Synthesis, Characterization and Electrical Properties of ZrO_2 Dispersed PEO-KNO_3 Nanocomposite Polymer Electrolyte Systems

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Abstract:

Polymer electrolytes have sparked widespread interest due to their potential applications in solid-state batteries and electrochemical devices. In this study, nanocomposite polymer electrolytes based on polyethylene oxide (PEO) and potassium nitrate (KNO3) were produced using variable quantities of zirconium dioxide (ZrO2) as an inorganic filler. The structural, morphological, and electrical properties were carefully examined. X-ray diffraction (XRD) indicated a decrease in crystallinity with increased ZrO2 loading, indicating expanded amorphous regions conducive to ionic transport. Scanning electron microscopy (SEM) demonstrated a uniform distribution of ZrO2 nanoparticles throughout the PEO-KNO3 matrix. Impedance spectroscopy revealed a considerable improvement in ionic conductivity at the appropriate ZrO2 concentration. The findings emphasize the complementing role of ceramic fillers in boosting the performance of polymer electrolytes, making the system an attractive choice for solid-state electrochemical applications.

Keywords: PEO–$KN0_3$, ZrO_2 nanoparticles, Ionic conductivity, Dielectric properties, Electric modulus, XRD, SEM, FTIR.

1.INTRODUCTION

Solid polymer electrolytes (SPEs) have been intensively studied as liquid electrolyte substitutes due to their flexibility, low flammability, and ease of manufacturing. Due to its ether oxygen groups, polyethylene oxide (PEO) is intensively explored as a polymer host for alkali metal ions. However, PEO's strong crystallinity at ambient temperature limits ionic transport, limiting its electrochemical device use. Ionic conductivity can be improved by adding inorganic fillers to the polymer–salt matrix. TiO2, Al2O3, and ZrO2 nanoparticles disturb PEO's crystalline phase, increase amorphous content, and induce polymer chain segmentation. The chemical stability, mechanical robustness, and high dielectric permittivity of ZrO2 make it a good choice for polymer electrolyte modification.

This study created PEO–KNO_3 polymer electrolytes via solution casting and changing ZrO2 nanoparticle concentrations. To assess solid-state energy storage device applicability, the nanocomposite systems' structural, morphological, and electrical properties were examined.

2. SYNTHESIS OF THE MATERIAL

Materials Required: Polyethylene Oxide (PEO- 1.4 grams) ,Potassium Nitrate (KNO_3- 0.6 grams),Zirconium dioxide (ZrO_2- 0.02 grams),Acetonitrile (anhydrous -35 ml, used as solvent) **2.1. Preparation of Polymer Electrolyte Films:** The polymer electrolyte films were prepared by the solution casting technique: 1. PEO and KNO_3 were dissolved in acetonitrile to obtain a 70:30 w/w ratio. 2. ZrO_2 nanoparticles were added to the solution in the weight fraction of 1%.3. Ultrasonication was applied for 1 hour to disperse nanoparticles homogeneously. 4. The solutions were cast into glass Petri dishes and left for slow solvent evaporation.5. Films were dried under vacuum at 60 °C for 24 hours to eliminate residual solvent.

3. CHARACTERIZATION

3.1 XRD ANALYSIS

The XRD study of the ZrO2–KNO_3 dispersed PEO nanocomposite shows considerable structural changes. Diffraction peaks at 2θ = 19.08°, 23.48°, 29.33°, 33.97°, and 38.51° indicate KNO_3 and PEO crystals with modest ZrO2 contributions. PEO is semi-crystalline, with a strong peak at 23.48°, whereas peaks at 19.08° and 29.33° indicate orthorhombic planes of KNO_3. ZrO2 incorporation reduces peak intensities and broadens, indicating partial PEO crystallinity disruption and amorphous area enhancement. Ionic conductivity improves because amorphous domains allow chain mobility and quicker ion transport. ZrO2 has a nucleating effect that prevents recrystallization and ensures ion dispersion in the polymer matrix. The equilibrium between crystalline and amorphous phases optimizes electrochemical performance. XRD results show that a structurally modified nanocomposite electrolyte with increased ionic conduction for solid-state energy storage was synthesized.

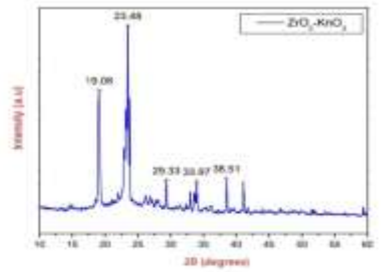


Fig.1: X-Ray Diffraction pattern of PEO-KNO_3 with ZrO_2 (1%) concentration

3.2. FOURIER TRANSFORM INFRARED ANALYSIS

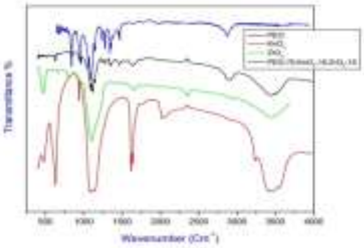


Fig.2: FTIR spectra of pure PEO, KNO3, ZrO2 and PEO-70: KNO3-15: ZrO2-15 dispersed nanocomposite polymer electrolyte systems

The ZrO2–KNO_3 dispersed PEO nanocomposite XRD investigation reveals significant structural changes. Diffraction peaks at 2θ = 19.08°, 23.48°, 29.33°, 33.97°, and 38.51° highlight KNO_3 and PEO crystals with minimal ZrO2 contributions. PEO is semi-crystalline, with a significant peak at 23.48°, while KNO_3 peaks at 19.08° and 29.33° imply orthorhombic planes. ZrO2 reduces peak intensities and broadens, indicating partial PEO crystallinity disruption and amorphous area enhancement. Ionic conductivity improves because amorphous domains allow chain mobility and faster ion transport. Nucleating ZrO2 prevents recrystallization and ensures polymer matrix ion dispersion. The crystalline-amorphous equilibrium optimizes electrochemical performance. A structured nanocomposite electrolyte with improved ionic conduction for solid-state energy storage was produced, according to XRD.

3.3 SCANNING ELECTRON MICROSCOPE ANALYSIS

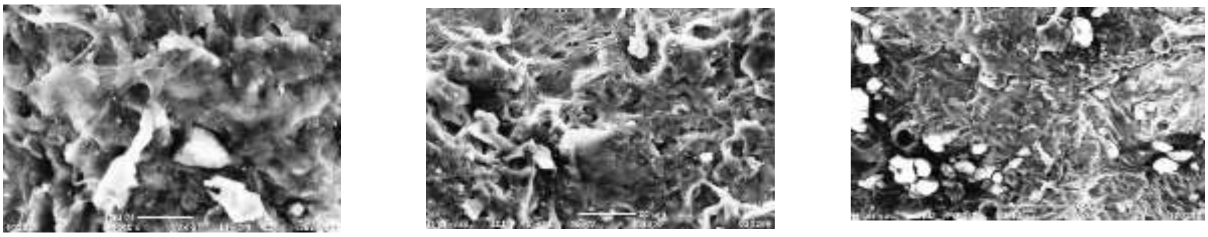


Fig.3: SEM picture of PEO-70: KNO3-15: ZrO2-15 dispersed solid polymer electrolyte systems with 500, 1000, and 2000 magnifications

SEM examination of ZrO2-dispersed PEO–KNO_3 nanocomposite polymer electrolytes at 500×, 1000×, and 2000× magnifications shows considerable morphological changes compared to pure PEO. Smooth polymer areas, porous domains, and brilliant granular clusters corresponding to well-dispersed ZrO2 nanoparticles are visible in the micrographs. The absence of large agglomerates ensures ceramic filler dispersion and good polymer–salt matrix interaction. ZrO2 destroys PEO's semi-crystalline structure, increasing its amorphous percentage, which is essential for polymer chain flexibility and segmental motion. Surface pores add free volume and ion transport channels. Additionally, ZrO2 nanoparticles serve as Lewis acid-base interaction sites for K^+ ions, promoting salt dissociation and minimizing ion pairing. The SEM results show that ZrO2 incorporation increases morphology, amorphicity, and ionic conduction, corroborating electrochemical tests of increased conductivity.

3.4. ELECTRON IMPEDANCE SPECTROSCOPY

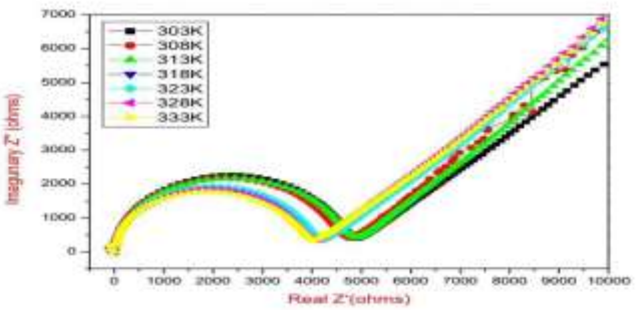
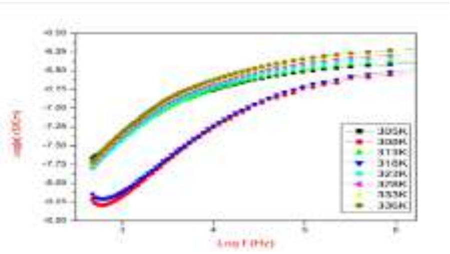
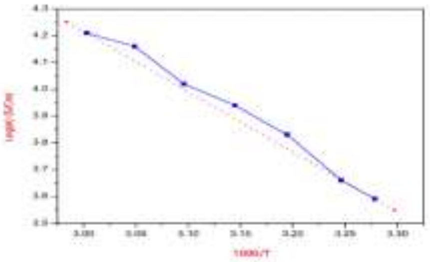


Fig.4: Nyquist plot of PEO-70: KNO$_3$-15: ZrO$_2$-15 dispersed solid polymer electrolyte systems at distinct temperatures

The SEM analysis of ZrO2-dispersed PEO–KNO_3 nanocomposite polymer electrolytes at 500×, 1000×, and 2000× magnifications reveals significant morphological changes compared to pure Micrographs show smooth polymer patches, porous domains, and bright granular clusters of well-dispersed ZrO2 nanoparticles. Without significant agglomerates, ceramic filler dispersion and polymer–salt matrix interaction are good. ZrO2 breaks PEO's semi-crystalline structure, making it more amorphous, which is necessary for polymer chain flexibility and segmental motion. Free volume and ion transport channels come from surface pores. ZrO2 nanoparticles promote salt dissociation and reduce ion pairing by acting as Lewis acid-base interaction sites for K^+ ions. SEM shows that ZrO2 inclusion increases morphology, amorphicity, and ionic conduction, supporting electrochemical conductivity studies.

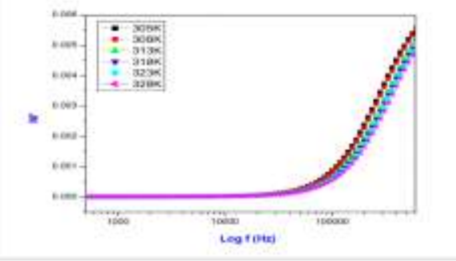
3.2. AC CONDUCTIVITY DC CONDUCTIVITY

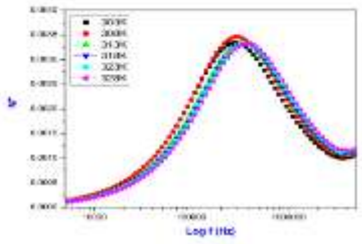




The conductivity spectra (log σ against log f) of ZrO2–PEO–KNO_3 nanocomposites exhibit three regions: a low-frequency plateau for dc conductivity, a mid-frequency dispersion zone, and a high-frequency saturation Raising the temperature from 305 to 336 K increases dc conductivity from 10^{-8} to 10^{-7} S/cm and increases crossover frequency. Faster ion dynamics and shorter relaxation durations make ion transport thermally active. The observed increase is attributable to ZrO2 nanoparticles, which reduce PEO crystallinity, speed up KNO_3 salt dissociation, and enhance ion conduction channels in the polymer matrix Therefore, the nanocomposite exhibits increased ionic mobility and conductivity at high temperatures. We found that the ZrO2–PEO–KNO_3 system is a promising solid polymer electrolyte for high-performance electrochemical devices. ZrO2–PEO–KNO_3 nanocomposite electrolytes exhibit Arrhenius behavior, with a linear trend as log(σ) versus 1000/T. The straight-line relationship illustrates that warmth activates ionic conduction, increasing conductivity. Higher temperatures make PEO chains more flexible, allowing ions to pass through the polymer matrix. Linearity of the data shows a single dominant conduction mechanism regulates ion transport without diverging from Arrhenius behavior. The slope's low activation energy reveals that ZrO2 nanoparticles disrupt PEO crystallinity and dissociate salt, improving charge carrier mobility. The nanocomposite electrolyte is appealing for advanced solid-state electrochemical devices that need conductivity and structural stability.

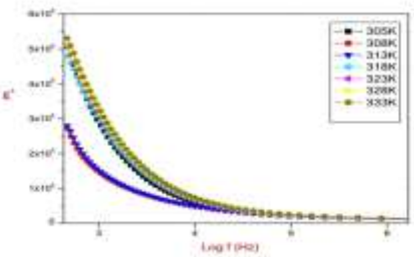
3.4. ELECTRIC MODULUS





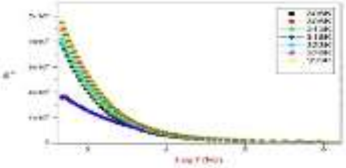
The electric modulus formalism minimizes electrode polarization by expressing the reciprocal of the complex dielectric permittivity, making it useful for studying ion dynamics in polymer electrolytes. Real part (M′) represents elastic response, whereas imaginary part (M″) represents energy dissipation. ZrO2–PEO–KNO_3 nanocomposites exhibit suppressed polarization and bulk relaxation, with M′ spectra near zero at low frequencies and abruptly rising at high frequencies. With rising temperature (305–328 K), M″s high-frequency dispersion shifts slightly, indicating quicker relaxation and ionic mobility. The M″ spectra show a relaxation peak that rises to higher frequencies with increasing temperature, indicating faster relaxation and enhanced ion transport. A single relaxation mechanism is suggested by the symmetric peaks. ZrO2 nanoparticles reduce PEO crystallinity, promote salt dissociation, and create effective conduction channels, proving the system's potential as an energy storage solid-state electrolyte.

3.5. DIELECTRIC PROPERTIEs



3.5.1. DIELECTRIC CONSTANT: The dielectric constant, defined as the ratio of a material's permittivity (ε) to empty space (ε_0), measures its electrical energy storage capabilities compared to a vacuum. ZrO2(1%) dispersed PEO–KNO_3 nanocomposite electrolytes exhibit a frequency-dependent dielectric response, with large ε′ values at low frequencies and decreasing with increasing frequency (305-333 K). At low frequencies, electrode polarization and space charge accumulation dominate, but at higher frequencies, dipoles and charge carriers cannot keep up with the fast fluctuating field. The low-frequency dielectric constant increases with temperature, indicating increased ionic mobility, charge carrier density, and polymer chain flexibility. ZrO2 nanoparticles reduce PEO crystallinity, aid salt dissociation, and increase dielectric responsiveness. The nanocomposite is a promising contender for solid-state electrochemical devices like batteries and supercapacitors due to its thermally stimulated conduction mechanism.

3.5.2. DIELECTRIC LOSS:



The loss tangent measures dielectric loss (ε″), which is the energy released as heat in a material when subjected to an alternating electric field. Polarization lags after the applied field. ZrO2(1%) dispersed PEO–KNO_3 nanocomposites exhibit large ε″ values at low frequencies in their frequency-dependent dielectric loss spectra from 305-333 K. Because of electrode polarization and charge build-up at the electrode–electrolyte interface. As frequency rises, ε″ significantly falls, indicating polarization suppression and dipolar relaxation dominance. High temperature increases low-frequency dielectric loss due to increased ionic mobility, charge carrier density, and polymer chain flexibility. The addition of ZrO2 nanoparticles improves dielectric performance by reducing PEO crystallinity, promoting KNO_3 salt dissociation, and enhancing interfacial polarization.

4. CONCLUSION

This study successfully develops and examines ZrO2-dispersed PEO–KNO_3 nanocomposite polymer electrolytes, assessing their structural, morphological, and electrical properties. XRD and FTIR measurements show that ZrO2 nanoparticles disrupt crystallinity and increase amorphous phase in the polymer–salt matrix. This structural change increases ionic mobility. ZrO2 is uniformly distributed in SEM micrographs, ensuring morphological stability and enhanced host polymer interaction. Impedance spectroscopy results reveal the nanocomposite's higher ionic conductivity than the PEO–KNO_3 system, indicating ZrO2's vital function in enhancing ion transport channels. The improved composite has conductivity suitable for rechargeable batteries and supercapacitors. ZrO2 nanoparticles alter the microstructure and improve electrical performance, laying the groundwork for new energy storage technologies using nanocomposite electrolytes.

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