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The Role of Glycerol in Modulating Ionic Transport and Electrochemical Performance of PEO:NaCl Solid Polymer Electrolytes

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Abstract

Solid polymer electrolytes (SPEs) are promising alternatives to liquid electrolytes, offering stability and versatility. However, low ionic conductivity remains a challenge, which can be addressed through strategies such as salt incorporation and plasticizer optimization. This study aims to enhance PEO-NaCl-based polymer electrolyte films by adding glycerol to modify crystallinity and improve electrical properties. Characterization included Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and electrochemical impedance spectroscopy (EIS) to analyze structural, spectroscopic, and electrochemical properties as a function of plasticizer content. The study demonstrated significant enhancements in the electrochemical and dielectric properties of PEO-NaCl polymer electrolytes with increasing glycerol content. Electrical Impedance Spectroscopy (EIS) revealed a marked improvement in DC conductivity, increasing from 1.38×10^{-8} S/cm for the glycerol-free sample to 1.74×10^{-4} S/cm at 32% glycerol concentration, attributed to reduced bulk resistance and enhanced ion mobility. Glycerol also improves the dielectric properties of PEO-NaCl electrolytes by increasing polarizability, enhancing ion motion, and reducing ion aggregation, which leads to better ionic conductivity and energy dissipation. Additionally, the relaxation dynamics

improved, as evidenced by sharper and higher dielectric loss tangent peaks ($\tan\delta$) with glycerol addition. The findings confirm that glycerol effectively reduces polymer rigidity, boosts ionic mobility, and improves conductivity, positioning it as a promising plasticizer for solid-state electrolytes.

Keywords: PEO; NaCl; Polymer electrolytes; plasticizer; Glycerol

1. Introduction

Electrolytes are essential in facilitating ionic mobility between electrodes, which is vital for the functioning of electrochemical devices. However, liquid electrolytes have several drawbacks, including leakage, high flammability, and chemical instability. Consequently, there is a growing trend to replace them with polymers [1]. Solid polymer electrolytes (SPEs) offer several advantages, including excellent electrochemical stability, versatility, high specific energy, and ease of fabrication into thin films [2]. The SPEs are suitable for a range of solid-state electrochemical devices, such as supercapacitors, batteries, fuel cells, and chemical sensors. Nevertheless, one major challenge with SPEs is their low electrical conductivity, which requires improvement for optimal performance [3, 4]. Dry polymer electrolytes, also referred to as solvent-free electrolytes, allow for the mobility of both positively charged ions (cations) and negatively charged ions (anions), as they are loosely bound.

Polyethylene oxide (PEO)-based polymer electrolytes remain among the most widely studied polymer ion conductors due to PEO's beneficial structure that supports fast ion transport. The main requirement for high conductivity appears to be the ability of the polymer's coordination groups to readily dissolve cations. Polymers containing Lewis bases (usually ether oxygens) can act as coordinating cations, thereby promoting the dissolution of salts. Due to the chain entanglement of the polymer host, these polymer salt complexes exhibit mechanical properties that are similar in most respects to those of real solids. For metal ions, the microscopic environment remains liquid, and the ionic conductivity is "coupled" with the local segmental motion of the polymer [5]. The relatively high crystallinity of PEO-based electrolytes at ambient temperature leads to poor ionic conductivity. Several strategies have been developed to enhance the conductivity of electrolytes, including salt incorporation, and the use of plasticizers. For example, the addition of ammonium salts to a chitosan-dextran blend has been shown to significantly improve DC ionic conductivity due to the increased concentration of mobile ions [6, 7]. The dissociation of salts within the polymer matrix is critical; as the salt concentration increases, the number of free ions available for conduction also increases, leading

to enhanced conductivity [8, 9]. However, excessive salt can lead to phase separation or crystallization, which can negatively impact conductivity.

Plasticizers, such as glycerol and succinonitrile, play a crucial role in modifying the properties of polymer electrolytes. For instance, Aziz et al. demonstrated that the addition of glycerol to chitosan-dextran polymer electrolytes significantly suppressed crystallinity, allowing for enhanced ionic conductivity due to increased ion dissociation and mobility [10]. Similarly, the study by Sadiq et al. highlighted that incorporating plasticizers into polyvinyl alcohol (PVA) and chitosan blends resulted in a substantial increase in ionic conductivity, approaching that of gel-based electrolytes [11]. The plasticization effect is attributed to the disruption of hydrogen bonding between polymer chains, which allows for greater segmental motion and, consequently, improved ion transport [12].

While the addition of plasticizers generally enhances the ionic conductivity of polymer electrolytes, it is essential to optimize their concentration to achieve the best performance. Excessive plasticization can lead to a reduction in mechanical strength and stability of the polymer matrix, which may compromise the overall performance of the electrochemical device [10]. For instance, Aziz et al. emphasized that finding the right balance in plasticizer content is crucial, as too much plasticizer can result in a decrease in the structural integrity of the polymer electrolyte, leading to potential leakage or failure in practical applications [13]. Research has shown that the optimal concentration of plasticizers varies depending on the specific polymer and salt used. Dannoun et al. stated that incorporating 42 wt% glycerol into a chitosan-based electrolyte significantly improved conductivity, but further increases in glycerol content led to diminishing returns in performance [14]. This highlights the importance of conducting systematic studies to determine the optimal plasticizer concentration for each specific polymer electrolyte system.

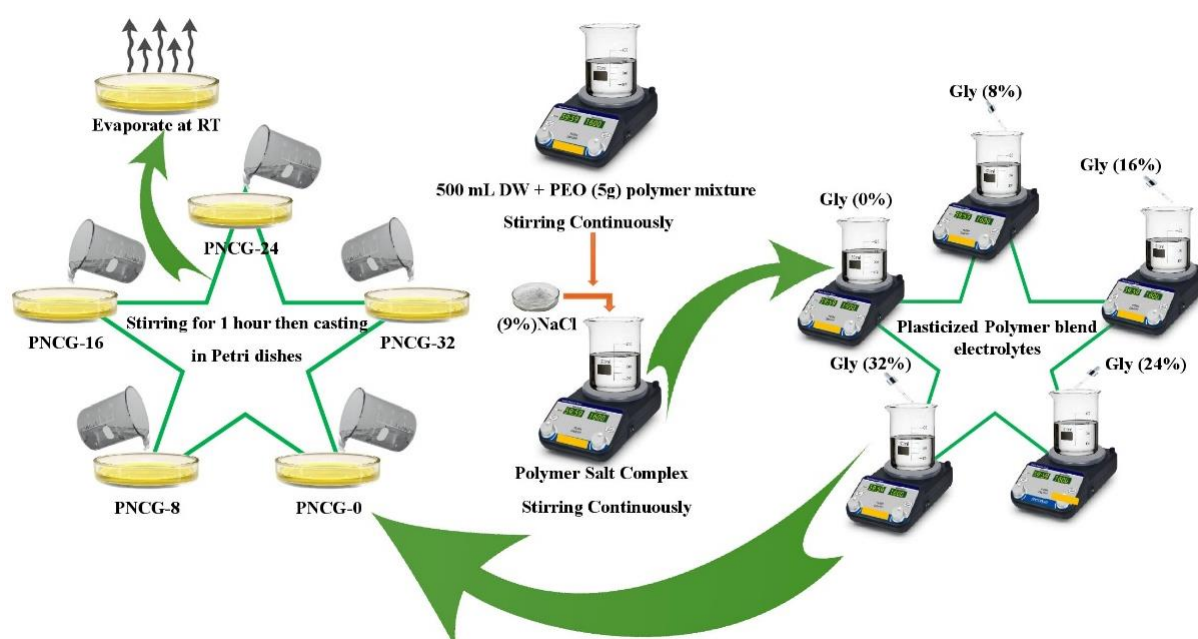
In this study, a 9% NaCl salt solution was dissolved in PEO, and glycerol was added to modify the polymer's crystallinity and improve its electrical properties. We conducted both electrochemical and non-electrochemical analyses, including crystal structure analysis via X-ray diffraction (XRD) and spectroscopic analysis using Fourier-transform infrared spectroscopy (FTIR), on the modified polymers. Electrochemical impedance spectroscopy (EIS) was employed to investigate the electrical phenomena associated with the chemical reactions of the polymer films as different amounts of plasticizer were introduced.

2. Experimental Procedure

The poly(ethylene oxide) (PEO) employed in this study, featuring a molecular weight of 2,000,000 and the chemical formula $(-\text{CH}_2\text{CH}_2\text{O}-)_n$, was obtained from Sigma-Aldrich. A weight of 5 g of PEO powder was dissolved in 500 mL of acetonitrile and 0.495 g of a 9% NaCl solution. The resulting solution was divided into five small beakers containing glycerol concentrations of 0%, 8%, 16%, 24%, and 32%. After adding each mixture, it was stirred for one hour and then left exposed to air at room temperature overnight to allow any bubbles formed during mixing to rise. A magnetic stirrer set to medium rotation was used to ensure that the PEO and salts were fully dissolved in the solution. Volumes of 60 mL and 40 mL of the solution were transferred to petri dishes. After casting, the dishes were placed at room temperature to allow the solvent to evaporate. Consequently, thick and thin polymer films were formed after one week. The materials used for the polymer films are listed in Table 1. Scheme 1 illustrates the synthesis of the PEO:NaCl polymer electrolyte films.

Table 1. The amount of PEO, NaCl, and glycerol in polymer films

Sample code	PEO (gram)	NaCl		Glycerol	
		(%)	(gram)	(%)	(gram)
PNCG-0	1	9%	0.099	0%	0
PNCG-8	1	9%	0.099	8%	0.0956
PNCG-16	1	9%	0.099	16%	0.2093
PNCG-24	1	9%	0.099	24%	0.3470
PNCG-32	1	9%	0.099	32%	0.5171



Scheme 1. Schematic Procedure for Preparing PEO:NaCl Solid Polymer Electrolytes

3. Results and Discussions

3.1. Electrical Impedance Spectroscopy

Electrical Impedance Spectroscopy (EIS) is a crucial technique for analyzing the impedance characteristics of materials across a range of frequencies. It provides valuable insights into charge transfer, ion mobility, and dielectric behavior, making it useful in fields such as energy storage, corrosion science, and biomaterials. EIS operates by applying an alternating current (AC) signal to a system and measuring its voltage response, which yields impedance with real and imaginary components [15, 16]. These components are analyzed using a Nyquist plot and modeled with equivalent circuits. Recent advancements in EIS focus on enhancing sensitivity, data analysis, and integration with machine learning for more accurate modeling. Portable EIS devices are also being developed for field applications [17-19]. EIS is a powerful tool for characterizing materials like polymer electrolytes, and when combined with techniques such as FTIR and XRD, it enables researchers to gain a comprehensive understanding of material properties, thereby supporting advancements in sustainable energy storage technologies.

The corresponding circuit, shown as an inset in Figure 1, is created by connecting the constant phase element (CPE1) and bulk resistance (R_b) in parallel. Together, these components form the semicircle portion of the Nyquist plot. Additionally, an extra constant phase element (CPE2) is connected in series with both CPE1 and R_b , resulting in the spike portion of the plot. The mathematical basis for the impedance of the CPEs (Z_{CPE}) is given by the following equation [20]:

$$Z_{CPE} = [\frac{1}{Y_m \omega^n} \cos(\varphi) - j \frac{1}{Y_m \omega^n} \sin(\varphi)] \quad (1)$$

where ($\varphi = n\pi/2$), representing the phase angle, Y_m corresponds to the capacitance of the constant phase element (CPE), and ω is the angular frequency, calculated using the formula $\omega = 2\pi f$. The parameter n indicates the degree of deviation of the plot from the imaginary axis. The imaginary component of the measured impedance (Z_i) is plotted on the y-axis, while the real component (Z_r) is plotted on the x-axis. For plots containing only a semicircle, as observed in PNCG-0, Z_r and Z_i can be determined using Equations (2) and (3) [21]:

$$Z_r = \frac{R_b + R_b^2 Y_1 \omega^{n_1} \cos(\varphi_1)}{1 + R_b Y_1 (2\omega^{n_1} \cos(\varphi_1) + R_b Y_1 \omega^{2n_1})} \quad (2)$$

$$Z_i = \frac{R_b^2 Y_1 \omega^{n_1} \sin(\varphi_1)}{1 + R_b Y_1 (2\omega^{n_1} \cos(\varphi_1) + R_b Y_1 \omega^{2n_1})} \quad (3)$$

Here, n_1 represents the extent to which the semicircle deviates from the vertical axis. Furthermore, the plots for PNCG-8, PNCG-16, PNCG-24, and PNCG-32 exhibit both a semicircular region and a spike. The values of Z_r and Z_i were determined as follows [22]:

$$Z_r = \frac{R_b + R_b^2 Y_1 \omega^{n_1} \cos(\varphi_1)}{1 + R_b Y_1 (2\omega^{n_1} \cos(\varphi_1) + R_b Y_1 \omega^{2n_1})} + \frac{1}{Y_2 \omega^{n_2}} \cos(\varphi_2) \quad (4)$$

$$Z_i = \frac{R_b^2 Y_1 \omega^{n_1} \sin(\varphi_1)}{1 + R_b Y_1 (2\omega^{n_1} \cos(\varphi_1) + R_b Y_1 \omega^{2n_1})} + \frac{1}{Y_2 \omega^{n_2}} \sin(\varphi_2) \quad (5)$$

here, n_2 represents the degree of deviation of the spike from the horizontal axis. Y_1 corresponds to the capacitance observed at high frequencies, whereas Y_2 refers to the capacitance measured at low frequencies.

Table 2 summarizes the results obtained from the Electrical Impedance Spectroscopy (EIS) analysis. The DC conductivity (σ_{dc}) is calculated using Eq. (6), which depends on the bulk resistance (R_b), film thickness (t), and electrode area (A) [21]:

$$\sigma_{dc} = \frac{t}{R_b A} \quad (6)$$

It has been observed that as glycerol concentration increases, the σ_{dc} values rise while R_b decreases. This can be attributed to the higher ion concentration in the electrolytes, which boosts electrode polarization and, as a result, increases capacitance at low frequencies. This also enhances ionic conductivity by facilitating greater ion mobility and dissociation. These findings suggest that glycerol molecules interact attractively with the polymer chain segments, leading to a reduction in cohesive forces [23]. Additionally, glycerol can improve the electrical characteristics of the polymer electrolyte and expand its application areas. As a plasticizer, glycerol breaks the bonds in the polymer, increasing the mobility of cations and anions within the polymer electrolyte. This is significant because the electrical conductivity value is directly proportional to the mobility of the electrical carriers [24].

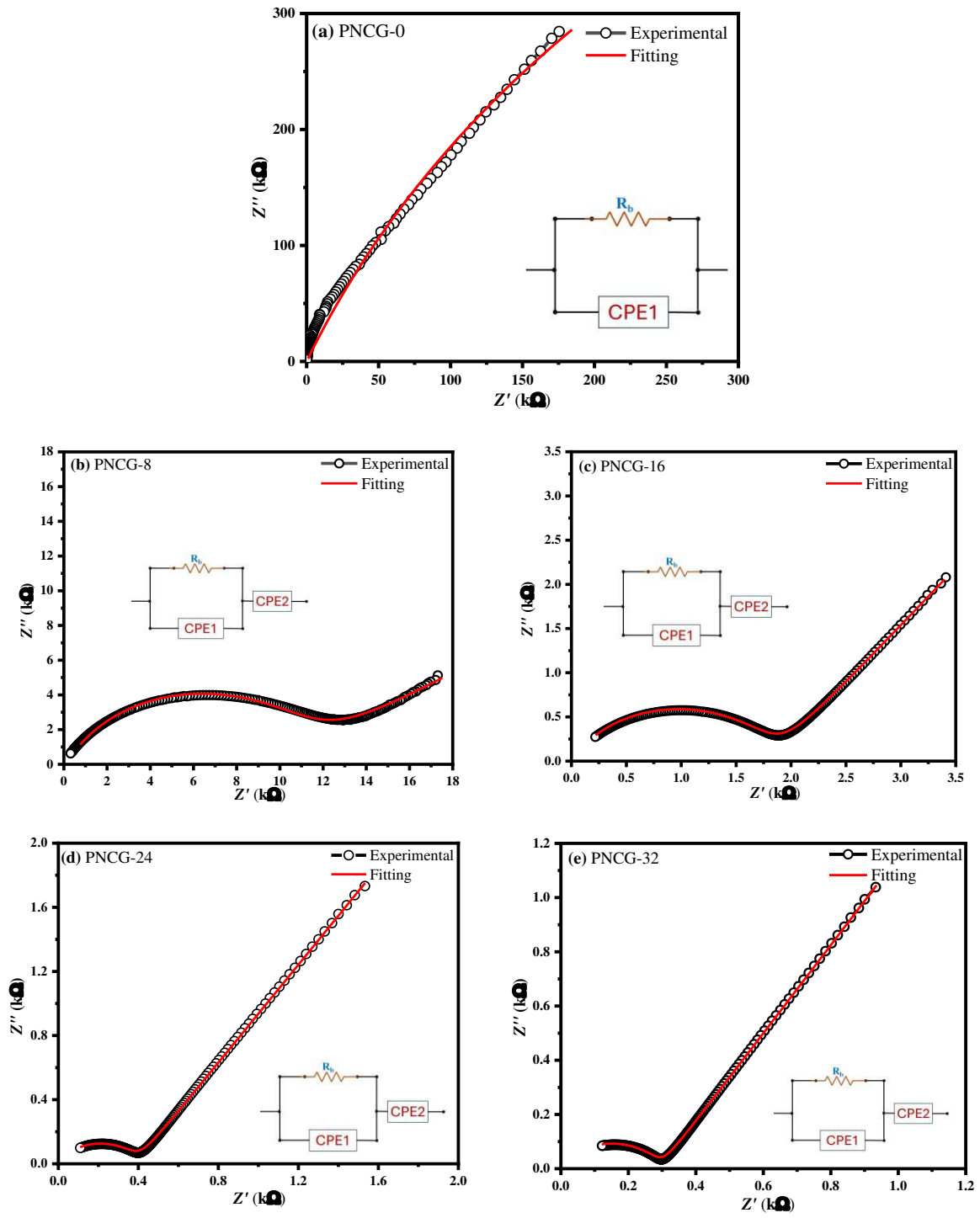


Figure 1. Impedance plot for MC:NaF samples with different ratios of glycerol

Table 2. The calculated EIS parameters after fitting the experimental data of PEO-NaCl polymer electrolyte samples.

Sample Codes	t (μm)	$\Phi 1$ (Rad)	$\Phi 2$ (Rad)	CPE1 (F^{-1})	CPE2 (F^{-1})	R_b (Ω)	σ_{dc} (S/cm)
PNCG-0	135	1.19	-	1.87×10^{-8}	-	1,590,400	1.38×10^{-8}
PNCG-8	250	1.19	0.58	4.11×10^{-9}	7.29×10^{-6}	10,282	3.94×10^{-6}
PNCG-16	279	1.10	0.91	2.87×10^{-8}	8.95×10^{-6}	1,840	2.46×10^{-5}
PNCG-24	215	1.09	0.99	5.81×10^{-8}	8.17×10^{-6}	390	8.94×10^{-5}
PNCG-32	315	1.10	1.02	4.75×10^{-8}	1.20×10^{-5}	294	1.74×10^{-4}

Relaxation time (τ) represents the time required for ions or electrons to return to equilibrium after being perturbed by an external force, such as an electric field [18, 19].

$$\tau = \frac{1}{2\pi f_{max}} \quad (7)$$

where maximum frequency f_{max} (in Hz) is the frequency of the relaxation peak. The diffusivity (D) of ions in polymer electrolytes calculated by follow equation

$$D = \frac{1}{16} \frac{\pi f_{max} \cdot t^2}{(\tan \delta_{max})^3} \quad (8)$$

where (t) is the sample thickness, ($\tan \delta_{max}$) is the maximum tangent loss and f_{max} is the frequency corresponding to maximum tangent loss. According to the Einstein equation, the number of charge carriers (N) in electrochemical systems, particularly in polymer electrolytes, can be expressed through a relationship that incorporates temperature, DC conductivity, and diffusivity, providing a comprehensive understanding of ion transport behavior.

$$N = \frac{\sigma_{dc} k_B}{D \cdot q^2} \times T \quad (9)$$

where q represents the electric charge (1.6×10^{-19} C), T is the ambient temperature (approximately 300. K in this study), and k_B denotes the Boltzmann constant (1.381×10^{-23} J/K). The DC conductivity (σ_{dc}) is a measure of the mobility (μ) of ions, which depends on the ion's charge (q) and the concentration of charge carriers (N).

$$\mu = \frac{1}{N} \frac{\sigma_{dc}}{q} \quad (10)$$

The conductivity of a material is fundamentally influenced by the mobility of charge carriers, with higher mobility generally correlating to increased conductivity. However, this relationship is also contingent on the concentration of charge carriers within the material. Table 3 outlines the ion transport parameters calculated using equations (7–10). The incorporation of 32 wt.% glycerol into the polymer electrolyte substantially reduced the relaxation time, which in turn enhanced ion diffusivity and mobility. These improvements in ion transport parameters mobility, diffusivity, and charge carrier concentration are critical for boosting the performance of energy storage devices like batteries and supercapacitors. The role of plasticizers, such as glycerol, is pivotal in optimizing the physicochemical properties of polymer electrolytes for efficient ion transport. Enhancements in these properties directly contribute to better energy storage performance, as demonstrated by studies on glycerolized polymer electrolytes. For instance, Aziz et al. and Adam et al. reported that glycerolized polymer electrolytes exhibited high specific capacitance and energy density over prolonged cycles, emphasizing glycerol's potential as an effective plasticizer in high-performance solid-state electrolytes [25]. Furthermore, Adam et al. (2023) observed that the addition of glycerol in potassium-ion-conducting solid biopolymer electrolytes increased ion mobility and facilitated the dissociation of ion aggregates, resulting in higher ion concentration and improved mobility [7]. Glycerol, as a plasticizer, plays a crucial role in enhancing the ion transport properties of polymer electrolytes. By increasing ion mobility, diffusivity, and number density while simultaneously reducing relaxation time, glycerol contributes significantly to the efficiency and durability of energy storage devices. These advancements underscore the importance of designing polymer electrolytes with optimized compositions to meet the demands of next-generation energy storage technologies

Table 3. Ion transport properties, including mobility, relaxation time, diffusivity, and charge carrier density.

Sample Codes	τ (μ s)	D (cm^2/s)	N (cm^{-3})	μ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
PNCG- 0	1591.5494	1.40×10^{-2}	1.59×10^{11}	5.43×10^{-1}
PNCG- 8	140.6273	1.00×10^{-3}	6.35×10^{14}	3.87×10^{-2}
PNCG- 16	27.440886	3.16×10^{-3}	1.26×10^{15}	1.22×10^{-1}
PNCG- 24	6.212161	1.05×10^{-2}	1.37×10^{15}	4.06×10^{-1}
PNCG- 32	5.095926	9.62×10^{-3}	2.94×10^{15}	3.72×10^{-1}

3.2. Dielectric Properties

The dielectric constant (ϵ_r) and dielectric loss (ϵ_i) describe the ability of materials to store and dissipate electrical energy [26-28]. The ϵ_r represents the polarization response to an applied electric field, while ϵ_i indicates the energy dissipated as heat due to ionic motion [29, 30]. The values of ϵ_r and ϵ_i were determined at different frequencies using the following equations [31]:

$$\epsilon_r = \frac{t Z_i}{\omega A \epsilon_o (Z_r^2 + Z_i^2)} \quad (11)$$

$$\epsilon_i = \frac{t Z_r}{\omega A \epsilon_o (Z_r^2 + Z_i^2)} \quad (12)$$

where ϵ_o is the permittivity of free space (8.85×10^{-12} F/m).

Figure 2 (a) and (b) display the amounts of ϵ_r and ϵ_i , respectively, at different frequencies for all samples. At low frequencies, both ϵ_r and ϵ_i exhibit higher values due to efficient ionic and dipolar polarization, as ions have enough time to orient themselves with the applied electric field [32]. However, as the frequency increases, these values decline sharply because the rapid oscillations of the field inhibit ionic and dipole responses. The convergence of dielectric constant values across glycerol concentrations at high frequencies highlights the diminishing role of ionic mobility under fast field reversals, emphasizing the system's relaxation dynamics [33].

Additionally, Figure 2 indicates that the glycerol additive, as a plasticizer, significantly enhances the dielectric properties. The hydroxyl groups in glycerol interact with ions from the polymer and salt, enhancing polarizability and promoting dipole alignment with the electric field. This interaction results in improved ionic conductivity and increased energy dissipation capacity [34]. This is achieved by enhancing ion motion within the polymer, which reduces ion aggregation and allows a greater number of free ions to participate in charge transport [32].

The high ionic mobility, particularly at low frequencies, leads to greater dielectric loss due to the dissipation of energy during ionic migration. However, dielectric loss decreases because the ions are unable to keep up with the field oscillations at higher frequencies [35]. The improvement in ionic conductivity underscores glycerol's significance in enhancing the electrochemical performance of polymer electrolytes.

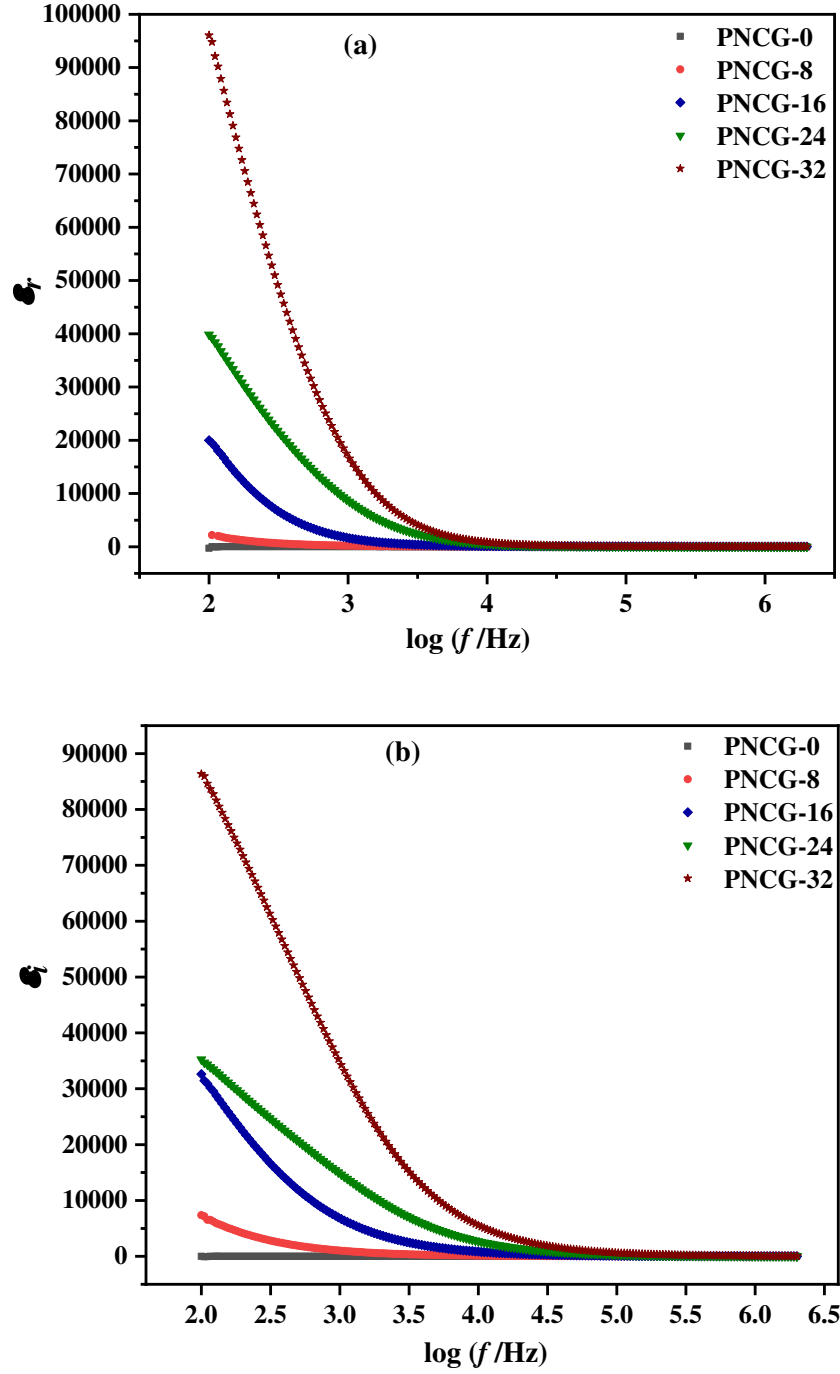


Figure 2. Frequency-dependent dielectric properties of the PEO:NaCl system with varying glycerol ratios: (a) real dielectric constant and (b) dielectric loss (imaginary component)

The ratio of the imaginary component (ϵ_i) to the real component (ϵ_r) defines a parameter known as the dielectric loss tangent ($\tan \delta$) [36], also referred to as the dissipation factor. It can be determined using the following expression [37]:

$$\tan \delta = \frac{\epsilon_i}{\epsilon_r} \quad (13)$$

Figure 3 reveals that the dielectric loss tangent ($\tan\delta$) varies as a function of frequency for PEO-NaCl polymer electrolytes with different glycerol concentrations (8–32%). The sample without glycerol (PNCG-0) exhibits lower $\tan\delta$ values, indicating limited ionic mobility and minimal energy dissipation. Distinct peaks emerge at specific frequencies, which shift toward higher frequencies with increasing glycerol content. This shift reflects reduced relaxation times due to enhanced polymer chain mobility [38]. The incorporation of glycerol produces sharper and more pronounced peaks, signifying improved relaxation dynamics. At the highest glycerol concentration (PNCG-32), the peaks display increased intensity along with a frequency shift, indicating further enhancement of energy dissipation and ionic mobility. These results demonstrate that glycerol effectively enhances dielectric properties and ionic mobility by reducing polymer rigidity [39].

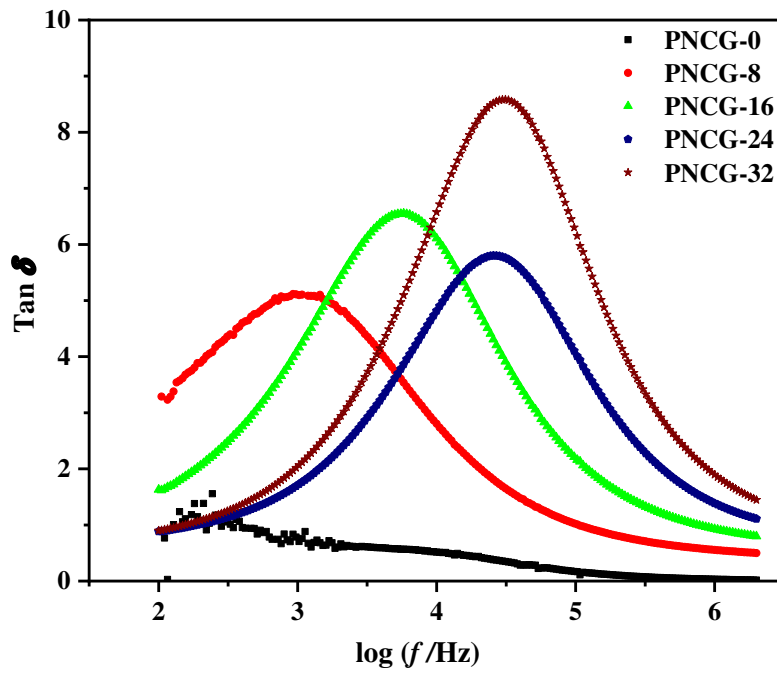


Figure 3. The dielectric loss tangent vs. frequency for PEO:NaCl system

The electrical modulus is a useful parameter for analyzing relaxation dynamics and ionic conduction in polymer electrolyte systems. It consists of two components: the real part (M_r) and the imaginary part (M_i), which can be calculated using the following expressions [20]:

$$M_r = \left[\frac{\epsilon_r}{(\epsilon_r^2 + \epsilon_i^2)} \right] \quad (14)$$

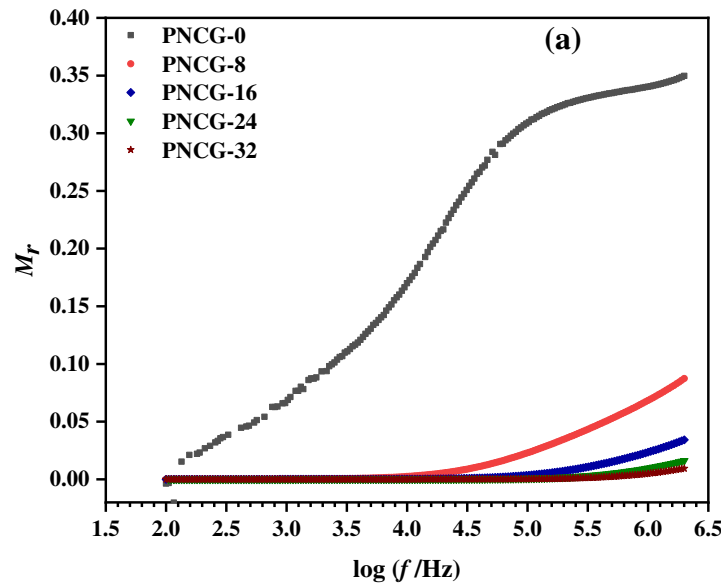
$$M_i = \left[\frac{\varepsilon_i}{(\varepsilon_r^2 + \varepsilon_i^2)} \right] \quad (15)$$

Figure 4 illustrates the frequency dependence of the real (M_r) and imaginary (M_i) components of the electrical modulus for the polymer electrolyte system:

(a) As shown in Figure 4a, M_r remains close to zero at lower frequencies, indicating the dominance of electrode polarization effects in this range. This behavior is associated with the material's high capacitance, which obscures relaxation processes [40]. As the frequency increases, M_r steadily rises, signifying the reduction of electrode effects and the increasing prominence of the material's intrinsic relaxation dynamics.

(b) Figure 4b displays the imaginary component M_i , which exhibits a distinct peak at higher frequencies. This peak corresponds to the conductivity relaxation process, involving ionic mobility and polymer matrix reorganization [41]. The relaxation frequency (f_{max}), associated with the peak, is inversely proportional to the relaxation time, as described by Equation (7) [42]. The height and width of the M_i peak provide insights into the degree of ionic interaction and the structural heterogeneity of the material [43].

The results reveal that the addition of a plasticizer to the polymer electrolyte system causes the M_i peak to shift dramatically toward higher frequencies. This shift becomes more pronounced with increasing plasticizer content, indicating enhanced ionic mobility and reduced relaxation times in the system.



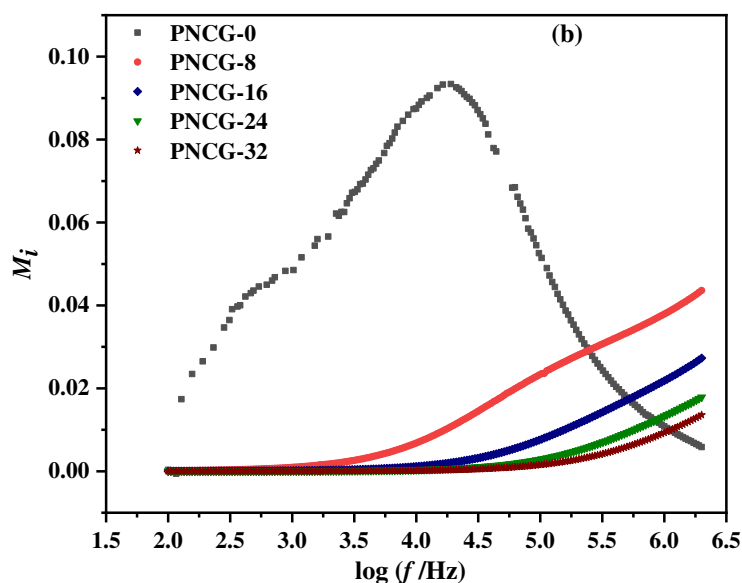


Figure 4. Electrical modulus components of PEO:NaCl polymer electrolytes with varying glycerol concentrations: (a) real part (M_r) and (b) imaginary part (M_i)

3.3. FTIR Spectroscopy

FTIR (Fourier-transform infrared) spectrum showing transmittance (%) as a function of wavenumber (cm^{-1}) for five samples, labeled S1 to S5. FTIR spectra are frequently utilized to detect functional groups in a substance by studying absorption bands that represent the vibrations of molecules. Figure 5 illustrates the FTIR spectra of PEO-NaCl with various percentages of glycerol added. The peaks in S2, S3, S4, and S5 that appear around 3300-3500 cm^{-1} are often attributed to O-H stretching vibrations, indicating the presence of hydroxyl groups in alcohols [44]. The broad intensity of PEO-NaCl at 3356 cm^{-1} increases from 0% to 32% with glycerol addition, due to the O-H group in the glycerol structure [20]. Peaks around 2880 cm^{-1} may signify C-H stretching vibrations [45], while the weak absorption band around 2361 cm^{-1} indicates the presence of complex salt [46]. The peak around 1461 cm^{-1} corresponds to CH_2 bending vibrations in the glycerol molecule [47]. The sharp and strong peak around 1096 cm^{-1} indicates C-O stretching vibrations [48]. This peak is common in compounds containing alcohols, such as glycerol, and arises from stretching vibrations of the C-O bond in the hydroxyl groups. The peak around 530 cm^{-1} in an FTIR spectrum is often associated with lattice and bending vibrations [48]. The observed peak could be related to glycerol or the polymeric system and the interaction between glycerol and salt [49]. Glycerol can enhance polymer mobility by forming hydrogen bonds with PEO and NaCl [50]. These findings generally suggest that glycerol increases hydrogen bonding, enhances polymer chain flexibility,

and alters the structural patterns of the PEO-NaCl systems [51]. This structural change is essential for applications that require increased flexibility and conductivity of ions.

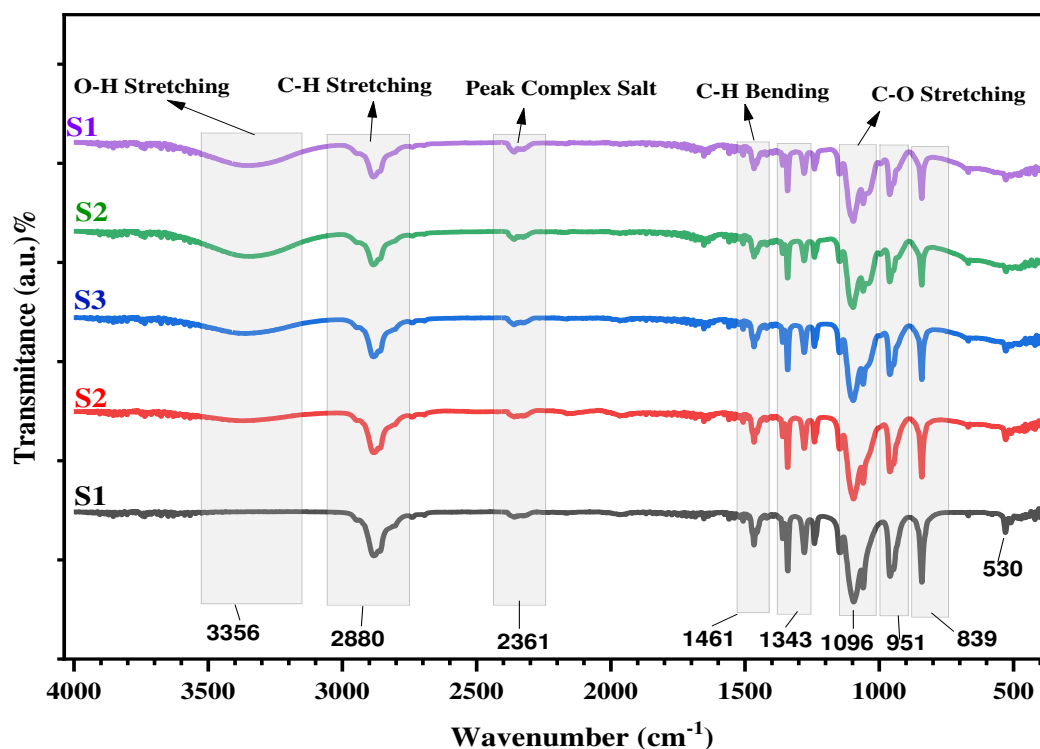


Figure 5. The FTIR spectra of the PEO-NaCl with different glycerol additives

Figure 6 reveals the schematic illustrates the polymer-salt complex formation involving sodium cations (Na^+) and Chloride (Cl^-) with PEO polymer. The interaction occurs as Na^+ coordinates with the hydroxyl groups present on the PEO polymer backbone, forming ionic crosslinks that enhance the structural stability of the polymer network. Simultaneously, Cl^- interacts through electrostatic forces with the positively charged regions of the PEO-salt system, further stabilizing the complex. The illustration highlights the spatial arrangement and binding mechanism within the PEO-salt complex.

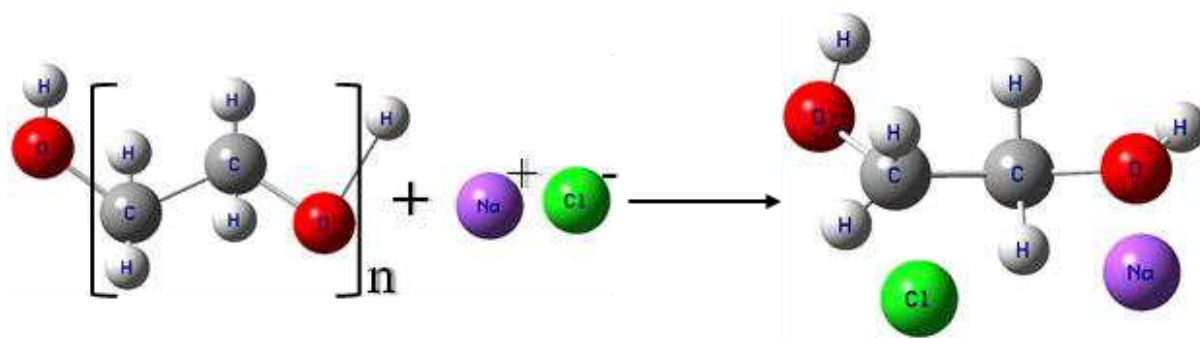


Figure 6. Polymer-Salt Complex Formation of cations (Na^+) and anions (Cl^-) with PEO

3.4. XRD Study

X-ray diffraction (XRD) is a powerful technique for investigating the structural composition of polymer electrolytes. By analyzing the diffraction peaks, researchers can gain valuable insights into the relationship between crystalline structures and their corresponding diffraction patterns [52]. The XRD analysis of the PEO-NaCl–glycerol complex provides detailed information on the crystalline structure and phase properties of the system. The incorporation of salts, such as NaCl, and plasticizing agents, like glycerol, induces significant changes in the crystalline structure of PEO, which is inherently semicrystalline [53].

Figure 7 presents the XRD patterns of PEO-NaCl complexes with varying glycerol concentrations. The semicrystalline PEO exhibits two distinct diffraction peaks at 18.37° and 22.24° , characteristic of its crystalline phase. Additional peaks at 30.71° and 44.61° correspond to undissolved NaCl, indicating incomplete salt dissolution in the polymer matrix [4].

At lower glycerol concentrations (0–8%), the XRD patterns exhibit sharp and distinct peaks, indicating higher crystallinity. At these levels, glycerol has a minimal impact on the crystalline structure of PEO [24]. With the incorporation of 16% glycerol, the observed peak intensities decrease, suggesting a reduction in crystallinity. However, as the glycerol concentration increases to 24%, two distinct peaks reappear with enhanced intensity, signifying a further reduction in crystallinity and an increase in the amorphous nature of the material [20]. At the highest glycerol concentration (32%), the peaks become broader and less defined, indicating a significant decrease in crystallinity. This behavior is attributed to glycerol acting as a plasticizer, disrupting the crystalline regions of PEO and promoting amorphous characteristics [21].

The crystallinity of the samples varies substantially, ranging from 84.95% (PNCG-0, the pure sample) to 34.57%. The pure sample exhibits the highest crystallinity and a more organized structure, which contributes to enhanced mechanical strength but limits flexibility due to rigid molecular packing. Glycerol, as a plasticizer, increases polymer chain flexibility by reducing crystalline domains and creating channels that facilitate ion transport. This increased flexibility and additional free volume improve ionic mobility [11].

Adjusting the glycerol concentration provides a means to optimize the polymer's structure and ionic conductivity for electrolyte applications. Electrochemical impedance spectroscopy (EIS)

results further support this, showing that higher glycerol concentrations reduce bulk resistance (R_b), thereby enhancing ionic conductivity, as described by Eq. (6). The complementary insights from XRD and EIS clearly demonstrate how structural changes in the polymer (as revealed by XRD) directly influence its electrical performance (as evidenced by EIS) in the PNCG system.

The degree of crystallinity (X_c) was calculated using Equation (16) [54]:

$$X_c = \frac{A_c}{A_c + A_a} \times 100 \quad (16)$$

where A_c represents the area of the crystalline region, A_a represents the area of the amorphous region, and X_c indicates the percentage of crystallinity. Figure 8 illustrates the crystallinity of the polymer/salt system before and after the incorporation of the plasticizer. The addition of glycerol generally reduced the crystallinity of the system, enhancing the dissociation of salt into cations and anions. This dissociation subsequently increased the concentration of charge carriers in the solid polymer electrolyte (SPE).

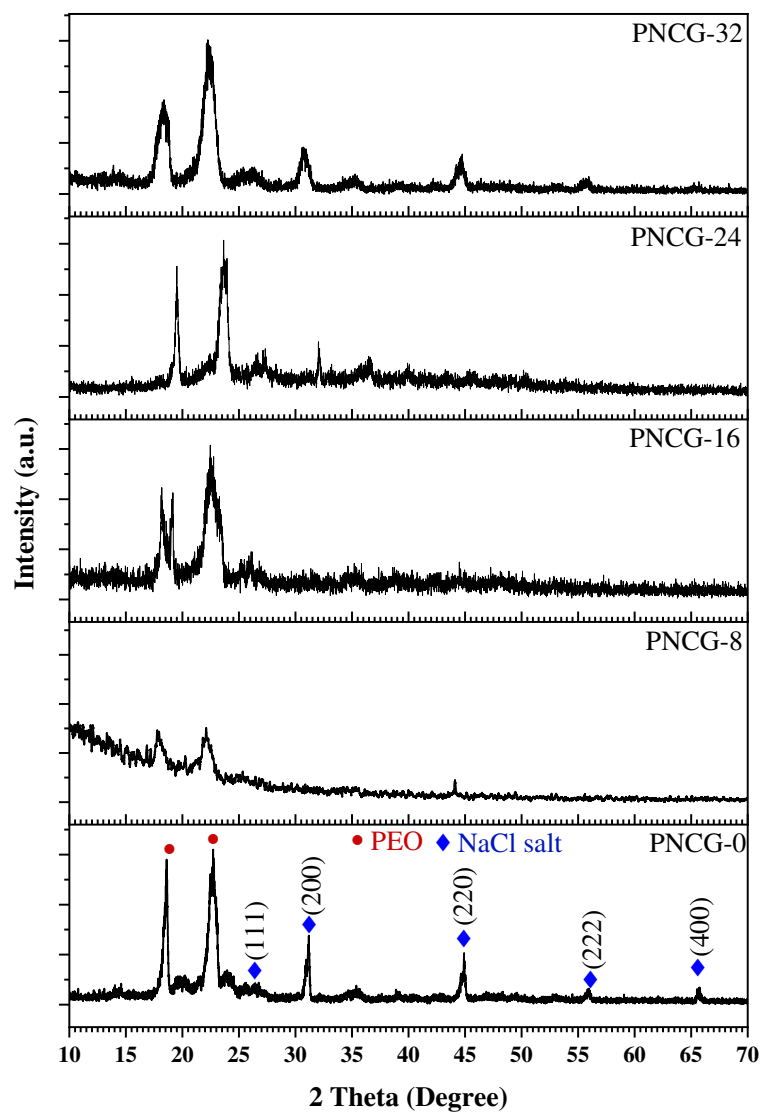


Figure 7. The XRD patterns of different glycerol of additives for the PEO-NaCl system

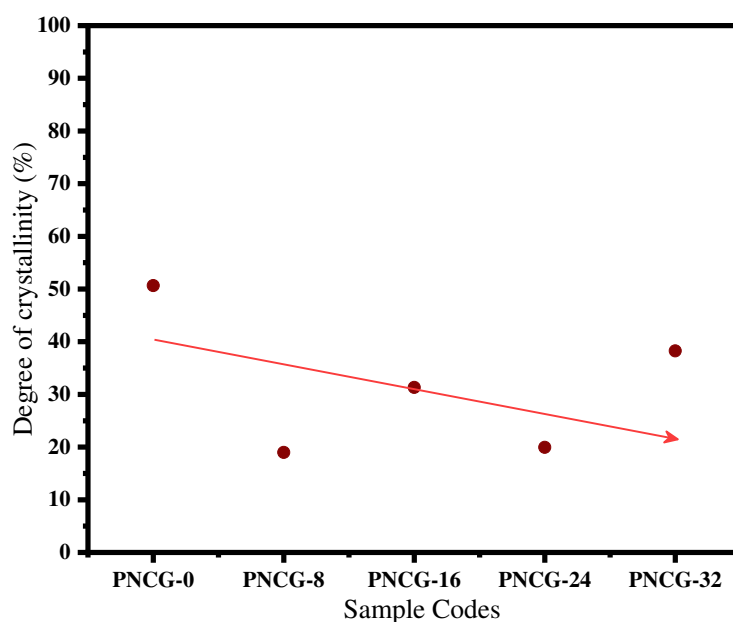


Figure 8. The degree of crystallinity was determined from the XRD pattern

4. Conclusion

This study demonstrates the potential of glycerol as a plasticizer for improving the electrochemical performance of PEO-NaCl-based polymer electrolytes. The addition of glycerol significantly reduced the crystallinity of PEO, enhancing ion mobility and conductivity. The EIS measurements revealed that the highest ionic conductivity, 1.74×10^{-4} S/cm, was achieved at a 32% glycerol concentration, i.e., the conductivity increased by approximately 12,609 times from the glycerol-free sample to the sample with 32% glycerol. This enhancement is attributed to improved ion dissociation and mobility due to reduced polymer rigidity and better interaction between the polymer chains and the salt ions. Dielectric property analysis confirmed that glycerol increases polarizability by promoting dipole alignment and reducing ion aggregation, leading to greater energy dissipation and improved charge transport. The sharp dielectric loss peaks at higher frequencies with increasing glycerol content indicate enhanced relaxation dynamics and reduced polymer matrix rigidity. The results underscore the importance of optimizing glycerol concentration to balance ionic conductivity and mechanical stability. Excessive plasticizer content may compromise structural integrity, but within the optimal range, glycerol demonstrates substantial improvements in conductivity and dielectric properties. These findings suggest that PEO-NaCl-glycerol-based polymer electrolytes are promising candidates for applications in solid-state electrochemical devices, such as batteries, fuel cells, and supercapacitors, providing an efficient, stable, and cost-

effective alternative to conventional liquid electrolytes. Future work should explore the long-term stability and scalability of these materials.

Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of Interest

There are no financial and non-financial competing interests.

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Author contributions:

S. B. Aziz: Supervision, Project administration, Conceptualization, Review.

I. N. Qader and S. Y. Omar visualization.

P. A. Ibrahim synthesis polymer films.

D. S. Muhammad, P. Aspoukeh, S. M. Hamad, and S. M. Hussein performed the characterizations.

K. A. Babakr, R. A. Omer, I. L. Salih, H. Hamad Rasul, S. S. Mohammed, D. A. Hamid, P. H. Mahmood, and A. W. Muhammed data analysis and writing.

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