscopy. SPE film containing 16 wt. % NH4Cl exhibited the highest ionic conductivity of 1.43 x 10-3 S/cm at ambient temperature, 303K. The temperature dependence SPE films showed an Arrhenius-type relation where the regression values obtained from the log conductivity versus reciprocal temperature is close to unity (R2≈1).

MN Chai,MIN Isa et.al.,[5] reported Biopolymer electrolyte based on carboxymethyl cellulose has been prepared by doping with different concentration of oleic acid via solution casting technique. Fourier Transform Infrared spectroscopy was used to study the complexation between the salt and polymer. New peak was observed at 1710, 2850, 2920 cm^{-1}. X-ray diffraction study reveals the amorphous nature of the biopolymer electrolyte. Impedance study shows the highest ionic conductivity, σ, was found to be 2.11×10^{-5} $S \cdot cm^{-1}$ at room temperature (303 K) for sample containing 20 wt% of oleic acid and the biopolymer electrolyte obeys Arrhenius behaviour.

Najam Sardar a, et.al.,[2] reported solidpolymer electrolyte based on sodium carboxymethylcellulose (NaCMC) and cationic gemini surfactants (16-*s*-16, *s* = 5, 6)/conventional surfactant (CTAB) in aqueous solutions is investigated by conductivity, fluorescence and viscosity techniques. Electrostatic and hydrophobic interactions play a dominant role in such systems. The conductivity results showed that the geminis interact strongly with NaCMC as compared to CTAB. Fluorescence measurements were used to calculate aggregation number for the three combinations which were found about the same as those for the corresponding free micelles. Addition of surfactants leads to an increase in relative viscosity after certain concentration of the surfactants. Further increase in relative viscosity is significant in case of geminis and this increase is ascribed to the physical cross-linking of surfactant micelles with NaCMC chains.

N. N. S. Baharun,et.al.,[1] reported solid polymer electrolyte based on Sodium-carboxymethylcellulose (NaCMC) by using solution casting and followed by soaking the film into the optimized polysulfide solution for 68 seconds. Impedance studies of the polymer electrolytes have been done using electrochemical impedance spectroscopy (EIS). The NaCMC/polysulfide electrolyte exhibited a room temperature (RT) ionic conductivity of 2.79×10^{-5} Scm $^{-1}$. The conductivity increased to 1.11×10^{-4} S cm $^{-1}$ when the NaCMC/polysulfide electrolyte was plasticized with 40 wt.% of ethylene carbonate (EC). The conductivity-temperature relationship of the plasticized electrolyte obeys the Arrhenius rule with activation energy for plasticized film at 40 wt.% EC is as low as 0.25 eV. The transport properties, Diffusion coefficient (D), number density of mobile ions (n), and its mobility (μ) were also calculated.

Francesca Colò et.al.[7], prepared solid polymer electrolyte based on homogeneously blended with sodium carboxymethyl cellulose (Na-CMC) and sodium perchlorate films were based on a classic polyethylene oxide (PEO). 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. The promising prospects of the newly elaborated hybrid electrolyte are investigated by means of galvanostatic charge/discharge cycling in lab-scale cell with TiO2-based or NaFePO4-based working electrode.

1.12 SCOPE OF THE WORK

It is proposed to prepare polymer based electrolyte in the form of thick films through solvent casting technique using Carboxyl methyl cellulose(NaCMC) and Sodium tetrafluoroborate ($NaBF_4$) with TiO_2 solvent. As prepared membranes were subjected to characterization techniques such as FTIR, ac impedance analysis. FTIR study has revealed the formation of complexes between the Carboxyl methyl cellulose and the Sodium tetrafluoroborate. From the ac impedance analysis, the ionic conductivity was calculated at the room temperature.

CHAPTER II

MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 INTRODUCTION

This chapter deals with the method of sample preparation of Carboxyl methyl cellulose and sodium salt (N
technique is explained in this chapter.

2.2 MATERIALS USED

Polymer :NaCMC(Mol wt: 263.2 g/mol)
Electrolyte :$NaBF_4$(Mol wt: 109.79 g/mol)
Solvent : Distilled water (Boiling point: 100 °C)
Filler:Titanium Dioxide (TiO_2)

2.3 CARBOXYL METHYL CELLULOSE AND SODIUM SALT

Carboxymethylcellulose (CMC), generally used as sodium salt NaCMC, is one of the most widely used polyelectrolyte cellulose derivatives.

NaCMC is an anionic, water soluble, polyelectrolyte with vast applications in the food, pharmaceutical, personal care/cosmetic, paper and other industries.

2.3.1 STRUCTURE OF NaCMC

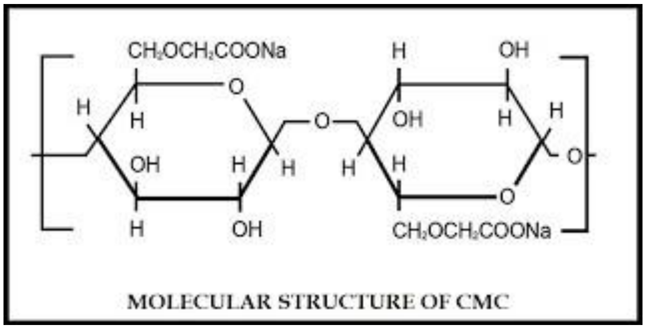


Figure 2.1 Shows the structure of NaCMC

2.3.2PHYSICAL PROPERTIES OF NaCMC

Chemical Formula **:**$C_8H_{16}NaO_8$

Molecular Weight **:**263.2 g/mol

Shape **:** powder

Color **:**white to light yellow

Odor **:**Odorless

Melting point **:**274^{o}c

Refractive index **:**1.48

Density **:**1.6g/cm^3

Glass transition temperature: 79 ^{o}c

Stability **:**Stable

2.3.3 Applications:

- Its ability to form strong, oil-resistant films is important to many applications. These strong, fairly flexible films are unaffected by oils, greases, or organic solvents.
- CMC has received considerable attention in the textile industry because of its readily solubility and excellent film-forming characteristics.
- Thickening action and suspending properties of CMC are mainly responsible for its use in emulsion paints. It performs best in anionic systems, such as acrylic emulsions, where its compatibility produces excellent leveling.
- It can be used in auto polish, in suspension polymerization, in molding extrusion of lead pencils and coal briquettes.

2.4 SODIUM TETRAFLUOROBORATE

Description. **Sodium tetrafluoroborate** is an organic compound that has the molecular formula NaBF4. The compound is a salt that forms white or colorless water-soluble rhombic crystals. It is less soluble in organic solvents and readily soluble in water.

2.4.1 STRUCTURE OF SODIUM TETRAFLUOROBORATE

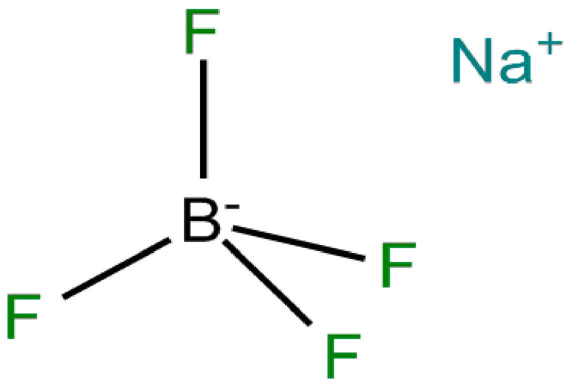


Figure 2.2 Shows the structure of $NaBF_4$

2.4.2 PHYSICAL PROPERTIES OF $NaBF_4$

Chemical Formula **:$NaBF_4$**

Molecular Weight **:37.83** g/mol

Shape : solid crystals very hygroscopic

Color :colorless or white

Odor :Odorless

Melting point :384^{o}c

Refractive index :1.48

Density :1.60g/cm^{3}

Stability :Stable.

2.4.3 APPLICATIONS

It is used inmanufacturing of metals, casting of metals, production of metals, surface treatment of metals, etc

Sodium tetrafluoroborate may be used as a catalyst for the synthesis of bio(indoyl) methane's via electrophilic substitution reaction of indoles with aldehydes and ketones.

It is also used in laboratory synthesis of boron fluoride.

It may be used for the synthesis of fluoro-nucleic acids andfluoroheterocyclic compounds**.**

2.5 TITANIUM DIOXIDE

Titanium dioxide is a titanium oxide with the formula TiO2. A naturally occurring oxide sourced from ilmenite, rutile and anatase, it has a wide range of applications. It has a role as a food coloring

2.5.1 SRTUCTURE OF TITANIUM DIOXIDE

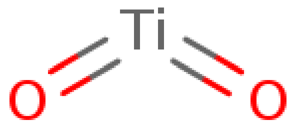


Figure 2.3 Shows the structure of TiO_2

2.5.2 PHYSICAL PROPERTIES OF TiO_2

Chemical Formula : TiO_2

Molecular Weight : 233.38 g/mol

Shape : White solid

Color : white power

Odor : Odorless

Melting point :1,843 °C

Density :4.23 g/cm^3

2.5.3 USES AND APPLICATIONS OF TiO_2

Uses:

- It is used in the casting of copper anode plates as a coating material.

- It is used as a radiopaque agent.
- It is used as a component in oil well drilling fluids.
- It is used to increase the density of the polymer by acting as a filler for plastics.
- Used to test the PH of the soil.
- Used as a filler or to modify the consistency in oil paints.
- It is used in imaging of the GI tract during barium meal.
- Used to diagnose certain disorders of the intestines, stomach.
- It is used in the manufacturing of alloys.

Applications:

- Titanium dioxide (TiO2) is a naturally occurring mineral used as a bright white pigment for painting, as a coloring in the food industry, in sunscreens and cosmetics, and in many industrial applications.
- Titanium dioxide is used as a UV filter in sunscreen products to protect the skin from harmful UV rays when exposed to sunlight.

2.6 COMPOSITION OF POLYMER SALT SYSTEM

The carboxyl methyl cellulose with sodium salt(NaCMC) based polymer electrolyte with sodium tetrafluoroborate ($NaBF_4$) the following compositions (weight percentage) were prepared.

Table 2.1 composition of (Wt%)

S.No:	**SAMPLE CODE**	**NaCMC+NaBF4 (Wt%)**	**TiO2 (g)**

1	S1	100%	--
2	S2	70+30%	--
3	S3	70+30%	0.02
4	S4	70+30%	0.04
5	S5	70+30%	0.06
6	S6	70+30%	0.08
7	S7	70+30%	0.10

2.7 METHODS OF POLYMER FILM PREPARTION

Polymer film preparation can be classified as chemical and physical. The solid polymer electrolytes are easy to fabricate as soft films of only a few microns and their flexibility permits interfaces with solid electrodes, which remain intact, when the device is in use. This makes the application and development of all electrochemical devices possible. In the present study, our interest is in the preparation of polymer films. There are various methods to prepare good quality polymer films. The preparation methods are given below.

- Solution –casting method
- Hot pressing method
- Blowing
- Evaporation method
- Laser evaporation method
- Flash evaporation method
- Polymerization of monomer
- Gaseous discharge
- Sputtering
- Photolytic Process
- Pyrolysis

2.8 SOLUTION CASTING METHOD

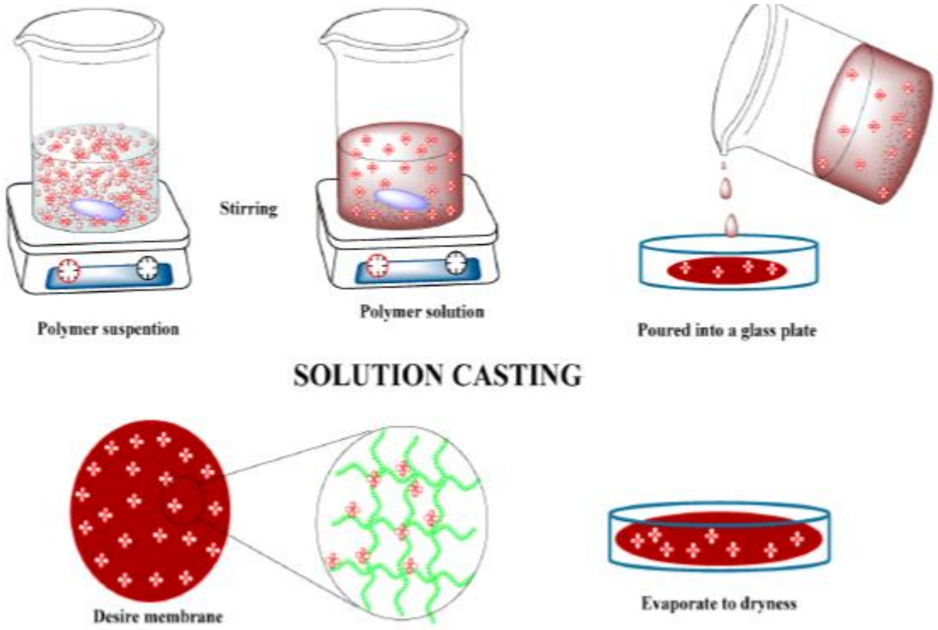


Figure 2.4 Shows the solution casting image

The solvent casting technique was one of the simplest method to prepare the polymer electrolyte. The required amount of NaCMC and $NaBF_4$ were added in sequence to distilled water.

After a complete dissolution of polymer and salt was added and further stirred for 5 hours .After stirring the prepared solution is involving

After a homogenous solution was obtained, and the resulting solution was poured on to a glass plate and water was allowed to evaporate in microwave oven at 60^0 c over one night.

The films were dried for another one day to remove any trace of water.

In this technique is varied from by the addition of different filler ratio with (0.02,0.04,0.06,0.08,0.10), polymer salt respectively.

CHAPTER III

CHARACTERIZATION TECHNIQUES

3.1 Introduction

To analyze the structural and electrical properties of the material, characterization is important process. The conductivity and structural properties of the prepared biopolymer electrolyte can be characterized by

- AC IMPEDANCE STUDIES
- FTIR STUDIES

3.2 CONDUCTIVITY STUDIES

For the conductivity studies, the ac impedance method is adopted. This method is used to characterize the electrical properties of materials and their interferences with electrically conducting electrodes. It is used to study the dynamics of the mobile charges in bulk of ionic, electronic and dielectric materials. This consists of applying an electric pulse across the electrode and studies their response.

The main advantage of impedance spectroscopy is,

- It involves relatively simple electrical measurements that can readily be
  automated.
- The results can be correlated with material variables such as compositions,microstructure, defect, dielectric properties,chemical reaction, etc.

Unlike de technique, the as impedance techniques use small pulse is the range of 5-10mV peak to peak. This cause only minimal perturbation of the electrochemical test system; thereby the error in measurements is reduced. This method provides the data on both the electrode capacitance and charges transfer kinetics.

The objective of ac impedance experiment is to determine the value of the various elements in the equivalent circuit. This is done by studying the response to an ac excitation over a wide range of frequencies. From the observation value the conductivity σ_{ac} can be determined.

Electrically conductivity measurements are normally carried out under ac conditions because under these condition polarization effects are minimized. This is because the alternating current is out of phase with applied ac voltage, perturbing the various processes within the cell such as surface and interfacial process bulk ionic transport and double layer formation are the electrode formation. The ac conductivity is calculated using the impedance plot. From the plot bulk resistance 'S' is calculated by extrapolating the curve to X-axis. This graph plotted between

Z cosɵ and Z sinɵ.

The intersection of X-axis gives the value of bulk resistance, then

$$\sigma_{ac} = \frac{thickness}{(area)X(resistance)}$$

Generally the conductivity of a material is measured at various frequencies; it is well known that several physical process such as the migration ion through the bulk of the electrolyte, charge transfer across the interfacial zone and conduction via grain boundaries occur with the passage of electrical current through a solid electrolyte. The individual processors passage of electrical current through a solid electrolyte.

Figure 3.1 shows the Impedance Analyzer that we have used.

Figure 3.1 shows the Impedance Analyzer

3.3 FTIR studies

FTIR is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time. The identification of the functional groups in organic compounds is extensively done using Infrared spectroscopy . As their spectra are generally complex and comprises of numerous maxima and minima which are useful for comparison of organic compounds. In fact, some of the physical properties of any organic compound can be truly inferred from its infrared absorption spectrum. This method functions on the fact that atoms in the molecule vibrate relative to each other with very well defined frequencies for a given set of atoms or functional groups .

In the present study FTIR spectra of all polymer electrolytes were recorded on the spectrophotometer, in the wave number range 400 – 4000 cm-1.

The light is measured using an infrared spectrometer which produces the output of an infrared spectrum. The IR spectrum is a graph oh infrared light absorbance by the substance on the vertical axis and the frequency on the horizontal axis.

- The Fourier transform converts the detector output to an interpretable spectrum
- The FTIR generates spectra with patterns that provide structural insights

3.3.1 FTIR THEORY

Radiation from the infra-red region of the electromagnetic spectrum can be absorbed by bonds between atom

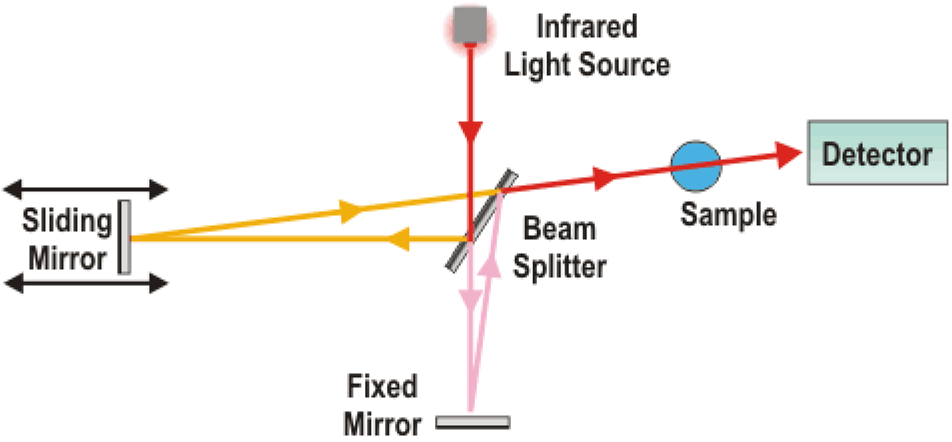


Figure 3.2 shows the instrumentation of FTIR

3.3.2 Principles of FTIR Spectrometer:

FTIR relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectru

The background emission spectrum of the IR source is first recorded, followed by the emission spectrum of the

The resultant absorption spectrum from the bond natural vibration frequencies indicates the presence of various chemical bonds and functional groups present in the sample. FTIR is particularly useful for identification of organic molecular groups and compounds due to the range of functional groups, side chains and cross-links involved, all of which will have characteristic vibrational frequencies in the infra-red range.

3.4 Components

3.4.1 IR sources

FTIR spectrometers are mostly used for measurements in the mid and near IR regions. For the mid-IR region, 2−

3.4.2 Detectors

Mid-IR spectrometers commonly use pyroelectric detectors that respond to changes in temperature as the intensity of IR radiation falling on them varies. The sensitive elements in these detectors are either deuterated triglycine sulfate (DTGS) or (LiTaO3). These detectors operate at ambient temperatures and provide adequate sensitivity for most routine applications. To achieve the best sensitivity the time for a scan is typically a few seconds. Cooled photoelectric detectors are employed for situations requiring higher sensitivity or faster response.

3.4.3 Beam splitter

An ideal beam-splitter transmits and reflects 50% of the incident radiation. However, as any material has a limi

that makes it semi-reflective. KBr absorbs strongly at wavelengths beyond 25 µm (400 cm^{-1}) so

CsI is sometimes used to extend the range to about 50 μm (200 cm^{-1}). ZnSe is an alternative where moisture vapor can be a problem but is limited to about 20μm (500 cm^{-1}).

3.5 APPLICATIONS

- FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs and contaminants.
- It is a simple and reliable technique widely used in both organic and inorganic chemistry, in research and industry.
- It is used in quality control, dynamic measurement, and monitoring applications such as the long-term unattended measurement of Co2 concentrations in greenhouses and growth chambers by infrared gas analyzers.
- It is also useful in measuring the degree of polymerization in polymer manufacture. Change in the character or quantity of a particular bond are assessed by measuring at a specific frequency over time [12]

CHAPTER IV

RESULT AND DISCUSSION

4.1 INTRODUCTION

In this chapter the results obtained through different characterization techniques such as AC impedance Analysis spectroscopy and FTIR are discussed. This chapter deals with detailed studies of the vibrational characterization carried out by IR Spectroscopy. It also gives information on the electrical property of polymer electrolyte before and after the addition of filler with the help of impedance spectroscopy analysis at different frequency.

4.2 FTIR ANALYSIS

The FTIR spectrum of NaCMC $NaBF_4$ and NaCMC+$NaBF_4$ and NaCMC+$NaBF_4$+TiO_2 are shown in Figure (4.1) to figure (4.4) and the band assignment for each absorption peaks are given in the table (4.1)

The vibrational peaks of functional group of NaCMC namely Carboxyl group, methyl group and hydroxyl group are analysed in the FTIR spectrum of polymer electrolyte (PE) and filler added polymer electrolyte (FPE) samples.

a) OH out of plane bending mode

The absorption peak at 936 cm^{-1} observed in FTIR spectrum of NaCMC is due to OH out of plane bending. This peak is shifted to 951 cm^{-1} after the addition of $NaBF_4$ and 950 cm^{-1} after the addition of TiO_2 to PE.

b) C-O Stretching mode:

A strong and broad peak observed at 1067 cm^{-1} in the FTIR spectrum of NaCMC is due to C-O stretching mode. This peak also show a shift in wavenumber. The peak is observed at 1087 cm^{-1} in both NaCMC+$NaBF_4$ and NaCMC+$NaBF_4$+TiO_2 spectrum. The absorption peak at 1223 cm^{-1} is also due to stretching. The intensity of this peak is reduced after the addition of $NaBF_4$ and TiO_2.

c) C=O stretching

In the FTIR spectrum of NaCMC, C=O stretching of carboxyl group result in an absorption peak at 1685 cm^{-1}.The intensity of this peak is reduced in the FTIR spectrum of NaCMC+$NaBF_4$ and NaCMC+$NaBF_4$ +TiO_2.

d) C-H stretching

The absorption peaks at 2981 and 2887 cm^{-1} are due to CH asymmetric and CH symmetric stretching respectively. These peaks are shifted to 2977 cm^{-1} and 2883 cm^{-1} for the NaCMC+$NaBF_4$ sample and 2976 and 2883 cm^{-1} for the NaCMC+$NaBF_4$ +TiO_2.

e) OH stretching

In the FTIR spectrum of NaCMC peaks at 3753 and 3659 cm^{-1} are attributed to the OH stretching mode. The change in peak position of these peaks are not analysed as they overlap with the OH stretching of $NaBF_4$.

4.3 Characteristic peaks of BF^{4-}

In the FTIR spectrum of $NaBF_4$ as shown in figure (4.2),the absorption peaks at 524,622,1030 and 1619 cm^{-1} are due to the vibrational mode of BF^{4-}.The peaks 524 and 622 cm^{-1} are shifted to 597 and 654cm^{-1} after for NaCMC+$NaBF_4$ and remains the same after the addition of TiO_2 to PE.The peak 1030 cm^{-1} shown no change in its position and the intensity of the peak 1619 cm^{-1} is reduced for both NaCMC+$NaBF_4$ +TiO_2 samples. These changes showed by the vibrational modes of NaCMC and $NaBF_4$ in the FTIR spectrum of NaCMC+$NaBF_4$ and NaCMC+$NaBF_4$+TiO_2 indicates that complex formation is there between polymer ,salt and filler.

The vibrational modes of $NaBF_4$ salt was analysed using FTIR in the wavenumber region of 4000-400cm^{-1}

The FTIR spectra of pure NaCMC biopolymer is shown in figure (4.1).

FTIR STUDIES FOR NaCMC:

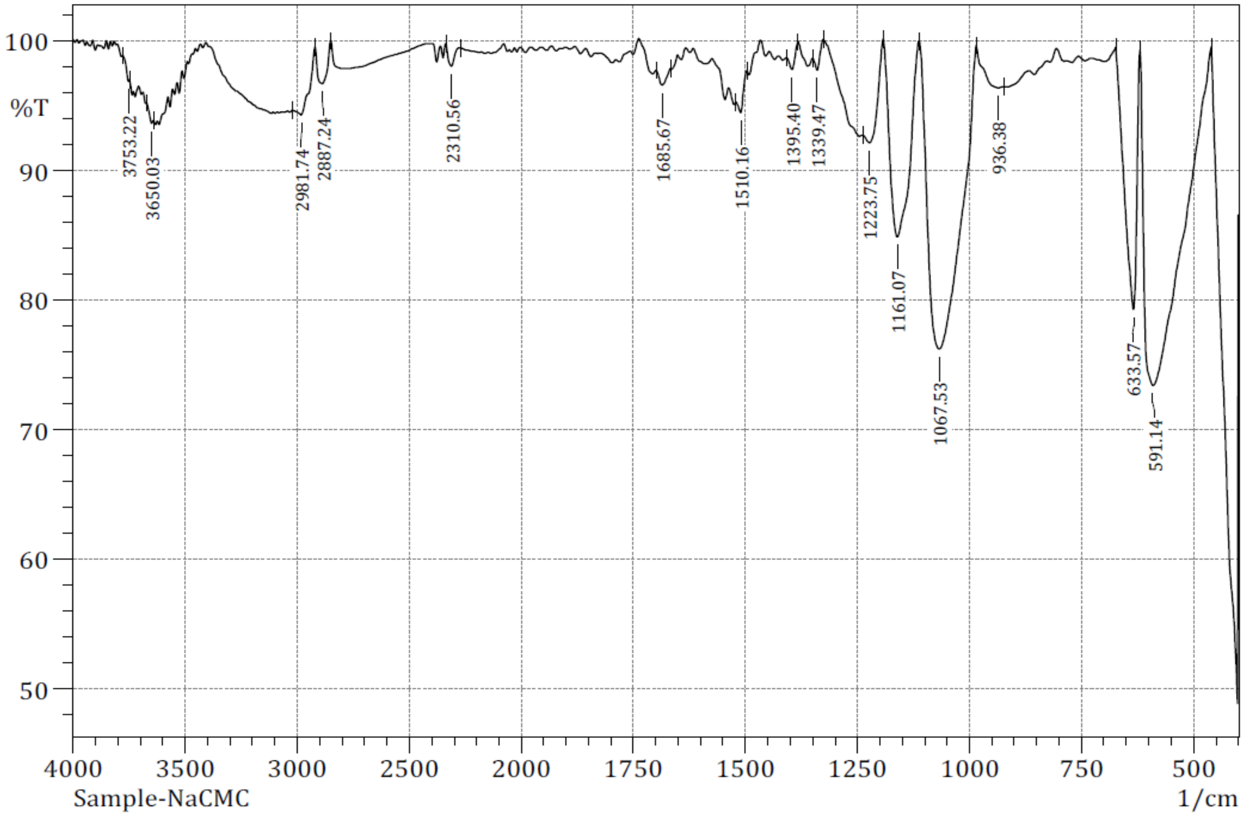


Figure (4.1) FTIR SPECTRUM OF PURE NaCMC

FTIR STUDIES FOR NaBF$_4$:

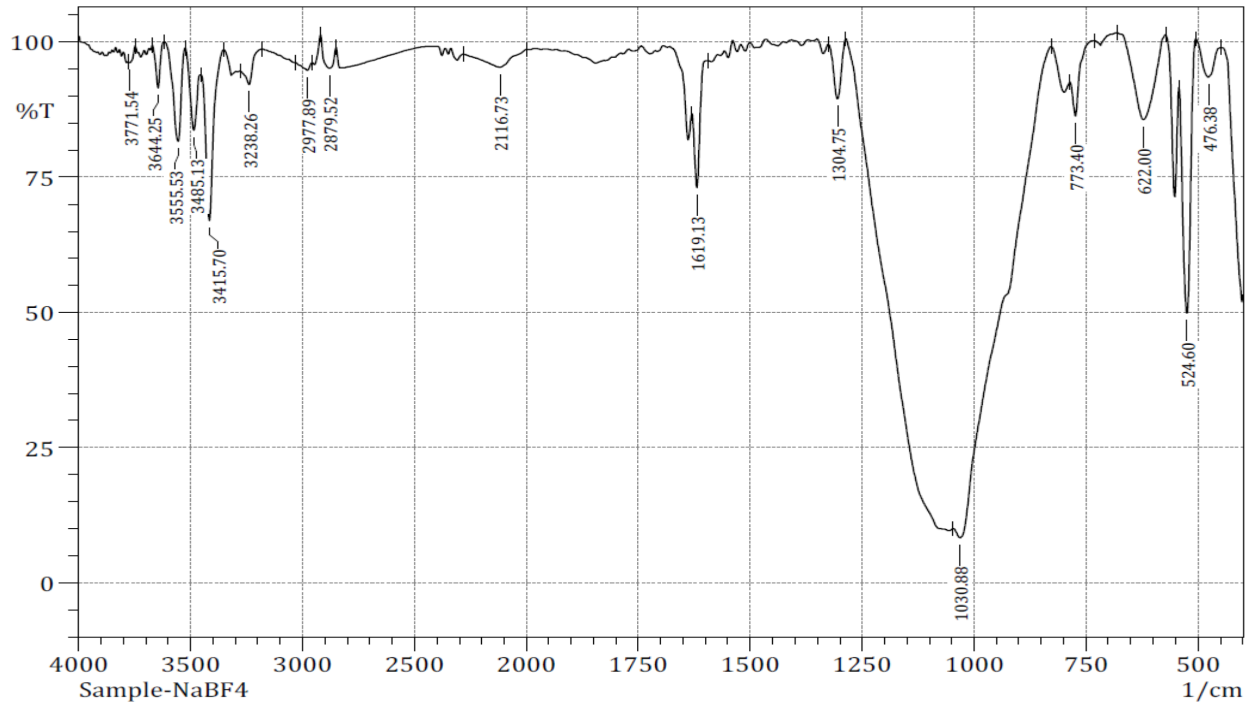
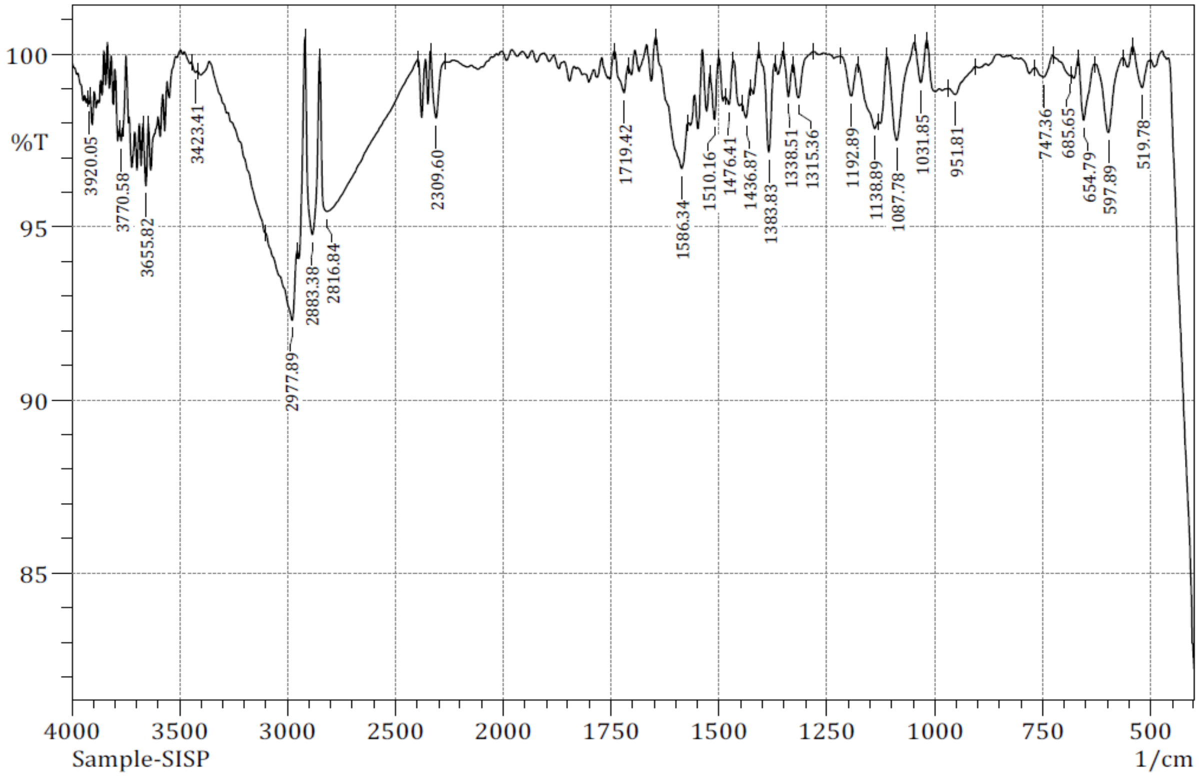


Figure (4.2) show the FTIR spectrum for $NaBF_4$



FTIR STUDIES FOR $NaBF_4$+NaCMC:

Figure (4.3) show the FTIR spectrum for $NaBF_4$+NaCMC

FTIR STUDIES FOR $NaBF_4$+NaCMC+TiO_2 (0.04%):

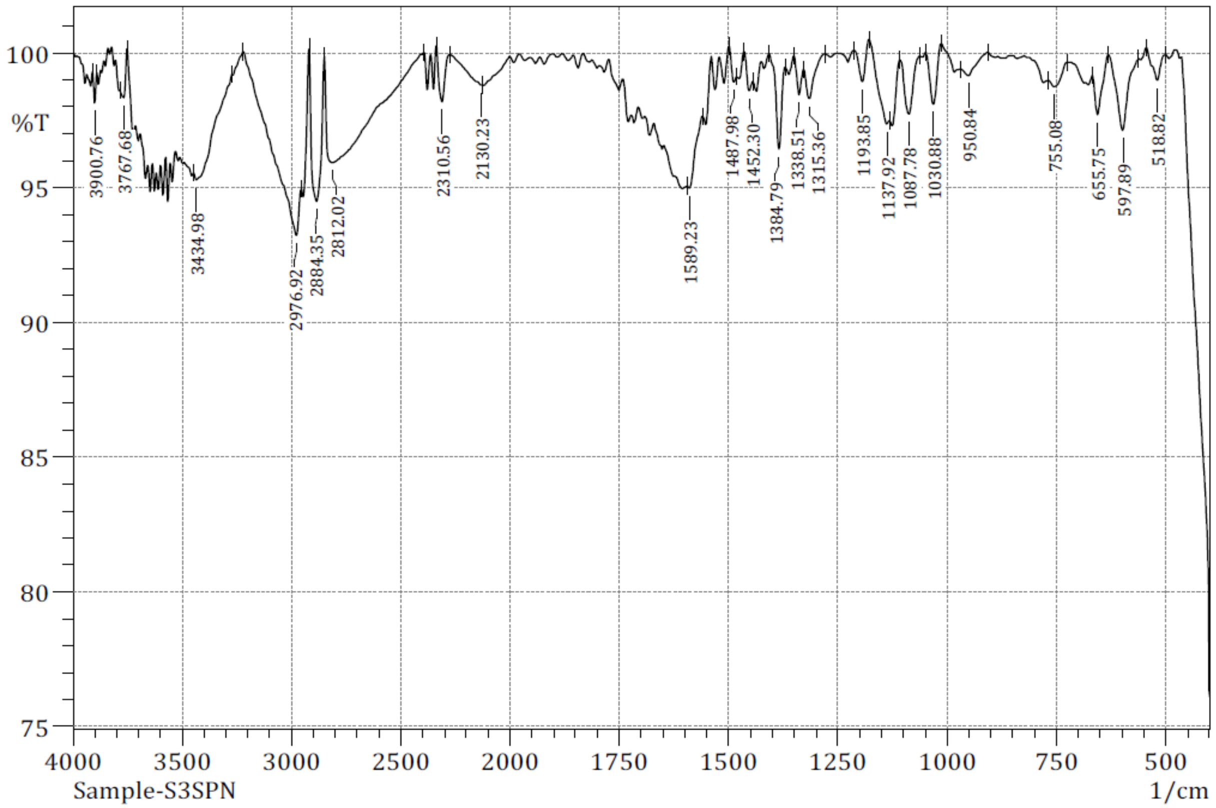


Figure (4.4) show the FTIR spectrum for $NaBF_4$+NaCMC+TiO_2(0.04%)

Table 4.1 Band assignments and corresponding wavenumber

	Wavenumber (cm^{-1})		
Band assignment	**NaCMC/NaBF$_4$**	**NaCMC+NaBF$_4$**	**NaCMC+NaBF$_4$+TiO$_2$**
STRETCHING	**For NaCMC**		
O-H	3753.22	3770.58	3434.98
C-H	--	2883.38	2976.92
C-Br	--	587.89	597.89
BENDING			
C-H	936.38	1436.87	1452.30
STRETCHING	**For NaBF$_4$**		
O-H	2977.89	3423.41	3434.98
C-H	2879.52	2883.38	2824.35
C-O	1030.88	--	--
C-Br	--	587.89	597.89
BENDING			
≡C-H	622.00	--	655.75
=C-H	--	685.65	655.75
C-H	--	1436.87	1452.30
CH_3 C-H	--	1383.83	1338.51

4.4 FREQUENCY DEPENDANCE CONDUCTIVITY

The electrical properties of solid bio polymer electrolyte with different concentration of TiO_2 filler have been studied using AC impedance spectroscopy analysis.

The figure (4.5) shows the complex AC impedance plot for NaCMC biopolymer. Figure (4.5) shows the AC impedance plot for NaCMC+ $NaBF_4$ solid biopolymer electrolyte system. Figure (4.3 to 4.7) shows the AC impedance plot for NaCMC+$NaBF_4$+X Wt% TiO_2 of filler added solid bio-polymer electrolyte system, where 5 the X varies from 0.02 to 0.10g.

The figure shows a semicircle due to the bulk and parallel combination of resistance and capacitance of bulk material. The extrapolated semicircle intercept X-axis which gives the value of bulk resistance R_b of the sample.

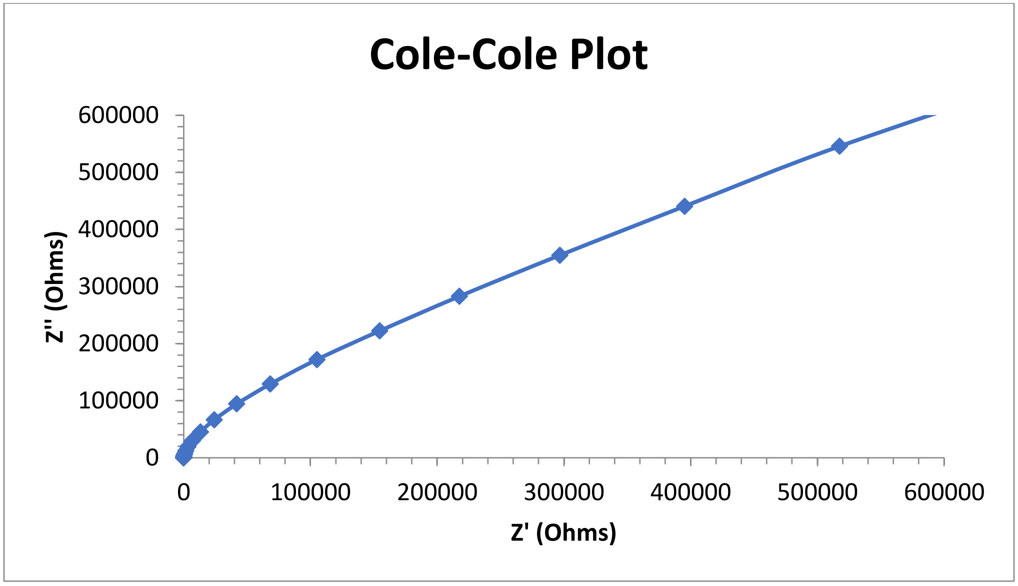


Figure (4.5) The AC impedance plot for pure NaCMC

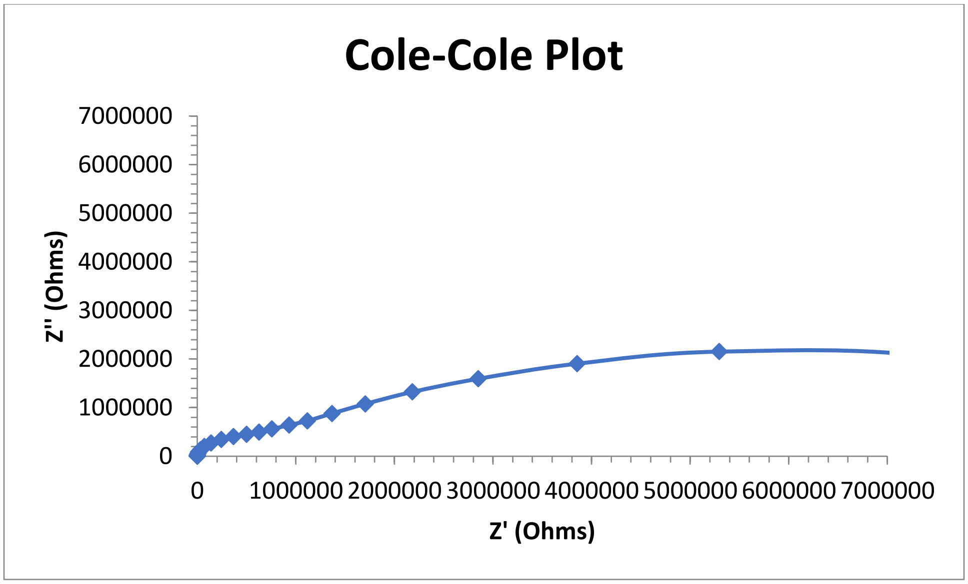


Figure (4.6) AC impedance plot for NaCMC+$NaBF_4$

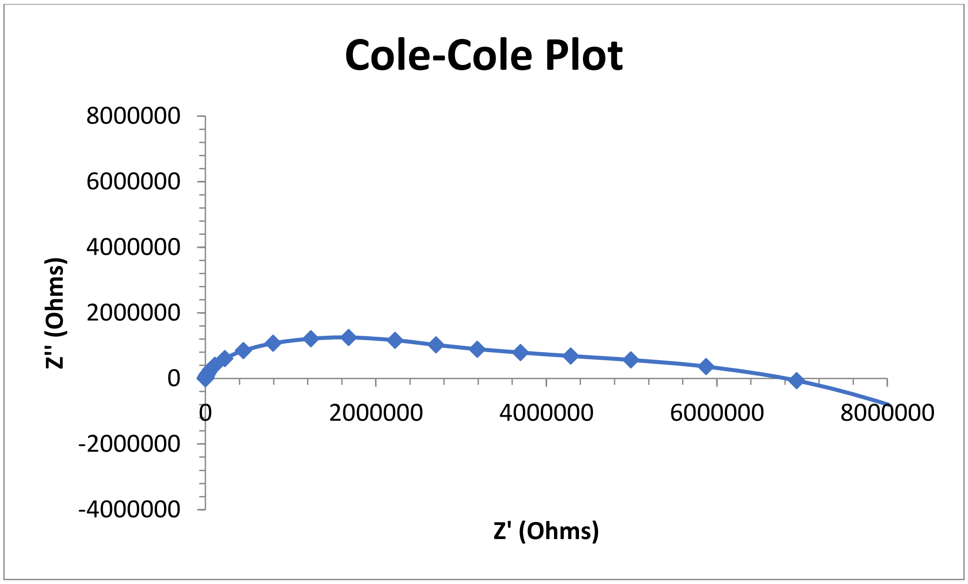


Figure (4.7) AC impedance plot for NaCMC+$NaBF_4$+TiO_2(0.02%)

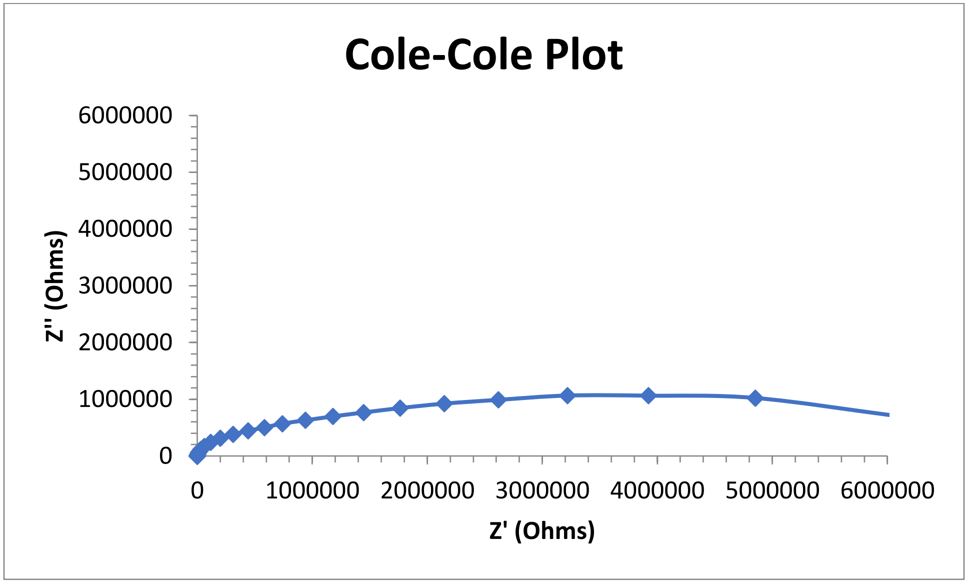


Figure (4.8) AC impedance plot for NaCMC+$NaBF_4$+TiO_2(0.04%)

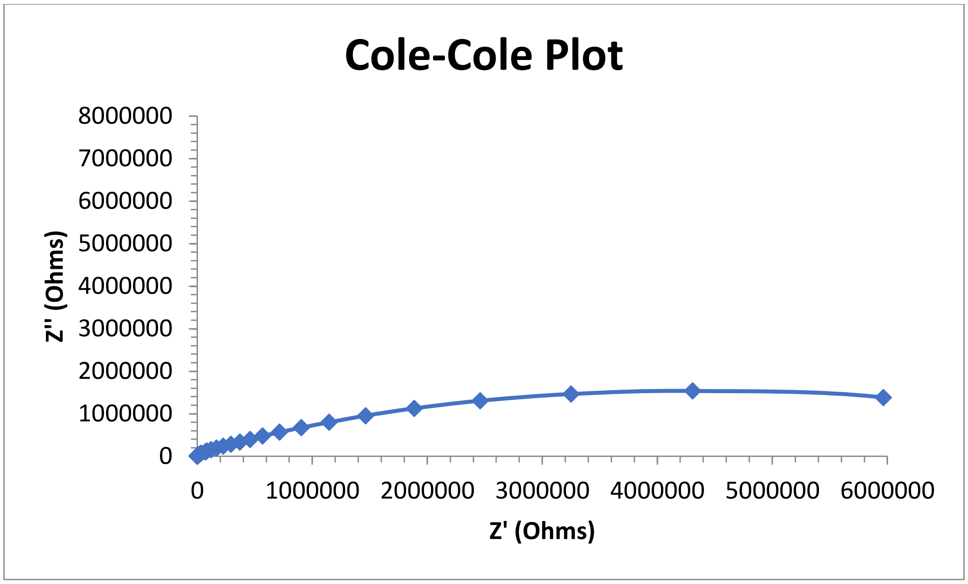


Figure (4.9) AC impedance plot for NaCMC+NaBF$_4$+TiO$_2$(0.06%)

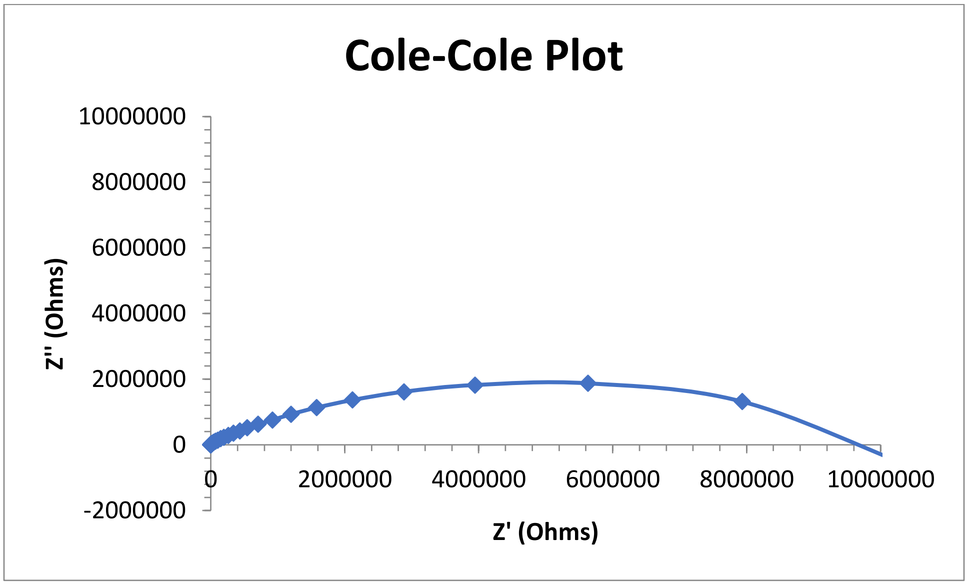


Figure (4.10) AC impedance plot for NaCMC+NaBF$_4$+TiO$_2$(0.08%)

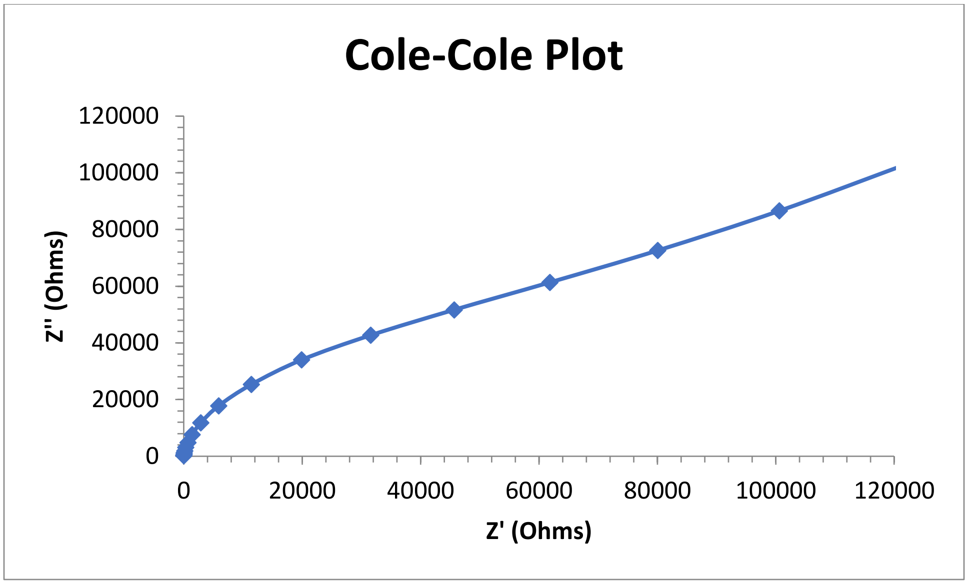


Figure (4.11) AC impedance plot for NaCMC+NaBF$_4$+TiO$_2$(0.10%)

The conductivity of the AC impedance spectroscopy is calculated at various frequency using the following expression and the values are given in table(4.2):

$$\sigma_{AC} = \frac{l}{R_b * A} \qquad \text{-----------------} \ 1$$

where,

l is the thickness of the sample

A is the contact area of the electrode

R_b is the bulk resistance of the sample

The conductivity of the pure NaCMC bio-polymer is found to be decrease the conductivity to $4.19*10^{-10}$ Scm^{-1}.This may be due to the interaction of NaCMC with NaBF$_4$ which inhibits the mobility of Na$^+$. The polymer is also not favourable for the disassociation of NaBF$_4$ into Na$^+$ andBF^{4-} ions. Addition of NaBF$_4$ salt to the pure NaCMC bio-polymer system .The ionic conductivity of NaBF$_4$+NaCMC the mobility of NA$^+$ ions which is allow the movement of ions within the polymer matrix. Usually the polymer electrolyte is a amorphous phase which is leads to the more more flexible polymer chain. Increase the mechanical strength of the solid bio-polymer electrolyte sample, In addition of TiO$_2$ filler.so, the highest ionic conductivity was attained at 0.04% TiO$_2$ filler concentration as the conductivity is $3.483*10^{-9}$ scm^{-1}.This is may be due to ion with filler and polymer with filler interaction.

After the addition of 2Wt% of TiO$_2$,the ionic conduction shows an increase in value from $4.19*10^{-10}$ to $6.34*10^{-10}$ Scm^{-1}.The value is further increased to $3.48*10^{-9}$ Scm^{-1} for 4Wt% TiO$_2$ added PE.This increase in ionic conductivity can be explained based on the interaction between TiO$_2$ and the polymer NaCMC. The filler,TiO$_2$ has the tendency to lower the polymer chain reorganization by acting as a cross linking center for the polymer segment. This enhances the amorphous nature of NaCMC which results in high ionic conductivity.

Further increase in concentration of TiO_2 decrease the ionic conductivity of polymer electrolyte.for high enough to each other imposing contain on the easy movement of polymer segment.

TABLE 4.2 CONDUCTIVITY VALUES FOR SAMPLES WITH VARIOUS RATIO OF TiO2 FILLER

SAMPLE	THICKNESS (cm)	RESISTANCE (Ohm) (10^6)	CONDUCTIVITY (Scm^{-1}) (10^{-10})
NaCMC (1g)	0.042	3.4413	7.07
$NaBF_4$+NaCMC (0.3 +0.7)	0.053	2.5284	4.19
$NaBF_4$+NaCMC+TiO_2 (0.02)	0.109	3.4413	6.34
$NaBF_4$+NaCMC+TiO_2 (0.04)	0.065	2.3732	$3.48*10^{-9}$
$NaBF_4$+NaCMC+TiO_2 (0.06)	0.052	2.9248	$1.78*10^{-9}$
$NaBF_4$+NaCMC+TiO_2 (0.08)	0.084	3.2417	5.19
$NaBF_4$+NaCMC+TiO_2 (0.1)	0.034	1.5024	4.53

CHAPTER V

SUMMARY AND CONCLUSION

Polymer electrolyte consisting of Carboxyl methyl cellulose and sodium salt and Sodium Tetrafluoroborate was prepared by solvent casting technique and its mechanical strength has been enhanced with the addition of TiO_2 filler. Distilled water has been used as the solvent. FTIR results confirm the complex formation of $NaBF_4$and the polymer NaCMC. The introduction of Na+ ions in NaCMC molecule reduced the crystalline nature of the NaCMC and thereby increase its amorphous nature leads to increase in conductivity. The X-Ray diffraction study confirms the occurrence of structural changes in NaCMC due to the addition of $NaBF_4$ and TiO_2

The ionic conductivity of $NaBF_4$- NaCMC is a result of mobility of Na+ which allows the ion movement within the polymer matrix. The impedance response of the electrolytes reveals that the conductivity is due to Na+ ions as observed in the earlier systems studied. The conductivity of a polymer electrolyte is usually due to the amorphous phase. This leads the polymer chain more flexible, which results in the segmental motion of the polymer.

The maximum ionic conductivity of the NaCMC +$NaBF_4$ + TiO_2 has been determined as $3.48*10^{-9}$ Scm-1 at room temperature.

REFERENCES

1.N. N. S. Baharun, M. A. Mingsukang, M. H. Buraidah, H. J. Woo, A. K. Arof **“** Journal of Ionics 26” , 1365–1378 (2020),published on 22 October 2019.

2.NajamSardar**,**MohammadKamil**,**Kabir-ud-Dinjournal of colloids and surfaces A :Physicochemical and Eingineering Aspects .volume of 415 and public shed on December 2012 ,Pages 413-420.

3.Supriya Shetty,Ismayil, Shreedatta Hegde, V Ravindrachary, Ganesh Sanjeev, Rajashekhar F Bhajantri & Saraswati P Masti “Journal of Ionics” and published on 25 March 2021.

4.Erlantz Lizundiaa,b, Carlos M. Costac,d , Raquel Alves c,e , Senentxu Lanceros-Méndez b,f Published on 1 July 2020 and “Journal of Elsevier” ,volume 1 ,25 December 2020,100001.

5. MN Chai, MIN Isa “ Journal of crystallization process and Technology” Vol.No3 publisedon 2013.

6. H.Buqa,M.Holzapfel,F.Krumeich,C.Veit, P.Novák, “Journal of power sources”,volume 161,page No.617-622, issue 1 October 2006.

7. Francesca Colòa , Federico Bellaa, Jijeesh R. Naira , Matteo Destroa,b , Claudio Gerbald “Journal of Elsevier and Electrochemica Acta 174”page no.185-190,Published on 29 may 2015.

8.Wenting Lan , Li He , and Yaowen Liu , “ Journals of coating” volume 8 publised on 19 August2018.

9.Mohd Ikmar Nizam Mohamad Isa, Nur Hidayah Ahmad, “Advanced material science” page no.247-252.publised on June 2015.

10.Y. Li É.S. Nagy M.N. Esmail Z. HórvölgyiWeak “Journals of Macro molecule” Symposia Volume 202,page No.307-324publised on 21 October 2003.

11. NK Zainuddin ,MA Saadiah,APP Abdul Majeed,AS Samsudin, “Journal of polymer analysis and charaterrization23(4)” page No.321-330.2018.

12.J. POLAVKA, Ľ. LAPClK, V. KELLO, L. HEBORT, and M. YVS Chemical papers 38 (5),page No.619-628,1984.

13. M.Jaipal Reedy, T.Sreekanth, “Journal of Mateerrial science”, 35 (2000)page No. 2841-2845.

14. M.Jaipal Reedy, T.Sreekanth, S. Ramalingaiah, “Journal of Power sources 79 “ page No.105-110,1999.

15.Siddaramaiah, “practicals in polymer science”, First edition : 2005, Reprint 2007.

16. Jinli Qiao, Jing Fu Lin,Rui Lin,Jianxin Ma, Jianshe Liu, “polymer” (2010) page No.4850-4859.

17. M.M.E.Jacbo, S.R.S Prabaharan, S,Tadhakrishna, “Solid state Ionics” 104(1997) 267.