Effect of SIO_2 Nano Filler on Structural Properties and Ionic Conductivity of PEO-$NACLO_4$ Polymer System

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Abstract

This thesis investigates sodium-ion solid polymer electrolytes reinforced with nano-alumina, synthesized via solution casting. The research focused on how nanoparticle dispersion influence's structure, morphology, thermal stability, and electrochemical behavior. Various techniques—XRD, SEM, FTIR, and impedance spectroscopy—were applied. XRD revealed reduced crystallinity of PEO upon SiO_2 incorporation, suggesting a shift toward an amorphous phase favorable for ion transport. FTIR confirmed complexation between PEO chains, sodium ions, and SiO_2, highlighting enhanced salt dissociation. SEM micrographs showed uniform nanoparticle distribution, while impedance spectroscopy indicated that ionic conductivity improved significantly with optimized SiO_2 loading, though excessive filler caused agglomeration and performance decline. The improvements are attributed to increased amorphous content, better ion mobility, and Lewis acid–base interactions at the SiO_2 interface. Overall, the findings demonstrate that SiO_2 nanoparticles effectively tune the microstructure and transport properties of PEO-based electrolytes, underscoring their potential in next-generation solid-state sodium-ion batteries. Index Terms— Polymer Electrolyte, SiO_2, XRD, FTIR, SEM, Impedance spectroscopy.

1. INTRODUCTION

The growing demand for safe, sustainable, and high-performance energy storage technologies has stimulated considerable research into alternatives to conventional lithium-ion batteries. Among these, sodium-ion batteries (SIBs) have gained attention due to the natural abundance, low cost, and wide geographical distribution of sodium resources compared to lithium. However, the successful realization of SIBs depends strongly on the development of efficient solid-state electrolytes capable of providing high ionic conductivity, thermal stability, and mechanical robustness.[1]

Solid polymer electrolytes (SPEs) have emerged as a promising class of materials because of their flexibility, lightweight nature, and ability to suppress dendrite growth. Polyethylene oxide (PEO), in particular, has been widely studied as a polymer host due to its strong coordinating ability with alkali metal salts. Nonetheless, its high degree of crystallinity at ambient temperature restricts ionic transport, thereby limiting overall conductivity.[2]

To address these challenges, the incorporation of inorganic nano-fillers has been proposed as an effective strategy to disrupt crystallinity and enhance ion mobility. Among different fillers, silicon dioxide (SiO_2) nanoparticles are of particular interest due to their large surface area, high thermal stability, and ability to interact with polymer chains through Lewis's acid–base interactions. These characteristics not only improve the amorphous fraction of the polymer but also facilitate salt dissociation and promote homogeneous ion transport pathways.[3]

In this work, solid polymer electrolytes based on PEO complexed with sodium perchlorate ($NaClO_4$) and reinforced with SiO_2 nanoparticles were prepared using the solution casting technique. The influence of nano-filler concentration on structural, morphological, thermal, and electrochemical properties was systematically investigated through X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and impedance spectroscopy. The study provides insights into the role of SiO_2 in tailoring the microstructure and transport behavior of PEO-based electrolytes, aiming to improve their suitability for next-generation sodium-ion battery applications.[4]

2. SYNTHESIS OF THE MATERIAL

The solution casting technique was employed to fabricate solid polymer electrolyte films, which are particularly suited for energy storage devices such as batteries. To begin, 1.4 grams of polyethylene oxide (PEO), sourced from Aldrich Inc., was dissolved in 35 mL of dimethylformamide (DMF). The solution was thoroughly stirred until a clear and uniform mixture was obtained. Its density was carefully regulated by controlled solvent evaporation, facilitated through the use of a microwave oven.[5].

To minimize particle agglomeration, 0.02 grams of sodium oxide powder with an average particle size of 60 nm was incorporated into the solution. Subsequently, 0.6 grams of sodium perchlorate ($NaClO_4$) was added. The mixture was then continuously stirred for 48 hours using a magnetic stirrer to ensure uniform dispersion, which is critical for achieving enhanced mechanical strength and improved electrochemical performance.[6]

Once homogeneity was attained, the solution was poured onto a flat glass substrate and spread evenly with a casting blade, allowing precise control over film thickness. The cast films were subjected to slow solvent evaporation under vacuum conditions to minimize imperfections such as trapped air bubbles [7]. After drying, the films were carefully peeled from the substrate and annealed, a step that not only improves crystallinity but also promotes stronger interactions between the polymer chains and nano-alumina. This treatment enhances the films' structural integrity and optimizes their suitability for electrochemical applications.[8]

3. CHARACTERIZATION

3.1. ANALYSIS OF X-RAY DIFFRACTION (XRD):

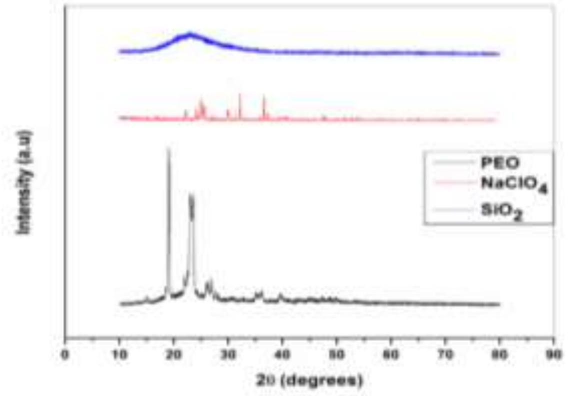

Fig.1: X-Ray Diffraction Pattern of pure PEO, $NaClO_4$ and SiO_2

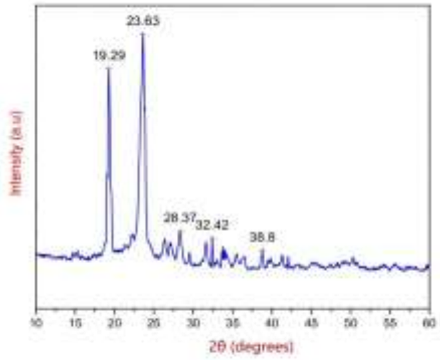

Fig.2: X-Ray Diffraction pattern of pure PEO-70: $NaClO_4$-15: SiO_2-15 samples

Figure-1 shows the XRD patterns of the. X-Ray Diffraction pattern of pure PEO-70: $NaClO_4$-15: SiO_2-15 samples and Figure-2 indicates PEO-70: $NaClO_4$-15: SiO_2-15 system. The peaks at 19.29°, 23.63° are related to pure PEO, which is the characteristic of crystalline host polymer. Sharp peaks at 28.37°, 32.42°, 38.8°, 38.72°, 40.76°, 45.25°, 47.26°, 49.45°, 50.0°, 55.50° are related to pure $NaClO_4$ and are correlated with earlier reported results.[9] The characteristic peak of $NaClO_4$ at 25.90° and 37.20° have disappeared PEO-70: $NaClO_4$-15: SiO_2-15 dispersed system, which confirms thea miscibility of salt in the dispersed system. The peaks that appeared around 19° and 23° in PEO-70: $NaClO_4$-15: SiO_2-15 systems correspond to the un-complexed PEO. [10]

3.2. ANALYSIS OF FOURIER TRANSFORM INFRARED:

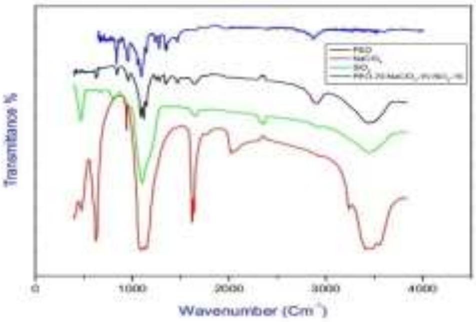

Fig.3. FT-IR of pure PEO, $NaClO_4$, SiO_2 and PEO-70: $NaClO_4$-15: SiO_2-15 samples

The FTIR spectra shed light on the molecular interactions within the PEO–$NaClO_4$–SiO_2 polymer electrolyte. A broad band at ~2800 cm^{-1} reflects hydroxyl group vibrations, typically linked to absorbed moisture or surface OH groups. [11] The SiO_2 nanofiller is confirmed by peaks at 1030.8 cm^{-1} (Si–O–Si stretching) and 1450.5 cm^{-1} (silica vibrations). Pure PEO shows a strong band at 1091 cm^{-1} due to C–O–C ether stretching. In the PEO-70: $NaClO_4$-15: SiO_2-15 composition, this band shifts to a lower frequency, signaling Na^+ coordination with PEO oxygen atoms. This bond weakening supports sodium ion complexation, enhancing ionic conductivity in the polymer electrolyte.[12]

3.3. ANALYSIS OF SCANNING ELECTRON MICROSCOPE:

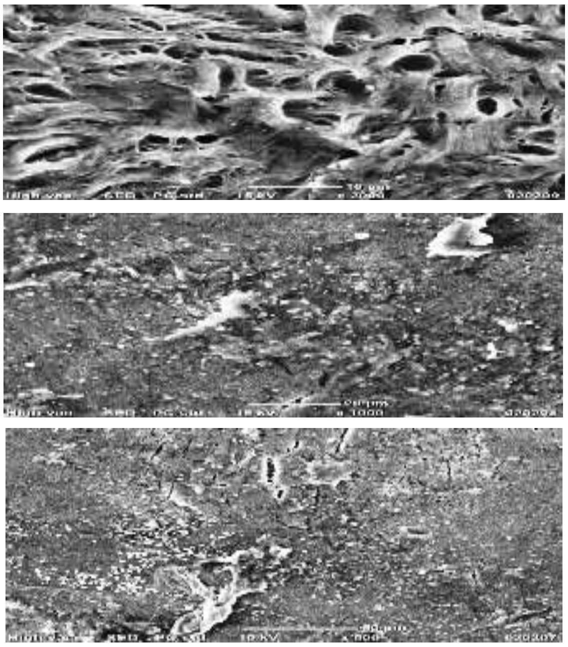

Fig.4. SEM micrographs of the polymer electrolyte at magnifications of 500 and 1000 show the general surface features and distribution of particles across the matrix.

When the magnification is increased to 5000 (Fig. 4), nano-alumina particles are distinctly visible, confirming their incorporation within the polymer host [13]. These nanoparticles appear irregularly dispersed, creating noticeable variations in surface texture and morphology. The uneven distribution of alumina leads to roughened regions, which may influence both mechanical stability and ionic pathways within the composite system. Such microstructural observations highlight the crucial role of nanofiller dispersion in tailoring the performance of solid polymer electrolytes.[14]

4. IMPEDENCE ANALYSIS

4.1. Complex Impedance Spectroscopy

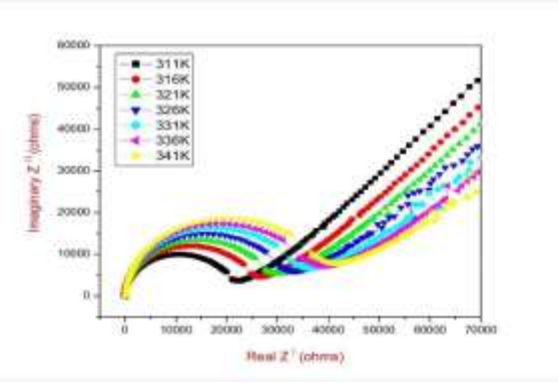

Fig.5. Picture of Nyquist plots of SiO_2, $NaClO_4$ and PEO

Impedance spectroscopy provides valuable insight into the conduction mechanism of polymer electrolytes. Nyquist plots typically show a semicircle at high frequency, reflecting bulk resistance and capacitance, followed by a spike at low frequency due to electrode polarization. [15] For SiO_2 nanofiller electrolytes, the intercept of the semicircle on the real axis indicates bulk resistance (Rb). With rising temperature, Rb decreases, signifying enhanced ion dissociation, increased charge carrier density, and greater ion mobility within the polymer matrix. This thermally activated ion transport underscores the effectiveness of nanofiller-based polymer electrolytes in boosting conductivity, making them promising candidates for advanced electrochemical energy storage systems.[16]

4.2. AC Conductivity

Joncher's power-law effectively explains the AC conductivity of polymer electrolytes across varying frequencies. The conductivity follows the relation σ(ω) = σ_dc + Aω^n, where σ_dc represents frequency-independent conductivity, A indicates polarization strength, and n is the frequency exponent. Typically, three dispersion regions are observed. At low frequencies, conductivity arises from space charge polarization effects. In the mid-frequency range, a dc saturation zone appears, reflecting stable charge transport. At high frequencies, a dc-to-ac transition occurs, influenced by coulombic interactions between charge carriers and polymer chain disruption. This model highlights the complex ion dynamics and frequency response of polymer electrolyte systems.[17]

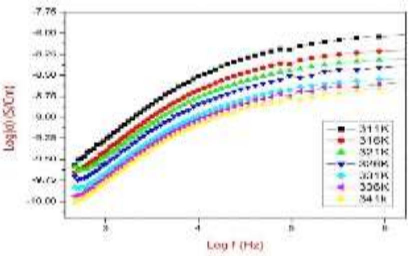

Fig.6. Frequency dependent conductivity of PEO-70:$NaClO_4$-15:SiO_2-15 solid polymer-electrolyte at different temperatures

4.3. DC Ionic Conductivity The DC ionic conductivity of an electrolyte system can be determined using the relation: σ=t\A·Rbt Here, A represents the electrode's cross-sectional area, t is the electrolyte thickness, and Rb is the bulk resistance obtained from impedance measurements

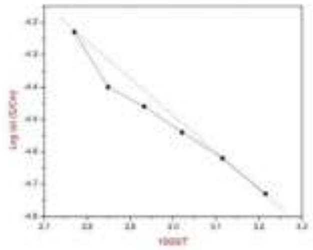

Fig.7. Variation of dc ionic conductivity of PEO-70:NaClO$_4$-15:SiO$_2$-15

The incorporation of SiO$_2$ nanofillers into the PEO–NaClO$_4$ polymer electrolyte system significantly influences both structural properties and ionic conductivity. Structurally, the nanofillers disrupt the crystalline regions of PEO, enhancing the amorphous phase, which provides a more flexible medium for ion migration. This structural modification facilitates polymer segmental motion, thereby promoting ion hopping between coordination sites. Consequently, the ionic conductivity improves due to increased charge carrier mobility and reduced bulk resistance. The temperature-dependent studies further confirm thermally activated conduction, with conductivity rising steadily and reaching higher values compared to filler-free systems, making SiO$_2$-based composites promising for electrochemical device applications [18].

4.4. Dielectric Properties

The complex dielectric permittivity (ε*) of a material as a function of frequency is expressed as:

$$\varepsilon^* = \varepsilon'(\omega) - j\varepsilon''(\omega)$$

Here, **ε′** represents the real part, also known as the dielectric constant, which indicates the ability of the electrolyte to store electrical energy during each cycle of the applied alternating field. Meanwhile, **ε″** corresponds to the imaginary part, which accounts for dielectric losses, reflecting the energy dissipated within the material due to polarization and conduction mechanisms [19].

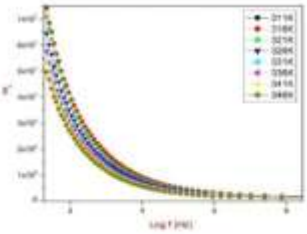

Fig.8. Frequency dependent dielectric constant of PEO-70: NaClO$_4$-15: SiO$_2$-15 polymer-electrolyte at distinct temperatures

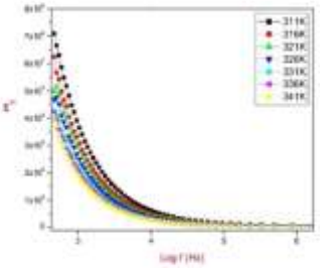

Fig.9. Frequency dependent dielectric constant of PEO-70:NaClO$_4$-15:SiO$_2$-15 polymer-electrolyte at distinct temperatures

The dielectric properties of PEO/$NaClO_4$/SiO_2 nanocomposite polymer electrolytes (NCPEs) are strongly affected by nanofiller concentration and temperature.[20] The dielectric constant rises markedly, peaking around 5×10^4, due to the homogeneous dispersion of SiO_2 nanoparticles that improve charge carrier mobility within the matrix. As shown in Figure 22, the dielectric loss (ε'') follows a similar trend. At low frequencies, ε'' remains high, reflecting amorphous phases introduced by nanofillers and electrode polarization at the polymer–electrode interface. Increasing temperature promotes ion pair dissociation, higher free carrier density, and enhanced interfacial polarization, while dipole relaxation and shorter relaxation times further raise dielectric loss.[21]

5. CONCLUSION

Incorporating SiO_2 nanofillers into the PEO–$NaClO_4$ polymer electrolyte markedly alters its structural and electrical behavior. XRD reveals reduced crystallinity, indicating enhanced amorphous phases that favor ion mobility, while FTIR confirms strong polymer–salt–nanofiller interactions promoting ionic dissociation. SEM images show dispersed nanoparticles disrupting surface uniformity and forming conductive pathways. Impedance spectroscopy highlights decreased bulk resistance and distinct Nyquist arcs, evidencing improved charge transport. Dielectric studies further demonstrate increased dielectric constant, linked to enhanced space charge polarization. Collectively, these findings confirm that SiO_2 nanoparticles effectively boost conductivity and stability, establishing the PEO–$NaClO_4$–SiO_2 system as a strong candidate for solid-state devices.

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