Effect of CeO_2 Nanoparticles on the Structural and Electrical Properties Of PEO–$KClO_4$ Nanocomposite Polymer Electrolytes

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ABSTRACT

This work presents the emulsion and disquisition of polyethylene oxide (PEO) – potassium perchlorate ($KClO_4$) solid polymer electrolytes dispersed with cerium oxide (CeO_2) nanoparticles. The polymer nanocomposites were fabricated via result casting and dominated to structural, morphological, and electrochemical characterization. X-ray diffraction (XRD) analysis confirmed that the addition of CeO_2 reduces the crystallinity of PEO, thereby increasing the amorphous regions that facilitate ion transport. Fourier transform infrared spectroscopy (FTIR) revealed polymer – tar – stuffing relations through shifts in vibrational bands and variations in intensity. Scanning electron microscope (SEM) indicated morphological variations and disbandment of filling tittles within the polymer matrix. Electrochemical impedance spectroscopy (EIS) demonstrated significant enhancement in ionic conductivity with CeO_2 loading, following Arrhenius-type temperature dependence. Dielectric and Electric modulus analyses show better polarization, relaxation dynamics, and non-Debye conduct. The findings suggest that CeO_2 - unravel PEO – $KClO_4$ nanocomposites are promising contenders for coming- generation solid- state electrochemical bias. Among them, polyethylene oxide (PEO) has been vastly studied as a polymer host because of its capability to solvate alkali hearties through ether oxygen collaboration and still, the high crystallinity of PEO at room temperature limits ionic transport, performing in low conductivity. To address this limitation, several strategies have been explored, including blending, plasticization, and the incorporation of inorganic nanofillers. The addition of nanofillers is particularly effective, as they disrupt crystalline regions, increase unformed content, and give new ion transport pathways. Cerium oxide (CeO_2) nanoparticles are of particular interest because of their high dielectric constant, face oxygen vacancies, and capability to interact with both cations and anions. These features meliorate tar dissociation and reduce ion aggregation, enhancing conductivity and dielectric response. Although numerous studies have excavated CeO_2 in lithium- predicated systems, lower reports live for potassium perchlorate ($KClO_4$) – predicated electrolytes. The present study investigates CeO_2- dispersed PEO–$KClO_4$ nanocomposite films prepared via result casting. Structural, morphological, and electrical characterizations were performed to understand the part of CeO_2 in modifying crystallinity, ion transport, and dielectric relaxation.

Keywords: PEO–$KClO_4$, CeO_2 nanoparticles, Ionic conductivity, Dielectric properties, Electric modulus, XRD, SEM, FTIR

1. INTRODUCTION

The solid polymer electrolytes (SPEs) have gained significant attention as promising substitutes for conventional liquid electrolytes owing to their inherent advantages such as enhanced mechanical flexibility, ease of processing, better dimensional stability, and improved operational safety. Among the various polymer hosts, polyethylene oxide (PEO) has been one of the most widely explored candidates. This is primarily due to its strong ability to solvate alkali metal salts through coordination between the ether oxygen atoms in the polymer backbone and the cations of the salt. Despite these advantages, PEO suffers from a major drawback—its high degree of crystallinity at ambient temperature severely restricts segmental chain motion, which in turn limits ionic transport and results in poor room-temperature conductivity [1]. To overcome this challenge, several modification strategies have been introduced, including polymer blending, incorporation of plasticizers, and addition of inorganic nanofillers. Among these, nanofiller incorporation has been shown to be particularly effective of dense packing and crosslinking density of polymer by retarding crystallization [2].

The presence of nanofillers not only interrupts the crystalline domains of PEO, thereby increasing the amorphous fraction, but also creates additional conduction pathways that facilitate ion migration [3-4]. In this context, cerium oxide (CeO_2) nanoparticles are especially concerned in their high dielectric constant, the presence of oxygen vacancies on the surface, and the ability to interact with both cations and anions make them valuable additives [5]. These properties promote efficient salt dissociation, reduce ion clustering, and enhance both ionic conductivity and dielectric performance. Although CeO_2 has been extensively studied as a reinforcing filler in lithium salt–based polymer electrolyte systems, investigations focusing on its effect in potassium perchlorate ($KClO_4$)–based electrolytes remain relatively limited [6]. This gap motivates the present work, which aims to explore the influence of CeO_2 nanoparticles on the structural, morphological, and electrochemical characteristics of PEO–$KClO_4$ solid polymer electrolytes [7-8]. Nanocomposite films were synthesized via a solution-casting approach, and a comprehensive set of characterizations—including X-ray diffraction (XRD), scanning electron microscopy (SEM), impedance spectroscopy, and dielectric analysis—were carried out. The objective is to elucidate the role of CeO_2 in modulating polymer crystallinity, improving ion transport behaviour, and tailoring dielectric relaxation processes [9-11].

2. MATERIALS AND EXPERIMENTAL METHODS

2.1 MATERIALS

Polyethylene oxide (PEO, high molecular weight) was selected as the polymer matrix. Potassium perchlorate ($KClO_4$) was employed as the ionic salt, and cerium oxide (CeO_2) nanoparticles were incorporated as inorganic fillers. Acetonitrile was used as the solvent. All reagents were utilized in their supplied form without additional purification.

2.2 FABRICATION OF POLYMER ELECTROLYTE FILM

The nanocomposite films were prepared by solution casting:

Figure 1: Process of Solution casting

Polyethylene oxide (PEO) was first dissolved in acetonitrile while maintaining continuous magnetic stirring. The stirring process was continued until the polymer was completely solubilized, giving rise to a transparent and homogeneous solution. In the next step, a separately prepared solution of potassium perchlorate ($KClO_4$) in acetonitrile was introduced drop by drop into the polymer medium. This gradual addition facilitated the interaction between the polymer chains and the salt ions, thereby promoting the formation of a stable polymer–salt complex. For the incorporation of the inorganic phase, cerium oxide (CeO_2) nanoparticles at concentrations of 1 and 2 wt% were dispersed in acetonitrile using ultrasonic agitation. Sonication ensured that the nanoparticles were broken down into smaller aggregates and uniformly suspended in the solvent. The well-dispersed CeO_2 suspension was then added slowly to the PEO–$KClO_4$ matrix under continuous stirring, which assisted in achieving homogeneous dispersion of the nanoparticles within the host polymer system. The final mixture, containing polymer, salt, and filler, was cast into clean Petri dishes to allow even spreading of the solution. These cast films were initially dried under ambient laboratory conditions to remove the bulk of the solvent through natural evaporation. To further ensure the elimination of residual solvent and to enhance film stability, the partially dried samples were subjected to vacuum drying at 60–70 °C. This final step produced flexible, mechanically stable, and uniform nanocomposite electrolyte films suitable for subsequent characterization and electrochemical studies.

2.3 ANALYTICAL TECHNIQUES

- X-ray Diffraction (XRD): Structural changes and crystallinity reduction.
- Fourier Transform Infrared Spectroscopy (FTIR): Polymer–salt–padding interactions.
- Scanning Electron Microscopy (SEM): Surface morphology and padding dispersion.
- Electrochemical Impedance Spectroscopy (EIS): Ionic conductivity, dielectric response, and modulus analysis.

3. RESULTS AND DISCUSSIONS

3.1 XRD Analysis of CeO_2 Dispersed Polymer Electrolytes:

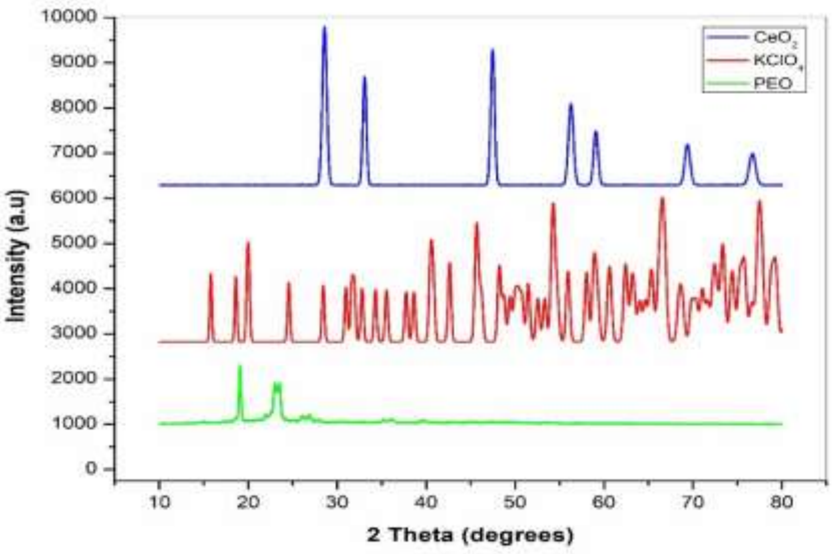

Figure 2: XRD analysis of pure PEO–$KClO_4$ and CeO_2

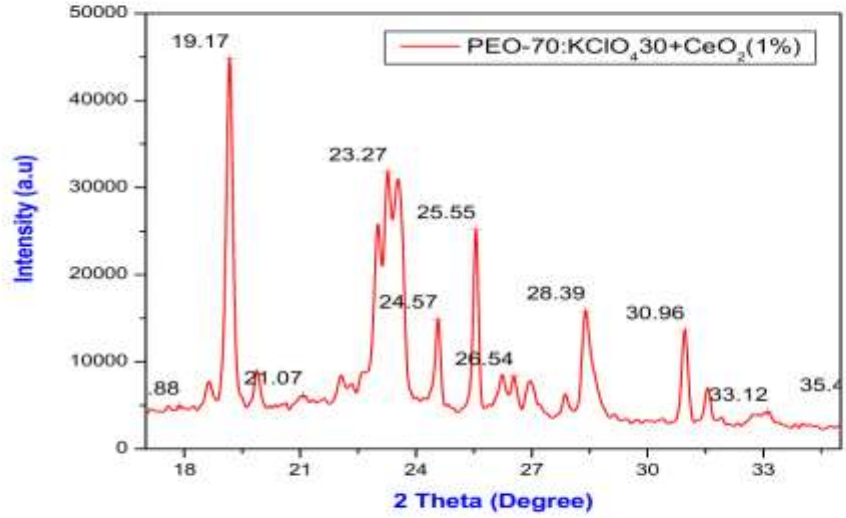

Figure 3: X-ray diffraction spectra of PEO–KClO$_4$ (70:30) polymer electrolytes containing CeO$_2$ (1 wt%)

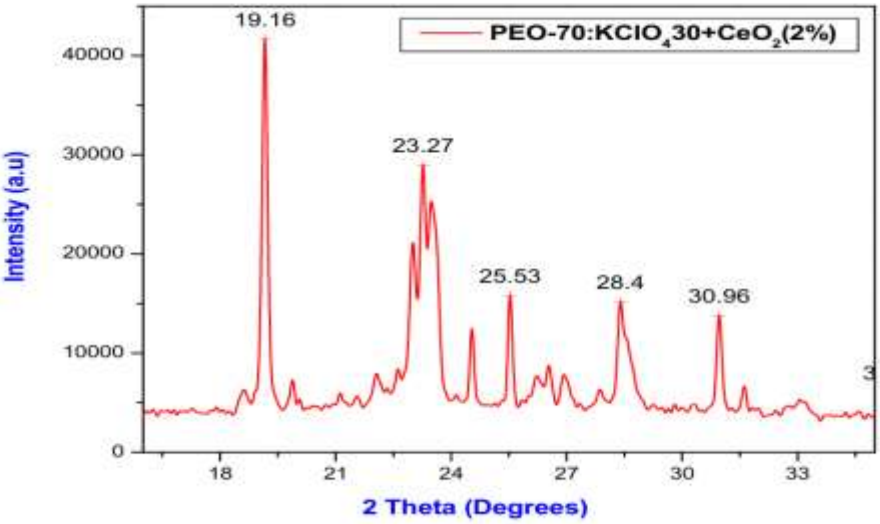

Figure 4: X-ray diffraction spectra of PEO–KClO$_4$ (70:30) polymer electrolytes containing CeO$_2$ (2 wt%)

The figure (2), figure (3) and figure (4) represent pure PEO displayed sharp reflections at 19° and 23°, characteristic of its semi-crystalline nature. KClO$_4$ and CeO$_2$ exhibited strong crystalline peaks consistent with their reported phases. The XRD profiles of PEO–KClO$_4$ (70:30) ratio of electrolytes incorporated with CeO$_2$ nanoparticles reveal distinct structural modifications. For the 1 wt% CeO$_2$ composite, sharp reflections at 19.17° and 23.27° correspond to crystalline domains of PEO, while changes in peak intensity indicate partial disruption of polymer crystallinity and the creation of new interaction sites. At higher filler loading (2 wt%), the diffraction pattern displays characteristic peaks at 19.16°, 23.27°, 25.53°, 28.40°, and 30.96°, with the most intense reflection at 19.16°. Compared to the lower CeO$_2$ content, the 2 wt% sample exhibits the reduced and redistributed intensities with their decreased crystallinity and an enhanced amorphous phase. These modifications signify stronger polymer–salt–filler interactions, which are expected to promote more efficient ionic transport within the nanocomposite matrix.

3.2 FTIR Spectroscopy:

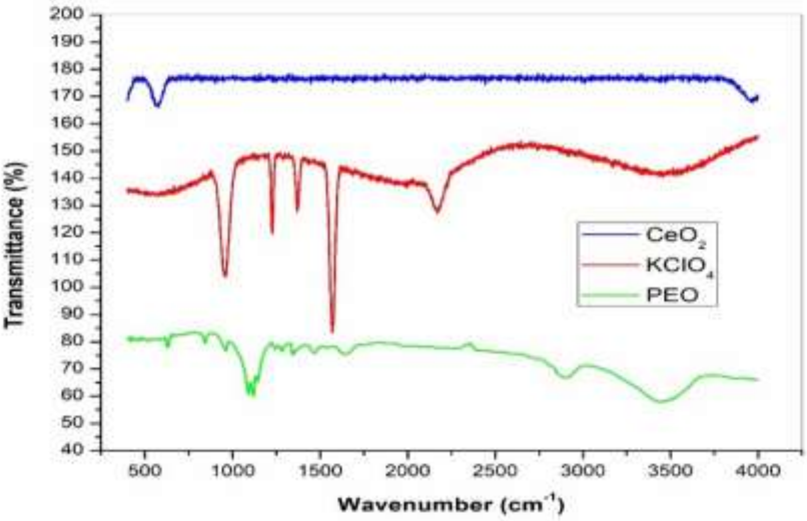

Figure 5: FTIR analysis of PURE PEO–KClO$_4$ and CeO$_2$

Figure (5) displays the FTIR spectra of PURE PEO, KClO$_4$, and CeO$_2$ where PEO displays distinct absorption peaks corresponding to its molecular vibrations within the 500–4000 cm^{-1} range. KClO$_4$ shows several intense bands between 900–1500 cm^{-1}, attributed to the vibrational modes of perchlorate ions. On the other hand, CeO$_2$ exhibits minimal features, reflecting its weak infrared response. The clear differences in spectral patterns validate the individual identity of each component and indicate possible interactions when incorporated into composite systems.

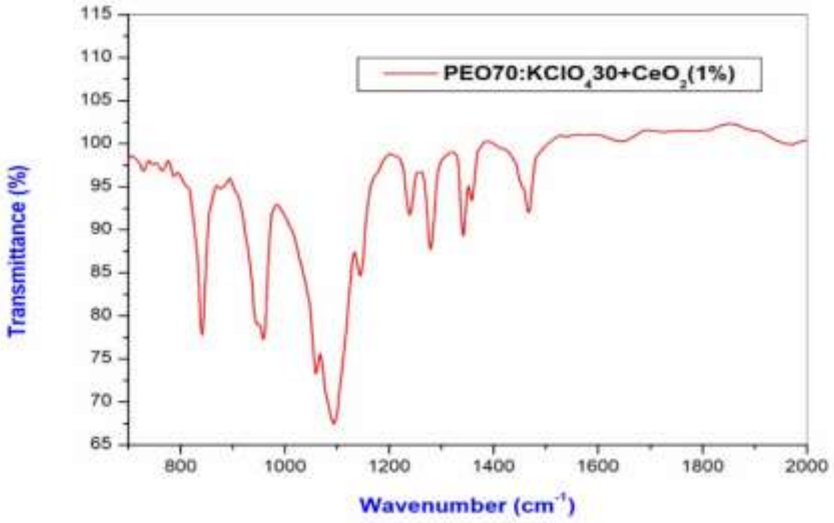

Figure 6: FTIR analysis of PEO–KClO$_4$ (70:30) nanocomposite electrolytes with CeO$_2$ (1 wt%)

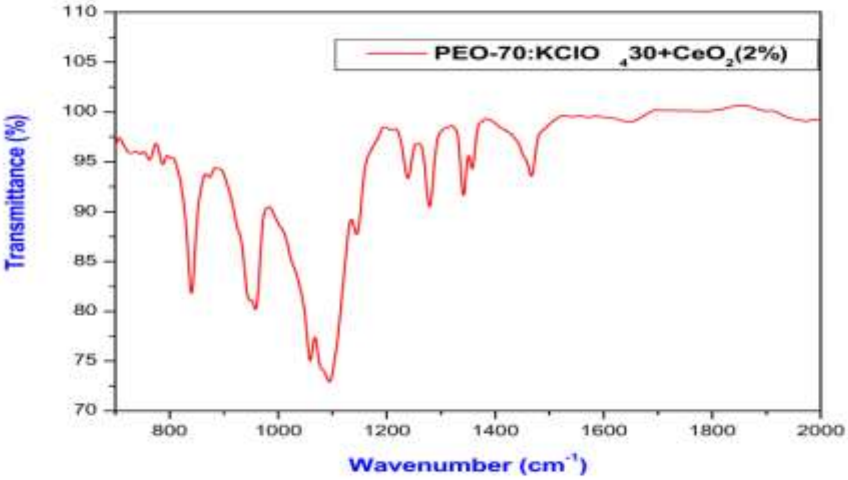

Figure 7: FTIR analysis of PEO–KClO$_4$ (70:30) nanocomposite electrolytes with CeO$_2$ (2 wt%)

Figure (6) and (7) illustrating the FTIR spectra of PEO–KClO$_4$ (70:30) nanocomposites incorporated with CeO$_2$ reveal characteristic absorption features between 600–1700 cm^{-1}. In both 1 wt% and 2 wt% CeO$_2$-loaded systems, the bands at 840–950 cm^{-1} are attributed to C–O–C stretching of the PEO backbone, while a strong absorption near 1100 cm^{-1} corresponds to ether group vibrations. Additional features observed in the 1250–1450 cm^{-1} region confirm coordination of K$^+$ ions with the PEO chains. The incorporation of CeO$_2$ results in slight shifts and changes in peak intensities, indicating strong polymer–salt–filler interactions. These modifications suggest a reduction in crystallinity and an increase in amorphous content, which are favourable for enhancing ionic transport in the nanocomposite electrolyte films.

3.3 SEM Morphology:

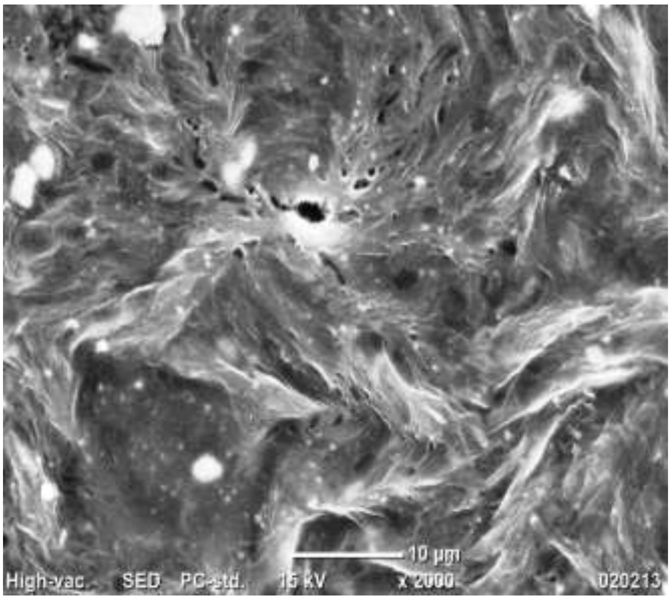

Figure (8)

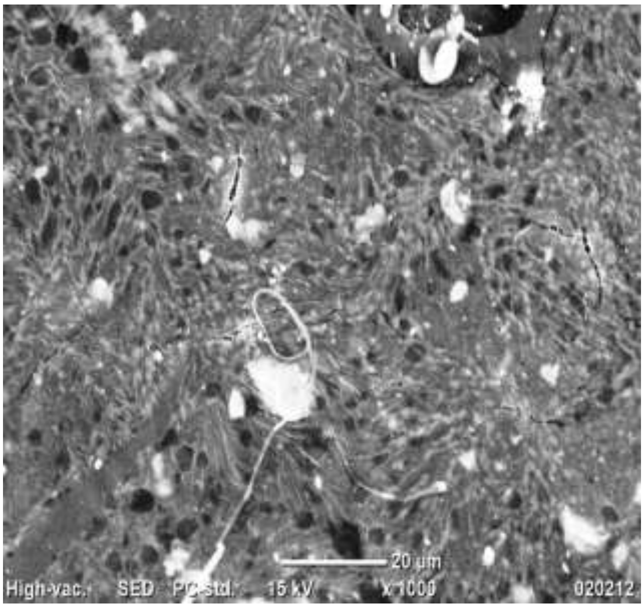

Figure (9)

Figure (8): SEM micrograph of PEO–KClO$_4$ (70:30) + CeO$_2$ (1 wt%) electrolyte at ×2000 magnification (scale bar: 10 µm) and figure showing fibrous morphology and embedded CeO$_2$ nanoparticles with reduced porosity.

Figure (9): SEM micrograph of PEO–KClO₄ (70:30) + CeO₂ (1 wt%) electrolyte at ×1000 magnification (scale bar: 20 µm) and here figure displaying a heterogeneous surface with uniformly distributed filler particles and polymer–salt–filler interactions.

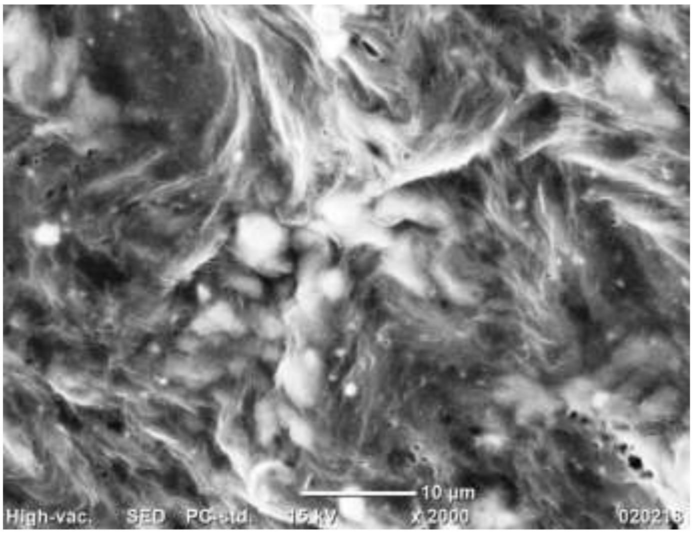

Figure (10)

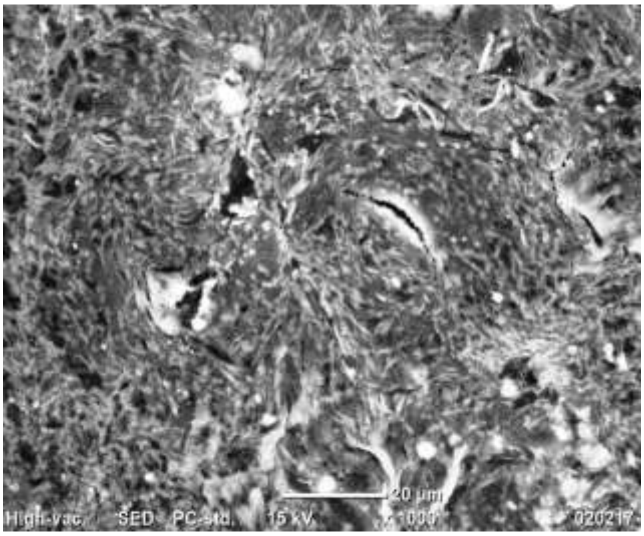

Figure (11)

Figure (10): SEM micrograph of PEO–KClO₄ (70:30) + CeO₂(2 wt%) electrolyte at ×2000 magnification (scale bar: 10 µm), and image displaying dense fibrous regions with embedded CeO₂ nanoparticles, indicating reduced crystallinity and enhanced amorphous domains.

Figure (11): SEM micrograph of PEO–KClO₄ (70:30) + CeO₂(2 wt%) electrolyte at ×1000 magnification (scale bar: 20 µm), and figure illustrating a relatively uniform surface with dispersed filler clusters and fewer micro voids, suggesting improved structural homogeneity.

3.4 Impedance Spectroscopy:

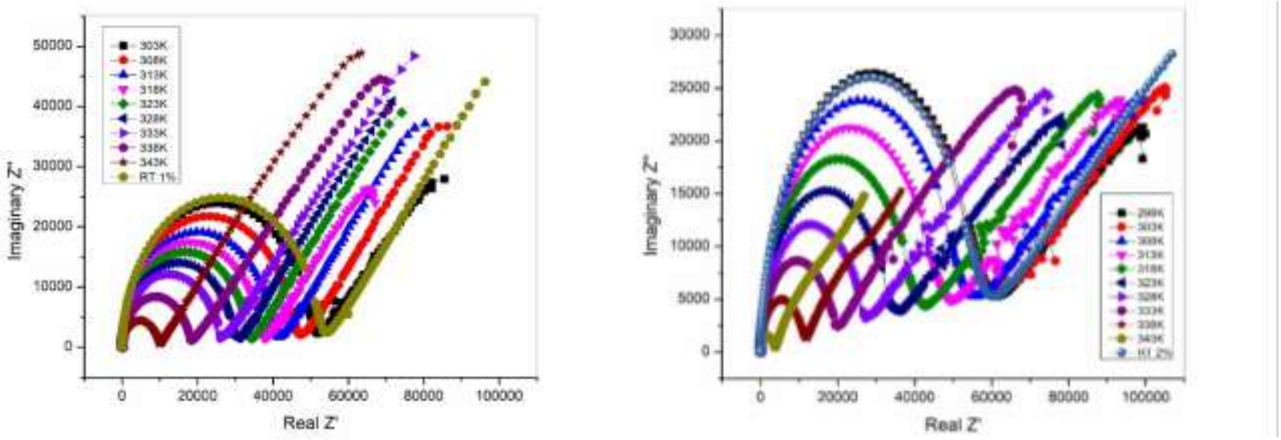

Figure (a)

Figure (b)

Figure 12: Nyquist plots of PEO–KClO₄ (70:30) composite polymer electrolytes containing (a) 1 wt% CeO₂ and (b) 2 wt% CeO₂, recorded at different temperatures, illustrating the effect of filler concentration on impedance behaviour and ion transport

The Nyquist plots of PEO–KClO₄ (70:30) electrolytes with 1 wt% and 2 wt% CeO₂ exhibit semicircular arcs followed by inclined tails, characteristic of bulk resistance and electrode polarization. In both systems, the semicircle diameter decreases with increasing temperature, signifying reduced resistance and enhanced ionic conductivity. The effect is more pronounced for the 2 wt% CeO_2 composite, indicating stronger polymer–salt–filler interactions and improved ion transport at elevated temperatures.

3.5 AC Conductivity:

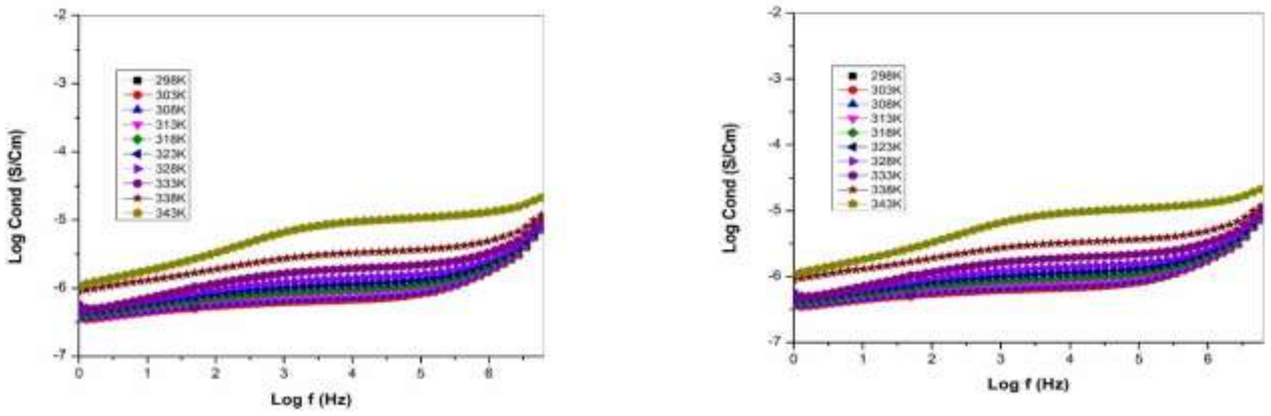

Figure (a)

Figure (b)

Figure13: Frequency-dependent conductivity studies were performed on the PEO:$KClO_4$(70:30) polymer electrolyte incorporated (a) with 1 wt% CeO_2 (b) 2 wt% under varying temperature conditions

Figure 13: (a) and (b) are illustrates the AC conductivity spectra of PEO:$KClO_4$ (70:30) with 1 wt% and 2 wt% CeO_2 show a low-frequency plateau followed by a dispersive rise at higher frequencies, typical of ion hopping in polymer electrolytes. Conductivity increases consistently with temperature from 298 K to 343 K, confirming thermally assisted ion transport. The 2 wt% CeO_2 sample exhibits higher conductivity than the 1 wt% CeO_2 system, indicating that increased filler content enhances salt dissociation, ion mobility, and overall charge transport.

3.6 Dielectric Properties:

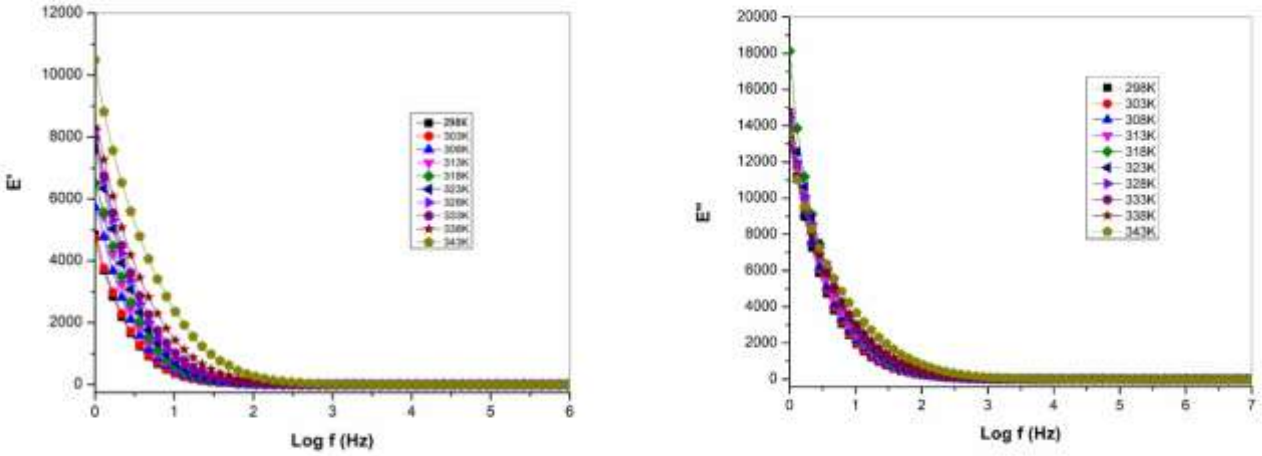

Figure (a)

Figure (b)

Figure 14: Frequency-dependent variation of (a) dielectric constant (E') and (b) dielectric loss (E'') for the PEO:$KClO_4$ (70:30) + 1 wt% CeO_2 nanocomposite electrolyte at different temperatures

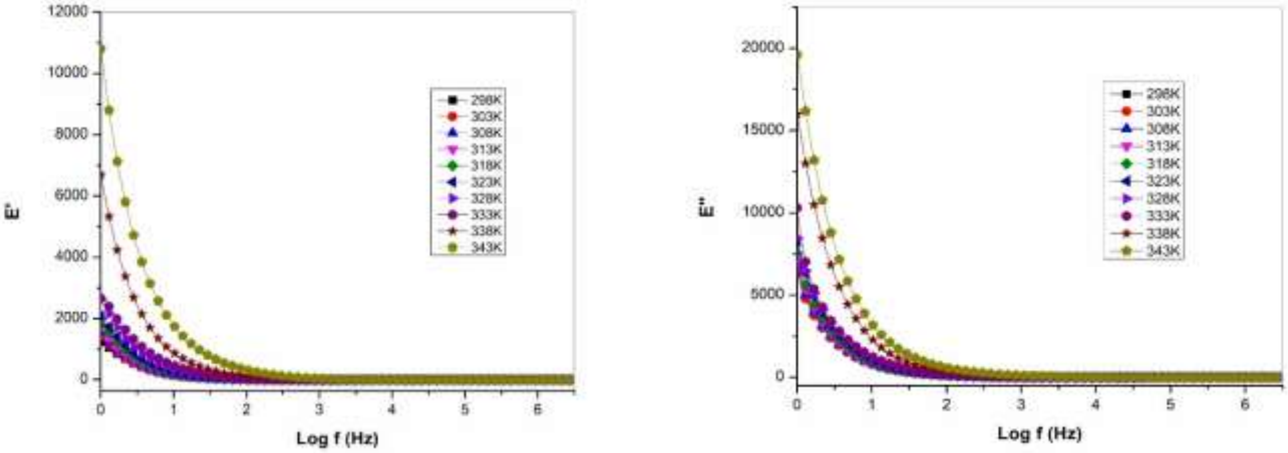

Figure (a) Figure (b)

Figure 15: Frequency-dependent variation of (a) dielectric constant (E') and (b) dielectric loss (E'') for the PEO:KClO$_4$ (70:30) + 2 wt% CeO$_2$ nanocomposite electrolyte at different temperatures

Figure (14,15): (a) and (b) Frequency-dependent dielectric constant (E′) and dielectric loss (E″) for PEO:KClO$_4$ (70:30) with 1% and 2% CeO$_2$ nanocomposite electrolytes at different temperatures. Both dielectric constant (E′) and dielectric loss (E″) show high values in the low-frequency region due to electrode and interfacial polarization, which decrease rapidly with increasing frequency as dipoles fail to follow the alternating field. Conductivity-related relaxation becomes evident at higher temperatures, confirming thermally assisted ion dynamics. The 2 wt% CeO$_2$ system exhibits higher dielectric response than the 1 wt% CeO$_2$ system, indicating improved salt dissociation and enhanced charge carrier mobility.

3.7 Electric Modulus Analysis:

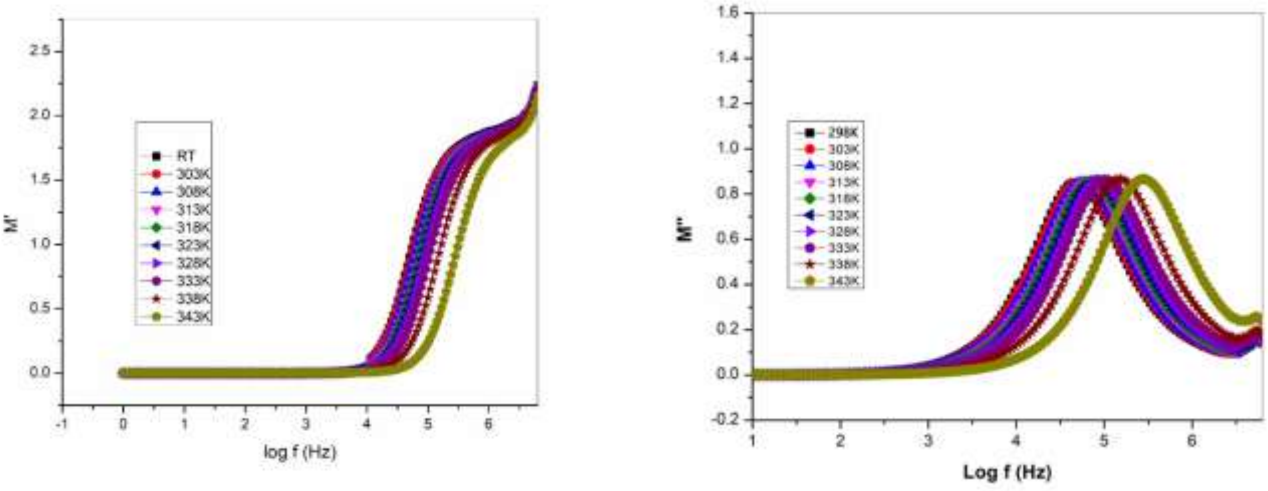

Figure (a) Figure (b)

Figure 16: Frequency-dependent variation of the (a) real part of electric modulus (M′) and (b) Imaginary part of electric modulus (M″) for PEO:KClO$_4$ (70:30) + 1 wt% CeO$_2$ nanocomposite electrolyte at different temperatures

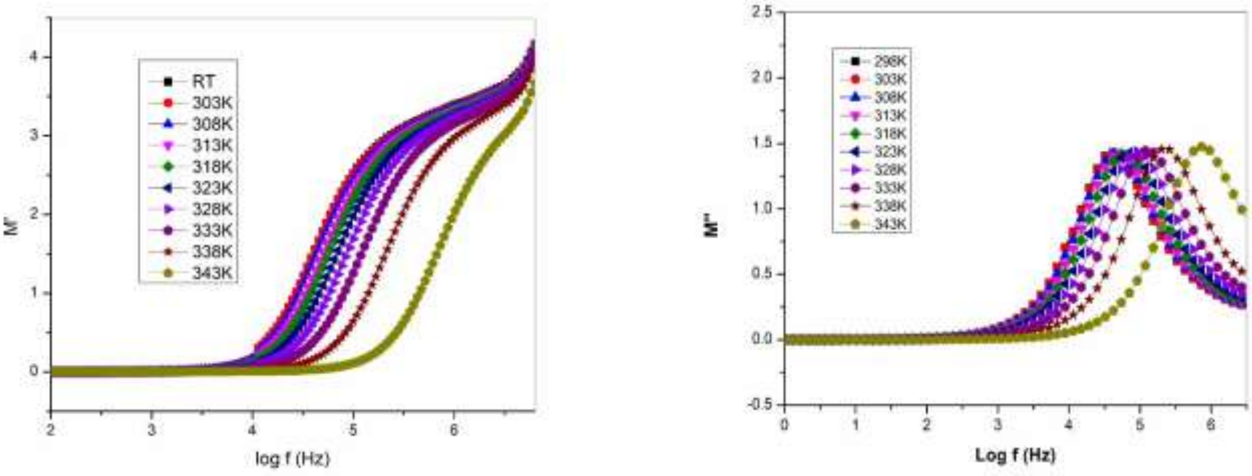

Figure (a) Figure (b)

Figure 17: Frequency-dependent variation of the (a) real part of electric modulus (M′) and (b) Imaginary part of electric modulus (M″) for PEO:KClO$_4$ (70:30) + 2 wt% CeO$_2$ nanocomposite electrolyte at different temperatures

Figures (16) and (17) shows the Frequency-dependent variation of the real (M′) and imaginary (M″) parts of the electric modulus for PEO:KClO$_4$ (70:30) with 1 wt% and 2 wt% CeO$_2$ nanocomposite electrolytes at different temperatures. The real part (M′) remains close to zero in the low-frequency region due to suppression of electrode polarization, and increases at higher frequencies, indicating bulk relaxation. The imaginary part (M″) exhibits relaxation peaks that shift toward higher frequencies with rising temperature, confirming thermally activated relaxation and reduced relaxation times. The broader and more intense peaks in the 2 wt% CeO$_2$ system suggest enhanced ion transport compared to the 1 wt% system. Furthermore, the asymmetry of the peaks indicates non-Debye type relaxation, reflecting a distribution of relaxation times within the polymer electrolyte matrix.

4. CONCLUSION

This study demonstrates that the incorporation of CeO$_2$ nanoparticles effectively modifies the structural, morphological, and electrical properties of PEO–KClO$_4$ polymer electrolytes. XRD confirmed crystallinity suppression, FTIR revealed polymer–salt–filler interactions, and SEM highlighted morphological changes. Electrochemical measurements established enhanced ionic conductivity, improved dielectric response, and favorable relaxation dynamics. The results establish CeO$_2$-doped PEO–KClO$_4$ composites as promising candidates for solid-state energy storage devices, such as potassium-ion batteries and electrochemical capacitors.

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