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SODIUM ION BASED NANO SILICON DIOXIDE (SiO_2) DISPERSED SOLID POLYMER ELECTROLYTE SYSTEM

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Abstract: This paper explores the development of sodium ion based nano SiO_2 dispersed solid polymer electrolytes for energy storage. Synthesized via the solution casting method, these materials ensure uniform nano SiO_2 dispersion within a polymer matrix, enhancing its mechanical strength and ionic conductivity key attributes for sodium ion batteries. Characterization techniques such as X-ray diffraction (XRD) assessed crystallinity, while Fourier transform infrared spectroscopy (FTIR) examined chemical interactions between the polymer and nano SiO_2, and Scanning electron microscopy (SEM) analyzed the morphology and nano particle distribution. Ionic conductivity, measured using an LCR meter, demonstrated promising electrochemical performance, validating these nano SiO_2 polymer systems as advanced candidates for sodium ion battery applications.

Keywords: SiO_2, Electrolyte, XRD, FTIR, SEM, Impedance.

1. Introduction:

This research explores the potential of sodium ion based nano silicon dioxide (SiO_2) dispersed solid polymer electrolytes (SPEs) for energy storage. SPEs are gaining attention in sodium ion batteries as they offer key advantages over liquid electrolytes, particularly improved safety and thermal stability. Sodium-ion batteries present a viable alternative to lithium ion due to sodium's abundance and cost effectiveness, but their development relies heavily on advancing electrolyte performance.

In this paper, Nano SiO_2 was dispersed in a polymer matrix using solution casting to achieve uniform distribution, which is essential for enhanced ionic conductivity and structural integrity. Nano SiO_2 interacts with polymer chains to create effective ion transport pathways, boosting both conductivity and mechanical strength. The selected polymer, polyethylene oxide (PEO), is commonly used due to its compatibility with sodium salts and potential for ionic conduction. However, PEO's crystalline structure limits ion mobility at room temperature, so strategies to improve performance include blending it with other polymers, adding plasticizers, and introducing nano SiO_2 to enhance chain flexibility [1].

The type of sodium salt, $NaClO_4$ used here, affects ionic conductivity, provides high dissociation and stability, but optimizing salt concentration is critical to avoid ion pairing that can limit free ion availability. Additionally, nano SiO_2 contributes to the SPE's electrochemical stability, reducing degradation risks at high voltages and preventing sodium dendrite formation, which can cause short circuits. Despite these advances, SPEs face challenges in achieving sufficient room temperature ionic conductivity for high-power applications. Future research is directed towards optimizing SiO_2 size, enhancing the polymer structure to reduce crystallinity, and developing porous matrices to facilitate ion transport [2]. Compatibility with sodium metal anodes, prone to reactivity issues, also requires further exploration. Promising recent studies indicate that controlled SiO_2 distribution can yield SPE ionic conductivities near those of liquid electrolytes at room temperature [3].

Sodium ion based nano SiO_2 SPEs represent a significant step forward in energy storage technology. While challenges remain, these materials offer a safer, cost effective alternative to lithium ion batteries and could transform the future of battery technology by improving energy density, durability, and cost efficiency.

2. Literature survey

This study focuses on developing sodium ion based nano silicon dioxide (SiO_2) dispersed solid polymer electrolytes (SPEs), which are promising for next generation energy storage. Sodium ion batteries offer a viable alternative to lithium-ion batteries due to sodium's abundance, cost effectiveness, and environmental friendliness [4]. SPEs, particularly those enhanced with nano SiO_2, provide advantages over liquid electrolytes, including better thermal stability and reduced leakage risks, crucial for safer, longer lasting batteries.

Nano SiO_2, with its high surface area and thermal stability, strengthens the polymer matrix, improving ionic conductivity by creating efficient ion transport pathways and increasing mechanical stability. Achieving its uniform distribution in the polymer is essential, as uneven dispersion can hinder ion transport [5]. Techniques like solution casting and in-situ polymerization aid in achieving uniformity. Polyethylene oxide (PEO) is widely used in SPE's for its ability to dissolve sodium salts, though its crystalline structure limits ionic mobility at room temperature. Adding nano SiO_2 and blending with other polymers, like PVDF, can improve conductivity by increasing chain mobility [6].

Sodium salts, such as $NaClO_4$, also influence the electrolyte's performance by supporting dissociation and thermal stability. However, optimal concentration is needed to prevent ion pairing. Nano SiO_2 enhances the electro-chemical stability of SPE's, protecting them from degradation and sodium dendrite growth, which are common issues that reduce battery performance. Although challenges remain, especially with achieving room-temperature conductivity, ongoing research focuses on optimizing SiO_2 size, polymer structure, and anode compatibility [7].

3. Synthesis of SiO_2

The solution casting method is essential in developing polymer based composites like solid polymer electrolytes (SPE's), particularly in fabricating advanced sodium ion battery materials. This process involves dissolving polymers and additives in a solvent, casting the solution onto a substrate, and evaporating the solvent to form a thin uniform film. In the context of sodium ion based SPE's, this method supports optimal dispersion of nano silicon dioxide (SiO_2) within the polymer, significantly enhancing ionic conductivity and mechanical robustness key attributes for efficient, stable battery performance.

The process begins by dissolving a selected polymer, such as polyethylene oxide (PEO), in a solvent like dimethylformamide (DMF). Here, 2.4 grams of PEO is carefully mixed with 40 milliliters of DMF. Continuous stirring is required to ensure thorough dissolution, creating a homogeneous base for the polymer electrolyte film. The polymer concentration can be adjusted to achieve specific film thicknesses, tailored to the battery's requirements. Once the polymer solution is prepared, nano fillers like SiO_2 are introduced. In this instance, 0.3 grams of nano SiO_2 is added, alongside sodium perchlorate ($NaClO_4$) salt, which serves as the ionic conductor in the electrolyte.

Adding these components requires continuous, thorough stirring to prevent particle aggregation and ensure even distribution of nano SiO_2 throughout the polymer matrix. This uniform distribution is crucial for the structural integrity of the film, allowing consistent ion transport and thereby enhancing both the mechanical and electro chemical properties of the SPE.

The prepared solution is then stirred for 48 hours using a magnetic stirrer, creating a stable dispersion of nano-particles. Once the solution reaches a homogeneous consistency, it is cast onto a smooth, flat substrate commonly glass or Teflon to form the film. After casting, the solvent evaporates, leaving behind a thin, flexible SPE film with evenly dispersed nano SiO_2. This method's effectiveness lies in producing high-performance polymer electrolytes with uniform nano-particle integration, supporting their application in advanced, stable sodium ion batteries.

4. Results and discussion

4.1. X-ray Diffraction (XRD)

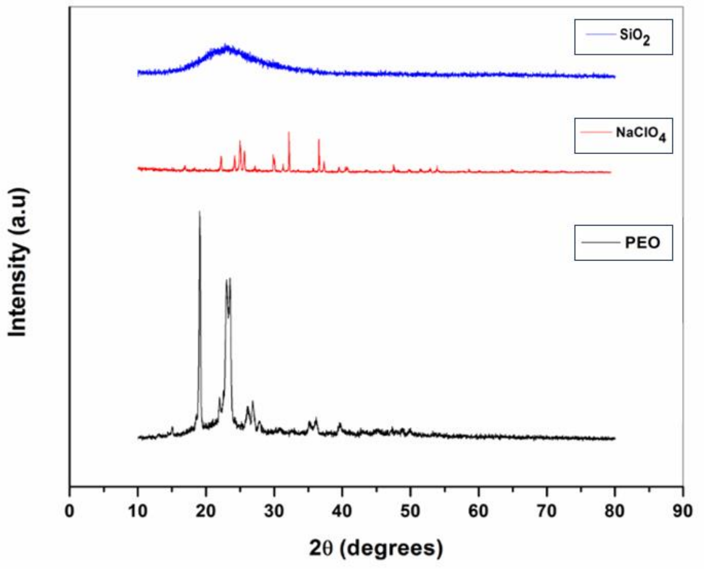

Figure 1(a): X-ray diffraction pattern of pure PEO, $NaClO_4$, SiO_2

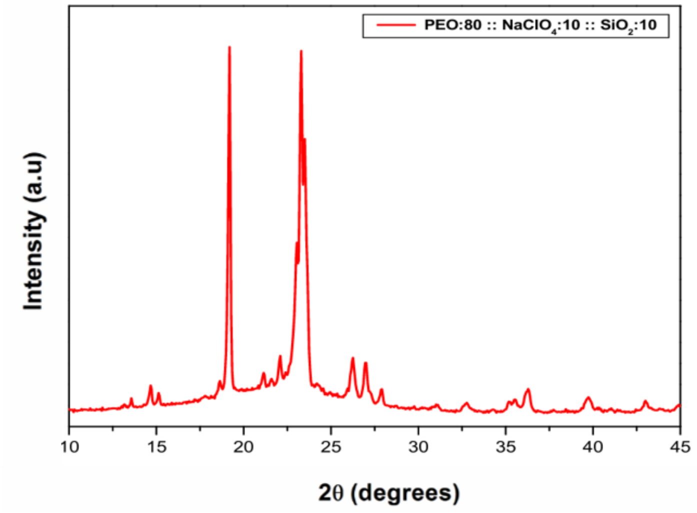

Figure 1(b): X-ray diffraction pattern of PEO-80: $NaClO_4$-10: SiO_2-10

Figures 1(a) and 1(b) represent the XRD configurations of the pure PEO, $NaClO_4$, SiO_2, and PEO-80: $NaClO_4$-10: SiO_2-10 dispersed system. The peaks at 19.18°and 23.29° are related to pure PEO, which is characteristic of the crystalline host polymer. Sharp peaks at 31.11°, 32.87°, 36.33°, 34.94°, 43.14°, 45.25°, 47.41°, 49.0°, 50.06° are related to pure $NaClO_4$ and are correlated to the earlier reported results. The characteristic peak of $NaClO_4$ at 31.11° and 43.14°, has disappeared in the PEO-80: $NaClO_4$-10: SiO_2-10 dispersed system, which confirms the complexation of salt in the dispersed system. The peaks that appeared around 19° and 23° in PEO-80: $NaClO_4$-10: SiO_2-10 dispersed systems correspond to the un-complexed PEO [8].

4.2. Fourier Transform infrared spectroscopy (FTIR)

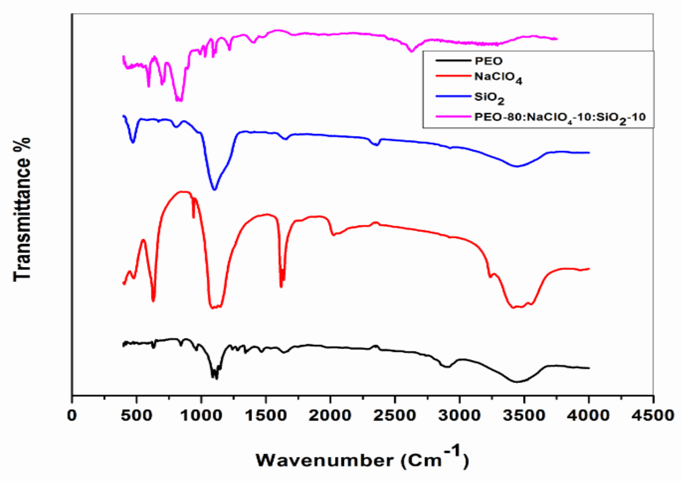

Figure (2): FTIR spectra of pure PEO, $NaClO_4$, SiO_2, and PEO-80: $NaClO_4$-10: SiO_2-10

The FTIR spectra of pure PEO, $NaClO_4$, SiO_2, and PEO-80: $NaClO_4$-10: SiO_2-10 dispersed solid polymer electrolyte system are shown in Figure (2). A peak around 3441 cm^{-1} in all systems is ascribed to the stretching hydroxyl group (O-H) [8]. In SiO_2 nanofiller dispersed system, the peak at 1087.8 cm^{-1} corresponds to Si-O-Si symmetric stretching, the peak at 1645.3 cm^{-1} relates to the characteristic peak of silica [9]. A peak at 1091cm^{-1} in PEO shifts to a lower frequency in PEO-80: $NaClO_4$-10: SiO_2-10 dispersed solid polymer electrolyte system. This shows that there is an interaction between sodium cation and the carbonyl group existing in the system.

4.3. Scanning Electron Microscopy (SEM)

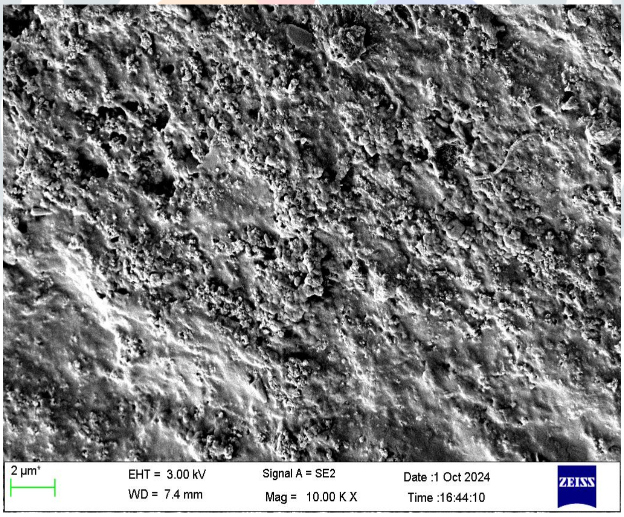

Figure 3(a): SEM picture of PEO-80: $NaClO_4$-10: SiO_2-10 dispersed solid Polymer electrolyte with 10000 magnifications

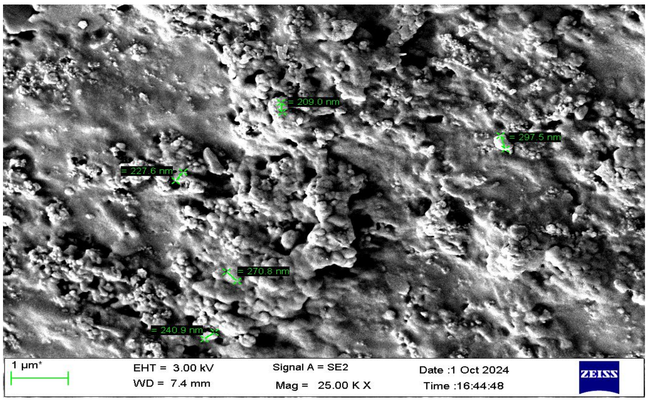

Figure 3(b): SEM picture of PEO-80: $NaClO_4$-10: SiO_2-10 dispersed solid Polymer electrolyte with 25000 magnifications

Figure 3(a) shows the SEM micrograph of SiO_2 dispersed PEO-80: $NaClO_4$-10: SiO_2-10 solid polymer-electrolyte with 10000 magnification. From the figure, the surface is smooth and the crystallites are arranged randomly. Voids between the crystallites are seen significantly.

Figure 3(b) shows the SEM picture of the same dispersed solid electrolyte system with 25000 magnification. The distribution of nano silicon dioxide particles can be observed clearly apart from an uneven surface morphology of the dispersed system.

4.4. Electrical and Dielectric Properties of SiO_2 dispersed nanocomposite polymer electrolyte

4.4.1. AC Conductivity

Joncher's power law behavior describes the AC conductivity of polymer electrolytes, particularly in the intermediate to high-frequency range. The total conductivity, expressed as a sum of frequency-independent and frequency-dependent components, follows this model. The frequency-dependent conductivity displays three regions: (i) a low-frequency space charge polarization region, (ii) a mid-frequency DC saturation zone, and (iii) a high-frequency DC to AC transition zone. This high-frequency behavior results from Coulomb interactions among charge carriers and disruptions in polymer chains, with a constant A, representing polarization strength and n as the frequency exponent.

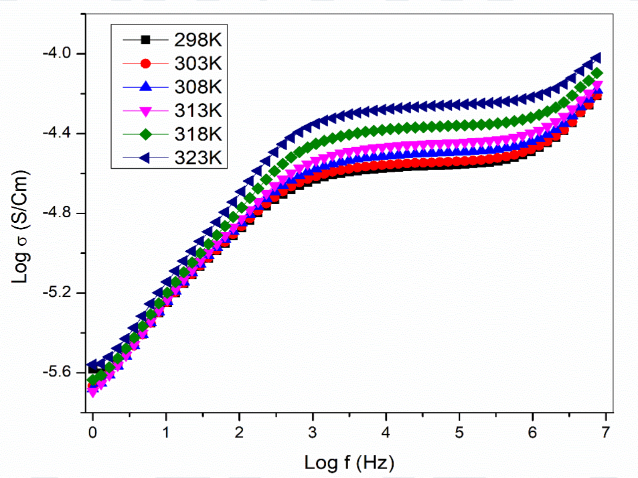

Figure 4(a): Frequency-dependent conductivity of SiO_2 dispersed nano composite at various temperatures

Figure 4(a) illustrates the frequency-dependent AC conductivity of SiO_2 nanofiller-dispersed electrolyte, showing a nearly frequency-independent plateau up to 10^6 Hz, indicating a DC component. At various temperatures, the conductivity remains frequency-independent over this range, but overall conductivity rises with temperature. This increase in conductivity with temperature is attributed to enhanced ion mobility due to thermally activated processes.

4.5.2. Complex Impedance Spectroscopy

Impedance spectroscopy effectively analyzes the conduction and ion transport in polymer electrolytes, that has shown in Figure 4(b) as Nyquist plots. The semicircle at high-frequency followed by spike at low-frequency indicates the electrolyte's characteristics, reflecting both bulk resistance and capacitance. In SiO_2 nanofiller-dispersed electrolytes, the x-axis intercept of the semicircle gives the bulk resistance (R_b), which decreases with rising temperature. This decrease suggests the increased ion dissociation and enhanced ion mobility at elevated temperatures.

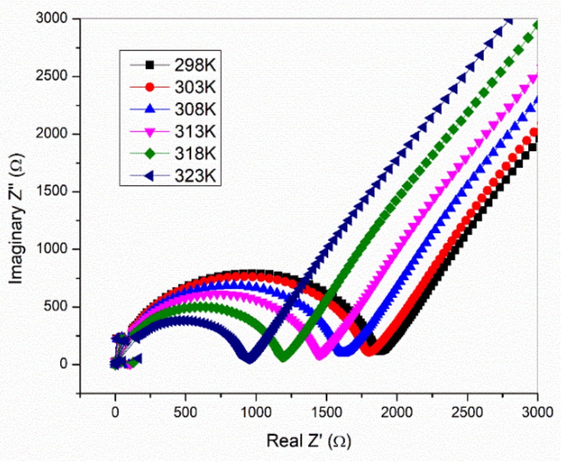

Figure 4(b): Nyquist plots of SiO_2 dispersed NCPEs at distinct temperatures

4.5.3. DC Ionic Conductivity

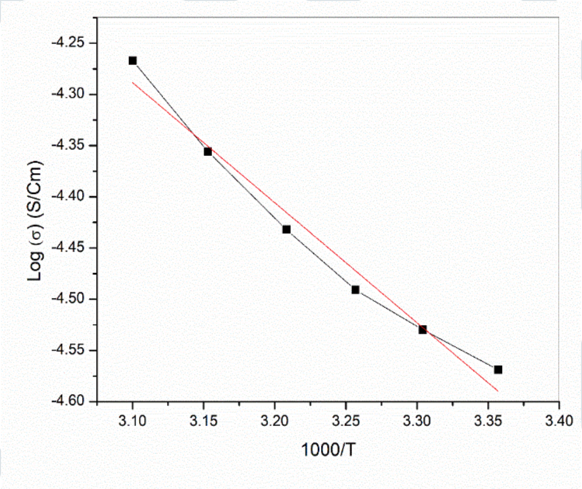

Figure 4(c): Arrhenius plot of SiO_2 dispersed NCPEs at distinct temperatures

The DC ionic conductivity of SiO_2 nanofiller-dispersed polymer electrolyte has been calculated using the cross-sectional area A, thickness t, and bulk resistance R_b. Conductivity has been increases with temperature according to the Arrhenius relationship. This rise in conductivity is likely due to enhanced ion dissociation and increased charge mobility.

In Figure 4(c), a plot of Log(σ) against 1000/T for various temperatures indicates that conductivity follows an upward trend with temperature and the conductivity is found to be 1.18×10^{-6} S/cm at room temperature. This may be attributed to ion hopping among coordination sites and polymer segmental motion. The activation energy E_a, deduced from the plot's slope, and found to be 0.493 eV.

4.5.4. Dielectric Properties

The complex dielectric permittivity (ϵ) of a material as a function of frequency describes its ability to store electrical energy in response to an alternating field. Here, ϵ is the standard dielectric constant of the electrolyte, which dictates the energy retained per cycle.

In Figure 4(d), the dielectric constant of SiO_2-dispersed NCPE systems across various temperatures shows a high permittivity at low frequencies, mainly due to space charge polarization and dipole alignment with the field. As frequency rises, permittivity decreases, attributed to reduced space charge polarization. At higher frequencies, this decline becomes more saturated.

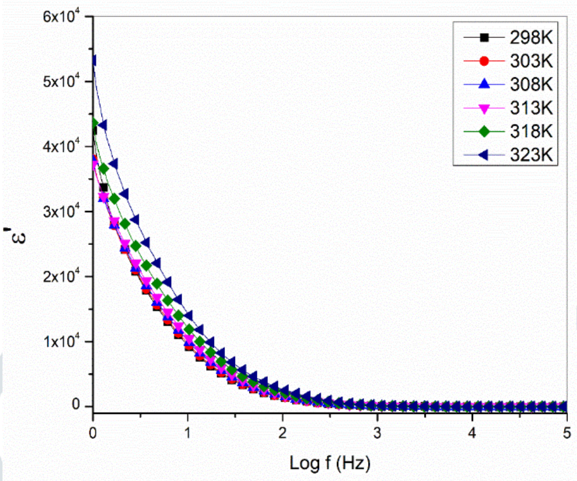

Figure 4(d): Frequency-dependent dielectric constant of SiO_2 dispersed NCPEs at distinct temperatures

Figure 4(d) illustrates the frequency-dependent dielectric constant of SiO_2-dispersed NCPE across temperatures. At low frequencies, a high dielectric constant arises primarily from space charge polarization and dipole alignment in the field's direction. As frequency increases, permittivity declines due to reduced space charge polarization, eventually stabilizing at high frequencies as dipolar polarization vanishes. The addition of nanofiller and elevated temperatures lead to a peak dielectric constant of 5×10^4, attributed to the increased charge carriers from uniformly dispersed nanoparticles in the $PEO/NaClO_4/SiO_2$ matrix.

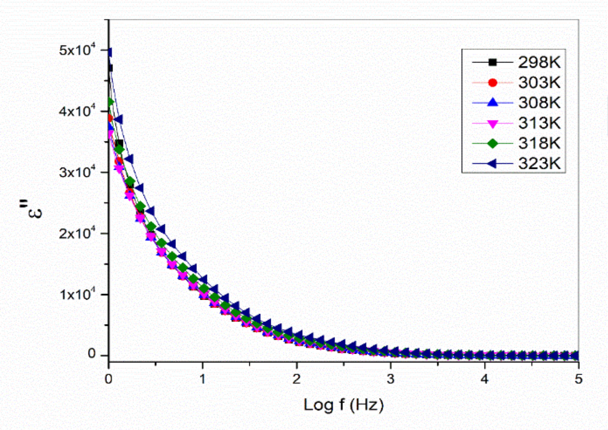

Figure 4(e): Frequency-dependent dielectric loss of SiO_2 dispersed NCPEs at distinct temperature

Figure 4(e) presents the dielectric loss of SiO_2-dispersed NCPEs across various temperatures, showing a similar trend to the dielectric constant. High dielectric loss at low frequencies indicates a more amorphous phase introduced by nanofiller. The steep increase at very low frequencies is attributed to electrode polarization, which overshadows other relaxation processes. With increasing temperature, enhanced ion pair dissociation boosts free carrier density at the interface, increasing dielectric loss due to dipole relaxation and a shorter relaxation time. This trend is consistent across all systems.

4.5.5. Electric Modulus Spectra

An electric modulus study helps to analyze conductivity relaxation while minimizing electrode polarization. The complex electric modulus, with real (M') and imaginary (M'') components, can quantify this.

Figure 4(f) shows the frequency-dependent real modulus M' for SiO_2-dispersed NCPEs across temperatures. At low frequencies, M' is near to zero, rising steadily with frequency before stabilizing at an asymptotic maximum, indicating short-range charge carrier mobility via hopping. Higher temperatures shift the dispersion toward higher frequencies due to polymer chain interactions, decreasing relaxation time and enabling greater charge carrier movement along polymer segments.

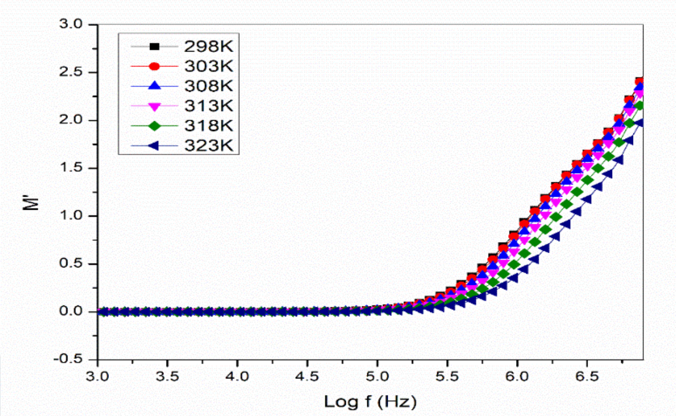

Figure 4(f): Frequency-dependent real electric modulus of SiO_2 dispersed NCPEs at distinct temperatures

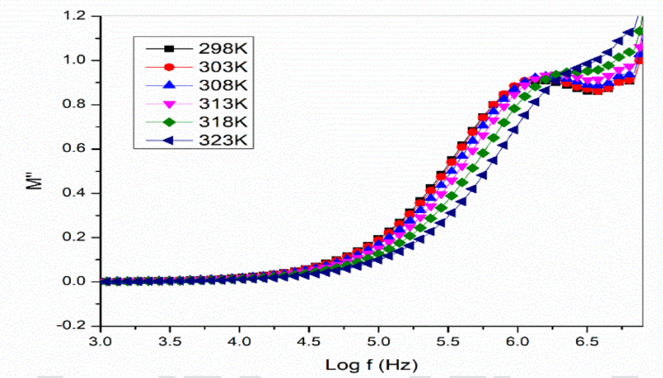

Figure 4(g): Frequency-dependent imaginary electric modulus of SiO_2 dispersed NCPEs at distinct temperatures

Figure 4(g) demonstrates the variation of M'' with the frequency of SiO_2 dispersed nano composite polymer electrolyte at distinct temperatures. The existence of relaxation peaks in M''suggests that the films are good ionic conductors [16]. Due to the presence of nano-filler, the broadening and shifting of the peaks have been observed. There is a shift in the peak towards the high-frequency region, with temperature indicating the increased movement of the charge carriers leading to a decrease in relaxation time [17-18].

Conclusion:

This paper investigates Solid polymer electrolyte using nano-silicon dioxide (SiO_2) within a sodium-ion framework, crafted through solution casting for uniform nano-particle distribution. The nano-SiO_2 enhances both electrical and ionic conductivity, positioning it as a promising material for sodium-ion batteries. Comprehensive characterization included X-ray diffraction (XRD) for crystallinity, Fourier-transform infrared spectroscopy (FTIR) for polymer SiO_2 bonding interactions, and Scanning electron microscopy (SEM) for nano-particle dispersion. Ionic conductivity measurements were conducted using an LCR meter, confirming the potential of this system to improve sodium-ion battery performance.

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