



Circuit Modeling and Dielectric of Solid state EDLC device based on Magnetism Ion Conducting Polymer

Research Project

Submitted to the department of Physic in partial fulfillment of
the requirement for the degree of B.A in physics

By :
Shajwan Omer Mohammed


Supervised by:
Asst. Prof. Dr. Mowfaq Jalil Ahmed

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Supervisor Certificate

This research project has been written under my supervision and has been submitted for the award of the degree of BSc. in (Physics).

Signature



Name: Asst. Prof. Dr. Mowfaq Jalil Ahmed

Date: 2024/04/12

I confirm that all requirements have been completed.

Signature:

Name: Asst. Prof. Dr. Asaad Hamed

Head of the Department of Physics

Date: / 4 / 2024

Dedication

My great parents, who never stop giving of themselves in countless ways.

My beloved and sisters.

To all my family and my friends who encourage and support me. All the people in my live who support me in academic life.

Acknowledgements

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List of Abbreviations

Abbreviation	Meaning
SPE	solid polymer electrolyte
CS	chitosan
POZ	poly (2-ethyl-2-oxazoline)
NH ₄ NO ₃	ammonium nitrate
GL	glycerol
FTIR	Fourier transform infrared
ITP	ion transport parameters
n	number of charge carriers
μ	ionic mobility
D	diffusion coefficient
M_r	real part of modulus
M_i	imaginary part of modulus
σ_{ac}	ac conductivity
LE	liquid electrolyte
PEO	poly (ethylene) oxide
σ_{dc}	dc conductivity
PEG	poly ethylene glycerol
PPE	plasticized polymer electrolyte
R	resistance
C	capacitance
ϵ_r	dielectric constant
ϵ_i	dielectric loss
PVA	poly vinyl alcohol
GPE	gel polymer electrolyte
PVdF	poly (vinyl denfluoride)
ϵ^*	dielectric permittivity
Li ⁺	Lithium ion
Mg ⁺²	Magnesium ion
IS	impedance spectroscopy
$\tan \delta$	loss tangent
Z_r	real part of impedance
Z_i	imaginary part of impedance
Z^*	complex impedance
EIS	electrochemical impedance spectroscopy
GL	glycerol
R	resistance
C	capacitance
D	diffusion coefficient

Abstract

The aim of the research was to better understand how polarization and ion conduction work in biopolymer-mix electrolyte systems. In order to comprehend energy storage and loss resulting from ion mobility better, the dielectric properties of CSPVMGNT were investigated. Chitosan (CS) and polyvinyl alcohol (PVA) were used to produce polymer blends, while magnesium nitrate ($Mg(NO_3)_2$), at a weight percentage of 50%, served as a source of magnesium ions. To improve ion conductivity, the CS:PVA: $Mg(NO_3)_2$ system was examined at different doses of glycerol plasticizer. To ascertain the produced films' suitability as energy storage materials, a number of analytical techniques were applied to examine their electrochemical characteristics. The dielectric constant significantly improved with increasing plasticizer concentration. Non-Debye relaxation is indicated by the existence of an asymmetric relaxation peak in $\tan\delta - M''$ spectra. At $7.34 \times 10^{-5} S/cm$ the biopolymer mix electrolyte with a plasticizer content of 55.8 percent exhibited the highest DC conductivity. The present plasticized magnesium ion-conducting biopolymer mix electrolyte exhibits promising findings for future use in energy storage devices.

Chapter one

1.1 Introduction

The increasing oil problem and environmental concerns have sparked interest in renewable energy sources, which include those that come from naturally renewing sources including the sun, wind, storms, seas, seeds, algae, geothermal energy, and biodegradable polymer materials. (Wang, 2020; Zhou, 2021). The large subject of polymer science, organic chemistry, electrochemistry, and inorganic chemistry are all included in polymer electrolyte (PE) science. (Wang, 2009). At room temperature, a polymer electrolyte is both a separator and an ion conducting membrane with moderate to high ionic conductivity. Recently, material science has placed a great deal of emphasis on polymers, particularly solid-state solutions, which are an example of an ion-conducting polymer (solid-state polymer electrolytes SPE). Ion-conducting polymers are being studied as a solid electrolyte example. due to its potential for usage in electrochemical devices such supercapacitors, fuel cells, and rechargeable batteries. Historically, the main power sources for various commercial electronic devices have been lithium-ion batteries (LIB) and conventional liquid electrolytes (LES). However, defects such volatile liquid electrolytes, high flammability, and chemical instability can cause combustion and even explosion in batteries. (Jian, 2022).

The study intended to investigate ion conduction and polarization effects in biopolymer-mix electrolyte systems. The dielectric characteristics of CSPVMGNT were examined to better understand energy storage and loss due to ion mobility.

1.2 Literature review

Wright (1975), a polymer scientist from Sheffield, invented conductive SPEs. (Wright, 1975) Poly(ethylene) oxide (PEO) has been utilized to dissolve inorganic salts and conduct ions at ambient temperature circumstances since its discovery by Wright and colleagues in 1975. (Hamdan, 2014). SPEs are regarded as really multifunctional materials because of their versatility as an ion transportation medium in critical applications such as energy storage and electrochemical displays. (Wright, 1998). SPEs are being developed to replace standard LEs. LEs are incompatible for use for a variety of reasons, including poor electrochemical stability, leakage, and environmental effect. SPE is offered as a solution to these issues in this work due to its compatibility with electrodes, ease of processing, low weight, and coast ability. (Hafiza, 2014). Because they are solvent-free, SPEs are recognized for their excellent safety performance. SPEs with strong elastic relaxation qualities under stress are simple to operate with and process (Ibrahim, 2014). Scientists are now looking for a novel polymer host that has improved conductivity and mechanical characteristics while being cost-effective and ecologically safe. . In comparison to gel and LE, SPE has several advantages, including no leakage and simple manufacture. However, because of its low conductivity value, it is challenging for researchers to develop high-quality polymer electrolytes with good ionic conductivity. (Hafiza, 2014). These problems can be solved in a variety of ways, such as by combining two polymers, adding nano-sized fillers to the polymer matrix, plasticizing it with a liquid additive, etc. (Hirankumar, 2018). Polymers are classified into two types: synthetic and natural. The removal of waste and the depletion of nonrenewable fossil fuels have driven the development of ecologically acceptable alternative energy sources. Because plastic rubbish does not degrade when it is abandoned, it continues to damage the environment. As a result, there has been a

drive to develop biodegradable polymers to replace those that are not. Furthermore, synthetic-based polymers are petroleum-derived, have a high material cost, and are nonbiodegradable in nature. To reduce the need for petroleum-based polymers, researchers have attempted to create natural biopolymers. (Rani, 2015). An ion-pairing effect appears to be associated to a decrease in conductivity and polarization, according to the literature. Due to the low dielectric permittivity of host polymers, a variety of methods have been suggested to improve DC conductivity (DC), including plasticization, salt doping, polymer grafting, polymer blending, and salt doping (Aziz, Hamsan, 2020). Plasticization, which increases salt dissociation, is an important stage that raises conductivity. (Asnawi, 2020). In addition to plasticization, utilizing two polymers as the host material for ionic conduction may enhance the conductivity of a polymer electrolyte (Rani, 2015). When two polymers are joined, extra complexation sites are formed, which increases ion movement, exchange, and conductivity. The electrical conductivity of natural CS films is very low. The hydrogen atoms in the CS monomer are strongly linked and cannot be mobilized by an electric field. Polymer blends based on POZ:CS electrolyte systems impregnated with varied NH_4NO_3 compositions electrolyte systems were created by solution casting in the presence of 1% acetic acid solvent (Rani, 2015).

POZ has been suggested as a possible biological candidate in several research investigations (Aziz, woo, 2020). Understanding how ions conduct through polymers is essential to create more efficient polymer electrolytes for electrochemical devices (Navaratnam, 2015). Plasticization is another approach to improve the conductivity of an electrolyte. Adding a little quantity of liquid to a polymer matrix can plasticize the polymer chain and accelerate the rate of salt dissociation. A high dielectric constant plasticizer may dissolve more salt and create more free mobile ions (Shukur, 2013). The plasticization process affects salt

dissociation through offering more conducting paths for mobile ions to travel, increasing the ionic conductivity of the polymer electrolyte (Asnawi, 2020). Furthermore, plasticizer has the ability to increase the amorphous nature of SPE, leading to an increase in the segmental motion of the polymer chain, which supports more ion mobility due to a lower energy barrier and is expected to increase ionic conductivity (Hafiza,Isa,M.I.N , 2020). Because of the polymers' strong connections, several researchers moved their emphasis to polymer mixing, one of the most effective ways for improving the electrical and mechanical properties of electrolytes systems (Rani, 2015). Researchers are interested in polymer blending because of the simplicity of the preparation and the ability to control the physical properties of the films (Shukur, Ithnin, Kadir, 2014). One aspect that influences the conductivity of polymer mixtures is their miscibility. Blends that do not have phase separation will have greater conductivities than blends that do. Magnesium nitrate salt ($Mg(NO_3)_2$) (Aziz, Ahmed 2023) was used in this study because Magnesium salts are known to be effective polymer matrix proton donors. CS is a popular polysaccharide in blending systems with other polymers. As a natural polymer, CS is used as a host polymer since it is non-toxic and biodegradable (Navaratnam, 2015). This natural biopolymer's availability, cheap cost, biocompatibility, biodegradability, and simplicity of chemical modification are all benefits. CS can be used in various applications, such as water treatment, pharmaceutical products, agriculture, and membrane formation. Biodegradable polymers, such as CS, can create solid electrolytes that are environmentally safe and have good processing capabilities for producing thin films, allowing for more creative battery system designs, such as multiple cell battery systems (Sudaryanto,2015). When two polymers are joined, additional complexation sites are formed, which increases ion movement, exchange, and conductivity. The electrical conductivity of natural CS films is quite low. The hydrogen atoms in the CS monomer are firmly linked and

cannot be mobilized by an electric field. Polymer blend electrolyte systems were developed by solution casting in the presence of 1% acetic acid solvent on the basis of POZ:CS electrolyte systems impregnated with varied $(\text{Mg}(\text{NO}_3)_2)$ compositions (Rani, 2015). POZ has been identified as a possible biological candidate in several research investigations (Aziz, Woo, 2020). Understanding how ions conduct through polymers is essential for developing more efficient polymer electrolytes for electrochemical devices (Navaratnam, 2015). Plasticization is another approach for improving the conductivity of an electrolyte. A small quantity of liquid added to the polymer matrix can plasticize the polymer chain and increase the rate of salt dissociation. A high dielectric constant plasticizer may dissolve more salt and create more free mobile ions (Shukur, 2013). The plasticization process affects salt dissociation by providing more conducting paths for mobile ions to travel, increasing the ionic conductivity of the polymer electrolyte. Furthermore, plasticizer has the ability to increase the amorphous nature of SPE, which promotes an increase in the segmental motion of the polymer chain, which encourages more ion mobility due to a lower energy barrier and is expected to increase ionic conductivity (Hafiza, Isa, M.I.N , 2020). Plasticized SPE is often inflexible due to the strong interactions of the polymers. The attraction forces between polymer chains can be lowered by adding plasticizer to improve their flexibility. Plasticizers are frequently composed of polymers with low molecular weight or nonvolatile organic solvents. Polyethylene glycol (PEG-200, PEG-400, PEG-600), and dimethylformamide are examples of acceptable plasticizers. (DMF), ethylene carbonate (EC), propylene carbonate (PC), etc. (Hirankumar, 2018). GL is a colorless, odorless liquid that is produced as an inevitable by-product of the transesterification of vegetable oils used to manufacture biodiesel. It can also be generated from less toxic materials such as microalgae or cellulose. It is frequently used in drugs due to its inexpensive cost, low toxicity, and unique physicochemical properties, such as water solubility and

hygroscopicity (Sadiq,Aziz, 2022). At room temperature, GL is a non-toxic chemical with a high boiling point (290 °C) and a low melting point (18 °C), preventing evaporation and solidification. According to its chemical formula (C₃H₈O₃), GL has a multi-hydroxyl group structure, which suggests it has more accessible electron lone pairs for ionic conduction. The high dielectric constant (GL) of glycerol (42.5) increases salt dissociation and decreases interactions between polymers. Polymer electrolytes frequently exhibit crystalline and amorphous phases. Considering the fact that ion conduction occurs mostly in the amorphous phase. Ion relaxation and charge transport processes are among the most studied concerns in SPE, a branch of condensed matter physics (Aziz, 2010). FTIR has previously been used to determine the complexation of polymers with salt. FTIR spectroscopy and electrochemical impedance spectroscopy (EIS) have been demonstrated to be efficient approaches for examining the polymer host's interactions with charge carriers and establishing the charge carriers' transport characteristics (Asnawi,Aziz, 2021). Sharma et al. (Kamboj, 2021) have investigated the polymer-ion interaction using FTIR. It was demonstrated that anion peak deconvolution is a new approach for distinguishing between regions associated with single free ions and regions associated with pairs of ions.

Chapter two

Methodology

2.1 Solution Casting Method

The solution casting method, also known as the direct casting method, is one of the most commonly used to prepare polymeric films for food, pharmaceuticals, and biomedical applications (Figure 2.1). This method is straightforward and has been used for a long time to develop film-based polymeric systems. Hence, many authors regard this method as the conventional solution casting method. The method involves the dissolution of the polymers in suitable solvents. The polymeric solutions, which may contain various additives, such as plasticizers.

The blends of chitosan can also be used to develop films. Blends are prepared by mixing two or more polymers to tailor the physical properties of the resultant films over the films made with pristine polymer(s). The polymeric blends may either form a homogenous matrix or a phase-separated matrix system. It has been reported that blends of chitosan with different polymers (natural or synthetic) can improve the physical, mechanical, thermal, optical, and barrier properties [Haghighi, 2020]. The natural polymers used for this purpose are classified as polysaccharides and proteins [Haghighi, 2020]. The derivatives of these polymers have also been employed. The examples of polysaccharide-based natural polymers include pectin, starches from different sources (e.g., cassava starch, purple yam starch, and potato starch), bacterial cellulose, carboxymethyl cellulose, and gum Arabic. Protein-based natural polymers include collagen, gelatin, fish myofibrillar protein, soy protein isolate, and zein [Haghighi, 2020].

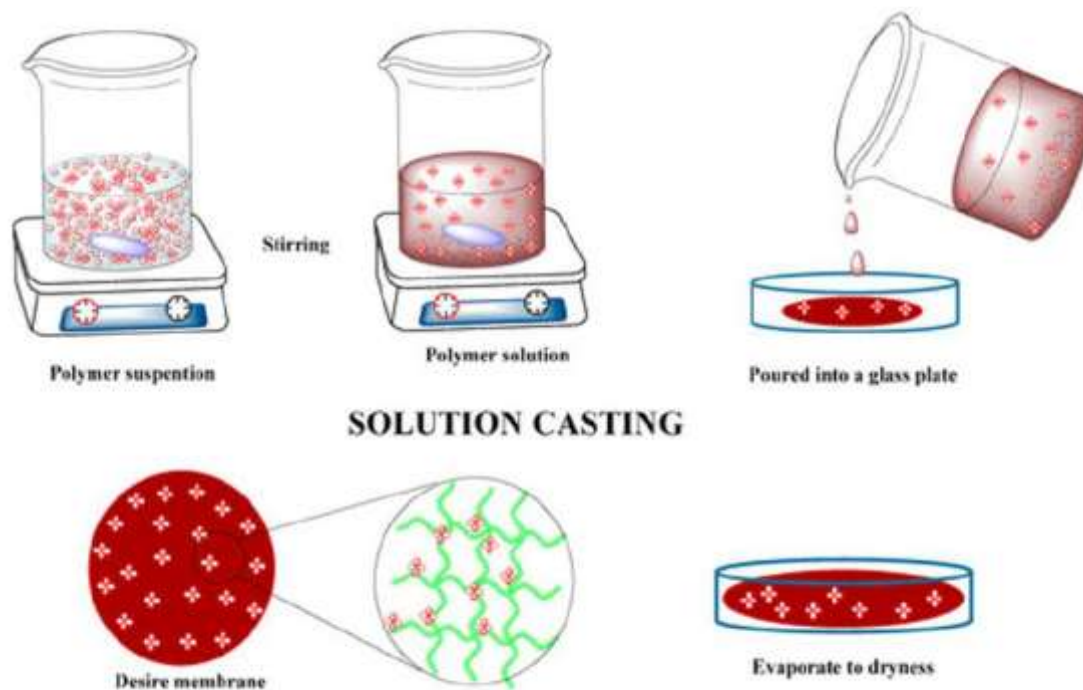


Figure (2.1) General steps in the solution casting method [Ilyas, etal 2022).

Some of the synthetic polymers employed in conjunction with chitosan include poly (vinyl alcohol), poly (ϵ -caprolactone), and ethylene-vinyl alcohol. These polymers are mixed with chitosan solution and homogenized before the degassing stage, and this is then used for the film casting.

The functionality of the chitosan films (pristine or blend) can further be improved by adding additives. Various additives, such as essential oils and nanoparticles, are being added to enhance the mechanical and barrier properties. These components are added to the chitosan solution or chitosan blends and are subsequently homogenized to form stable emulsions or dispersions.

2.2 Sample Preparation

Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$), polyvinyl alcohol (PVA), and chitosan (CS) are required to create the CS:PVA: $\text{Mg}(\text{NO}_3)_2$ matrix of hosts. Magnesium nitrate provides Mg-ions to the mixture. The solvent acetic acid (CH_3COOH) and double-distilled water were needed as agents for polymeric materials in the solution-cast method.

The present samples have been prepared previously using the solution casting method (Aziz,2023).

To prepare the biopolymer mix host matrix, 1g of CS was disseminated in 60 mL of 1% acetic acid solution using a magnetic stirrer for several hours at room temperature. Meanwhile, 1g of PVA was completely dissolved in 60mL of double-distilled water after constant stirring at 80^0c for many hours.

After the PVA solution had cooled to room temperature, the two polymer solutions were constantly mixed to form a homogeneous viscous solution. Following that, 50 wt.% $\text{Mg}(\text{NO}_3)_2$ salt was added to the CS: PVA blended solutions while stirring to ensure a homogeneous mixture. Following that, glycerol concentrations ranging from 11 to 55 wt.% were gradually added to each solution in increments of 11 wt. percent. Each prepared solution was then placed in a clean, labeled Petri dish, and the solvent was allowed to evaporate at room temperature to produce the film gradually. Finally, the electrolyte systems with glycerol incorporation of 11, 22, 33, 44, and 55 wt.% were coded as CSPVMGNT1, CSPVMGNT2, CSPVMGNT3, CSPVMGNT4, and CSPVMGNT5, respectively.

2.3 Fabrication of the EDLC device

An EDLC is made by blending 6.25% carbon black (CB) and 81.25 % activated carbon (AC) in a planetary ball mill for 20 minutes at 500 rpm. The resulting powder mixture (AC: CB) is then dissolved in 15 mL of N-methy-2-pyrrolidone (NMP) with a 12.5% polyvinylidene fluoride (PVdF) binder until the solution becomes thick and black. Next, use the doctor blading technique to apply the black solution on the 0.25 mm thick metal foil. The coated aluminum foils are then quickly dried in an oven at 60°C. After drying the electrodes, a disk with a geometric area of 2.01 cm^2 is created. Figure (2,2) depicts an EDLC assembly with the AC electrode, highest conductive electrolyte, and AC electrode positioned in that sequence. This design included the cell within a CR2032 coin, which was then put in a Teflon housing as shown in figure (2.2).

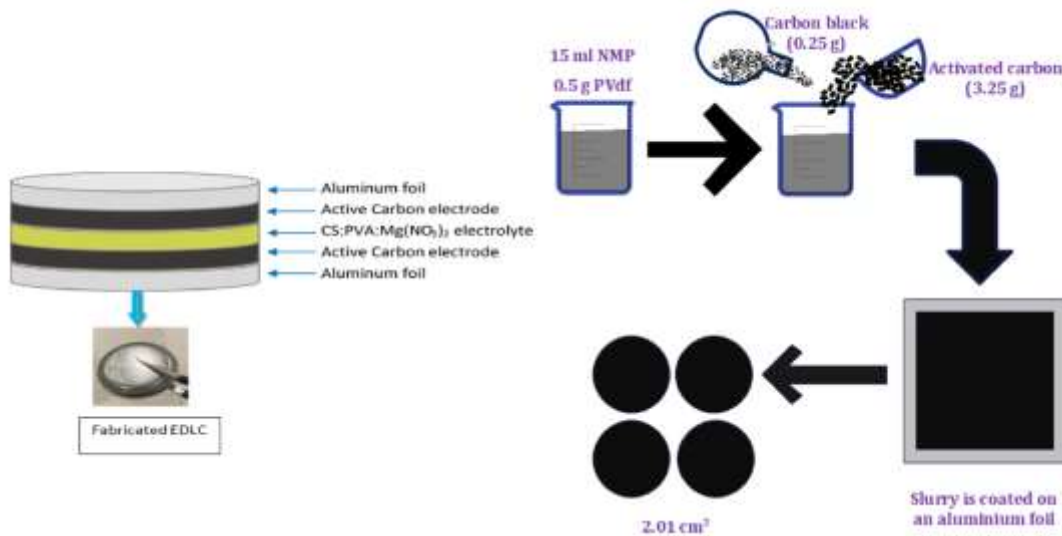


Figure (2.2) Schematic of the EDLC arrangement and electrode formation.

2.4 Impedance Related Function

Impedance spectroscopy, or IS, is an effective method for determining many of the electrical characteristics of materials and their interactions with electrically

conducting electrodes. It may be used to study the dynamics of bound or mobile charge in the bulk or interfacial areas of many kinds of solid or liquid materials, including ionic, semiconducting, mixed electronic-ionic, and even insulators (dielectrics). Several additional measured or calculated impedance variables frequently play an essential role in IS. Other similar functions used in IS include complex admittance ($Y(\omega)$), complex permittivity $\varepsilon(\omega)$, and complex electric modulus $M(\omega)$. The four fundamental impedance response values can be indicated by the generic phrase immittance, whereas the two quantities are commonly characterized as the complex dielectric constant or dielectric permittivity.

$$\varepsilon^* = (j\omega C_0 Z^*)^{-1} = \varepsilon_r - j\varepsilon_i \quad \dots (2.1)$$

$$M^* = j\omega C_0 Z^* = M_r - jM_i \quad \dots (2.2)$$

The dielectric parameters such as dielectric constant (ε_r), dielectric loss (ε_i), loss tangent ($\tan\delta$), complex electric modulus (M_r and M_i) and σ_{ac} was derived from the impedance-related functions as follows (Nofal, 2022) :

$$\varepsilon_r = \frac{Z_i}{\omega C_0 (Z_r^2 + Z_i^2)} \quad \dots(2.3)$$

$$\varepsilon_i = \frac{Z_r}{\omega C_0 (Z_r^2 + Z_i^2)} \quad \dots (2.4)$$

$$\tan \delta = \frac{\varepsilon_i}{\varepsilon_r} \quad \dots(2.5)$$

$$M_r = \frac{\varepsilon_r}{(\varepsilon_r^2 - \varepsilon_i^2)} \quad \dots(2.7)$$

$$M_i = \frac{\varepsilon_i}{(\varepsilon_r^2 - \varepsilon_i^2)} \quad \dots(2.8)$$

$$\sigma_{ac} = \omega \varepsilon_0 \varepsilon_i = \left[\frac{Z_r}{(Z_r^2 + Z_i^2)} \right] \left(\frac{t}{A} \right) \quad \dots (2.9)$$

here, C_0 is vacuum capacitance of the cell and is equal to $\frac{\varepsilon_0 A}{d}$, where ε_0 is the

permittivity of free space 8.85×10^{-12} F/m, A and d are the area and the thickness of the sample, respectively and $\omega = 2\pi f$, where f is frequency of the power source, z_r is the real part of impedance, z_i is the imaginary part of impedance, and $\tan \delta$ is loss tangent.

Chapter Three

Results and discussion

3.1 Dielectric Constants

The dielectric constant determined the polarity of the polymers and the energy stored in each cycle, whereas the dielectric loss characterized the energy lost owing to ion mobility (Liu,2020).

The study examined a material's dielectric characteristics under various situations, including ambient temperature and different frequencies.

Figures 2 and 3 show the measured values of the dielectric constant and dielectric loss. At low frequencies, large dielectric properties were observed, indicating that the electrodes were being polarized due to space-charge effects. The polarization area's size was critical for predicting mobility and effective ion concentration, both of which are important elements in the creation of high capacitance EDLC devices (Machappa,2009).

The results also revealed that at low frequencies, the dielectric constant and dielectric loss values were larger, owing to interfacial polarization. This phenomenon was caused by a rise in charge carrier concentration at the interface, rather than by the electrolyte's bulk properties. At higher frequencies, the dielectric constant and dielectric loss values dropped nonlinearly before reaching a steady state. The dielectric constant and dielectric loss measurements were predicted to plateau at lower frequencies and then show power law dispersion at higher frequencies. This was consistent with Klein et al.'s theoretical study of electrode polarization. The present electrolyte system's ϵ' and ϵ'' spectra clearly demonstrate these characteristics.

Figures 3.1 and 3.2 indicate a rise in ϵ' and ϵ'' values as a fraction of the plasticizer content in the system, owing to an increase in charge carrier concentration (Bhajantri,2021). The present plasticized CS-PVA-Mg (NO₃)₂ biopolymer blend electrolyte systems, notably the CSPVMGNT5 sample, show a significant rise in the ϵ' due to the sample's strong ionic conductivity in the low frequency region. On the other hand, a higher dielectric constant of SPE corresponds to a better ability of the matrix to dissolve salts (Wang,2016). The relaxation behavior of the CSPVMGNT biopolymer blend electrolyte systems was determined by examining the loss tangent ($\tan \delta$).

Figure 3.3 illustrates how the tangent loss ($\tan \delta$) of CSPVMGNT films varies with frequency and temperature. The $\tan \delta$ increased with frequency and peaked at a given frequency before continuously falling after that. This is due to the active (ohmic) component rising quicker than the reactive (capacitive) component at low frequencies. At higher frequencies, the ohmic component loses its frequency dependency, but the capacitive component increases according to frequency.

This pattern of change has already been seen in numerous SPE systems. The system exhibits a wide single peak at the mid-frequency of $\tan \delta$, indicating a non-Debye type dielectric relaxation process (Tripathi,2020). The relaxation time of all plasticized SPEs was calculated using the peak location of $\tan \delta$, which listed in table (3.1).

Table 3.1 The relaxation time of all plasticized SPEs samples

Sample code	relaxation time (s)
CSPVMGNT1	1.32×10^{-3}
CSPVMGNT2	7.58×10^{-4}
CSPVMGNT3	6.06×10^{-5}
CSPVMGNT4	9.23×10^{-6}
CSPVMGNT4	$1.63 \times 10^{-6}s$

As a consequence, the appearance of tan peaks and the resulting shift in their position with increasing plasticizer concentration support the dielectric relaxation phenomena. SPE films are polarized when an external electric field is applied via microscopic rearrangements of ions, electrons, atoms, and molecules to line up with the external field.

According to previous research, when polymers are mixed together to produce a SPE matrix, the amorphous phase expands and more salts dissolve. This resulted in increased chain length and polymer segmental mobility. Increased polymer chain segmental mobility has been demonstrated to minimize relaxation time, hence accelerating up the ion transport process. When glycerol plasticizer is introduced, the ϵ' rises, and the relaxation peak in the $\tan \delta$ plot changes to higher frequencies, which indicates a shorter relaxation period. Because of a rise in segmental motion within the system, which produces an increase in the mobility of the ions, the ion conductivity rises.

3.2 Electric Modulus Analysis

The Electric Modulus Formalism is a useful tool for understanding the conductivity relaxation processes that occur in ion-conducting fluids. The complex electric modulus (M^*), the inverse of complex electric permittivity, may be used to investigate how ion relaxation impacts polymer electrical characteristics ($M^* = 1/\epsilon^*$). This technique has the benefit of reducing the electrode polarization effects caused by charge formation in the interfacial area (Chérif, 202-).

Figures 3.4 and 3.5 show the real (M') and imaginary (M'') graphs of the electric modulus vs frequency. It is obvious that M' and M'' increase as the frequency scans toward relatively high values, reducing electrode polarization processes at low

frequencies. The fact that M' approaches maximum saturation when the dielectric constant drops at a certain frequency is highly intriguing.

In particular, the more stronger relaxation peak, which appears to vary with glycerol content, occurs in the middle-frequency region of M'' . As the glycerol concentration increases, the loss maxima decrease monotonically. As frequency increases, the peak frequency signifies a transition from long-range to short-range mobility, while the peak value in M'' reflects the components' real dielectric spin relaxation process. This demonstrates that when plasticizer concentration rises, relaxing time decreases.

3.3 Conductivity Analysis

The effect of applied frequency on AC conductivity (σ_{ac}) for all plasticized CS: PVA:Mg(NO₃) Figure 3.6 shows two biopolymer mix electrolyte samples at room temperature. The high salt concentration samples may be divided into three sectors: low, intermediate, and high-frequency areas (CSPVMGNT3, CSPVMGNT4, and CSPVMGNT5).

The conventional electrode polarization effect is visible at low frequencies. The low-frequency dispersion zone is defined as a parabolic region that corresponds to bulk DC conductivity and is correctly connected to compound concentration. A significant finding is that when salt content increases, the relaxation process switches, resulting in the production of AC conductivity in the high-frequency region. Ions are more likely to travel to a more advantageous location before returning to their original place at higher frequencies.

This increased probability explains why higher frequencies have more conductivity, which indicates dispersion. Charge carrier confinement across the sample causes the AC conductivity phenomenon. According to Jonscher's universal power law (Papathanassiou,2006), the large dispersion zone of AC conductivity at high frequency is determined by frequency as a power law with a near to one exponent.

The AC conductivity data in Fig. 7 and table 3.2 were used to estimate the DC conductivity value of each plasticized biopolymer electrolyte.

Table 3.2 AC conductivity of samples at ambient temperature

Sample code	$\sigma_{ac} (Scm^{-1})$
CSPVMGNT1	9.17×10^9
CSPVMGNT2	1.69×10^7
CSPVMGNT3	2.98×10^6
CSPVMGNT4	1.57×10^5
CSPVMGNT4	7.34×10^5

The DC conductivity clearly rises with increased plasticizer content, while the relaxation time decreases (Fig.4). In other words, the variation in DC conductivity contradicts the interpretation in relaxation time. As more plasticizer is used, the amorphous region grows, resulting in weak and loose molecular packing. As a result, with high glycerol concentration, the polymer chain is simpler to align, resulting in a shorter relaxation time.

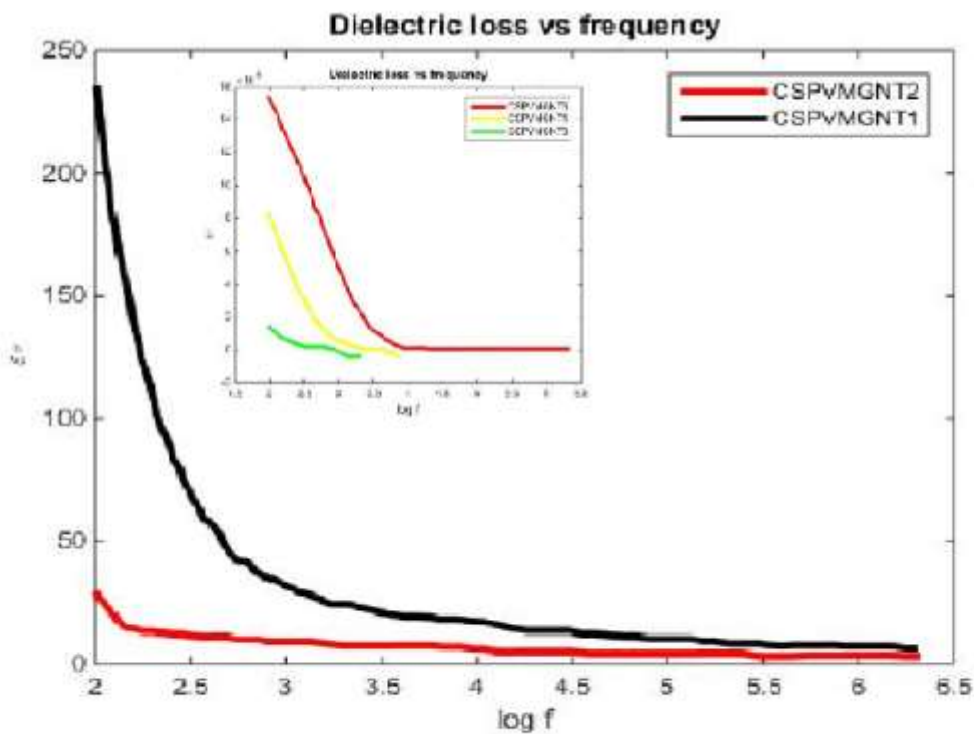


Fig. 3.1. The change of dielectric constant with respect to frequency for biopolymer blend electrolyte systems of CSPVMGNT at room temperature.

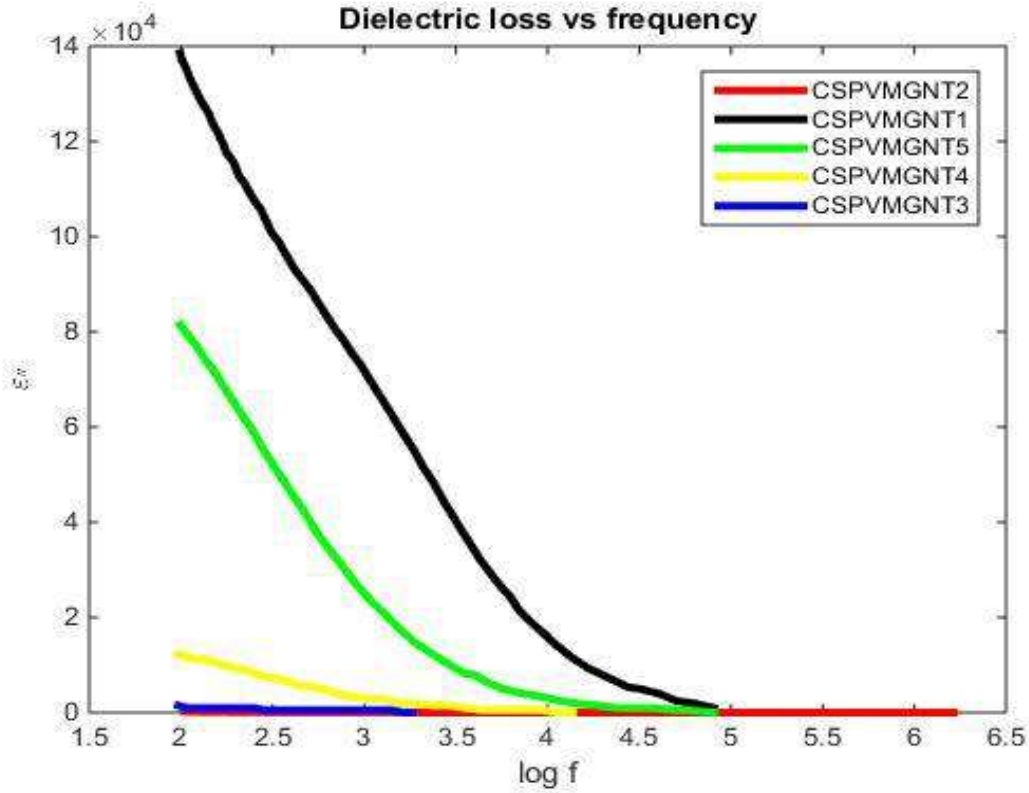


Fig.3.2. The change of dielectric loss with respect to frequency for biopolymer blend electrolyte systems of CSPVMGNT at room temperature.

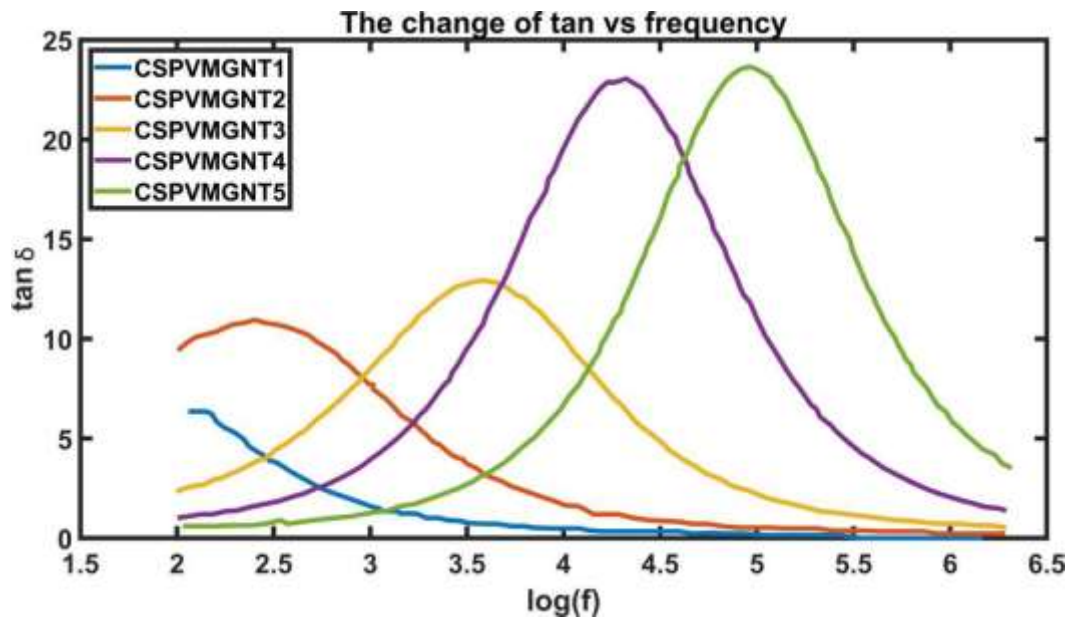


Fig. 3.3. The change of ($\tan \delta$) with respect to frequency for biopolymer blend electrolyte systems of CSPVMGNT at room temperature.

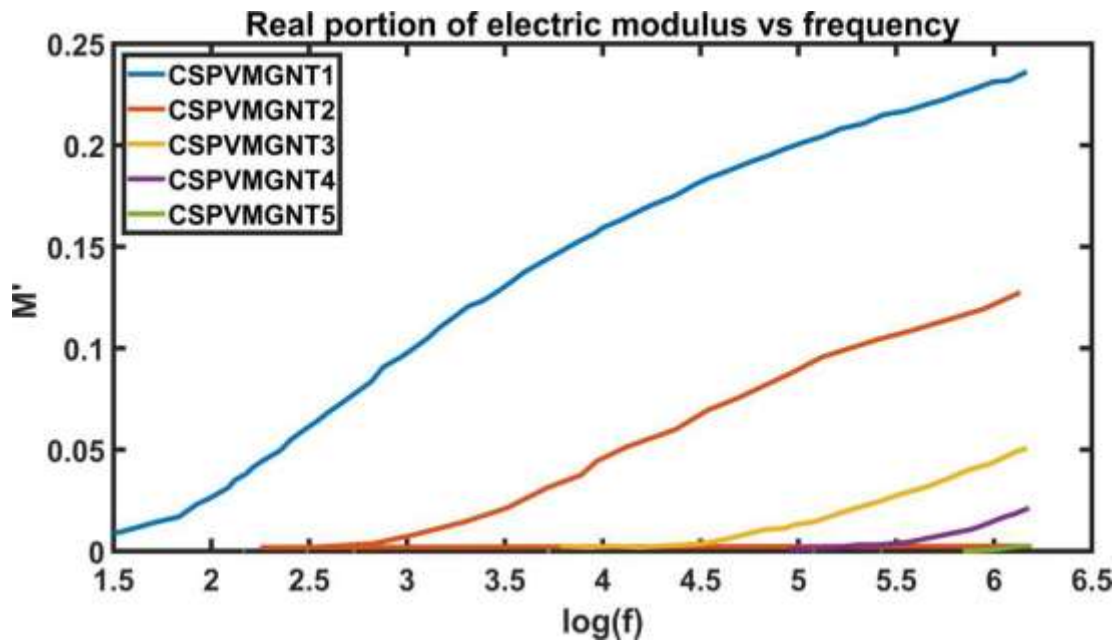


Fig. 3.4. Real portion of electric modulus (M') with respect to frequency for plasticized CS:PVA:Mg(NO₃)₂ biopolymer blend electrolyte systems at ambient temperature

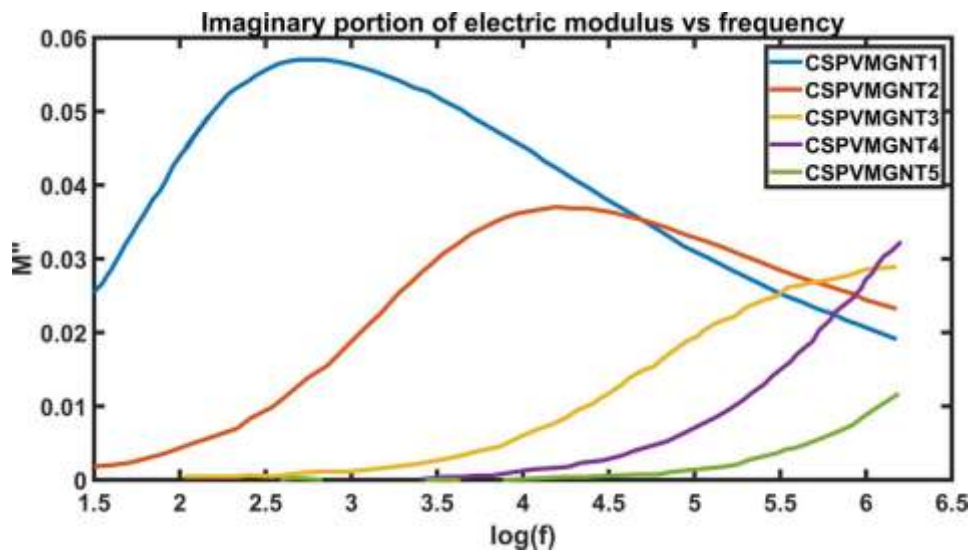
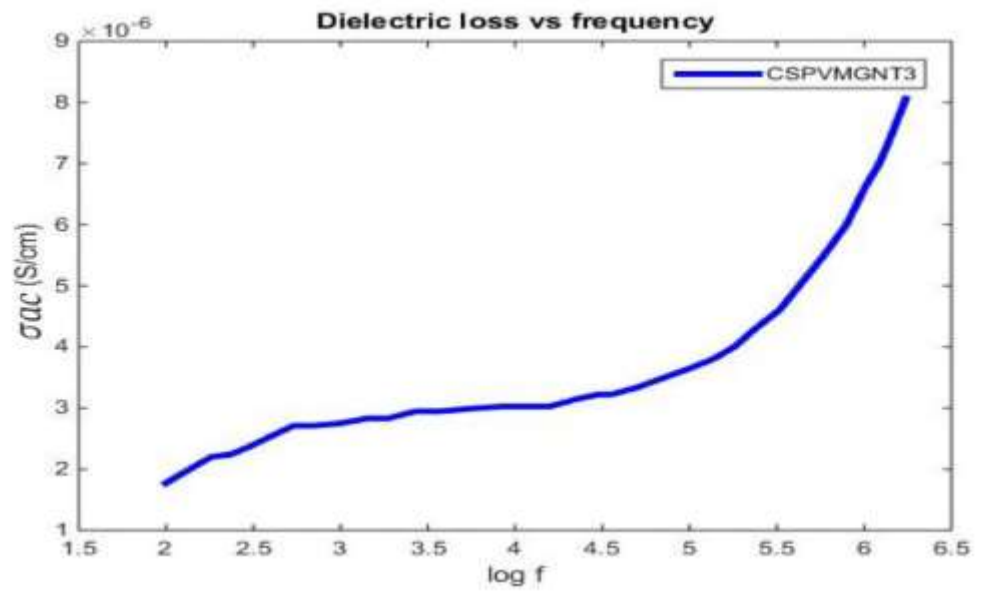
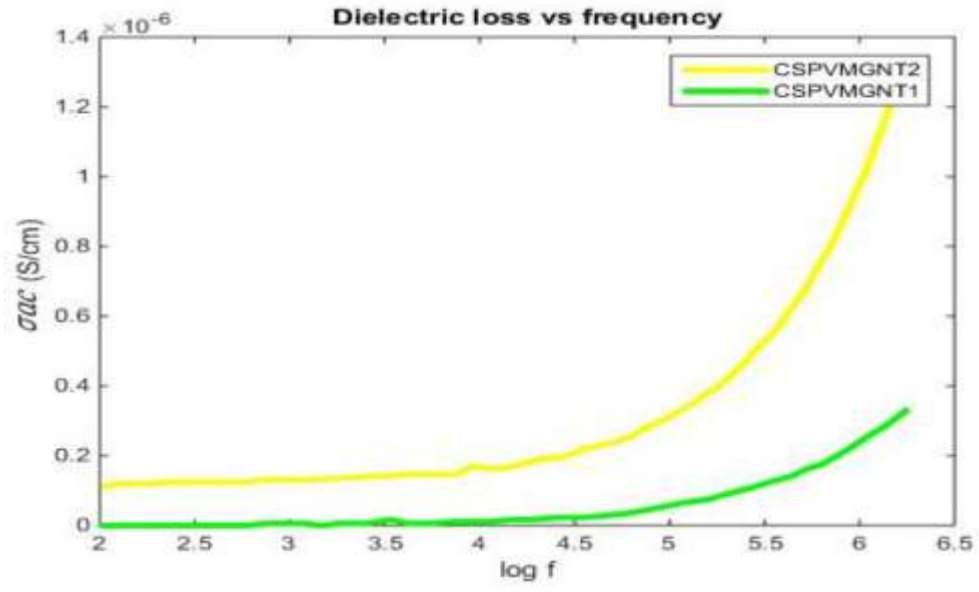


Fig. 3.5. Imaginary portion of electric modulus (M'') with respect to frequency for plasticized CS:PVA:Mg(NO₃)₂ biopolymer blend electrolyte systems at ambient temperature



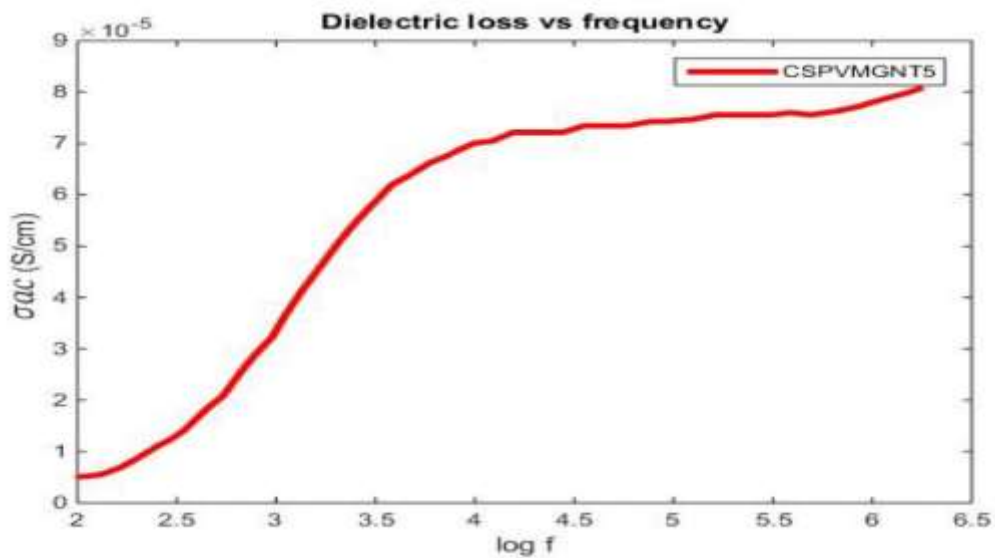
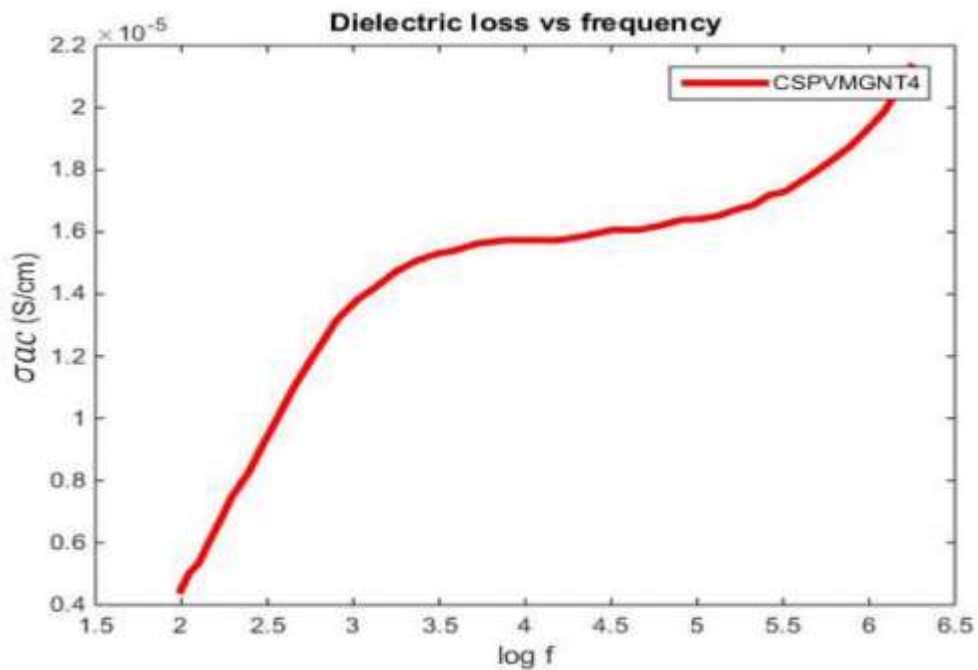


Fig.3.6. AC conductivity spectra for all plasticized CS:PVA:Mg(NO₃)₂ biopolymer blend electrolyte systems at ambient temperature.

Conclusion

Plasticized biopolymer blend electrolytes based on CS:PVA:Mg (NO₃)₂ with varying amounts of glycerol which were fabricated using a solution casting method to facilitate the transport of magnesium ions. The peak appearance for the current compounds displayed a non-Debye type.

References

Asnawi, A.S., Aziz, S.B., Brevik, I., Brza, M.A., Yusof, Y.M., Alshehri, S.M., Ahamad, T. and Kadir, M.F.Z., 2021. The study of plasticized sodium ion conducting polymer blend electrolyte membranes based on chitosan/dextran biopolymers: Ion transport, structural, morphological and potential stability. *Polymers*, 13(3), p.383.

<https://doi.org/10.3390/polym13030383>

Asnawi, A.S., Aziz, S.B., Nofal, M.M., Yusof, Y.M., Brevik, I., Hamsan, M.H., Brza, M.A., Abdulwahid, R.T. and Kadir, M.F., 2020. Metal complex as a novel approach to enhance the amorphous phase and improve the EDLC performance of plasticized proton conducting chitosan-based polymer electrolyte. *Membranes*, 10(6), p.132.

<https://doi.org/10.3390/membranes10060132>

Asnawi, A.S., B. Aziz, S., M. Nofal, M., Hamsan, M.H., Brza, M.A., Yusof, Y.M., Abdilwahid, R.T., Muzakir, S.K. and Kadir, M.F., 2020. Glycerolized Li⁺ ion conducting chitosan-based polymer electrolyte for energy storage EDLC device applications with relatively high energy density. *Polymers*, 12(6), p.1433.

<https://doi.org/10.3390/polym12061433>

Aziz, S.B., Abidin, Z.H.Z. and Arof, A.K., 2010. Effect of silver nanoparticles on the DC conductivity in chitosan–silver triflate polymer electrolyte. *Physica B: Condensed Matter*, 405(21), pp.4429-4433.

<https://doi.org/10.1016/j.physb.2010.08.008>

Aziz, S.B., Ahmed, M.J., Abdullah, O.G., Murad, A.R., Hamad, S.M. and Hadi, J.M., 2023. Magnesium ion conducting biopolymer blend-based electrolyte for energy storage application: Electrochemical characteristics. *Electrochimica Acta*, 461, p.142659.

<https://doi.org/10.1016/j.electacta.2023.142659>

Aziz, S.B., Hamsan, M.H., Brza, M.A., Kadir, M.F.Z., Muzakir, S.K. and Abdulwahid, R.T., 2020. Effect of glycerol on EDLC characteristics of chitosan: methylcellulose polymer blend electrolytes. *Journal of Materials Research and Technology*, 9(4), pp.8355-8366.

<https://doi.org/10.1016/j.jmrt.2020.05.114>

Aziz, S.B., Hamsan, M.H., Kadir, M.F.Z. and Woo, H.J., 2020. Design of polymer blends based on chitosan: POZ with improved dielectric constant for application in polymer electrolytes and flexible electronics. *Advances in Polymer Technology*, 2020, pp.1-10.

<https://doi.org/10.1155/2020/8586136>

Basak, P., Manorama, S.V., Singh, R.K. and Parkash, O., 2005. Investigations on the Mechanisms of Ionic Conductivity in PEO– PU/PAN Semi-interpenetrating Polymer Network– Salt Complex Polymer Electrolytes: An Impedance Spectroscopy Study. *The Journal of Physical Chemistry B*, 109(3), pp.1174-1182.

Bhajantri, R.F. and Masti, S.P., 2021. Dielectric relaxations and ion transport study of NaCMC: NaNO₃ solid polymer electrolyte films.

Chérif, S.F., Chérif, A., Dridi, W. and Zid, M.F., 2020. Ac conductivity, electric modulus analysis, dielectric behavior and Bond Valence Sum analysis of Na₃Nb₄As₃O₁₉ compound. *Arabian Journal of Chemistry*, 13(6), pp.5627-5638.

<https://doi.org/10.1016/j.arabjc.2020.04.003>

Hafiza, M.N. and Isa, M.I.N., 2014. Ionic conductivity and conduction mechanism studies of CMC/chitosan biopolymer blend electrolytes. *Research Journal of Recent Sciences*, ISSN, 2277, p.2502.

<http://www.isca.me/rjrs/archive/v3/i11/8.%20ISCA-RJRS-2014-839.pdf>

Hafiza, M.N. and Isa, M.I.N., 2020. Correlation between structural, ion transport and ionic conductivity of plasticized 2-hydroxyethyl cellulose based solid biopolymer electrolyte. *Journal of Membrane Science*, 597, p.117176.

<https://doi.org/10.1016/j.memsci.2019.117176>

Hafiza, M.N., Bashirah, A.N.A., Bakar, N.Y. and Isa, M.I.N., 2014. Electrical properties of carboxyl methylcellulose/chitosan dual-blend green polymer doped

with ammonium bromide. *International Journal of Polymer Analysis and Characterization*, 19(2), pp.151-158.

<https://doi.org/10.1080/1023666X.2014.873562>

Haghighi, H., Licciardello, F., Fava, P., Siesler, H.W. and Pulvirenti, A., 2020. Recent advances on chitosan-based films for sustainable food packaging applications. *Food Packaging and Shelf Life*, 26, p.100551.

<https://doi.org/10.1016/j.fpsl.2020.100551>

Hamdan, K. Z., and Azwani Sofia Ahmad Khair. "Conductivity and dielectric studies of methylcellulose/chitosan-NH₄CF₃SO₃ polymer electrolyte." *Key Engineering Materials* 594 (2014): 818-822.

<https://doi.org/10.4028/www.scientific.net/KEM.594-595.818>

Hirankumar, G. and Mehta, N., 2018. Effect of incorporation of different plasticizers on structural and ion transport properties of PVA-LiClO₄ based electrolytes. *Heliyon*, 4(12).

<https://doi.org/10.1016/j.heliyon.2018.e00992>

Ibrahim, S., Yasin, S.M.M., Ahmad, R. and Johan, M.R., 2012. Conductivity, thermal and morphology studies of PEO based salted polymer electrolytes. *Solid state sciences*, 14(8), pp.1111-1116.

<https://doi.org/10.1016/j.solidstatesciences.2012.05.019>

Jian, S., Cao, Y., Feng, W., Yin, G., Zhao, Y., Lai, Y., Zhang, T., Ling, X., Wu, H., Bi, H. and Dong, Y., 2022. Recent progress in solid polymer electrolytes with various dimensional fillers: a review. *Materials Today Sustainability*, 20, p.100224.

<https://doi.org/10.1016/j.mtsust.2022.100224>

Kamboj, V., Arya, A., Tanwar, S., Kumar, V. and Sharma, A.L., 2021. Nanofiller-assisted Na⁺-conducting polymer nanocomposite for ultracapacitor: structural, dielectric and electrochemical properties. *Journal of Materials Science*, 56, pp.6167-6187.

<https://link.springer.com/article/10.1007/s10853-020-05667-3>

Ilyas, R.A., Aisyah, H.A., Nordin, A.H., Ngadi, N., Zuhri, M.Y.M., Asyraf, M.R.M., Sapuan, S.M., Zainudin, E.S., Sharma, S., Abrial, H. and Asrofi, M., 2022. Natural-fiber-reinforced chitosan, chitosan blends and their nanocomposites for various advanced applications. *Polymers*, 14(5), p.874.

<https://doi.org/10.3390/polym14050874>

Liu, J., Khanam, Z., Muchakayala, R. and Song, S., 2020. Fabrication and characterization of Zn-ion-conducting solid polymer electrolyte films based on PVdF-HFP/Zn (Tf) 2 complex system. *Journal of Materials Science: Materials in Electronics*, 31(8), pp.6160-6173.

Navaratnam, S., Ramesh, K., Ramesh, S., Sanusi, A., Basirun, W.J. and Arof, A.K., 2015. Transport mechanism studies of chitosan electrolyte systems. *Electrochimica Acta*, 175, pp.68-73.

<https://doi.org/10.1016/j.electacta.2015.01.087>

Nofal, M.M., Aziz, S.B., Ghareeb, H.O., Hadi, J.M., Dannoun, E.M. and Al-Saeedi, S.I., 2022. Impedance and dielectric properties of PVC: NH₄I solid polymer electrolytes (SPEs): steps toward the fabrication of SPEs with high resistivity. *Materials*, 15(6), p.2143.

<https://doi.org/10.3390/ma15062143>

Machappa, T. and Prasad, M.A., 2009. AC conductivity and dielectric behavior of polyaniline/sodium metavanadate (PANI/NaVO₃) composites. *Physica B: Condensed Matter*, 404(21), pp.4168-4172.

<https://doi.org/10.1016/j.physb.2009.07.194>

Rani, M.S.A., Mohamed, N.S. and Isa, M.I.N., 2015. Investigation of the ionic conduction mechanism in carboxymethyl cellulose/chitosan biopolymer blend electrolyte impregnated with ammonium nitrate. *International Journal of Polymer Analysis and Characterization*, 20(6), pp.491-503.

<https://doi.org/10.1080/1023666X.2015.1050803>

Papathanassiou, A.N., 2006. Novel feature of the universal power law dispersion of the ac conductivity in disordered matter. *Journal of non-crystalline solids*, 352(50-51), pp.5444-5445.

<https://doi.org/10.1016/j.jnoncrysol.2006.08.019>

Sadiq, N.M., Aziz, S.B. and Kadir, M.F., 2022. Development of flexible plasticized ion conducting polymer blend electrolytes based on polyvinyl alcohol (PVA): chitosan (CS) with high ion transport parameters close to gel based electrolytes. *Gels*, 8(3), p.153.

<https://doi.org/10.3390/gels8030153>

Shukur, M.F., Ithnin, R. and Kadir, M.F.Z., 2014. Electrical properties of proton conducting solid biopolymer electrolytes based on starch–chitosan blend. *Ionics*, 20, pp.977-999.

<https://link.springer.com/article/10.1007/s11581-013-1033-8>

Shukur, M.F., Ithnin, R., Illias, H.A. and Kadir, M.F.Z., 2013. Proton conducting polymer electrolyte based on plasticized chitosan–PEO blend and application in electrochemical devices. *Optical Materials*, 35(10), pp.1834-1841.

<https://doi.org/10.1016/j.optmat.2013.03.004>

Sudaryanto, Yulianti, E. and Jodi, H., 2015. Studies of dielectric properties and conductivity of chitosan-lithium triflate electrolyte. *Polymer-Plastics Technology and Engineering*, 54(3), pp.290-295.

<https://doi.org/10.1080/03602559.2014.977424>

Wang, Y.P., Gao, X.H., Li, H.K., Li, H.J., Liu, H.G. and Guo, H.X., 2009. Effect of active filler addition on the ionic conductivity of PVDF-PEG polymer electrolyte. *Journal of Macromolecular Science®*, Part A: Pure and Applied Chemistry, 46(4), pp.461-467.

<https://doi.org/10.1080/10601320902740277>

Wang, Z., He, S., Nguyen, V. and Riley, K.E., 2020. Ionic liquids as “Green solvent and/or electrolyte” for energy interface. *Engineered Science*.

<https://par.nsf.gov/servlets/purl/10188714>

Wright, P.V., 1975. Electrical conductivity in ionic complexes of poly (ethylene oxide). *British polymer journal*, 7(5), pp.319-327.

<https://doi.org/10.1002/pi.4980070505>

Wright, P.V., 1998. Polymer electrolytes—the early days. *Electrochimica Acta*, 43(10-11), pp.1137-1143.

[https://doi.org/10.1016/S0013-4686\(97\)10011-1](https://doi.org/10.1016/S0013-4686(97)10011-1)

Wang, W.X., Feng, S.S. and Zheng, C.H., 2016. A comparison between conventional liposome and drug-cyclodextrin complex in liposome system. *International journal of pharmaceutics*, 513(1-2), pp.387-392.

<https://doi.org/10.1016/j.ijpharm.2016.09.043>

Zhou, Y., Wang, P., Ruan, G., Xu, P. and Ding, Y., 2021. Synergistic effect of P [MPEGMA-IL] modified graphene on morphology and dielectric properties of PLA/PCL blends. *ES Mater Manuf*, 11, pp.20-29.

https://www.espublisher.com/uploads/article_pdf/esmm5f928.pdf

Tripathi, N., Shukla, A., Thakur, A.K. and Marx, D.T., 2020. Dielectric modulus and conductivity scaling approach to the analysis of ion transport in solid polymer electrolytes. *Polymer Engineering & Science*, 60(2), pp.297-305.

<https://doi.org/10.1002/pen.25283>